

Relationship between Structure and Mechanical Properties in Hierarchical Nanoporous Gold

Vom Promotionsausschuss der
Technischen Universität Hamburg
zur Erlangung des akademischen Grades
Doktor der Naturwissenschaften (Dr. rer. nat.)
genehmigte Dissertation (Monografie)

von
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aus
Herzberg am Harz

2026

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Tag der mündlichen Prüfung: 25. März 2026

"Entities must not be multiplied beyond necessity."

—William of Ockham

Acknowledgments

First of all, I want to thank my doctoral supervisor Prof. Dr. Shan Shi for the provision of a fruitful approach, for helpful guidance, and for inspiring discussions. From my first day in Geesthacht, her advice was an indispensable contribution to the creation of this work. I also thank Prof. Dr. habil. Patrick Huber for serving as the 2nd reviewer and Prof. Dr. Roland Aydin for chairing the examination board. I am grateful to Prof. Dr. Jörg Weissmüller who contributed his expertise and his experience, in particular in the field of small-angle X-ray scattering. Besides, I am indebted to Dr. Jürgen Markmann who provided aid in technical, scientific, and all kinds of other matters.

Thanks also go to Dr. Robert Günther and Nina Petersen for their technical support, to Dr. Henry Ovri and Dr. Markus Ziehmer for their support in electron microscopy and focused ion beam, and to Haide Alfort-Springer and Stephanie Kropf-Eilers for their administrative support. Furthermore, I want to thank my colleagues Dr. Seoyun Sohn, Celina Passig, Wei-Che Chang, Lena Dyckhoff, Dr. Stefan Berger, Dr. Yong Li, Dr. Nadiia Mameka, Dr. Olga Matts, Dr. Lukas Lührs, Ulrike Dette, Haonan Sun, Dr. Zhongyang Li, Dr. Xinyan Wu, Dr. Marine Bossert, and Gideon Henkelmann. I acknowledge financial support by the German Research Foundation (DFG) through SFB 986, "Tailor-Made Multi-Scale Materials Systems – M3," project number 192346071.

Finally, I am deeply grateful to my parents Thomas and Irene and to my brother Paul. Without their unconditional help this work would not exist.

Abstract

Hierarchical nanoporosity represents a novel type of material which enables the combination of mechanical stability with a reduced solid fraction. The impact of a 2nd hierarchy level on the mechanical behavior is not yet fully understood. This thesis aims to unveil the various effects of structural parameters in hierarchical nanoporous gold on the mechanical properties.

Monolithic samples of hierarchical nanoporous gold (HNPG) are produced by a three-step procedure which consists of a 1st electrochemical dealloying, a coarsening step by annealing and a 2nd electrochemical dealloying. The variation of synthesis parameters enables the independent adjustment of the ligament size and the solid fraction on the upper and the lower hierarchy level.

Scanning electron microscopy (SEM) as well as small- and ultra-small-angle X-ray scattering (SAXS/USAXS) are employed for the structural analysis. In preparation for SAXS/USAXS, thin walls are cut out of the bulk material by plasma focused ion beam (PFIB). Two distinct length scales are identified for hierarchical nanoporous gold. The comparison between the ligament size or diameter determined by SEM and the ligament spacing determined by SAXS/USAXS results in a conversion factor which is dependent on the solid fraction. Furthermore, the specific surface area, which is detected on the basis of the scattering intensity, shows a good agreement with the specific surface area expected from the ligament spacing.

A mechanical characterization is performed by macroscopic compression tests. Coarsening on the lower hierarchy level is accompanied by a distinct decrease of stiffness and strength if the lower level solid fraction is about 0.30, which is explained by the influence of the lower level connectivity. A reduction of stiffness and strength is detected if the ratio between the upper and the lower level ligament size is reduced to about 2. The Young's modulus is lower than expected on the basis of the modified Roberts-Garboczi-law, which is associated with the early yielding of ligaments. This assumption is supported by the general impairment of the Young's modulus by the strength. During compression, the flow stress of several HNPG variants reaches the maximum value which is estimated according to the theoretical shear strength of gold and the modified Roberts-Garboczi-law. Altogether, this thesis provides a comprehensive study on the multiple interactions between structure and mechanical behavior in hierarchical nanoporosity.

Zusammenfassung

Bei hierarchischer Nanoporosität handelt es sich um eine neuartige Materialklasse, welche mechanische Stabilität mit einem verminderten Festphasenanteil kombiniert. Der Einfluss einer 2. Hierarchieebene auf das mechanische Verhalten ist bislang nicht vollständig verstanden. Diese Dissertation zielt darauf ab, das Verständnis für die verschiedenartigen Auswirkungen der Strukturparameter in hierarchisch nanoporösem Gold (HNPG) auf die mechanischen Eigenschaften zu verbessern.

Monolithische Proben aus hierarchisch nanoporösem Gold werden im Rahmen eines 3-Stufen-Prozesses hergestellt, welcher im Einzelnen aus einer 1. elektrochemischen Entlegierung, einer Vergröberung durch Anlassen und einer 2. elektrochemischen Entlegierung besteht. Die Variation der Herstellungsparameter ermöglicht die unabhängige Einstellung der Ligamentgröße und des Festphasenanteils auf der oberen und der unteren Hierarchieebene.

Rasterelektronenmikroskopie (SEM) sowie Klein- und Ultra-Kleinwinkelröntgenstreuung (SAXS/USAXS) werden für die strukturelle Analyse herangezogen. Für die Vorbereitung von Proben für SAXS/USAXS werden dünne Scheiben mittels einer plasmagestützten Ionenfeinstrahlanlage (PFIB) aus dem massiven Material herausgeschnitten. In hierarchisch nanoporösem Gold werden zwei deutlich ausgeprägte Längenskalen festgestellt. Der Vergleich zwischen der durch SEM bestimmten Ligamentgröße, welche dem Ligamentdurchmesser entspricht, und dem durch SAXS/USAXS bestimmten Ligamentabstand ergibt einen Korrelationsfaktor, welcher eine Abhängigkeit zu dem Festphasenanteil aufweist. Schließlich zeigt die spezifische Oberfläche, welche anhand der Streuintensität ermittelt wird, eine gute Übereinstimmung zu der anhand des Ligamentabstands erwarteten spezifischen Oberfläche.

Eine mechanische Charakterisierung wird durch makroskopische Druckversuche durchgeführt. Eine Vergröberung auf der unteren Hierarchieebene geht mit einer deutlichen Verminderung der Steifigkeit und der Festigkeit einher, falls der Festphasenanteil auf unterer Ebene bei etwa 0.30 liegt. Diese Beobachtung wird mit dem Einfluss der Vernetzung auf unterer Ebene erklärt. Eine Abnahme der Steifigkeit und Festigkeit wird festgestellt, wenn das Verhältnis zwischen der Ligamentgröße auf oberer und unterer Ebene auf etwa 2 herabgesetzt wird. Der E-Modul ist geringer, als anhand des modifizierten Roberts-Garboczi-Gesetzes erwartet wird, was mit dem frühzeitigen plastischen Fließen der Ligamente in Verbindung gebracht wird. Diese Annahme wird durch die generelle Beeinflussung des E-Moduls durch die Festigkeit gestützt. Während des Druckversuchs erreicht die Fließspannung einiger hierarchisch nanoporöser Strukturen

den Maximalwert, welcher anhand der theoretischen Scherfestigkeit von Gold sowie des modifizierten Roberts-Garboczi-Gesetzes erwartet wird. Insgesamt bietet diese Dissertation eine umfassende Studie zu den vielfältigen Wechselwirkungen zwischen der Struktur und dem mechanischen Verhalten in hierarchischer Nanoporesität.

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Chapter 1

Introduction

1.1 The concept of hierarchical nanoporosity

Nature is a rich source of inspiration for the usage of structural hierarchy. Famous examples are wood, bamboo, bone, nacre and tooth enamel. Hierarchy fulfils a variety of functions, such as weight reduction, mass transport, self-healing and fracture toughness. Ideal examples of the latter function are bone, nacre and tooth enamel, which are composites of protein and mineral. Structural hierarchy circumvents the rule of mixture and greatly enhances the fracture toughness by prohibition of crack propagation. Many man-made materials contain hierarchy as well. However, in comparison with natural materials the structural complexity is generally lower. Examples can be found in architecture, where the main purpose is weight reduction. Another example is fibrous laminate [1–5].

The diagnosis of structural hierarchy requires several structural levels which are characterized by some type of recurring element. Even if a stochastic structure is considered, this structure typically possesses certain characteristics with regard to dimension and extent. If a hierarchy of a specific order is present, a corresponding number of structural levels exist, which differ from each other in terms of structure and length scale. While a structure can refer to various features such as grain boundaries, the term *cellular foam* is more precise. It refers to composite materials in which one phase is solid and the other phase is liquid, gas or empty space. From the examples mentioned above, wood, bamboo and trabecular bone fulfil this criteria [1, 2]. There are many application possibilities for cellular foams [5], such as filtration [6], insulation [7], heat exchanging [8, 9] and catalysis [10, 11]. Often, these methods make use of the high surface area of nanoporous foams. A maximum surface area is desirable if it is the rate limiting step. Accordingly, the length scale has to be minimized. In particular, this criterion applies to catalysis, where surface reactions take place at the interface between fluid and solid. If the length scale of a cellular foam is continually reduced, material transport through convective flow is restricted due to the decreasing pore diameter. In this respect, an obvious advantage of hierarchical nanoporosity is the combination of large pores and a large surface, which enables the combination of high reactivity with fast mass transport [12]. However, cellular foams with structural hierarchy are rarely

used in technical applications. One example are heat exchangers with a metal foam as lower hierarchy level and a sandwich structure, which can be stacked to layers, as upper hierarchy level. The heat passes through the plates at top and bottom of the cellular structure. Heat transfer between different fluids is possible if they are pressed through adjacent layers [13, 14]. Even in this case, on the upper level hierarchy is 1-dimensional, it occurs in only one dimension.

In order to create materials with a minimum length scale, dealloying is an appropriate technique, since it enables the synthesis of structures with length scales as low as several nanometers [15]. Several attempts are made to find possible catalytic applications for nanoporous metals by dealloying. Indeed, a catalytic effect is detected for some reactions [11, 16]. Nanoporous gold (NPG) catalyzes the oxidation of carbon monoxide (CO) [17, 18]. Furthermore, nanoporous gold [19] or platinum-decorated nanoporous gold [20] can be utilized for the electrooxidation of methanol, for application in methanol fuel cells. Similar applications for platinum-decorated nanoporous gold are the electrooxidation of ethanol, formic acid and formaldehyde [21]. Other studies examine the utilization of bimetallic dealloyed nanoparticles with platinum as one constituent for the oxygen-reduction-reaction in fuel cells [22–24]. A catalytic effect during this reaction is confirmed for bulk nanoporous nickel-platinum, filled with ionic liquid, too [25]. Other possible applications are functional materials [26, 27] such as materials which change their mechanical behavior due to an applied voltage [28], or materials which deform as a result of an applied potential [29]. A limiting factor for utilization in high-temperature processes is the occurrence of coarsening [16]. All examples listed above have in common that they are far from practical application. The situation is different with a class of materials which is similar, but not identical to nanoporous metals by dealloying: Raney nickel catalysts. These porous materials are synthesized by the selective dissolution of phases which are rich in certain alloying elements, typically aluminum, sometimes silicon. The insoluble portion is a phase which is rich in nickel or a mixture of nickel with other elements, and poor in the soluble alloying element [30–32]. The decisive difference to dealloying is the absence of surface diffusion of nickel [33]. During the selective dissolution, Al-rich phases are leached, while Ni-rich phases remain unleached. After the completed generation of a pore-like structure, at the surface of the struts a capping layer of nickel has evolved. This type of metallic porous material is widely used in the industrial hydrogenation of organic molecules [30–32]. Nanoporous metals by dealloying however, as mentioned above, still need to prove their applicability. If now *hierarchical nanoporous metals* are considered, it must be stated that their utilization is still in its infancy. So far, the focus is more on the development of basic strategies for the synthesis of this type of material. For an assessment of the current state of research it is meaningful to gain an overview of existing approaches for the generation of the material of interest.

A large variety of methods exists for the production of metals which firstly exhibit a pore-like structure in the range of nanometers to millimeters, and secondly show some type of hierarchy inside their structure [5, 34]. This variety requires some specification, to which type of material the term *hierarchical nanoporous metal* refers to. Notable advances in the area of additive manufacturing (3D printing) enable the production of microarchitectures with multiple hierarchy levels, whose length scale differ by several

order of magnitude [4]. To reach the highest possible surface area, the length scale of the lowest hierarchy must be reduced as far as possible. This objective can be achieved by dealloying. The following classification refers to materials where one hierarchy level, typically the lowest one, is produced by dealloying. A more precise term is *hierarchical nanoporous metals by dealloying*.

Structures on the individual hierarchy levels do not need to be 3-dimensional. For example, the upper level structure can take the form of tubes [35] or nanowires [36], which are supplemented by a nanoporous lower-level structure made by dealloying. On the other hand, the lower level structure can consist of nanoscaled hollow tubes [4]. In the interest of simplification, only hierarchical materials with three-dimensional and continuous structures on every level are considered. This excludes hybrid materials, such as a nanoporous gold coating on a nickel foam, which is synthesized by the electrochemical deposition of a precursor alloy on the surface of the nickel foam, and subsequent dealloying [37]. Some type of surface roughening of nanoporous gold by electrochemical redox cycling [38] is excluded as well. Taken together, these conditions result in a structure like the one presented in Figure 1.1. Regions where upper level ligaments are fractured illustrate the continuity of the lower level structure along the cross section.

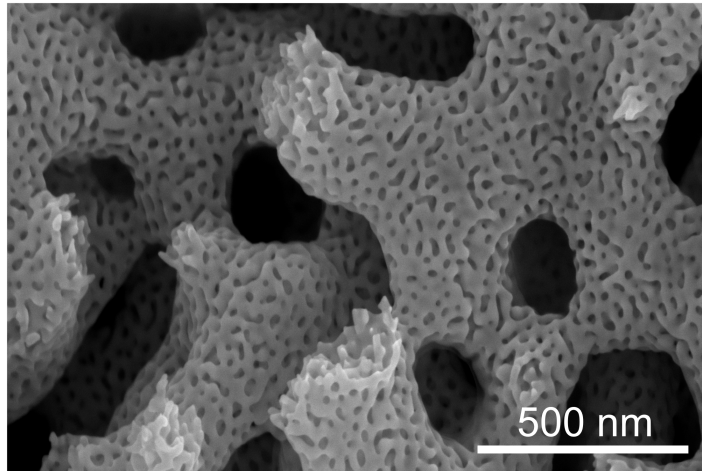


Figure 1.1: Exemplary scanning electron micrograph of hierarchical nanoporous gold. Fractured ligaments are clearly recognizable.

The various synthesis methods for this type of *hierarchical nanoporous metal by dealloying* can be divided into three classes: 1. templating of the topmost hierarchy level, supplemented by dealloying for the insertion of lower levels; 2. creation of a hierarchical structure by one-step dealloying; 3. two dealloying steps for the implementation of the upper and the lower hierarchy level, linked by an annealing step to increase the length scale of the upper level.

Two examples of the first class are the templating by 3D printing for the synthesis of hierarchical nanoporous gold (HNPG) [39] and hierarchical nanoporous copper [40]. As starting material for the 3D printing, a silver-gold composite ink or a manganese-copper composite ink is used, respectively. The lowest hierarchy level is inserted by dealloying, that is the removal of the less noble element, silver or manganese, respec-

tively. In both examples, the evaporation of the solvent creates a third hierarchy at intermediate level. This additional structural level consists of pores with a diameter of several μm . However, it is rather less pronounced [39, 40]. Another example of templating is a hierarchical nanoporous gold foam which is synthesized by blending of silver and gold powder with sodium chloride (NaCl). The dissolution of the NaCl, whose crystal size is much larger than the metal particle diameter, creates the topmost hierarchy. Here again, an intermediate, pore-like structural level is formed, most probably due to the evaporation of water. The lowest hierarchy is generated by dealloying [41]. Other approaches use polystyrene beads as template. In one case, a silver-gold coating is deposited on the surface of the polystyrene beads [42]. In another case, the polystyrene spheres are used for the generation of an inverse template made by silica, which is subsequently filled with a silver-gold alloy by electrodeposition [43]. This list is completed by two procedures which use porous structures made of polymers as a template. The first example describes the utilization of cellulosic fibers, denoted as *Washi paper*. This template is infiltrated by a slurry of silver-gold powder and water-soluble binder. The complete surface of the fibers is covered by metal particles. Sintering then decomposes the organic material and forms a porous alloy structure [44]. The other procedure [45] is based on a polymerized bijel. A bijel is formed by spinodal decomposition, driven by reduction of the surface area. Aside from the length scale, the structure of one of the phases of a bijel is not dissimilar to a nanoporous metal formed by dealloying [46]. The polymerized phase of the former bijel is impregnated with a solution of gold salt. Afterwards, heating pyrolyzes organic compounds. In this case, a hierarchical structure is generated solely by the template, without subsequent dealloying. Alternatively, an impregnation with a solution of silver salt can be added to the synthesis, which enables subsequent dealloying for the insertion of a lower hierarchy [45].

The second class covers hierarchical nanoporous metals produced by a single-step dealloying. This class can be subdivided into two subclasses, based on the precursor alloy: heterogeneous, two-phase alloys, and homogeneous single-phase precursor alloys. Several procedures starting from aluminum alloys can be classified into the first subclass: hierarchical nanoporous gold based on $\text{Al}_{80}\text{Au}_{20}$ or $\text{Al}_{70}\text{Au}_{30}$ [47], hierarchical nanoporous palladium based on $\text{Al}_{80}\text{Pd}_{20}$ [48], and hierarchical nanoporous nickel based on $\text{Al}_{80}\text{Ni}_{20}$, $\text{Al}_{75}\text{Ni}_{25}$, or $\text{Al}_{68.5}\text{Ni}_{31.5}$ [49]. Before the one-step dealloying procedure, an Al-phase coexists next to a more noble phase (Al_2Au -phase; Al_3Pd -phase; Al_3Ni - and Al_3Ni_2 -phase, in the respective procedure). During the dealloying, first the less noble Al-phase oxidizes under formation of large channels, which represent the upper hierarchy level. Immediately afterwards, the more noble phase is dealloyed, leading to the formation of the lower hierarchy level [47–49].

To give an example of the second subclass, hierarchical nanoporous palladium can be produced from $\text{Pd}_{30}\text{Ni}_{50}\text{P}_{20}$ metallic glass [50]. The evolution of hierarchical nanoporosity is attributed to different dissolution rates between phosphor and nickel. First, the oxidation of phosphor dominates, and large pores are generated. Later, the dissolution of nickel inserts the lower hierarchy level [50]. In another study [51], hierarchical nanoporous silver is produced from $\text{Ag}_x\text{Na}_{1-x}\text{Cl}$. Strictly speaking, the nanoporous structure does not evolve by dealloying, but by reduction-induced decom-

position. The dissolution of NaCl creates the upper hierarchy, while the dissolution of chloride inserts the lower one [51]. Apart from the above procedures, in some cases the reason for the development of a hierarchical nanoporosity is not clearly identified. One example is the fabrication of hierarchical nanoporous gold from a Au-Cu-alloy [52], which may be caused by an inhomogeneous composition. Another example is the production of hierarchical nanoporous palladium by dealloying of $\text{Cu}_{85}\text{Pd}_{15}$. Both hierarchy levels evolve simultaneously during the primary dealloying. As reason for the emergence of the two hierarchy levels, the "local structure collapse due to low solid fraction" is proposed [53, 54].

The third class refers to hierarchical nanoporous metals which are synthesized by two separate dealloying steps, linked by an annealing step. One advantage of this variant is the precise tuning of the upper hierarchy length scale by annealing time and/or temperature. A first example is given by Ding & Erlebacher [55], who deposit a silver layer on annealed nanoporous gold. After another annealing step for homogenization, a 2nd dealloying inserts the lower hierarchy level [55]. Qi & Weissmüller [12] introduce another strategy, which is based on the partial dealloying of a silver-rich AgAu-alloy. During the 1st dealloying, a certain share of the silver content is dissolved. Annealing then leads to the coarsening of the structure. In a 2nd dealloying step, the lower hierarchy is inserted, and the silver is removed completely [12]. This procedure is illustrated by Figure 1.2, which anticipates the synthesis method used in this study. At this point, it simply describes the basic process.

Qi & Weissmüller [12] start from a $\text{Ag}_{95}\text{Au}_5$ precursor alloy. Their procedure is adopted by several studies. In detail, the composition of the precursor alloy is varied to $\text{Ag}_{80}\text{Au}_{19}\text{Pt}_1$ [56], $\text{Ag}_{95}\text{Au}_5$ [44], $\text{Ag}_{85}\text{Au}_{15}$ [57], $\text{Ag}_{93}\text{Au}_7$ [58], $\text{Ag}_{95}\text{Au}_5$ [59], $\text{Ag}_{85}\text{Au}_{15}$, $\text{Ag}_{80}\text{Au}_{20}$, $\text{Ag}_{75}\text{Au}_{25}$, and $\text{Ag}_{70}\text{Au}_{30}$ [60], $\text{Ag}_{90}\text{Au}_{10}$ [61], and $\text{Ag}_{85}\text{Au}_{15}$ [62]. By two of them, the two-step dealloying is combined with templating, which results in the creation of nanoporous gold with three levels of hierarchy [44, 59]. Finally, a two-step dealloying does not ultimately require a partial dealloying. The consecutive removal of two different alloying elements is an alternative, as shown for the synthesis of hierarchical nanoporous nickel based on $\text{Mn}_{70}\text{Cu}_{15}\text{Ni}_{15}$ [63]. During the 1st dealloying, manganese is dissolved. After the 1st dealloying, which has removed most of the manganese content, the structure is annealed. In the course of the 2nd dealloying, copper dissolves despite its higher reduction potential, because nickel is passivated under the respective conditions [63–65].

1.2 Parametrization of the length scale

Essential parameters for the structural characterization are the ligament size and the solid fraction. Examinations on nanoporous metals typically employ scanning electron microscopy (SEM) for the characterization of the nanoporous structure. While the solid fraction is difficult to be determined by SEM [66], the presentation of SEM images frequently comes along with the statement of a ligament size L [58, 61, 67–75]. Normally, the ligament diameter L is measured by manually drawing lines in the SEM micrograph. In very few cases the statement is added that the diameter of the ligaments is measured at the thinnest position of the ligaments [61, 72, 76]. However, the

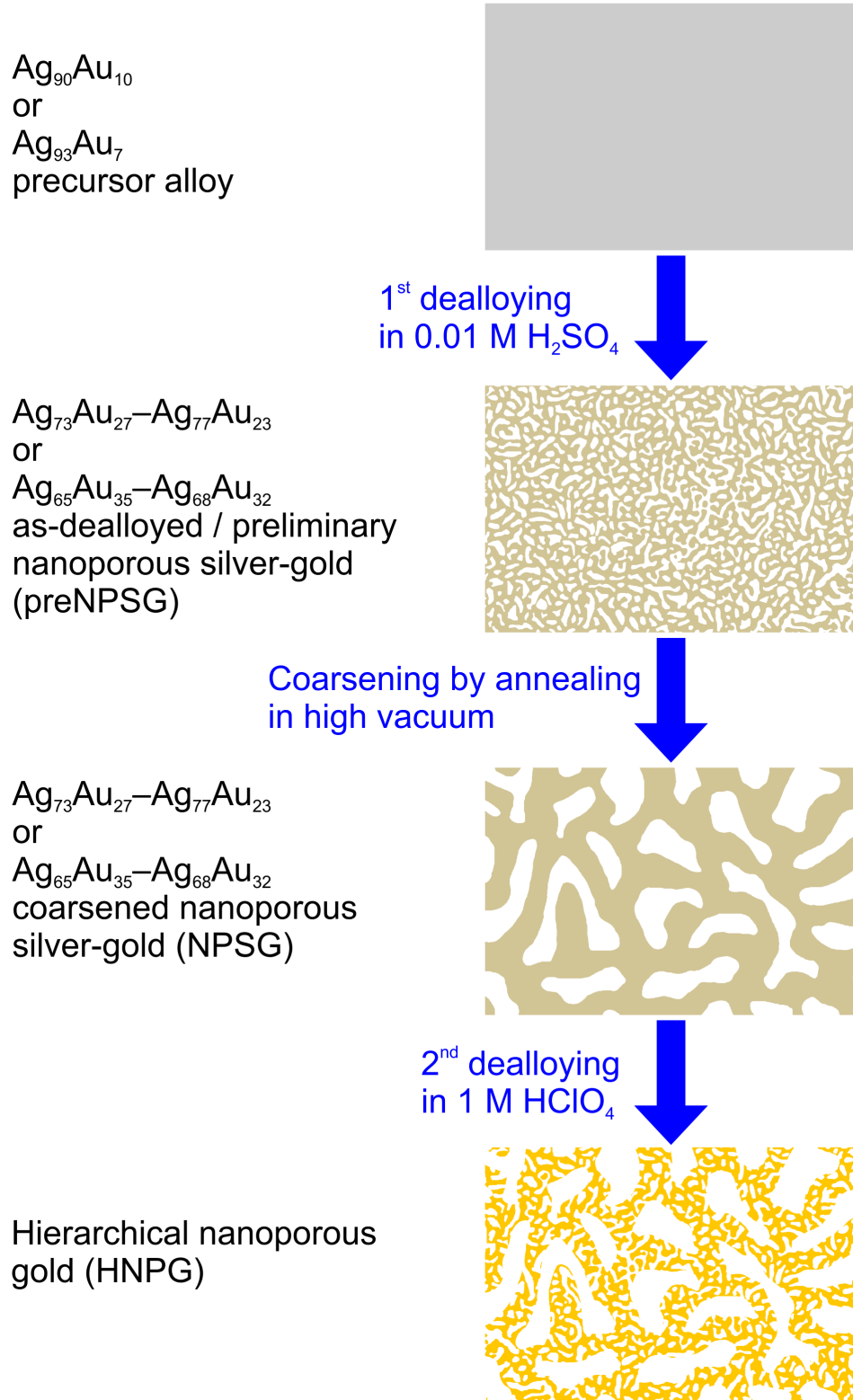


Figure 1.2: Schematic illustration of the synthesis of hierarchical nanoporous gold. The procedure consists of three basic steps: 1st dealloying, coarsening and 2nd dealloying. This illustration presents the synthesis used in this study. The variant of the synthesis, which starts from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy, is identical to the procedure used by Shi *et al.* [58].

selection of the ligament's necks as the measured distance occurs automatically if the analysis is done by hand. While this method is comparatively easy and straightforward, a disadvantage is a certain degree of uncertainty due to the manual selection of the ligaments to be measured. McCue *et al.* [66] collect SEM images in literature and reevaluate them with an automated image analysis software. The comparison between the ligament diameter yielded by their reevaluation and the ligament diameter stated in the respective study reveals a deviation in a scattered manner. Although this variance is partly due to different approaches used for the determination of the ligaments size in the studies collected by McCue *et al.* [66], there still remains some discrepancy.

Other methods for the evaluation of a SEM image with respect to a characteristic ligament size are, as already mentioned above, automated image analysis software [66, 77–79], and furthermore the fast Fourier transformation of the scanning electron micrograph [80, 81]. The latter one is applied to transmission electron microscopy images as well [80, 82–84]. Tomographic reconstructions of nanoporous metals, either by electron nanotomography [85] or by focused ion beam tomography [76, 86], often measure the ligament size by means of granulometry. Every voxel of the solid phase is assigned to the greatest sphere which can be fitted into the solid phase and which contains this voxel. Subsequently, a volumetric average over all voxels is calculated [87]. The resulting parameter, which is denominated as mean ligament thickness, L_G , must necessarily be higher than L , because the latter refers to the smallest diameter along the ligament axis. Compared with the ligament diameter, averaged over the ligament axis, L_G is higher as well, if the ligament shows curvature [88]. This last-mentioned method, which measures the diameter as distance to the ligament center, finds application in the analysis of tomographic reconstructions as well [89]. Finally, the usage of the inverse specific surface area is another alternative for the determination of a length scale [90, 91]. In the analysis of 3D porous structures, the utilization of a consistent parameter for the characterization of the length scale has not prevailed.

An alternative to tomography is the creation of nanoporosity by simulation. Advantages are the free adjustability of structural parameters such as solid fraction and length scale, and the possibility to analyze larger sample volumes. One possible method is the simulation of a spinodal decomposition by a phase-field model, whereat the generated structures are subsequently used for the simulation of mechanical deformation [92–94]. Another method is the creation of two-phase structures by a level cut of Gaussian random fields [95–98]. This model is also referred to as leveled-wave model. Respective structures are applied for the simulation of deformation [58], coarsening processes [99] or relaxation processes [75]. A Gaussian random field $f(\vec{x})$ is generated by the superposition of a total number of N waves. The wave number $|\vec{q}_j| = q_0$ of all waves is identical and constant. In contrast, the waves differ from each other in their direction and phase ϕ_j in a random manner. As a consequence, the random field function $f(\vec{x})$ shows a stochastic, 3-dimensional behavior [95, 98]:

$$f(\vec{x}) = \sqrt{\frac{2}{N}} \sum_{j=1}^N \cos(\vec{q}_j \cdot \vec{x} + \phi_j). \quad (1.1)$$

The generation of a 3-dimensional structure is possible by a cut with ξ as threshold. Space becomes pore if it fulfils the condition according to which $f(\vec{x})$ is larger than

the threshold ξ . If on the other hand $f(\vec{x}) \leq \xi$, then the space becomes solid. The resulting structure resembles a stochastic foam, such as a nanoporous metal. This type of structure can be described as a function $T(\vec{x})$, which takes the values 1 or 0, referring to solid or pore. For the determination of a characteristic length scale of this structure, an autocorrelation function is employed. Soyarslan *et al.* [98] compute several expressions of the autocorrelation function of $T(\vec{x})$ for various solid fractions [98]. In addition to that, Soyarslan *et al.* [98] examine the autocorrelation function of the random field function $f(\vec{x})$, which is also described by an analytical solution:

$$C(r) = \langle f(\vec{x}_1)f(\vec{x}_2) \rangle = \frac{\sin(q_0 r)}{q_0 r}. \quad (1.2)$$

The autocorrelation function $C(r)$ thus shows a simple dependency on the shift $r = |\vec{x}_1 - \vec{x}_2|$. For the purpose of illustration, this function is presented in Figure 1.3. The first maximum is most pronounced. It is located at a position of

$$r_m = 1.23 \frac{2\pi}{q_0}. \quad (1.3)$$

Consecutive maxima follow at distances of about $2\pi/q_0$. The position of the maxima is dictated by the fundamental properties of the sine function which shows maxima at $\pi/2$, $5\pi/2$, $9\pi/2$ and so on. On a structural level, a maximum of the autocorrelation function can be interpreted as a characteristic length scale. In their evaluation of the autocorrelation function of $T(\vec{x})$, Soyarslan *et al.* [98] find that it is almost identical to $C(r)$, which is the autocorrelation function of $f(\vec{x})$, and which is presented in Figure 1.3. For $T(\vec{x})$, which replicates an open-cell foam, a maximum of the autocorrelation function can be regarded as a characteristic distance of the ligaments. The solid fraction, which is incorporated into the investigation by Soyarslan *et al.* [98], shows a minor effect on the autocorrelation function, and no effect on the peak position. Thus, the following expression can be derived for the relation between q_0 and ligament distance (of 1st order), $\tilde{L}$, also called ligament spacing:

$$\tilde{L} = 1.23 \frac{2\pi}{q_0}. \quad (1.4)$$

Initially, this result is restricted to the leveled-wave model. It enables the determination of a distinctive size indicator using the wave number q_0 , which is inherent in the model [98]. For the purpose of structural description, $\tilde{L}$ is a desirable parameter. However, it cannot be determined from a SEM image. Although it is possible to measure the distance between ligaments in a SEM image, this length only considers the 2-dimensional part of the distance, while the real, 3-dimensional ligament distance remains unknown. Since SEM is ubiquitous, versatile and relatively less expensive with respect to experimental resources, the establishment of a link between the ligament distance or ligament spacing $\tilde{L}$ and the ligament size L determined by SEM is a promising approach towards improved methods for the structural characterization of nanoporous metals.

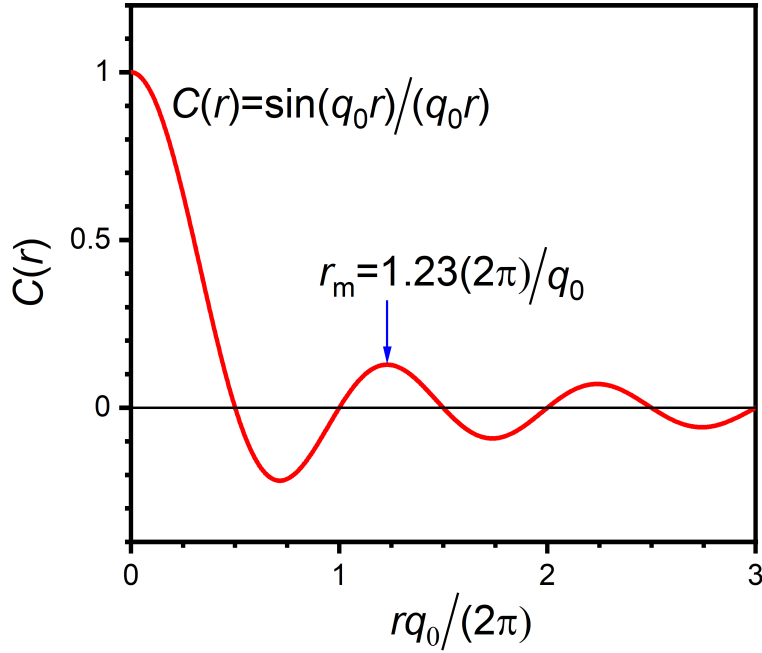


Figure 1.3: Autocorrelation function $C(r)$ of the random field function $f(\vec{x})$. The shift r is normalized to the wavelength $\lambda = 2\pi/q_0$. The first maximum is located at $r_m = 1.23(2\pi)/q_0$, while consecutive maxima follow at distances of about $2\pi/q_0$ to the first maximum and to each other. Inspired by a similar graphic in [98].

1.3 Mechanical behavior of hierarchical nanoporous gold

The influence of structural parameters on the mechanical behavior of nanoporous gold was extensively studied in the last two decades. A detailed overview is beyond the scope of this introductory chapter. Instead, the reader is referred to Section 2.2. Nevertheless, for the purpose of familiarization with the motivation of this thesis a brief introduction to the mechanical behavior of hierarchical nanoporous metals is provided below.

From the studies on hierarchical nanoporous metals listed above, hardly any investigation examines the mechanical behavior. This drawback is at least partly due to the difficulty of the production of macroscopic and mechanically stable samples. The only exception is a study by Shi *et al.* [58] which analyzes the connections between structural and mechanical parameters in hierarchical nanoporous gold. Their investigation serves as a basis for this thesis with respect to sample production and mechanical characterization. Relevant results are presented in Figure 1.4. The synthesis is based on the procedure established by Qi & Weissmüller [12], which is mentioned above, and which is illustrated by Figure 1.2. As precursor alloy, $\text{Ag}_{93}\text{Au}_7$ is used. After the 1st dealloying, the solid fraction is $\varphi = 0.31$ and the composition is $\text{Ag}_{74}\text{Au}_{26}$ – $\text{Ag}_{78}\text{Au}_{22}$. In Figure 1.4, which illustrates the procedure used in this study, a composition of $\text{Ag}_{73}\text{Au}_{27}$ – $\text{Ag}_{77}\text{Au}_{23}$ instead of $\text{Ag}_{74}\text{Au}_{26}$ – $\text{Ag}_{78}\text{Au}_{22}$ is stated, which is a negligible difference. Annealing temperatures employed by Shi *et al.* [58] are 300 °C, 400 °C or 500 °C, which leads to a coarsening of the structure in the 2nd step of the synthesis. During the 2nd dealloying, a

lower hierarchy is inserted into the structure, representing the 3rd step of the procedure. Parameters during the last step are not varied, which results in a constant lower level ligament size L^L of 15 nm for all samples. The upper level ligament size L^U is varied according to the annealing temperature. Respective values are 45 nm, 110 nm or 180 nm for 300 °C, 400 °C or 500 °C; they are inserted into Figure 1.4. It is worth mentioning that the ligament size L of coarsened nanoporous silver gold (NPSG) is identical to the upper level ligament size L^U of hierarchical nanoporous gold (HNPG) in each case. Mechanical compression tests are conducted both on NPSG and on HNPG. As a result of the examination of the stress-strain curves, the Young's modulus E is detected against the solid fraction φ , as shown in Figure 1.4. During the mechanical test, the solid fraction increases. Every line of connected datapoints in Figure 1.4 refers to one sample. Hierarchical nanoporous gold starts at a lower solid fraction compared with NPSG. Accordingly, data values for HNPG are located in the left half of the graphic. Based on these results, several conclusions can be drawn [58]:

- Coarsening results in a severe decrease of the Young's modulus of nanoporous silver gold. If the ligament size is larger, stiffness values for NPSG are lower. As a possible explanation, the reduction of the connectivity during coarsening is proposed, in accordance with previous studies [99, 100]. A more detailed description of the issue is presented in Subsection 2.2.4.
- A direct transfer of this sequence, according to which larger ligament sizes are associated with lower stiffness values, to HNPG seems reasonable, since the upper level structure is not suspected to change during the 2nd dealloying. However, HNPG shows a different dependence on the upper level ligament size L^U . Comparable with NPSG, the Young's modulus is lowest for the sample annealed at 500 °C in the 2nd synthesis step, which results in the highest L^U of 180 nm. In contrast to NPSG, HNPG annealed at 300 °C in the 2nd synthesis step features lower stiffness values than HNPG annealed at 400 °C. As a possible explanation, Shi *et al.* [58] point out the role of dangling ligaments, which can occur if the ratio between upper and lower level ligament size is too small. The load-bearing share of the structure can be reduced, and the risk of a complete disconnection is existent. The respective sample exhibits a L^U of 45 nm and a L^L of 15 nm. Consequently, the ligament size ratio is 3. The emergence of a ligament size ratio effect is possible for this ratio [101].
- With respect to the course of the Young's modulus of HNPG as a function of the solid fraction, Shi *et al.* [58] notice a good reproduction by an advanced version of the Roberts-Garboczi scaling law [98, 102, 103]. This law is modified in such a way that it can be applied to nanoporous materials with several hierarchy levels. The prediction of the Young's modulus according to this law is inserted into Figure 1.4. Additional information is given in Subsection 2.2.2.
- Although the course of the Young's modulus of HNPG can be described well by a modified Roberts-Garboczi-law, the measured values are lower than calculated by this scaling law. The mismatch concerning the absolute level is observable for NPSG, too. It can thus be concluded that HNPG deviates from the respective scaling law for the same reason as NPSG. As pointed out above, a decline of the connectivity of NPSG during coarsening is a possible explanation for the size-

dependent stiffness. According to this explanation, the connectivity of NPSG annealed at 300 °C, and correspondingly the upper level connectivity of HNPG, is already substantially reduced. In Subsection 2.2.2 it is demonstrated that the Roberts-Garboczi-law for unimodal nanoporous materials provides a good reproduction of the Young's modulus of nanoporous gold in many studies. The discrepancy observed by Shi *et al.* [58] is one of several exceptions. Whether this observation is related to a reduced connectivity still needs to be verified.

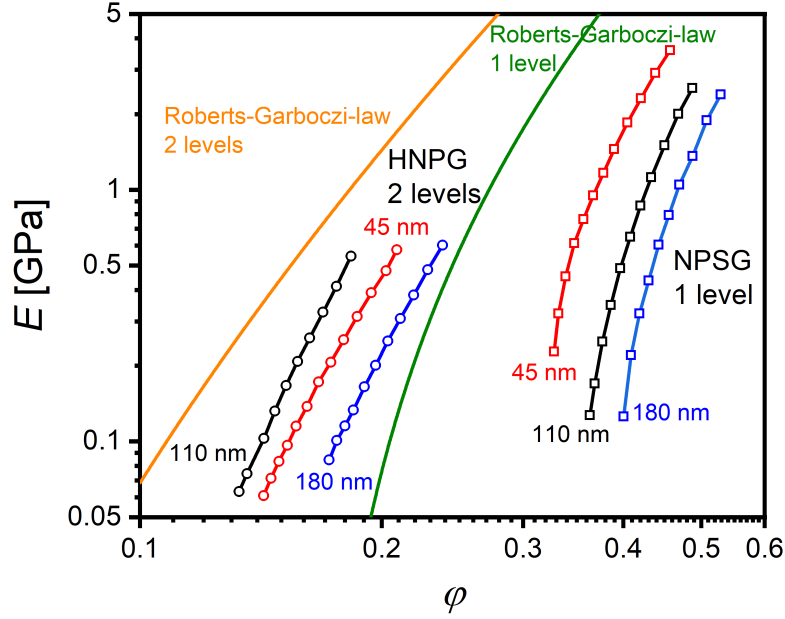


Figure 1.4: Previous results for structure-mechanical interactions in hierarchical nanoporous gold. The Young's modulus E of nanoporous silver gold (NPSG) and hierarchical nanoporous gold (HNPG) is depicted against the solid fraction ϕ . Values for NPSG are on the right side of the graphic, values for HNPG are on the left side. During the annealing step, the samples are annealed at 300 °C (red), 400 °C (black) and 500 °C (blue), which adjusts the ligament size of NPSG and correspondingly the upper level ligament size of HNPG, L^U , to 45 nm, 110 nm or 180 nm. The lower level ligament size L^L of HNPG is 15 nm for all HNPG samples. Solid lines depict E according to the modified Roberts-Garboczi-law for one as well as for two levels. The graphic is adopted from [58].

1.4 Research objectives and experimental approaches

The main objective of this thesis is the analysis of the influence of structural parameters on the mechanical characteristics in hierarchical nanoporosity. As exemplary test material, hierarchical nanoporous gold (HNPG) is examined. Within this thesis, three different topics are considered: These are the generation of HNPG, the structural characterization of HNPG and the mechanical characterization of HNPG. All of these fields are related to each other, since the structural parameters are varied to detect an impact on the mechanical behavior. Structural parameters need to be defined and determined.

At this point, four structural parameters are specified; these are the ligament size on upper and lower hierarchy level and the solid fraction on upper and lower hierarchy level. Two related parameters, which emerge from these, are the total solid fraction and the ligament size ratio between upper and lower hierarchy level ligament size (ligament size ratio). Other structural parameters, which are assumed to be of importance for the mechanical characteristics, are the connectivity on the upper hierarchy level and the connectivity on the lower hierarchy level [58, 98]. The approach followed in this thesis is to vary certain structural parameters of HNPG while keeping other structural parameters constant, and to investigate the impact on the mechanical behavior. HNPG is synthesized on the basis of the three-step procedure presented in Figure 1.2 [58], which is modified in many ways to enable the adjustment of different structural features. The separation of the influence of the lower hierarchy level structure from the influence of the upper hierarchy level structure requires a separate investigation of nanoporous silver gold (NPSG), which represents a preliminary stage. As precursor alloy, $\text{Ag}_{90}\text{Au}_{10}$ is selected, in contrast to the $\text{Ag}_{93}\text{Au}_7$ precursor alloy used in [58]. In this regard, the intent is to increase the solid fraction of NPSG and, relatedly, the upper level solid fraction of HNPG. At this point, the objective of the investigation is not restricted to hierarchical nanoporosity. Instead, the aim is to investigate a possible dependence of the connectivity evolution during coarsening on the solid fraction. Hierarchical nanoporous gold can be affected by this effect as well.

The mechanical behavior is analyzed by macroscopic compression tests. Three different methods are employed for the structural analysis: macroscopic mass and volume measurements for the determination of the solid fraction φ , scanning electron microscopy (SEM) for the morphological characterization and for the determination of the ligament size/diameter L , and small-angle X-ray scattering (SAXS) as well as ultra-small-angle X-ray scattering (USAXS) for the determination of the ligament spacing $\tilde{L}$ and the specific surface area α . The comparison between ligament size L and ligament spacing $\tilde{L}$ or, more generally, the comparison between SEM and SAXS/USAXS represents an additional topic, which affects the structural characterization of HNPG, but which is not restricted to hierarchical nanoporosity. Furthermore, the examination by SAXS/USAXS allows further conclusions about the nanoporous structure of HNPG and NPSG.

1.5 Outline of the thesis

An overview of the relevant theory is given in Chapter 2. First, an introduction to the generation of nanoporosity by dealloying is presented. The next section explains the theoretical basics of the mechanical behavior of nanoporous metals. Starting with the Gibson-Ashby-model, this part continues with more recent approaches such as the connectivity. Finally, the last section introduces the very basics of small-angle X-ray scattering (SAXS), before proceeding with the application of SAXS to nanoporous structures.

At the beginning of Chapter 3, the synthesis of hierarchical nanoporous gold is described. Every substep of the procedure is considered separately, and the determination of the residual silver concentration and the solid fraction is specified in detail.

Diagrams, which depict the electrochemical procedure, can be found in this section. Subsequently, the analysis by SEM and the implementation of focused ion beam (FIB) is outlined. Descriptions of the mechanical analysis and of the analysis by SAXS and USAXS are presented afterwards.

The experimental results of this thesis are presented in Chapter 4 and Chapter 5. Supported by SEM images, Chapter 4 first gives an overview of all synthesis variants which are implemented for the variation of structural parameters in HNPG. Table 4.1, which summarizes various control variables, solid fraction data and length scale values resulting from the structural analysis, is already recommended at this point. Afterwards, SAXS and USAXS scattering data are introduced. The procedure for the analysis of the scattering data is described there, because the analysis is developed from the scattering data. Length scale data are then presented and evaluated. A subsection focuses on the determination of the specific surface area. The majority of the results of this chapter is published in [61].

Chapter 5 is designated for the investigation of the mechanical behavior of HNPG. Certain datasets are compared with each other to assess the impact of selected structural parameters on the mechanical behavior. First, the effect of a variation of the upper level ligament size is examined. Two subsequent sections focus on a variation of the lower level ligament size, whereat the method for the adjustment of the lower level ligament size is different. In the discussion, the measured values are evaluated by means of scaling laws. A separate subsection discusses the stiffness decrease during coarsening.

The major results are summarized in Chapter 6, followed by an outlook. In the Appendix, a complete compilation of all mechanical tests is attached, whereas in Chapter 5 selected measurement series are depicted.

Chapter 2

Theoretical background

2.1 Nanoporous metals by dealloying

2.1.1 Creation of nanoporosity

Dealloying is the selective dissolution of one or more components from an alloy under formation of a nanoporous structure. Electrochemical dealloying, which is driven by different reduction potentials of the components, can be distinguished from liquid metal dealloying, caused by a negative enthalpy of mixing of one of the components in a molten metal bath or molten salt bath. The electrochemical dealloying in turn is differentiated into dealloying by free corrosion, which is carried out without an applied potential, and dealloying by an applied potential [16, 27, 33, 104]. The latter one is the method used for the synthesis of hierarchical nanoporous gold. During this type of dealloying, atoms of the less noble element oxidize and dissolve. The dealloying front proceeds layer by layer. Meanwhile, atoms of the more noble element diffuse along the alloy/electrolyte interface and agglomerate under formation of a mound, where the dealloying is stopped. In regions alongside these mounds, the dealloying front moves on and undercuts the mounds, which, in the end, leads to the creation of ligaments. The surface diffusion of the more noble element is a necessary condition for dealloying, along with an alloy with miscible components, and a difference in the reduction potential [16, 33]. After the passage of the dealloying front, known as primary dealloying [15], a nanoporous structure has evolved. The surface of the ligaments consists of a layer of passivating gold atoms, while the interior still has the original composition [105]. Subsequent to the primary dealloying, the secondary dealloying occurs, which is characterized by coarsening, combined with a further decrease of the concentration of the less noble element. The coarsening is driven by surface diffusion [15, 82]. If a small amount of platinum is added to a gold-silver alloy, the ligament size of the synthesized nanoporous metal is clearly reduced compared with a gold-silver alloy, while the residual silver content is increased. This effect is attributed to the suppression of surface diffusion and, accordingly, coarsening by the platinum [15, 56, 106].

With respect to the electrochemical dealloying by an applied potential, two syn-

thesis parameters are of significant importance: the critical potential for dealloying E_c , and the parting limit or dealloying threshold P_l . E_c indicates the dealloying potential below which the dealloying stops, recognizable by a low dealloying current. To maintain the dealloying process, the potential must exceed E_c . To be more specific, two definitions are available for the critical potential for dealloying, these are the massive dealloying potential (MDP) and the loss of passivation potential (LPP). In this thesis, the massive dealloying potential is used to determine E_c . According to the definition of the MDP, E_c is determined by the recording of a polarization curve. E_c is then the potential where a certain value for the current density is reached. By contrast, during the determination of the LPP a constant potential is applied. In this case, E_c is the lowest potential where a steady dealloying current is still measurable [12, 107–110].

The other parameter mentioned above, the parting limit P_l , refers to the composition of the alloy which is necessary to avoid the complete passivation of the surface. In case of a gold-silver alloy, the parting limit amounts to a portion of 0.55 silver. If the silver content is lower, the dealloying stops [16, 27, 109, 111]. Kinetic Monte Carlo simulations reproduce this value [112, 113].

2.1.2 Coarsening of nanoporous metals

As mentioned above, the underlying process of electrochemical coarsening, which takes place during the secondary dealloying, is surface diffusion of the more noble element [82]. This type of coarsening increases the ligament size from about 5 nm after the primary dealloying [82] to typically about 30 nm [15, 113]. A further increase to ligament sizes of several hundreds of nanometers is possible by annealing-induced coarsening [74, 86, 114], which is driven by surface diffusion, too [91, 115]. The increase of the length scale is the consequence of a reduction of the surface energy. In this respect, coarsening is an example of the Plateau-Rayleigh instability, which explains the breaking of a jet into droplets. Driven by gradients in the surface chemical potential, material moves away from convex regions. This results in the disappearance of small ligaments, which pinch off, before they retract [109, 116, 117].

2.2 Mechanical behavior of nanoporous metals

2.2.1 Gibson-Ashby-model

For the classification of mechanical parameters, the Gibson-Ashby-model [118–120] is widely used in the literature on nanoporous metals [68–70, 98, 114, 121–123]. The corresponding set of equations applies to cellular foams of which open-cell foams are of interest for the comparison with nanoporous materials. Open-cell foams are characterized by a truss structure, with recurring cells being formed by struts, connected by knots. These materials, which feature length scales of millimeters or micrometers, can be made of polymers, ceramics or metals, whereat polymer foams are most frequently investigated. Solid fractions vary in a wide range between 0.001 to 1.0, whereat a solid fraction above 0.3 changes the character of the material to a solid phase with holes [118, 120, 124, 125]. If a hierarchy is inserted into the structure, the solid fraction can be reduced to 0.0001 [126]. The following consideration is based on a unit cell

presented in Figure 2.1. The cubic cell features a length, width and height k , while the struts exhibit a width and height t . If a vertical force F acts on the cell, the horizontal struts bend and deform with a maximum displacement δ . The complete cell will deform by 2δ in vertical direction. It is important to note that the behavior is bending-dominated, in contrast to a stretch-dominated behavior. The displacement δ obeys the proportionality [118, 120]

$$\delta \sim \frac{Fk^3}{E_s I} \quad (2.1)$$

where E_s is the Young's modulus of the solid material and I is the 2nd moment of area of the cross section of the struts, which is determined by [127]

$$I = \frac{t^4}{12}. \quad (2.2)$$

The following proportionality can be determined for the solid fraction φ :

$$\varphi \sim \frac{t^2}{k^2}. \quad (2.3)$$

These equations are combined with expressions for the stress $\sigma \sim F/k^2$, for the strain $\epsilon = 2\delta/k$ and for the Young's modulus of the cell $E \sim \sigma/\epsilon$. A combination of all equations yields a dependence of the Young's modulus on the solid fraction,

$$E \sim E_s \varphi^2. \quad (2.4)$$

A continuation until $\varphi = 1$ finally yields

$$E = E_s \varphi^2 \quad (2.5)$$

which is the Gibson-Ashby-law for the Young's modulus of open-cell foams [118–120]. The proportionality factor of 1 is confirmed by experiments [118]. As long as the deformation is bending dominated, metallic microlattices with embedded structural hierarchy follow this law [126]. Other foams with embedded structural hierarchy, e.g. carbon nanotube foams [128], possess a deformation behavior with the proportionality $E \sim \varphi^3$ instead of $E \sim \varphi^2$, which is attributed to an inefficient load transfer between ligaments [126]. For the determination of the yield strength σ_y , a similar approach is available. The plastic section modulus of the cross section of the struts Z_p is

$$Z_p = \frac{t^3}{4}. \quad (2.6)$$

The plastic moment M_p is dependent on Z_p and on the yield strength of the solid material, $\sigma_{y,s}$ [129, 130]:

$$M_p = \sigma_{y,s} Z_p. \quad (2.7)$$

For the course of the plastic moment, the following relation is valid:

$$M_p \sim F k. \quad (2.8)$$

Assembling with equations presented above leads to an expression for the dependence of the yield strength on the solid fraction:

$$\sigma_y \sim \sigma_{y,s} \varphi^{1.5}. \quad (2.9)$$

By comparison with experiments, the factor of proportionality is found to be 0.3 [118, 131]. Therewith the Gibson-Ashby-law for the yield strength of open-cell foams is [118–120]

$$\sigma_y = 0.3 \sigma_{y,s} \varphi^{1.5}. \quad (2.10)$$

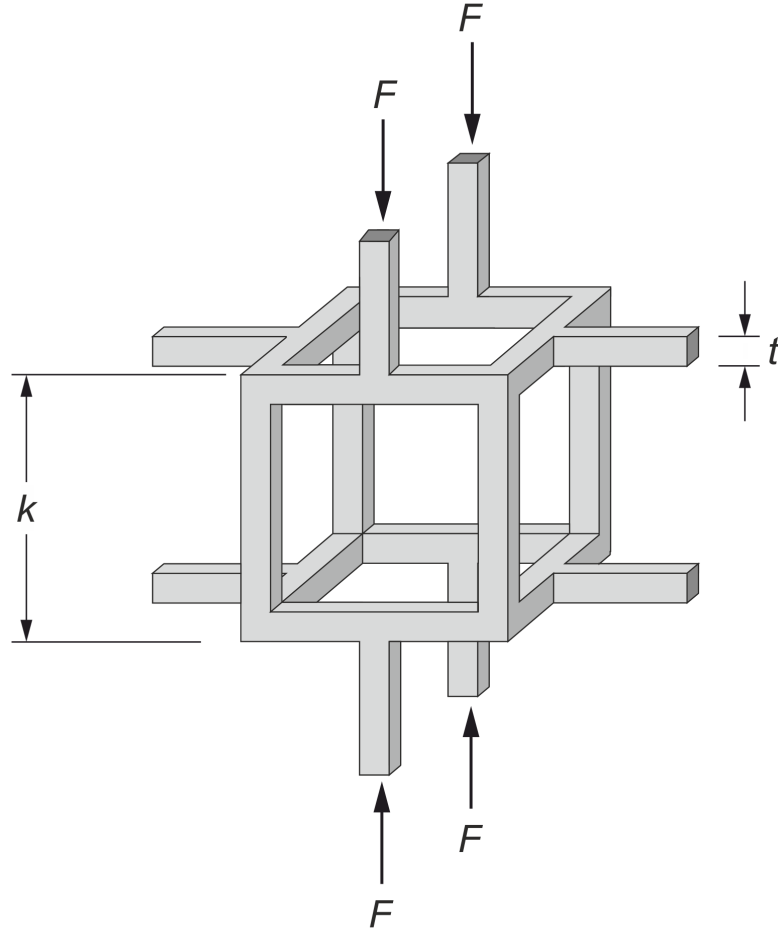


Figure 2.1: Structure of a unit cell as recurring component of an open-cell foam, used in the Gibson-Ashby-model. Redraw after [120].

2.2.2 Roberts-Garboczi-law

In a first study, Roberts & Garboczi [102] present theoretical measurements on the elastic behavior of closed-cell foams. The results are obtained by examinations on structures generated through Voronoi tessellations or Gaussian random fields (see Section 1.2). Closed-cell foams differ from open-cell foams insofar as they consist of faces instead of struts. For closed-cell foams, Gibson & Ashby [118] propose a proportionality

$E/E_s \sim \varphi^n$ with $n = 3$, if bending is the dominant deformation mechanism. However, they also argue that in closed-cell foams, the solid tends to accumulate in cell edges, so that closed-cell foams are similar to open-cell foams, described by Equation 2.5. Experiments on closed-cell foams show a proportionality of $1 < n < 2$, which suggests that face-stretching, instead of bending, is the deformation mechanism [102, 132]. Roberts & Garboczi [102] find that their values for the Young's modulus are best described by the equation

$$E = E_s \left(\frac{\varphi - p_0}{1 - p_0} \right)^w \quad (2.11)$$

with $p_0 \approx -0.15$ and $w \approx 2$. In this equation, p_0 is a fitting parameter with no physical meaning [102]. The fact that p_0 is negative leads to an increase of E , compared with Equation 2.5. In a second study, Roberts & Garboczi [103] note that Equation 2.11 is equally applicable to other structure types generated by Gaussian random fields, including single-cut Gaussian random fields, which are more comparable to nanoporous metals. In the same study, with respect to the dependence of the Poisson's ratio ν to the Poisson's ratio of the solid material, Roberts & Garboczi [103] notice a relationship to the percolation limit. The percolation limit is the solid fraction below which the structure becomes disconnected. Hodge *et al.* [70] mention the approach of Roberts & Garboczi [102] in the context of the reduced stiffness of nanoporous gold in comparison with the Gibson-Ashby-law. In an investigation on single-cut Gaussian random fields, Soyarslan *et al.* [98] propose a modified version of the Roberts-Garboczi-law, which includes the percolation limit φ_0 into the scaling relation:

$$E \approx 2 E_s \left(\frac{\varphi - \varphi_0}{1 - \varphi_0} \right)^{2.5}. \quad (2.12)$$

This relation is found to give a good reproduction of the Young's modulus values generated by their model, but also of experimental values yielded by measurements on nanoporous gold. Like the original Roberts-Garboczi-law, this equation is empirical, i.e. it is modelled on the basis of measured values. The value of the percolation limit φ_0 is given as 0.16 [98]. This value is used throughout this thesis. Another indication of the percolation limit, which is also derived from single-cut Gaussian random fields, is 0.13. Other mathematical models for the generation of porous materials yield different percolation limits [103, 133]. A comparison of the Young's modulus estimated by the Gibson-Ashby-law and the modified Roberts-Garboczi-law, Equations 2.5 and 2.12, with experimental values measured on nanoporous gold is shown in Figure 2.2. For the Young's modulus E_s of massive gold, a value of 77 GPa is assumed [134], as in this entire thesis. The comparison reveals that the E of samples which are not annealed, marked by black or blue symbols, indeed shows a downward trend if the solid fraction falls below 0.35. This trend can be described well by the modified Roberts-Garboczi-law, and it indicates the disconnection of ligaments if the solid fraction approaches the percolation limit.

From Equations 2.5, 2.10 and 2.12, Shi *et al.* [58] derive an enhancement of the Roberts-Garboczi-concept with regard to the yield strength σ_y . They utilize an approach of Liu *et al.* [74] which introduces an effective solid fraction φ_{eff} . This parameter describes the share of ligaments which contribute to the mechanic response. Thus, the ratio $\varphi_{\text{eff}}/\varphi$ describes the share of ligaments which are connected; the forming of this

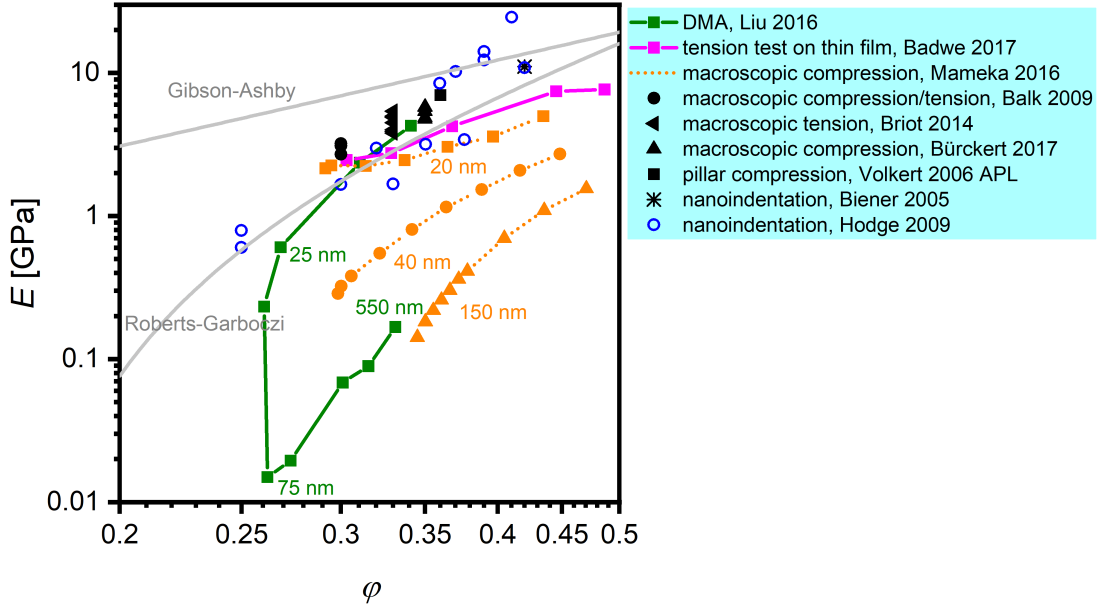


Figure 2.2: Compilation of Young’s modulus values of nanoporous gold from the literature against the solid fraction ϕ . Young’s modulus values E are determined by DMA [74], by tension tests on thin films [79], by the deformation of macroscopic samples [71, 73, 114, 123], by pillar compression [67], and by nanoindentation [70, 121]. E according to the Gibson-Ashby-equation, Equation 2.5, and E according to the modified Roberts-Garboczi-equation, Equation 2.12, are inserted. Dashed lines connect measurements on one single sample whose solid fraction increases during the compression test, while solid lines connect samples whose ligament size and solid fraction increase during annealing or during electrochemical coarsening. Black data points relate to as-dealloyed nanoporous gold with a ligament size between 15 nm and 100 nm. Data from the study by Hodge *et al.* [70] are based on a variety of synthesis routes, including annealing and the additional deposition of a silver coating. The ligament size varies between 50 nm and 250 nm. Samples analyzed by Liu *et al.* [74] first undergo a completion of dealloying, accompanied by a decreasing ϕ . After completed dealloying, the solid fraction increases, which indicates shrinkage.

ratio is one possible method for the determination of the connectivity [74]. If the Gibson-Ashby-law for the Young’s modulus, Equation 2.5, is considered to be valid, and if a deviation of the measured Young’s modulus E_{eff} from the expected Young’s modulus E_{GA} is explained by the disconnection of a certain share of ligaments, then the effective solid fraction can be determined by [74]:

$$\phi_{\text{eff}} = \sqrt{E_{\text{eff}}/E_s}. \quad (2.13)$$

Summarized, the comparison of Equation 2.13 and Equation 2.12, written with E_{eff} , yields an expression for the effective solid fraction as a function of the solid fraction. This term is subsequently inserted into Equation 2.10, written with ϕ_{eff} instead of ϕ . The modified Roberts-Garboczi-law for the yield strength is then [58]:

$$\sigma_y \approx 0.5 \sigma_{y,\text{loc}} \left(\frac{\phi - \phi_0}{1 - \phi_0} \right)^{15/8}. \quad (2.14)$$

The parameter $\sigma_{y,\text{loc}}$ is the local yield strength of the struts, which may differ from the yield strength of the bulk, $\sigma_{y,s}$. Furthermore, Shi *et al.* [58] develop advanced forms of Equations 2.12 and 2.14, which take into account the existence of multiple hierarchy levels. Their assumption is based on a generalized approach for the structure-dependent properties of hierarchical materials. For a hierarchical material with m hierarchy levels, a non-defined property P is dependent on the value of the bulk material, P_s , and on the same structure-dependent term $p(\varphi_j)$ including the solid fraction at the j -th hierarchy level φ_j :

$$P = P_s \prod_{j=1}^m p(\varphi_j). \quad (2.15)$$

If the Young's modulus of a nanoporous material with 2 hierarchy levels is considered, first Equation 2.12 is formed for the lower hierarchy level with solid fraction φ^L . The resulting value for the Young's modulus on the lower level is then inserted as E_s into the respective equation for the upper level with solid fraction φ^U :

$$E = 4E_s \left(\frac{\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{2.5} \left(\frac{\varphi^U - \varphi_0}{1 - \varphi_0} \right)^{2.5}. \quad (2.16)$$

A comparable procedure for the yield strength results in:

$$\sigma_y = \frac{\sigma_{y,\text{loc}}}{4} \left(\frac{\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{15/8} \left(\frac{\varphi^U - \varphi_0}{1 - \varphi_0} \right)^{15/8}. \quad (2.17)$$

Both approaches can be simplified and extended to a higher number of hierarchy levels, if the same solid fraction φ_E on every hierarchy level, $\varphi_j = \varphi_E = \varphi^{1/m}$, is assumed [58]. In this manner, equations can be summarized to

$$E = E_s 2^m \left(\frac{\varphi^{1/m} - \varphi_0}{1 - \varphi_0} \right)^{5m/2} \quad (2.18)$$

and

$$\sigma_y = \sigma_{y,\text{loc}} \frac{1}{2^m} \left(\frac{\varphi^{1/m} - \varphi_0}{1 - \varphi_0} \right)^{15m/8}. \quad (2.19)$$

2.2.3 Size effect on plasticity

Frequently used methods for the mechanical characterization of nanoporous or nanosized metals are nanoindentation [68–70, 121, 135], the compression of micropillars, fabricated by focused ion beam (FIB), using nanoindenters [67, 68], and macroscopic tensile or compression tests [71, 73, 114, 123, 136]. Other notable methods are the bending of beams or nanowires [137], and dynamic mechanical analysis (DMA), whereat this method determines the Young's modulus, but not the yield strength [74]. The display of values for the yield strength against the solid fraction of nanoporous or nanosized gold, presented in Figure 2.3(a), shows that the measured yield strength σ_y is in many cases more than one order of magnitude higher than estimated using the Equation 2.10. A clear correlation is not evident. For the assessment of σ_y with Equation 2.10, plotted in Figure 2.3(a), 200 MPa is assumed as the yield strength of massive gold, $\sigma_{y,s}$. This

estimate, which is often used in literature, e.g. [69, 121, 138], is in the upper range of possible yield strength values of gold which are dependent on the preceding treatment (annealing, cold working) [137]. [139] specifies a range of 55 MPa to 220 MPa. A different picture emerges if Equation 2.10 is rearranged and used to determine the yield strength of the solid material of the ligaments, $\sigma_{y,loc}$, which is already introduced in the preceding subsection:

$$\sigma_{y,loc} = \frac{\sigma_y}{0.3 \varphi^{1.5}}. \quad (2.20)$$

As can be seen from Figure 2.3(b), the local yield strength $\sigma_{y,loc}$ shows a negative correlation to the ligament size L . This downward trend for increasing ligament sizes is called smaller-is-stronger-effect and is demonstrated by several single examinations [68, 69, 74, 136, 140]. It is often described by a power law,

$$\sigma_{y,loc} = A L^u, \quad (2.21)$$

with A being a constant. As value of the exponent u , Volkert & Lilleodden [140] propose -0.61 , Briot & Balk [135] propose -0.55 , whereas Liu *et al.* [74] get a value of -0.34 . Hodge *et al.* [69] suggest a value of -0.5 , but in addition to a y-axis intercept. A closer look at Figure 2.3(b) reveals that several local yield strength values, which are derived from deformation tests on macroscopic samples, namely by Jin *et al.* [136] and Balk *et al.* [71], are slightly lower in comparison with values by other examinations. In previous reports, this discrepancy was considered to be larger [109, 136, 141]. This deviation led to a reevaluation of the factor used for the conversion of hardness data, derived by nanoindentation, to the yield strength. Initially, an equality of the hardness to the yield strength, i.e. $H = \sigma_y$, was assumed [68, 69, 121]. Based on the findings that dislocations are able to pass distances much longer than the ligament size, that the grain size is much larger than the ligament size, and that these conditions lead to a uniform deformation of the ligaments inside the grain, Jin *et al.* [136, 142] proposed the usage of the relationship $H = 3 \sigma_y$, which is used for massive materials. In Figure 2.3(b), the equation $H = 2.65 \sigma_y$ is used for the conversion of indentation hardness and Vickers hardness data into the yield strength, as proposed by Briot & Balk [135].

The increase of the yield strength with decreasing ligament size is similar to the increase of the yield strength with smaller grain sizes, described by the Hall-Petch relationship. This consideration states an increase of the yield strength with the inverse square root of the average grain size. Grain boundaries are regarded as barrier to the movement of dislocations, which pile up along the glide plane behind the grain boundary. Piled-up dislocations exert an additional stress to the dislocation next to the grain boundary and facilitate the overcoming of this obstacle. Larger grain sizes allow a larger pile-up, thereby reducing the stress necessary for the movement of dislocations, lowering the yield strength [146, 147].

For the smaller-is-stronger-effect of the yield strength with respect to the ligament size, several possible explanations are provided, which differ from the Hall-Petch relationship. Some approaches can be summarized by the concept of dislocation starvation. Accordingly, smaller ligaments exhibit lower dislocation densities, accompanied by an increased yield strength. One possible reason for the lowered dislocation density is the spatial delimitation of dislocation sources, such as Frank-Read sources. Smaller

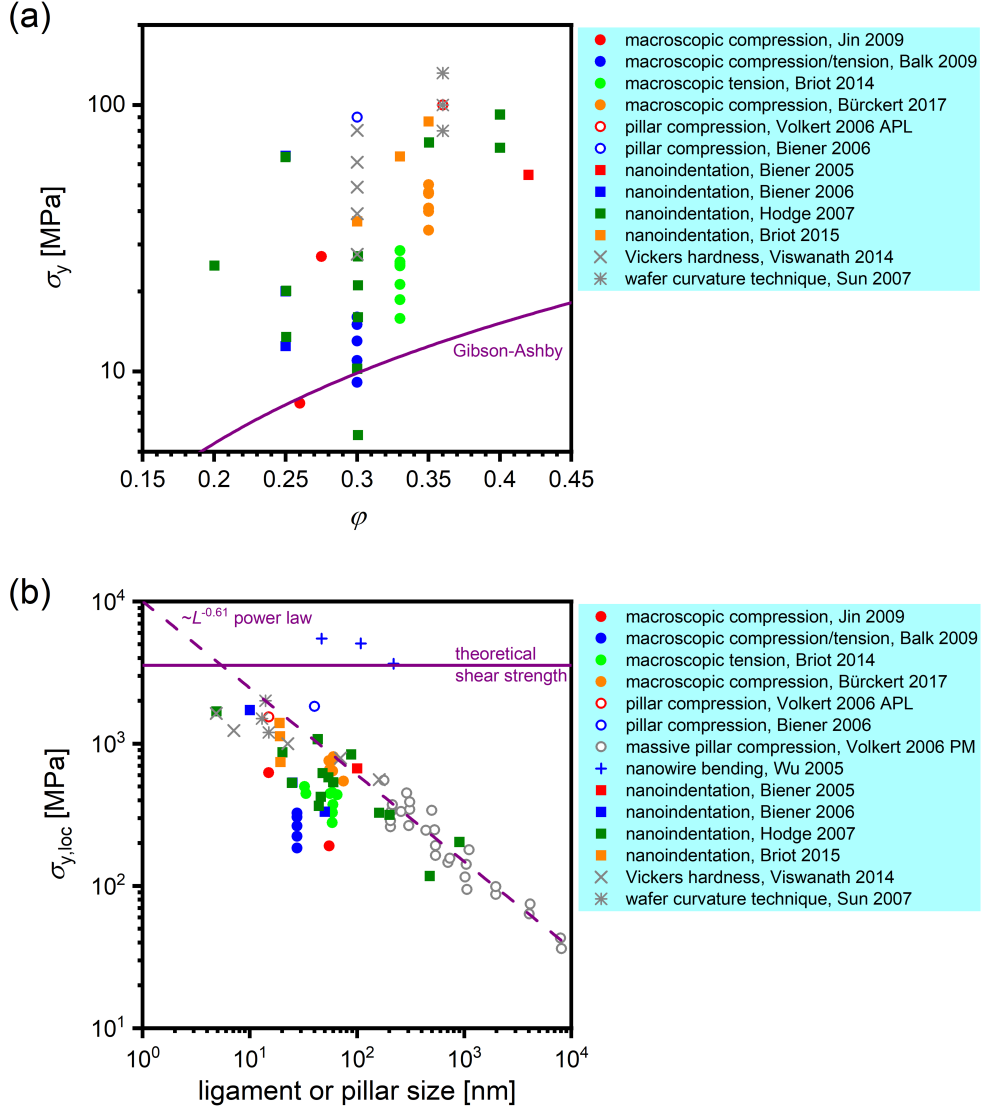


Figure 2.3: (a) Compilation of yield strength values of nanoporous or nanosized gold from the literature against the solid fraction ϕ . The solid line indicates the prediction by the Gibson-Ashby-law, Equation 2.10, with $\sigma_{y,s} = 200$ MPa. (b) Collection of local yield strength values of nanoporous or nanosized gold, $\sigma_{y,loc}$, calculated on the basis of Equation 2.20, against the ligament or pillar size L . The dashed line denotes a power law with exponent -0.61 , as proposed by [140]. As factor A in Equation 2.21, a value of $10000 \text{ nm}^{0.61}$ MPa is inserted, in accordance with [109]. The solid line indicates the theoretical shear strength and thus the maximum yield strength of gold, 3.56 GPa [143]. Yield strength values are determined by the deformation of macroscopic samples [71, 73, 123, 136], by the compression of nanoporous pillars [67, 68], by the compression of massive pillars [140], by nanowire bending [137], by nanoindentation [68, 69, 121, 135], by the Vickers hardness measurement [144] or by wafer curvature technique [145]. Adopted from [109, 138, 141], with new data sets being included and several existing data sets being newly evaluated. This concerns nanoindentation and hardness data which are evaluated by usage of a hardness-to-yield-strength ratio of 2.65 [135].

dislocation sources need higher stresses for activation. If smaller ligaments lead to a narrowing of the dislocation sources, the number of generated dislocations at a certain stress level decreases [68, 138]. Another explanation, which is used in this context, is the egress of dislocations from the ligaments' surface. This alone leads to a decreasing dislocation density. Furthermore, since dislocations go along with internal stress, which supports the activation of dislocation sources, a decreased dislocation density attenuates the generation of new dislocations as part of a feedback process. Irrespective of which effect is responsible for a low dislocation density in particular, the dislocation starvation scenario is most often suspected of being responsible for the smaller-is-stronger-effect of the yield strength [140, 148, 149].

Another possible reason for the size-effect of the yield strength observed in nanoporous metals is the obstruction of the free movement of dislocations by a surface layer. This is thinkable if an oxide-layer is present or if the surface is damaged by focused ion beam. In this case, the egress of dislocations from the surface is inhibited. A third concept are dislocation interactions. In this scenario, smaller ligament sizes possess a higher dislocation density, which requires a blocking of the dislocation release from the surface. Interactions between dislocations hinder the movement of a single dislocation, if their density reaches a sufficient scale (Taylor hardening [150, 151]). However, these explanations are regarded as unlikely [140].

2.2.4 Role of network connectivity

In Figure 2.2, three investigations are included which examine NPG samples coarsened to a various extent. In all three data sets, coarsening, induced by annealing or by electrochemical treatment, is combined with shrinkage and thus an increase of the solid fraction. Mameka *et al.* [114] observe that increasing the ligament size from 20 nm to 150 nm goes along with an increase of φ from 0.27 to 0.32. Badwe *et al.* [79] observe an increase of φ from 0.30 to 0.49 when the ligament size is coarsened from 50 nm to 750 nm. Samples of Liu *et al.* [74] are firstly dealloyed, whereat the dealloying is combined with electrochemical coarsening. During this synthesis step, the solid fraction decreases. Once the dealloying is completed, the samples are annealed and the ligament size increases from 75 nm to 550 nm, while the solid fraction rises from 0.26 to 0.33 [74]. It is remarkable that the two examinations by Mameka *et al.* [114] and Liu *et al.* [74] observe a distinct reduction of the Young's modulus upon annealing. By both studies, as a possible explanation a decline of the connectivity during coarsening is proposed. However, they utilize different concepts for the connectivity. The approach of Liu *et al.* [74] is already introduced in Subsection 2.2.2. For a nanoporous material with solid fraction φ , the measured E_{eff} is compared with the E_{GA} predicted by the Gibson-Ashby-law, Equation 2.5. The discrepancy between both values is explained by the disconnection of a certain share of the ligaments. The effective solid fraction φ_{eff} , which is introduced by Equation 2.13, describes the share of connected ligaments, referred to the total volume. As a measure of the connectivity β_{L} , the ratio between effective solid fraction and total solid fraction is calculated:

$$\beta_{\text{L}} = \frac{\varphi_{\text{eff}}}{\varphi} = \sqrt{\frac{E_{\text{eff}}}{E_{\text{GA}}}} = \sqrt{\frac{E_{\text{eff}}}{E_{\text{s}}\varphi^2}}. \quad (2.22)$$

Thus, according to this definition, the Young's modulus is affected by the square of the connectivity [74]:

$$E_{\text{eff}} = \beta_L^2 E_s \varphi^2. \quad (2.23)$$

Another approach is applicable to the analysis of 3D structures. First, the topological genus G is determined, which can be regarded as the absolute number of closed rings of the solid phase. Since G increases with the analyzed volume, the scaling of G to the absolute volume V is necessary for the determination of an independent parameter. Furthermore, with smaller structure sizes, the number of closed rings per unit volume is higher. This requires the scaling to a characteristic structure size. One method is the scaling with the specific surface area [90, 94, 117, 152]. An alternative is the usage of the mean ligament diameter L_G [86], calculated by granulometry [87]. The sum of mean ligament diameter and mean pore diameter is proposed as well [141]. Finally, the mean ligament spacing $\tilde{L}$ can be selected as scaling parameter [98, 99]. In this case, the scaled genus g is determined by the equation

$$g = \frac{G \tilde{L}^3}{V}. \quad (2.24)$$

A connection between both definitions of the connectivity is given by Sohn et al. [153]. The scaled genus g , which is defined using the ligament spacing $\tilde{L}$, is referred to a reference value g_0 . In addition to that, the impact of the size of g relative to g_0 is assumed to be similar to the ratio between φ and φ_{eff} . Starting from Equation 2.23, the scaling law takes the form:

$$E_{\text{eff}} = \left(\frac{g}{g_0} \right)^2 E_s \varphi^2. \quad (2.25)$$

A comparison with experimental data yields 2.93 as the value for g_0 [153]. The observation of a combination of coarsening with a decline in stiffness, which is mentioned above in the course of the description of Figure 2.2, leads to a closer examination of the development of the connectivity during coarsening. Liu & Jin [100] compare the coarsening of samples with a different initial solid fraction. The connectivity is estimated using the model by Liu *et al.* [74] which is presented in Equation 2.22. In other words, the measured E is converted into a value for the connectivity. If the solid fraction at the beginning is 0.46, the connectivity remains constant during coarsening. A φ of 0.35 causes a distinct decrease, while a φ of 0.26 – this data row is presented in Figure 2.2 – leads to a strong decrease of the connectivity during annealing-induced coarsening [100]. A similar result is yielded by kinetic Monte Carlo simulations on the coarsening of structures generated by Gaussian random fields. There, a solid fraction of about 0.29 is found to be a transition value. If $\varphi \geq 0.30$, the connectivity, defined by Equation 2.24, remains constant during coarsening. On the other side, the condition $\varphi \leq 0.27$ results in a decline of the connectivity [99].

During the coarsening, three mechanisms work against each other, these are ligament pinch-off and ring collapse, which result from the Plateau-Rayleigh instability [116, 117], and ligament reattachment. The first two effects reduce the connectivity, while the latter one leads to a connectivity increase. A descending connectivity is driven by ligament pinch-off and ring collapse. Since the characteristic size in Equation 2.24

increases during coarsening, a ligament reattachment is not inevitably required to keep the connectivity constant. On the other side, based on the comparison with particle sintering, ligament reattachment is proposed to be responsible for shrinkage, which is often an accompanying process next to coarsening, such as in the three coarsening procedures presented in Figure 2.2 [90, 154].

Other simulative [117] or experimental [91] evaluations support the finding that the process of coarsening is not self-similar, which is an indication that a declining connectivity is indeed a factor with significant influence on the mechanical properties. However, the theory of a severe connectivity decrease during coarsening is not undisputed. A series of measurements on annealed nanoporous gold samples, which analyzes the connectivity by conducting FIB tomography reconstructions, finds the connectivity to be constant. Furthermore, the ligament width distribution shows self-similarity in the course of coarsening. The solid fractions vary between 0.30 and 0.36 while the structure is coarsened from 26 nm to 420 nm [86]. Another study by Ngô *et al.* [155] observes both experimentally and in molecular dynamics simulations that the Young's modulus of NPG is significantly lower than estimated by the Gibson-Ashby-law. This dataset is not included into Figure 2.2, but the measured values show a good agreement with the dataset by Mameka *et al.* [114], 40 nm. The deviation is attributed to the early yielding of ligaments, which in turn is explained by a high level of prestress without external load. As underlying reason for the prestress, surface-induced stresses are suggested. A single length scale is analyzed in the experiment, so that the study is not explicitly associated with the process of coarsening. However, due to the similarity to the dataset by Mameka *et al.* [114], a surface-induced prestress and the early yielding of ligaments would serve as an alternative explanation apart from the concept of a connectivity decrease [155].

2.3 Small-angle X-ray scattering

2.3.1 Fundamentals of small-angle X-ray scattering

A sketch of the experimental setup which is used for small-angle X-ray scattering is given in Figure 2.4. The meaning of several basic parameters can be gathered from this drawing. An incident X-ray beam with wave vector $\vec{k}_i$ and wavelength λ , generated by a monochromatic X-ray source, hits the sample. The scattering wave vector $\vec{q}$ is given by the difference between the final wavevector $\vec{k}_f$ of the scattered beam and the wave vector $\vec{k}_i$ of the incident beam:

$$\vec{q} = \vec{k}_i - \vec{k}_f. \quad (2.26)$$

In elastic scattering processes, the length of $\vec{k}_i$ and $\vec{k}_f$ is identical and has the value $|\vec{k}| = 2\pi/\lambda$, while the length of $\vec{q}$, denominated as wavenumber q , is related to θ , which is half of the scattering angle [156]:

$$|\vec{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}. \quad (2.27)$$

The differential cross section $d\Sigma/d\Omega$ is determined from the Fourier transform of the electron density $n(\vec{x})$, which is subsequently squared and related to the sample volume,

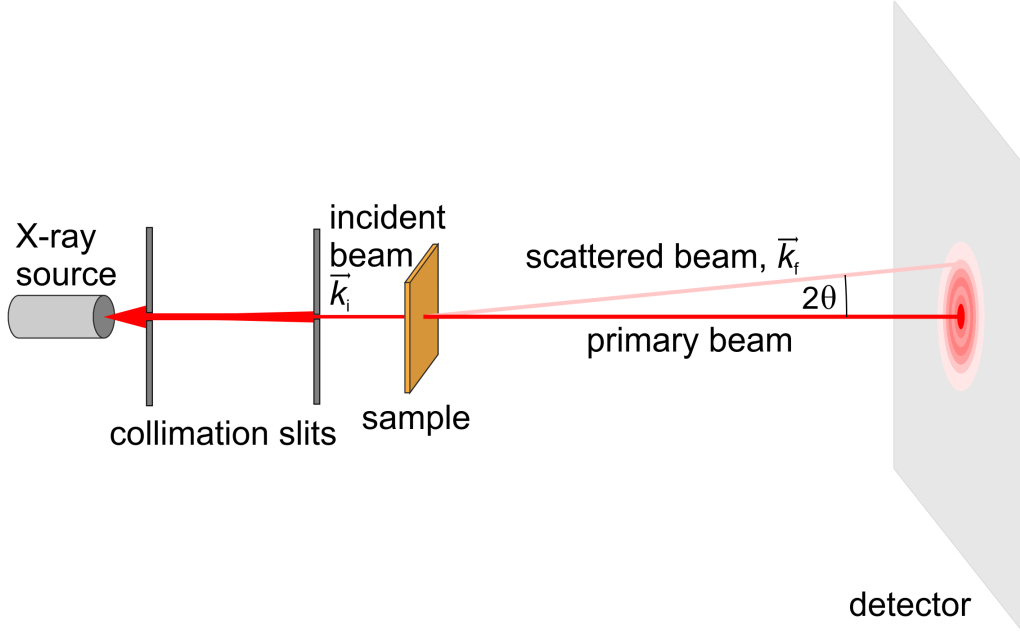


Figure 2.4: Schematic illustration of the setup used for small-angle X-ray scattering. Measurement parameters, which are not included in the graphic, are the sample thickness and the sample-detector distance. The drawing is not true to scale and the scattering angle 2θ is highly exaggerated. After [156, 157].

V . In that regard, an equal differential scattering cross section r_e^2 is assumed for every electron. If this condition is not satisfied, as for higher q -values, the following expression does not hold true [156, 158]. r_e is the classical electron radius, its value is $r_e = 2.818 \cdot 10^{-15} \text{ m}$ [156]. The differential cross section has the unit area per volume and can be seen as material-specific constant:

$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} \left| \int_V r_e n(\vec{x}) e^{i\vec{q} \cdot \vec{x}} d^3\vec{x} \right|^2. \quad (2.28)$$

For the derivation of an equation used in the calculation of the specific surface area, a simplified structural model is applied. Instead of a porous structure, spherical particles are utilized for solving Equation 2.28. The integral over the complete sample volume is transformed into a single integral for one particle, and multiplication with the number of particles, N . A length scale x is introduced, which is zero at the center of the particle. Intermediate steps, which are not shown here, lead to integration over the electron density difference function $\hat{n}(x) = n_p(x) - n_0$ for $x \leq R$, where $n_p(x)$ is the electron density inside the particles and n_0 is the electron density of the surrounding phase. R is the radius of the particles [156]. In this way, one arrives at

$$\frac{d\Sigma}{d\Omega} = \frac{N}{V} \left| \int_{V_{\text{sphere}}} r_e \hat{n}(x) e^{i\vec{q} \cdot \vec{x}} d^3\vec{x} \right|^2. \quad (2.29)$$

The following equation has proven useful for the transformation of volumetric Fourier transforms under the condition of spherical symmetry [156]:

$$\int f(x) e^{i\vec{q}\cdot\vec{x}} d^3\vec{x} = 4\pi \int x^2 f(x) \frac{\sin(qx)}{qx} dx. \quad (2.30)$$

Application to Equation 2.29 results in the following expression. The integral goes from 0 to R . Inside the particles, a constant electron density and thus a constant electron density difference $\hat{n}(x) = n_s - n_0$ is assumed. This allows to remove the electron density difference from the integral. Electron density fluctuations caused by the crystal structure of the particle material and electron density fluctuations caused by the arrangement of electrons inside single atoms are neglected:

$$\frac{d\Sigma}{d\Omega} = \frac{16\pi^2 N r_e^2 (n_s - n_0)^2}{V q^2} \left| \int_0^R x \sin(qx) dx \right|^2. \quad (2.31)$$

Solving the integral results in [156]:

$$\frac{d\Sigma}{d\Omega} = \frac{16\pi^2 N r_e^2 (n_s - n_0)^2}{V q^6} [\sin(qR) - qR \cos(qR)]^2. \quad (2.32)$$

This equation describes the differential scattering cross section of spherical particles in solution. Figure 2.5 shows a test measurement of silica particles. The differential scattering cross section according to Equation 2.32 is inserted next to the measurement signal.

For higher q -values, the term $qR \cos(qR)$ becomes dominant against $\sin(qR)$, which can be neglected. If the intensity is averaged over a certain q -range, the fluctuation caused by the term $\cos^2(qR)$ can be transformed into an averaged value of 0.5. Furthermore, a specific surface area $\alpha = 4\pi R^2 N/V$ is introduced, which describes the area per total volume. It is calculated by referring the surface area of the N particles to the total volume V [156]:

$$\lim_{q \rightarrow \infty} \frac{d\Sigma}{d\Omega} = \frac{16\pi^2 N R^2 r_e^2 (n_s - n_0)^2}{V q^4} \left(\frac{1}{2} \right) = \frac{2\pi \alpha r_e^2 (n_s - n_0)^2}{q^4}. \quad (2.33)$$

For $q \rightarrow \infty$, the relationship $d\Sigma/d\Omega \sim q^{-4}$ is observed, which is known as Porod's law [156, 159]. The proportionality to $q^{-\kappa}$ with $\kappa = 4$ is valid for smooth interfaces with abrupt transition of electron density. For rough interfaces, κ decreases to 3–4. In this context, an increasing roughness leads to an approximation to the value $\kappa = 3$. More generally, the power law concerning q is related to the fractal dimension of the scattering object. On the other side, κ increases up to 6 if the transition in electron density extends continuously over a boundary layer, instead of being discontinuous [156, 160–162]. If Equation 2.33 is applied to nanoporous metals, whose pores are filled with air, n_0 is set to 0. The electron density of the solid material n_s is determined by $n_s = \langle Z \rangle \rho_0$, where ρ_0 is the atomic density and $\langle Z \rangle$ the atomic number, averaged over the composition. Taking the atomic numbers of gold and silver, which are 79 and 47 [134], $\langle Z \rangle$ is calculated on the basis of the portion of the elements. To give an example, the composition $\text{Ag}_{75}\text{Au}_{25}$ corresponds to $\langle Z \rangle = 55$. Gold and silver feature

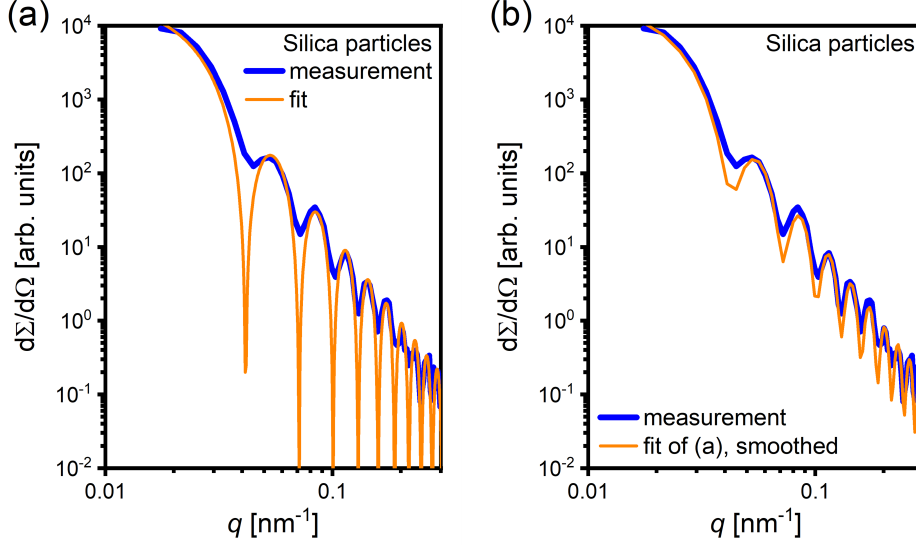


Figure 2.5: Test measurement of silica particles. (a) and (b) show the same scattering graph. A fit based on Equation 2.32 is inserted into (a). The equation used for the fit is $d\Sigma/d\Omega = Aq^{-6}[\sin(qR) - qR\cos(qR)]^2$ with adjustable parameters A and R . The fit is done by hand, the resulting particle diameter D is $D = 2R = 217\text{ nm}$. This value differs slightly from the indication by the manufacturer, who specifies an average particle diameter of $D = 213 \pm 6\text{ nm}$. In (b), the fit shown in (a) is smoothed by a 3-point moving average, which increases conformance with the scattering data. The physical background of the smoothing is the dimension of the sample parallel to the beam.

almost the same atomic density. The lattice constant of gold is $a_{\text{Au}} = 408\text{ pm}$, while the lattice constant of silver is $a_{\text{Ag}} = 409\text{ pm}$ [163]. For simplification, a_{Au} is used, which results in a uniform value for the atomic density, $\rho_0 = 4a^{-3} = 5.89 \times 10^{28}\text{ m}^{-3}$ [134]. Rearranging Equation 2.33 to the specific surface area results in [156, 158, 164]:

$$\alpha = \frac{1}{2\pi r_e^2 \langle Z \rangle^2 \rho_0^2} \lim_{q \rightarrow \infty} \frac{d\Sigma}{d\Omega} q^4. \quad (2.34)$$

This equation is one variant for the analysis of the scattering intensity data with respect to the specific surface area. Another method applies the invariant Q , which is a measure of the total scattering intensity [164]:

$$Q_\varphi = 2\pi^2 \langle Z \rangle^2 r_e^2 \rho_0^2 \varphi (1 - \varphi). \quad (2.35)$$

Starting from the scattering signal, the invariant can also be determined by integration of the radially averaged differential cross section [158, 164]:

$$Q_S = \int_0^\infty \frac{d\Sigma}{d\Omega} q^2 dq. \quad (2.36)$$

Insertion of Q_φ from Equation 2.35 into Equation 2.34 and subsequent exchange of Q_φ by Q_S results in [158]:

$$\alpha_{\text{Porod}} = \frac{\pi \varphi (1 - \varphi)}{Q_S} \lim_{q \rightarrow \infty} \frac{d\Sigma}{d\Omega} q^4. \quad (2.37)$$

This expression represents the second variant for the determination of the specific surface area. Equations 2.34 and 2.37 both exhibit the same evaluation of the scattering intensity in the Porod regime. The integral of the radially averaged $d\Sigma/d\Omega$ is incorporated into Equation 2.37 as a second experimentally determined parameter. An ideal measurement results in $Q_\varphi = Q_S$ and $\alpha = \alpha_{\text{Porod}}$. If, for some reason, all $d\Sigma/d\Omega$ -values are halved, α will be halved, too. Because Q_S will be halved as well, α_{Porod} will be unaffected. Calculating the specific surface area by means of Equation 2.37 is a way to omit measurement errors, which affect the total intensity. Equation 2.37 does not determine the specific surface area by utilization of the absolute scattering intensity in the Porod regime, but by evaluation of the scattering intensity in the Porod regime in relation to the scattering intensity of the complete scattering graph. Consequently, the detection of absolute units is not required for the identification of the specific surface area.

2.3.2 Length scale analysis by small-angle X-ray scattering

In Section 1.2, a relation between the ligament spacing $\tilde{L}$ and q_0 is derived, as presented in Equation 1.4. q_0 is the wave number used for the generation of the Gaussian random field. Based on such a leveled-wave generated structure, Shi *et al.* [58] compute a small-angle interference function by execution of a Fast Fourier Transform. More precisely, their underlying structure is hierarchical and generated by the multiplication of two single structures with different q_0 . The small-angle interference function shows two clear peaks whose q -values q_{peak} are identical to the corresponding values of q_0 [58]. With $q_0 = q_{\text{peak}}$, Equation 1.4 is modified to:

$$\tilde{L} = 1.23 \frac{2\pi}{q_{\text{peak}}}. \quad (2.38)$$

This expression enables the determination of the ligament spacing $\tilde{L}$ as a result of the evaluation of a scattering graph. While the derivation presented above is "experimental", Equation 2.38 is the result of basic laws of scattering [165]. The Debye scattering equation permits the calculation of the scattering intensity as a function of the interatomic distances [166]. On that basis, the following equation is obtained [167–169]:

$$\frac{d\Sigma}{d\Omega} \sim \int_V \int_V \tilde{n}(\vec{x}) \tilde{n}(\vec{x} + \vec{r}) e^{-i\vec{q} \cdot \vec{r}} d^3\vec{x} d^3\vec{r}. \quad (2.39)$$

The electron density fluctuation $\tilde{n}(\vec{x})$ is the local deviation from an average electron density $\bar{n}$ at point $\vec{x}$. With φ being the solid fraction and n_s being the electron density of the solid phase and with the electron density of the voids being negligible, $\bar{n}$ is determined by $\bar{n} = \varphi n_s$. $\vec{r}$ is a displacement vector, so that $\vec{x} + \vec{r}$ describes a shifted structure. An autocorrelation function $\gamma(\vec{r})$ can be defined in dependence on $\vec{r}$ [167–169],

$$\int_V \tilde{n}(\vec{x}) \tilde{n}(\vec{x} + \vec{r}) d^3\vec{x} = \bar{n}^2 V \gamma(\vec{r}), \quad (2.40)$$

where $\dot{n}^2$ is the mean square fluctuation which is the average value of $\tilde{n}(\vec{x})^2$ and which is calculated by $\dot{n}^2 = \varphi(1-\varphi)n_s^2$. Insertion of $\gamma(\vec{r})$ into Equation 2.39 results in [167–169]:

$$\frac{d\Sigma}{d\Omega} \sim \dot{n}^2 V \int_V e^{-i\vec{q}\cdot\vec{r}} \gamma(\vec{r}) d^3\vec{r}. \quad (2.41)$$

Finally, Equation 2.30 is used for the conversion of the volume integral [167–169]:

$$\frac{d\Sigma}{d\Omega} \sim 4\pi \dot{n}^2 V \int_0^\infty r^2 \gamma(r) \frac{\sin(qr)}{qr} dr. \quad (2.42)$$

Equation 2.38 is a direct result of this expression. If $\gamma(r)$ is a function with a sharp maximum at $r = r_m$, the integral $\int_0^\infty r \gamma(r) \sin(qr) q^{-1} dr$ as a function of q looks similar to the autocorrelation function shown in Figure 1.3, which illustrates the inverse case. While there the wavenumber is fixed to a single value, in this example the autocorrelation function $\gamma(r)$ is restricted to a single maximum. The integral $\int_0^\infty r \gamma(r) \sin(qr) q^{-1} dr$ is highest for q -values near 0. A first minimum is located at $q = 0.72 \cdot 2\pi/r_m$, while a first maximum can be found at $q = 1.23 \cdot 2\pi/r_m$. Consequently, the factor 1.23 derives directly from the autocorrelation function and is not restricted to the leveled-wave model. It is noted that the differential scattering cross section $d\Sigma/d\Omega$ cannot become negative, and that an autocorrelation function $\gamma(r)$ with a single maximum at $r \neq 0$ is not realistic. The autocorrelation function of a realistic structure, such as two spheres with distance r_m , exhibits a maximum at $r = 0$ with a value of 1 and a smaller maximum at $r = r_m$, and the high correlation for $r \rightarrow 0$ prevents the differential cross section from becoming negative [168].

In Equation 2.35, the determination of the invariant Q is presented. A derivation is possible starting from Equation 2.42. There, $d\Sigma/d\Omega(q)$ is the Fourier transform of $\gamma(r)$. If the inverse Fourier transform is formed, $\gamma(r)$ can be isolated. By setting $r = 0$, by insertion of Equation 2.36, and by bringing in absolute units, Equation 2.35 is obtained [169].

2.3.3 Characterization of nanoporous metals by small-angle X-ray scattering

The structural analysis by SEM is restricted to the material's surface. If the structure on the surface is expected to deviate from the bulk material, a scanning electron micrograph can be taken on the fracture surface. However, in the case of a specific type of structural inhomogeneities, like preexisting cracks, grain boundaries or regions with a lower solid fraction, the crack develops from these regions. In this case, the fracture surface is only conditionally representative for bulk structures. Unlike SEM, small-angle X-ray scattering enables the structural investigation of the bulk material. The structural parameters determined by this technique can be considered as averaged over the whole volume. Another advantage is the *in situ* characterization of processes under conditions which are not compatible with SEM. Accordingly, a possible application of SAXS is the investigation of dealloying processes. This includes two *in situ* studies on the dealloying of gold-silver alloys [170, 171], one *ex situ* study on the dealloying of a

gold-silver alloy [172], one *in situ* study on the dealloying of a copper-palladium alloy [84] and one *in situ* study on the dealloying of a copper-zinc alloy [173]. In addition, the application of *in situ* small-angle neutron scattering (SANS) in the investigation of the dealloying of a gold-silver alloy [174, 175] and the application of *in situ* grazing-incidence small-angle X-ray scattering (GISAXS) in the investigation of the dealloying of a gold-silver alloy or a copper-palladium alloy [84] are worth mentioning. The category of *in situ* investigations by SAXS also includes an analysis of the coarsening of nanoporous gold by heating [115] and an analysis of the coarsening of nanoporous gold during the later stage of the dealloying [176]. Furthermore, SAXS and GISAXS find application in the investigation of the lithiation of nanoporous gold [177] and in the structural characterization of nanoporous gold [169, 178] or hierarchical nanoporous gold [56].

Most approaches mentioned above start from thin foils or sputtered films with thicknesses between 100 nm and 25 μm . Two exceptions are the study employing SANS [174, 175] with a thickness of about 130 μm and the study by Gößler *et al.* [84], where the samples have an initial thickness of 200 μm –250 μm . Neutron scattering, utilized in the first exception [174, 175], is characterized by a poor scattering signal, which enables, but on the other hand also requires, the deep penetration of materials [156]. The second exception [84] is designed as GISAXS measurement where the vertical thickness of the sample is irrelevant. The SAXS measurement, which is conducted simultaneously with the GISAXS measurement, is not intended. Instead, it is caused by the bending of the sample during the measurement, which changes the condition under which the X-ray beam hits the sample from grazing incidence to transmission. However, the distance the beam passes through the sample is not known [84]. Summarized, none of the studies mentioned above presents a SAXS analysis of the bulk material of samples in the range of millimeters and a continuous nanoporous structure. One objective of this thesis is the application of SAXS to volumes which are representative for mm-sized bulk material. For this purpose, μm -sized walls are cut out of mm-sized samples.

The analysis of the scattering data is handled in various ways. In several cases [170, 172, 177], a characteristic length scale is determined by the equation $2\pi/q_{\text{peak}}$, whereat the determination of the peak position q_{peak} is not described in detail. It is assumed that the q -value with the highest intensity is selected. Other studies [56, 176] explicitly consider the factor 1.23 and make use of Equation 2.38. As exemplified by Welborn & Detsi [169], several models are proposed for the analysis of the scattering data of porous materials; among them are the Berk model [97, 179], the Teubner-Strey model [180] and the Choi & Chen model [181]. The latter two models determine, among other parameters, the ligament spacing $\tilde{L}$. All models find application in the analysis of small-angle X-ray scattering data [84, 115, 169, 174, 175]. The fitting of SAXS data on nanoporous gold by a particle diameter distribution, performed by SAXS analysis software, can be found in the literature as well [171].

Chapter 3

Methods and Synthesis

3.1 Equipment for electrochemical procedures

Electrochemical procedures are carried out in a 3-electrode chemical cell, as shown in Figures 3.1(a) and 3.1(b). The cell, which is custom-made [141], consists of a main chamber and additional pipes attached thereto. One of the pipes exhibits a larger opening to the main chamber, while the other pipe ends up with a Luggin capillary, whose opening is located in the center of the main chamber, as shown in Figure 3.1(c). This latter tube contains the reference electrode, whereas the counter electrode and the working electrode are located in the first-mentioned tube or in the main chamber, respectively. A current flow between counter electrode and working electrode leads to overpotentials, caused by the ohmic resistance of the electrolyte and the electrodes. Due to this effect, the counter electrode is not suitable for use as potential reference. Hence, the working electrode is connected to the reference electrode via a voltmeter which measures the potential difference E_D . Since virtually no electric current flows between working electrode and reference electrode, the potential of the latter one is unaffected by overpotentials and considered to be constant during the measurement. Furthermore, the working electrode, in Figure 3.1(c) represented by sample and sample holder, is placed directly next to the opening of the Luggin capillary, so that E_D is not distorted by the change of the potential caused by the ohmic resistance of the electrolyte. During the measurement, the concentration of the electrolyte changes due to the oxidation of the alloy material. The small opening of the Luggin capillary and the long distance to the actual electrode prevent an impact of a change in concentration in the main chamber. In this thesis, the potential is always the input parameter, while the current is the output parameter. From a technical point of view, the potentiostat adjusts the electric current to such an extent that E_D shows the desired value [182, 183].

A Metrohm Autolab PGSTAT302N or Metrohm Autolab Cabinet M/101 is used as potentiostat. Typically, a coiled silver wire (0.5 mm diameter, 99.9%, Fisher Scientific) is used as counter electrode. During the running of potential cycles, and only there, the silver wire is replaced by a rolled piece of carbon cloth (Kynol activated carbon fabrics, specific surface area $> 1800 \text{ m}^2/\text{g}$) which is used as counter electrode instead. Self-made Ag/AgCl-electrodes, referred to as (pseudo) ps-Ag/AgCl-electrodes, serve as

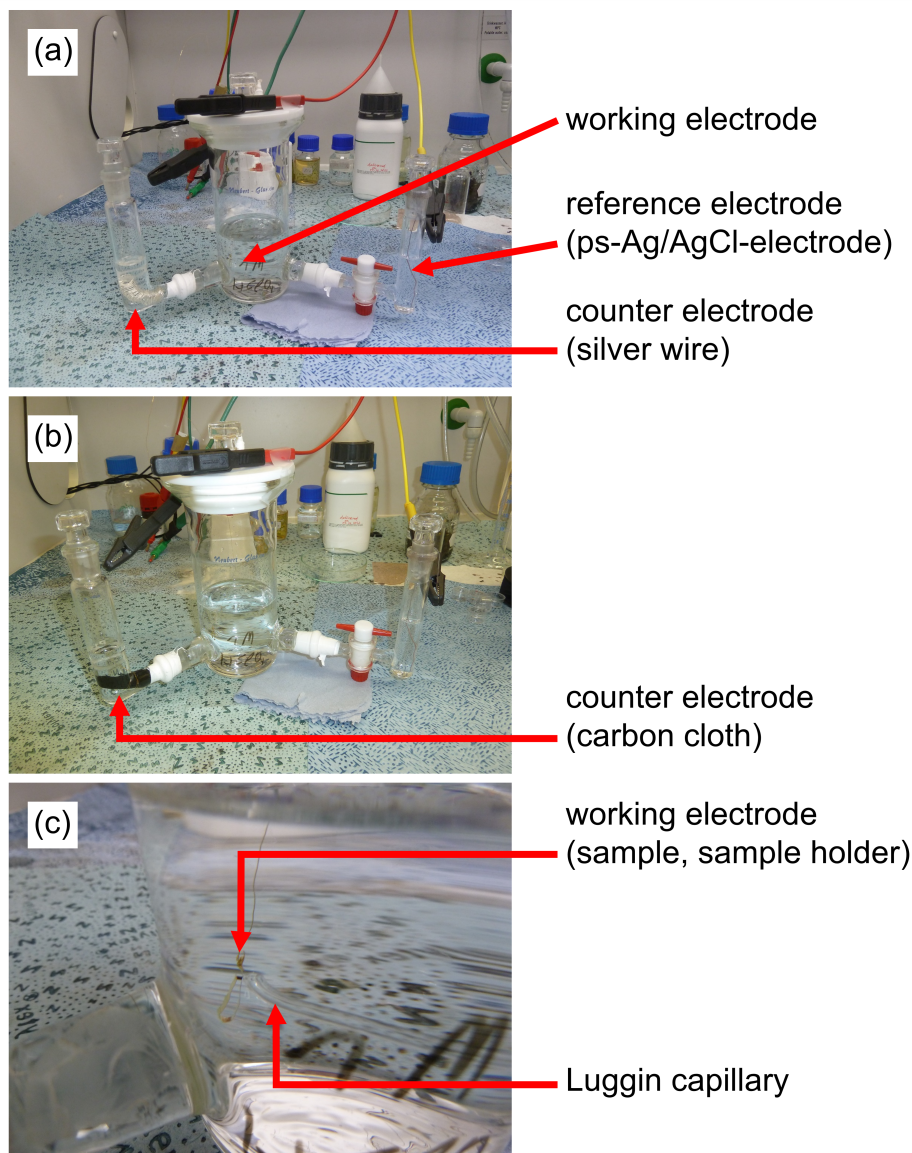


Figure 3.1: Images of an electrochemical cell used for dealloying. The cell exhibits a three-electrode design, as seen in (a) and (b). The working electrode is placed in the main body, while the pipes connected on the right and left side contain the counter electrode (left side) and the reference electrode (right side). In (a), a silver wire is used as counter electrode, while in (b) it is replaced by a rolled piece of carbon cloth. (c) shows a close-up of the sample which is clamped in a gold sample holder. The sample is placed next to the opening of the Luggin capillary.

reference electrodes. They are synthesized on the basis of silver wires of the same type as those used as counter electrodes. In 1 M HCl (1 N, J.T. Baker), a voltage of 0.9 V is applied for 120 s between a silver wire which serves as a working electrode and another silver wire which serves as a counter electrode and reference electrode, connected to each other. After the electrochemical deposition the silver wire which has been used as working electrode is existent as ps-Ag/AgCl-electrode [141]. Gold sample holders are self-made as well. They are produced on the basis of gold pieces (99.99%, Sindlhauser

Materials) and thin gold wires (0.127 mm diameter, 99.99%, Premion, Alfa Aesar). Two different types of gold sample holders are used: sample holders which carry one sample, and sample holders which carry four samples. An image of a gold sample holder for one sample is presented in Figure 3.1(c).

Two different electrolytes are used for dealloying: 0.01 M H_2SO_4 (98% Rotipuran) and 1 M HClO_4 (60% Emsure ACS, Merck Millipore). Before every procedure, the potential of the ps-Ag/AgCl-electrode is measured against a standard hydrogen electrode (SHE, Hydroflex, Gaskatel) in the respective electrolyte. The potential of the ps-Ag/AgCl-electrode is 0.621 ± 0.001 V vs. SHE in 0.01 M H_2SO_4 and 0.513 ± 0.004 V vs. SHE in 1 M HClO_4 . This routine measurement cannot be seen as a real calibration; instead, it is used as a quality control for the reference electrode and the electrolyte. In this thesis, potential values generally relate to the potential against the ps-Ag/AgCl-electrode, unless specified otherwise. Electrolytes are prepared with ultrapure water (Sartorius Arium Comfort, conductivity $0.055 \mu\text{S}/\text{cm}$) which is used for cleaning steps as well. Ethanol ($\geq 99.9\%$, Emsure ACS, Merck Millipore) is another chemical employed for cleaning purposes. Silica particles ($0.213 \mu\text{m}$, microParticles) are solely used for the test measurement presented in Figure 2.5.

3.2 Synthesis of hierarchical nanoporous gold

3.2.1 Preparation of precursor alloys

Two types of precursor alloys are used for the sample preparation: $\text{Ag}_{90}\text{Au}_{10}$ and $\text{Ag}_{93}\text{Au}_7$. However, the vast majority of specimens are synthesized out of the $\text{Ag}_{90}\text{Au}_{10}$ precursor alloy. The precursor alloys are produced by arc melting (MAM-1 Edmund Bühler) of silver wires (99.99%, WIELAND Edelmetalle) and gold wires (99.99%, Sindlhauser Materials). During the arc melting, which takes place in an argon atmosphere, about 25 subsequent alloying sequences are conducted to ensure a homogeneous composition. Afterwards the ingots are sealed in a quartz glass tube under a vacuum of about 10^{-1} mbar. Encapsulated by the quartz glass tube, the ingots are then annealed at 850°C for 5 days and subsequently quenched in water. Taken out from the quartz glass tube, the homogenized ingots are cold rolled to a thickness of about 0.8 mm by a rolling machine (Dima W 40 B Blechwalzmaschine). Finally, the ingots, which have a weight of about 2.5 g, are cut into cuboidal samples of dimension $0.8 \times 0.6 \times 0.6 \text{ mm}^3$ by a diamond wire saw (Well 3032-4). Single samples have a typical weight of about 4 mg before dealloying. To examine the homogeneity of the composition, energy dispersive spectroscopy (EDS) is applied to the fracture surface of a $\text{Ag}_{90}\text{Au}_{10}$ sample. 8 measurements at different positions yield an average silver concentration of $x_{\text{Ag}}^{\text{EDS}} = 0.900 \pm 0.002$, which confirms the accuracy of the alloy preparation. It is unclear if the standard deviation is partly caused by the measurement uncertainty of the EDS measurement or by a minor variance of the composition.

3.2.2 Partial electrochemical dealloying

A brief introduction to the synthesis is already given in Section 1.3. Figure 1.2 provides an overview. Monolithic samples of hierarchical nanoporous gold are synthesized

by a three-step procedure which consists of 1st dealloying, coarsening and 2nd dealloying. After completion of the respective steps samples are referred to as preliminary nanoporous silver gold (preNPSG), nanoporous silver gold (NPSG) and hierarchical nanoporous gold (HNPG). Parameters of every step can be varied. However, all synthesis variations can be classified into one of three categories, based on the composition of the precursor alloy and the composition of preNPSG: dealloying of Ag₉₀Au₁₀ to Ag₇₃Au₂₇–Ag₇₇Au₂₃, dealloying of Ag₉₀Au₁₀ to Ag₆₅Au₃₅–Ag₆₈Au₃₂ and dealloying of Ag₉₃Au₇ to Ag₇₃Au₂₇–Ag₇₇Au₂₃.

During the 1st dealloying, which is conducted in 0.01 M H₂SO₄, a certain amount of silver is extracted from the precursor alloy. Based on the change in composition, the amount of charge required for the dealloying is determined. If the dealloying is stopped at this value, the desired composition can be achieved. Another issue, which must be taken into account, is the homogeneity of the composition. As presented in Subsection 2.1.1, dealloying generally proceeds in two phases: primary dealloying and secondary dealloying. During the primary dealloying, the dealloying front moves from the outer surface of the sample to the center. Behind the dealloying front, secondary dealloying starts to further decrease the silver concentration. After the dealloying front has proceeded through the complete sample and the primary dealloying has been finished, a large concentration gradient from the outer surface to the center is still existent. Subsequently, dealloying goes on, and the dealloying progress in regions where the silver concentration is still higher must catch up with regions with lower silver concentration. In order to attain this objective, the dealloying speed is reduced to the minimum. Consequently, the dealloying potential E_D should be as low as possible, but still high enough to drive forward the dealloying progress. This condition is fulfilled by the critical dealloying potential E_c which is introduced in Subsection 2.1.1. Figure 3.2 shows a Tafel plot of a massive Ag₉₀Au₁₀ sample, where the current density is recorded in dependence on E_D . E_c is the potential where the current density is 1 mA/cm² [12, 107]. This value is reached at a potential of 0.397 V vs. ps-Ag/AgCl. However, E_D can also be determined by the rule according to which the dealloying time should not exceed one week. The course of the dealloying current is shown in Figure 3.3(b). Eventually, $E_D = 0.396$ V is applied for the dealloying of Ag₉₀Au₁₀ to Ag₇₃Au₂₇–Ag₇₇Au₂₃, as shown in Figure 3.3(a). For the dealloying of Ag₉₀Au₁₀ to Ag₆₅Au₃₅–Ag₆₈Au₃₂, E_D is increased to 0.402 V. For the dealloying of the last category, the dealloying of Ag₉₃Au₇ to Ag₇₃Au₂₇–Ag₇₇Au₂₃, E_D can be taken over from [58], which states a value of 0.364 V.

The dealloying potential is applied until a cut-off charge is reached. This value is calculated by multiplying the mass with the cut-off charge density K whose unit is C/g. K itself can be determined stoichiometrically [184]:

$$K = \frac{zF}{x_{Au}^{St} M_{Au} + x_{Ag}^{St} M_{Ag}} \left(x_{Ag}^{St} - \frac{x_{Ag}^{De} x_{Au}^{St}}{x_{Au}^{De}} \right). \quad (3.1)$$

x_{Ag}^{St} and x_{Au}^{St} are the silver and gold concentration of the precursor alloy, while x_{Ag}^{De} and x_{Au}^{De} are the silver and gold concentration after 1st dealloying. For the dealloying of Ag₉₀Au₁₀ to Ag₇₅Au₂₅, x_{Ag}^{St} , x_{Au}^{St} , x_{Ag}^{De} and x_{Au}^{De} have the values 0.9, 0.1, 0.75 and 0.25. The charge number z is 1, while the Faraday constant F is 96485.309 C/mol [163]. The molar mass of silver and gold is $M_{Ag} = 107.868$ g/mol and $M_{Au} = 196.967$ g/mol, respec-

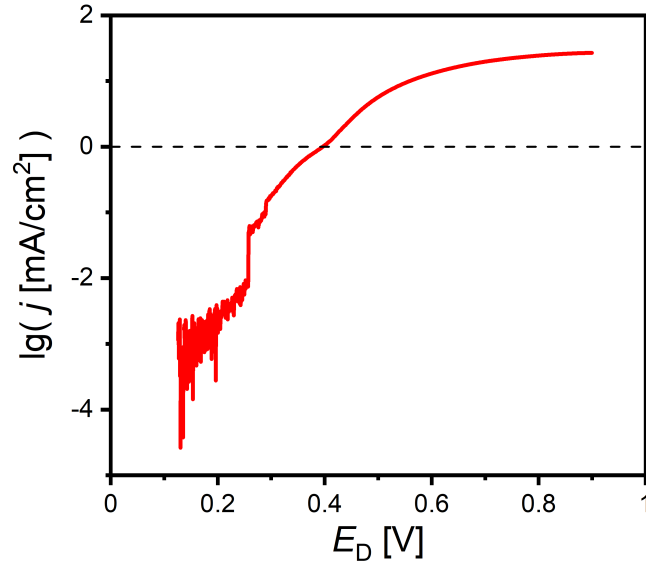


Figure 3.2: Tafel plot of a $\text{Ag}_{90}\text{Au}_{10}$ sample. The scan rate is 1 mV/s. The four larger sides of the cuboidal sample are considered as the area of the sample. The two smallest, roughly square-shaped sides, which are covered by the gold sample holder, are not included. A current density of 1 mA/cm² is reached at 0.397 V vs. ps-Ag/AgCl.

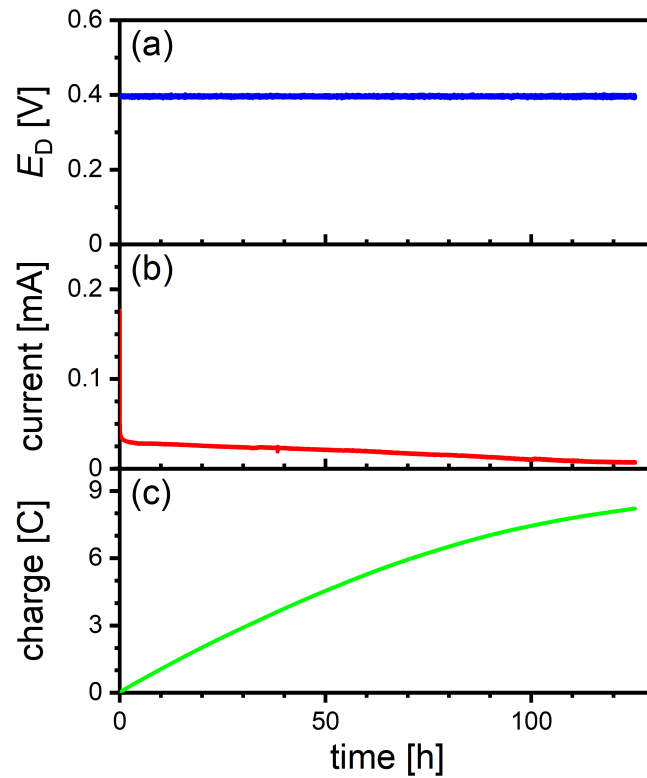


Figure 3.3: Course of the 1st dealloying. (a), (b) and (c) show the dealloying potential E_D , the dealloying current and the total charge, respectively. $E_D = 0.396$ V is applied until a cut-off charge of 8.217 C is reached.

tively [163]. If K is calculated this way, a value of 495.7 C/g results for the dealloying of $\text{Ag}_{90}\text{Au}_{10}$ to $\text{Ag}_{75}\text{Au}_{25}$. For the dealloying of the 2nd category, which implies a composition change from $\text{Ag}_{90}\text{Au}_{10}$ to $\text{Ag}_{67}\text{Au}_{23}$, K is 575.9 C/g, while for the dealloying of the 3rd category, which implies a composition change from $\text{Ag}_{93}\text{Au}_7$ to $\text{Ag}_{75}\text{Au}_{25}$, K is 608.8 C/g. In practice, secondary reactions appear during the 1st dealloying, and the values calculated by Equation 3.1 are not sufficient to obtain the desired composition. Due to the side reactions, Equation 3.1 is not used, and cut-off charge density values are determined empirically. For the dealloying of the 1st, 2nd or 3rd category, K is 517 C/g, 598 C/g or 622 C/g.

During the 1st dealloying, four samples are clamped in a corresponding sample holder and dealloyed together. After completion, the samples are cleaned in ultrapure water for 6–12 h and in ethanol for 3–6 h. To slow down the subsequent drying, the samples are left with a small amount of ethanol at the bottom of a 25 ml bottle whose opening is clogged by a towel. Drying lasts 1–2 days. Eventually, the transformation of the precursor alloy into preNPSG is completed.

The fact that four samples are dealloyed together results in a slight deviation of single samples from the pursued composition of either $\text{Ag}_{75}\text{Au}_{25}$ or $\text{Ag}_{67}\text{Au}_{23}$, while the average composition of the four samples is close to these values. Samples whose composition is outside the range of $\text{Ag}_{73}\text{Au}_{27}$ – $\text{Ag}_{77}\text{Au}_{23}$ or $\text{Ag}_{65}\text{Au}_{35}$ – $\text{Ag}_{68}\text{Au}_{32}$, respectively, are sorted out. The silver concentration is estimated by the following equation:

$$\begin{aligned} x_{\text{Ag}}^{\text{De}} &= \frac{n_{\text{Ag}}^{\text{De}}}{n_{\text{Ag}}^{\text{De}} + n_{\text{Au}}^{\text{De}}} \\ &= \left(\frac{x_{\text{Ag}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} - \frac{m^{\text{St}} - m^{\text{De}}}{M_{\text{Ag}}} \right) \\ &\quad \left(\frac{x_{\text{Ag}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} - \frac{m^{\text{St}} - m^{\text{De}}}{M_{\text{Ag}}} + \frac{x_{\text{Au}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} \right)^{-1}. \end{aligned} \quad (3.2)$$

m^{St} and m^{De} are the mass of the sample before and after the 1st dealloying. It is assumed that no gold is dealloyed, which implies that the amount of substance of gold is equal before and after the 1st dealloying, $n_{\text{Au}}^{\text{St}} = n_{\text{Au}}^{\text{De}}$. The variable $n_{\text{Ag}}^{\text{De}}$ describes the amount of substance of silver after the 1st dealloying. By insertion of the volume V^{De} of the sample after 1st dealloying the solid fraction φ^{De} in this state can be determined:

$$\varphi^{\text{De}} = \left(\frac{1}{\rho_{\text{Au}}} \left(\frac{M_{\text{Au}} x_{\text{Au}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} \right) + \frac{1}{\rho_{\text{Ag}}} \left(m^{\text{De}} - \frac{M_{\text{Au}} x_{\text{Au}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} \right) \right) \left(\frac{1}{V^{\text{De}}} \right). \quad (3.3)$$

The values $\rho_{\text{Ag}} = 10.49 \text{ g/cm}^3$ and $\rho_{\text{Au}} = 19.32 \text{ g/cm}^3$ are inserted as density of silver and gold [163]. On two samples at this stage, EDS analyses are conducted to confirm the correctness of Equation 3.2 and to verify a homogeneous composition. 12 EDS measurements at different positions of a sample, whose $x_{\text{Ag}}^{\text{De}}$ is 0.753 according to Equation 3.2, yield an average composition of $x_{\text{Ag}}^{\text{EDS}} = 0.767 \pm 0.018$. A tendency of a higher silver concentration towards the center of the sample is recognizable. In regions next to the surface $x_{\text{Ag}}^{\text{EDS}}$ is 0.756, while in more central regions $x_{\text{Ag}}^{\text{EDS}}$ is 0.778. Thus, the concentration difference inside the sample is about 0.02. On another preNPSG sample, 13 EDS

measurements yield a composition of $x_{\text{Ag}}^{\text{EDS}} = 0.682 \pm 0.013$, compared with $x_{\text{Ag}}^{\text{De}} = 0.679$ according to Equation 3.2. For this sample, the agreement between both measured variables is higher compared with the EDS analysis on the other sample. A slight underestimation of $x_{\text{Ag}}^{\text{De}}$ by Equation 3.2, which is conceivable according to the EDS analysis first mentioned, is therefore refuted.

3.2.3 Annealing

The 1st dealloying is followed by thermal coarsening, which is the 2nd fundamental step of the synthesis. Samples are annealed for 20 min in an infrared furnace (MILA-5000, ULVAC) under high vacuum at a pressure of 5×10^{-6} mbar. Three different temperatures T_{A} are applied: 300 °C, 400 °C or 500 °C. The purpose of the thermal treatment is the increase of the ligament size, as outlined in Subsection 2.1.2. After completion of this step, samples are denominated as nanoporous silver gold (NPSG). Again, the solid fraction φ^{An} is determined by volume and mass measurement. The approach is similar to Equation 3.3, whereby only volume and mass are adapted:

$$\varphi^{\text{An}} = \left(\frac{1}{\rho_{\text{Au}}} \left(\frac{M_{\text{Au}} x_{\text{Au}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} \right) + \frac{1}{\rho_{\text{Ag}}} \left(m^{\text{An}} - \frac{M_{\text{Au}} x_{\text{Au}}^{\text{St}} m^{\text{St}}}{x_{\text{Au}}^{\text{St}} M_{\text{Au}} + x_{\text{Ag}}^{\text{St}} M_{\text{Ag}}} \right) \right) \left(\frac{1}{V^{\text{An}}} \right). \quad (3.4)$$

3.2.4 Final electrochemical dealloying

A 2nd dealloying is conducted on NPSG samples for the insertion of the lower hierarchy. In the course of this process samples are transformed into HNPG. 1 M HClO₄ is used as electrolyte. The 2nd dealloying itself consists of three substeps which directly follow each other. On samples of the 1st category, which feature a composition of Ag₇₃Au₂₇–Ag₇₇Au₂₃ ($x_{\text{Ag}}^{\text{DE}} = 0.73$ – 0.77), a potential of 0.76 V, 0.80 V or 0.83 V is applied for 2 hours during the 1st substep. For samples of the 2nd category, whose composition is Ag₆₅Au₃₅–Ag₆₈Au₃₂ ($x_{\text{Ag}}^{\text{DE}} = 0.65$ – 0.68), E_{D} is increased to 0.90 V. Due to the higher gold concentration, a potential of 0.83 V or lower results in no significant dealloying current. For samples of the 3rd category, the complete procedure would be identical to samples of the 1st category. However, the 2nd dealloying is not conducted on any sample of this category. During the 2nd substep, which is identical for all categories, $E_{\text{D}} = 0.99$ V is applied for another 2 hours. Finally, either 5 or 60 potential cycles within a potential range of 0.30 V and 0.95 V are applied, which represents the 3rd substep. The variant with a number N_{CY} of 60 cycles is applied only on samples of the 2nd category. All cycles are run at a scan rate of 5 mV/s. As can be seen from Figures 3.4(d), 3.5(d) and 3.6(d), the cycles start at $E_{\text{D}} = 0.80$ V and the potential first goes upward. In the end, the potential stops at $E_{\text{D}} = 0.32$ V. The sample is then removed from the sample holder and cleaned and dried in the same way as after the 1st dealloying. As stated earlier, during the 3rd substep a rolled piece of carbon cloth is used as counter electrode instead of the silver wire, which is illustrated by the comparison of Figures 3.1(a) and 3.1(b).

An exemplary 2nd dealloying with $E_{\text{D}} = 0.80$ V during the 1st substep and 5 potential cycles during the 3rd substep is illustrated by Figure 3.4. The course of current and charge during all substeps is similar for samples annealed at different temperatures. If

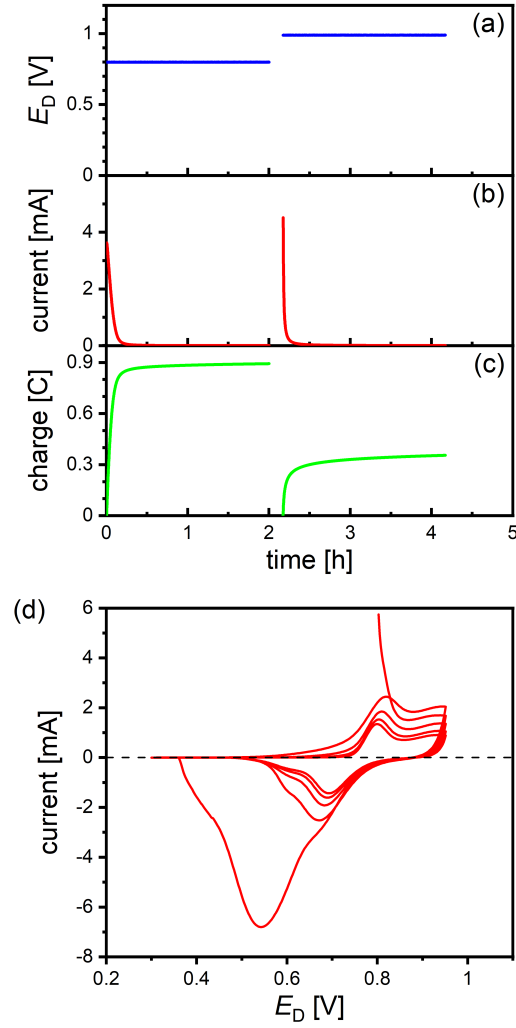


Figure 3.4: Course of the 2nd dealloying with $E_D = 0.80$ V during the 1st substep. (a), (b) and (c) show the dealloying potential E_D , the dealloying current and the total charge of the first two substeps, while (d) presents the subsequent 5 potential cycles. Between the 1st and the 2nd substep, a break of 10 minutes is inserted. The potential is not detected during this time and the charge is set to 0. During the reduction of the 1st potential cycle, a pronounced current maximum is existent. This peak has disappeared in subsequent cycles.

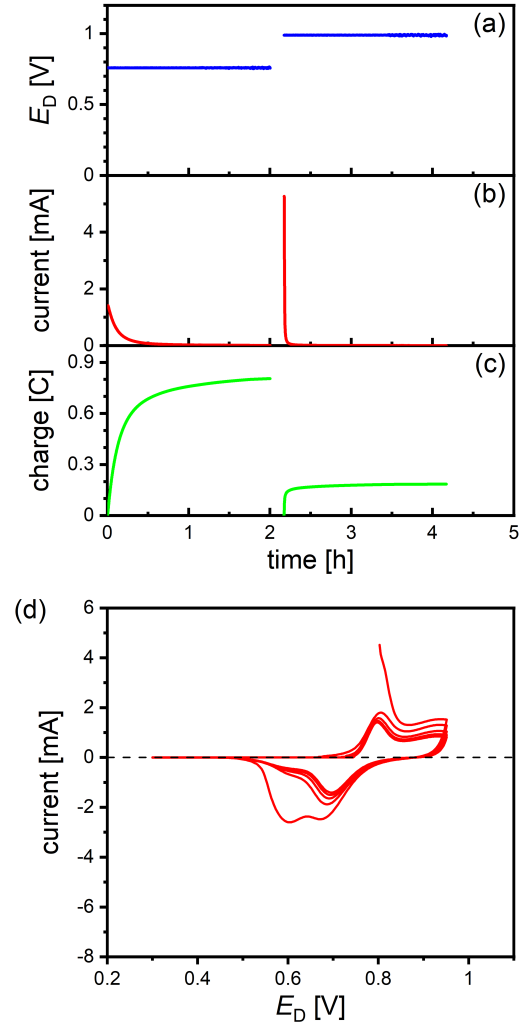


Figure 3.5: Course of the 2nd dealloying with $E_D = 0.76$ V during the 1st substep. In (a), (b) and (c), the dealloying potential E_D , the dealloying current and the total charge of the first two substeps of an exemplary sample is shown. (d) presents the subsequent 5 potential cycles. Compared with Figure 3.4, the current maximum during the reduction of the 1st potential cycle is less pronounced. Furthermore, the ratio between the completed charge of the 1st and the 2nd substep tends to be higher than for $E_D = 0.80$ V.

E_D is 0.83 V during the 1st substep, this similarity exists as well. During the reduction of the 1st potential cycle, a pronounced current maximum at $E_D = 0.54$ V is observable. After the 1st potential cycle, this peak has disappeared completely. A linkage to the reduction of a superficial oxide layer is proposed, whereat the composition of this layer remains unknown [141, 185]. The peak also occurs if E_D has been 0.90 V during the

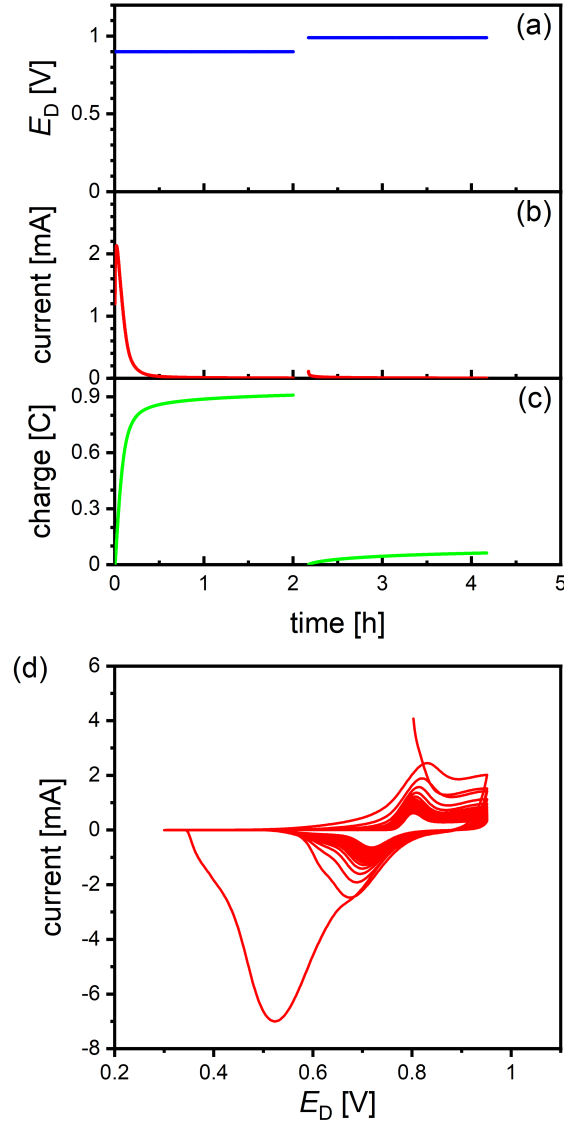


Figure 3.6: Course of the 2nd dealloying with $E_D = 0.90$ V during the 1st substep and 60 potential cycles during the 3rd substep. Applied potential E_D , current and charge are shown in (a), (b) and (c). (d) presents the subsequent 60 potential cycles. Because of the higher potential during the 1st substep, dealloying has proceeded further, and current and charge during the 2nd substep are considerable low.

1st substep, as presented in Figure 3.6(d). A different picture is shown if E_D has been 0.76 V during the 1st substep. As can be seen from Figure 3.5(d), the current maximum is less pronounced. Subsequent cycles show interrelated current maxima during oxidation and reduction. From the potential of the peak maxima, a half-wave potential of $E_D^H = 0.75$ V can be deduced [183, 186]. This redoxreaction is typically explained by the adsorption/desorption of oxygen species [15, 28, 187, 188]. Current values decrease with an increasing number of cycles, which suggests that the surface area of the sample decreases [141, 185]. Indeed, the purpose of increasing the number of cycles to 60 is the electrochemical coarsening of the nanoporous structure.

The residual silver content of the HNPG samples is not estimated by the mass measurement, as done for preNPSG or NPSG. Instead, $x_{\text{Ag}}^{\text{EDS}}$ is determined by an EDS measurement on a representative sample. $x_{\text{Ag}}^{\text{De}}$ is necessary to sort out respective samples. Thereby, $x_{\text{Ag}}^{\text{De}}$ is a process-relevant parameter which must be determined for every sample in a non-destructive way. Furthermore, $x_{\text{Ag}}^{\text{De}}$ naturally shows a variation among different samples, such as "Ag₆₅Au₃₅–Ag₆₈Au₃₂". Since $x_{\text{Ag}}^{\text{EDS}}$ is expected to be mainly constant among HNPG samples of the same procedure, the determination of the residual silver content by EDS is considered as the superior method with regard to HNPG. For the investigation of the solid fraction φ^{Fn} at this stage, the residual silver content is neglected, and the volume V^{Fn} of the HNPG sample is referred to the volume which is filled by a massive gold sample of weight m^{Fn} :

$$\varphi^{\text{Fn}} = \frac{m^{\text{Fn}}}{V^{\text{Fn}} \rho_{\text{Au}}} . \quad (3.5)$$

3.3 Microscopy and electron microscope techniques

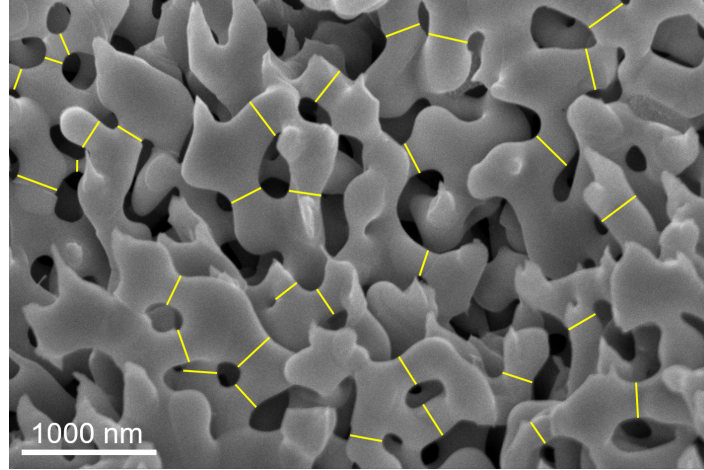


Figure 3.7: Exemplary analysis of a scanning electron micrograph in respect of the ligament size or ligament diameter L . The image shows NPSG annealed at 500 °C. A ligament size of $L = 229 \pm 56$ nm results from the analysis of 33 ligaments [61].

To investigate the outer appearance of the samples and to determine the volume necessary for Equations 3.3–3.5, images are recorded by an optical microscope (Olympus SZX10). Images are acquired on the 4 larger, rectangular sides of the cuboidal samples, whereat on every image 3 length and 3 width measurements are conducted by drawing lines. The x - and y -dimension of the sample are then calculated as the average of 6 values, while the z -dimension is calculated as the average of 12 values.

In preparation for scanning electron microscopy, the samples are split by a scalpel to enable the analysis of the fracture surface. Afterwards, the samples are glued to an aluminum specimen stub with conductive silver paste (Acheson Silver DAG 1415). High-resolution images are acquired by a FEI Helios G3 or a FEI Helios G4 PFIB at a distance of 4 mm, at an acceleration voltage of 10 kV, and at a beam current of

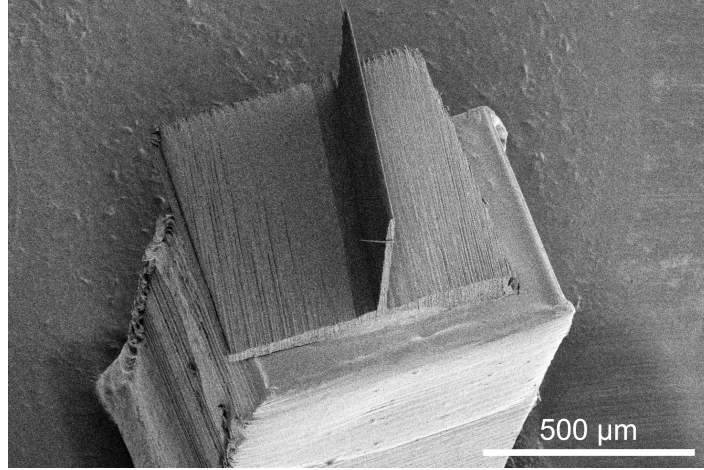


Figure 3.8: Scanning electron micrograph of a NPSG sample from which a thin wall is cut out by plasma focused ion beam in preparation for small-angle X-ray scattering [61].

25 pA–100 pA. The Through Lens Detector is used to achieve the maximum resolution. SEM micrographs are analyzed with respect to the ligament size or ligament diameter L by using the option "Analyze - Measure" of the software ImageJ [189]. Lines are drawn manually at the narrowest section of at least 25 ligaments, as illustrated by Figure 3.7. From the length values obtained, L and the error bar are calculated as the average and the standard deviation.

In addition to the acquisition of high-resolution SEM micrographs, energy-dispersive X-ray spectroscopy (EDS) is applied for the composition analysis. The energy-dispersive spectrometers (Oxford Instruments X-Max 80 or EDAX Octane Elite Super) are integrated components of the electron microscopes. The acceleration voltage is increased to 15 kV, while the beam current is set to 100 pA. If not specified otherwise, EDS measurements are conducted at 3–8 positions on the fracture surface of a single sample. Some percent of oxygen are frequently detected, while traces of chlorine or aluminium, which is the constituent of the specimen stub, are rarely observed. For the composition analysis of NPSG, of preNPSG, or of the precursor alloy, only the silver and gold content are included. Other additives are neglected, and the silver and gold concentration are raised to 1.0. With regard to the residual silver in HNPG, additional elements are not excluded. However, they are not systematically investigated since they are not in the focus of interest. Irrespective of the sample type, the silver concentration determined by EDS is denominated as $x_{\text{Ag}}^{\text{EDS}}$.

In preparation for the X-ray scattering analysis, a thin wall is cut out of the bulk material by plasma focused ion beam (PFIB). During the cutting process, the FEI Helios G4 PFIB is operated at ion beam currents between 100 pA and 2.5 μA and at an acceleration voltage of 30 kV. In order to avoid that the Xenon ion beam touches the aluminum specimen stub, the sample is mounted on a socket which in turn is glued to the specimen stub. A massive $\text{Ag}_{93}\text{Au}_7$ precursor sample is used as a socket. A scanning electron micrograph of a NPSG sample after completion of the FIB cutting process, mounted on a socket, is shown in Figure 3.8. The thickness of the wall is determined on the basis of a SEM micrograph with a viewing direction parallel to the

wall. On the other hand, the area of the wall can be determined by the acquisition of optical images. The thickness of the wall, which varies between $9\text{ }\mu\text{m}$ and $49\text{ }\mu\text{m}$, is the decisive factor for an optimal transmission during SAXS. A maximum scattering intensity is obtained when the transmission amounts to $1/e$ [190]. In contrast, the area of the wall, which is about $0.5 \times 0.5\text{ mm}^2$ in the ideal case and which thereby is equivalent to the transverse section of the sample, is of importance only inasmuch as it must be larger than the beam diameter. For some samples, breakage cause a reduction of the wall area.

3.4 Implementation of mechanical tests

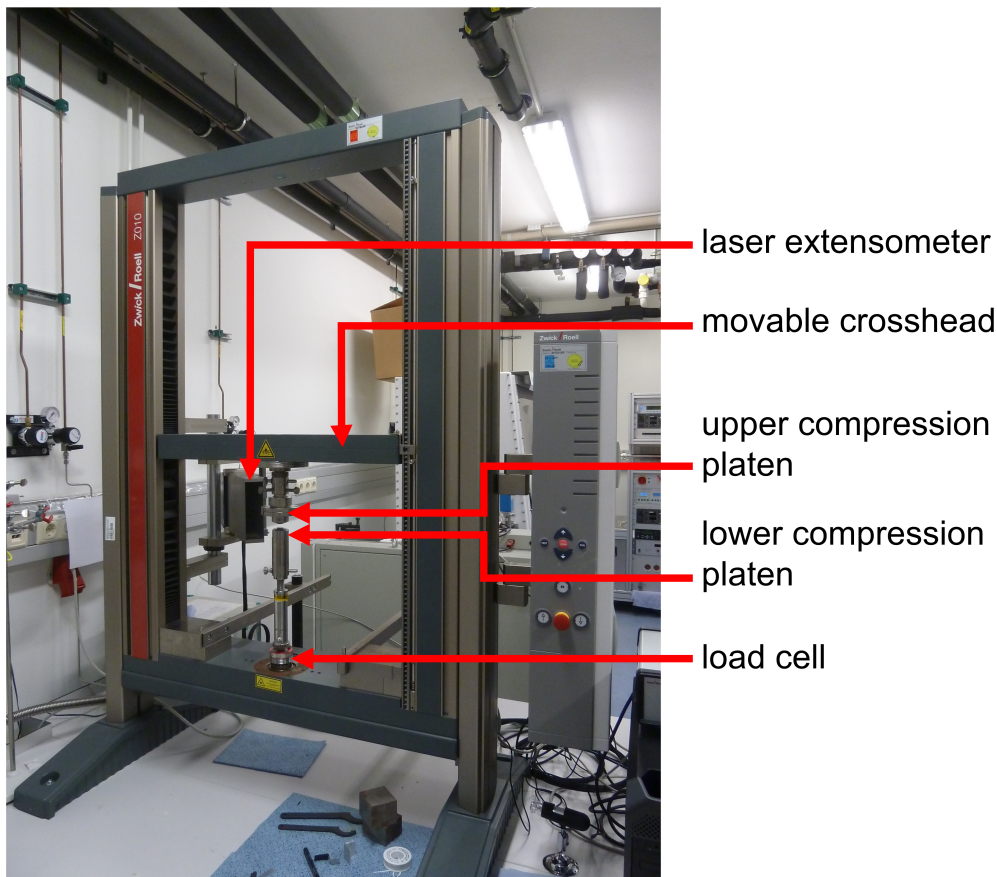


Figure 3.9: Z010 TN Allround Line testing machine from ZwickRoell. The sample (not shown) is positioned between the compression platens.

Figure 3.9 shows a picture of the Z010 TN Allround Line testing machine from ZwickRoell which is used for compression tests. The testing machine is equipped with a 2.5 kN load cell and a laser extensometer (ZwickRoell laserXtens) which measures the strain contactlessly by a reconciliation of the speckle pattern of the grips. The feed rate is set to $0.01\text{ \%}/\text{s}$. During the test, the feed rate is constant and independent of the direction of motion. Data recording starts after the first detection of a stress $\geq 0.5\text{ MPa}$. At lower stress values it is not ensured that the complete sample deforms uniformly, since samples are not perfectly cuboidal and are initially touched at corners

rather than at contact areas. Figure 3.10(a) exemplifies that the principal stress-strain-curve is interrupted by unload-load-cycles. During these unload-load-cycles, which start at predefined strain values, the stress is reduced to 1.0 MPa. Unload-load-cycles at a strain lower than 5% are not included in the analysis. Figure 3.10(b) illustrates that the stress-strain-curve exhibits a hysteresis loop. A secant is drawn between the point of intersection and the reversal point. The slope of the secant represents the secant modulus which is used as Young's modulus E in this thesis [141, 191]. For the determination of the flow stress σ_F , an extension is drawn from the lower end of the secant to the principal stress-strain-curve [58, 74]. Actually, the flow stress can be regarded as a single value $\sigma(\epsilon)$ of the principal stress-strain-curve at a random technical strain ϵ . Strain values are converted into the solid fraction φ by using the plastic Poisson's ratio ν and the solid fraction before compression φ^{Bc} which is identical to φ^{An} or φ^{Fn} [58]:

$$\varphi = \frac{\varphi^{Bc}}{(1 - \epsilon)(1 + \epsilon \nu)^2}. \quad (3.6)$$

For the determination of the plastic Poisson's ratio ν , optical images are acquired on compressed samples. ν is then determined by a comparison of the dimensions before and after compression [134]:

$$\nu = 0.5 \left(\frac{z^{Bc}}{z^{Bc} - z^{Ct}} \frac{x^{Ct} - x^{Bc}}{x^{Bc}} + \frac{z^{Bc}}{z^{Bc} - z^{Ct}} \frac{y^{Ct} - y^{Bc}}{y^{Bc}} \right). \quad (3.7)$$

x^{Bc} , y^{Bc} and z^{Bc} are the dimensions of the sample before compression, while x^{Ct} , y^{Ct} and z^{Ct} represent the corresponding values after compression. On the basis of measurements on 7 NPSG samples and 20 HNPG samples, ν is estimated to be 0.18 ± 0.04 for NPSG and 0.07 ± 0.04 for HNPG, respectively.

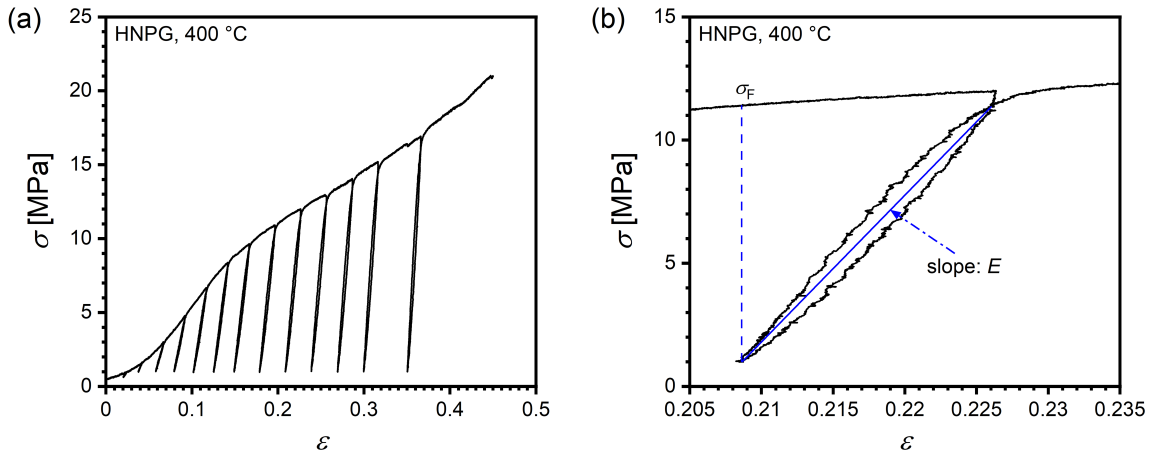


Figure 3.10: Illustration of a mechanical test on a HNPG sample. In (a), a stress-strain-curve of HNPG with $T_A = 400^\circ\text{C}$ is presented. (b) shows an enlarged view of one of the unload-load-cycles. A secant (blue line) is drawn into the unload-load-cycle. The Young's modulus E is determined from the slope of the secant. The extension of the lower end of the secant to the principal stress-strain-curve (blue dashed line) defines the flow stress σ_F . The strain existent at the level of the blue dashed line is assigned to σ_F and E and used for the determination of φ .

3.5 Setup for small- and ultra-small-angle X-ray scattering

A XEUSS 3.0 is used for SAXS and USAXS measurements. For illustration, Figures 3.11(a) and 3.11(b) show pictures of the device. All measurements are performed using a copper microfocus source (Genix 3D) and a 2D solid-state detector (Pilatus 300K) with a pixel size of $172 \times 172 \mu\text{m}^2$. The copper anode is operated at an acceleration voltage of 50 kV and at a current of 0.6 mA. A paraboloidal multilayer monochromator isolates the wavelength of the Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ line which is $\lambda = 0.154 \text{ nm}$ and which is relevant for Equation 2.27 [192]. For the implementation of X-ray scattering experiments, the thin wall, which is cut out by plasma focused ion beam as described in Section 3.3, is removed with a scalpel and attached to scotch tape. Figures 3.11(c) and 3.11(d) show that the scotch tape is then mounted on a circular opening of the solid sample holder which in turn is mounted into the beam line. Due to the small sample area, the beam diameter is reduced to the minimum by setting the slit aperture of the second and last slit to 0.1 mm, which results in a full width at half maximum of approximately 0.2 mm. For single samples, SAXS measurements are conducted with a fully evacuated beam path at sample-to-detector distances of either 1800 mm and 500 mm or 1800 mm, 500 mm, and 300 mm. After data reduction, the respective sections of the scattering signal, which are obtained at different distances, are pieced together without further correction, which results in a measurement range from 1.0 nm^{-1} down to 0.015 nm^{-1} .

A measurement series at a single distance consists of a measurement on the sample, a measurement on a scotchtape without sample, and a measurement of the incident, uninterrupted beam. In the course of the data reduction, which is performed using the software XSACT from XENOCSS [193], the data is first corrected for transmission and referred to the incident flux. For the ascertainment of the transmission, intensity values are evaluated at $q = 0$. The scotchtape itself features a transmission of 78%. Afterwards, the background measurement, which is the measurement on scotchtape, is subtracted from the measurement on the sample. In the end, the data is divided by the sample thickness, which results in the differential scattering cross section $d\Sigma/d\Omega$ in the unit mm^{-1} .

For USAXS measurements, a Bonse-Hart module [194, 195], which consists of a channel-cut monochromator crystal and an analyzer crystal, is mounted into the beam-line. Figure 3.12 illustrates the operation principle. In contrast to the drawing, some part of the beam bypasses the sample, which prevents the output of absolute units. A low beam intensity requires a substantial increase of the beam diameter compared with SAXS, so that the slit aperture of the second slit is increased to 0.6 mm–1.0 mm. The monochromator crystal is an integrated component of the device and driven into the beam path. On the other hand, the analyzer crystal is a separate component, as shown in Figure 3.11(e). For USAXS measurements, it is mounted into the beamline. During data recording, the measurement range of the angle of inclination β is passed through. The count rate and thus the intensity $I(\beta)$ is not radially averaged. Instead, it is averaged over horizontal lines at the detector, so that β -value cannot be converted directly into corresponding q -value. For this reason, the data is desmeared [196] after

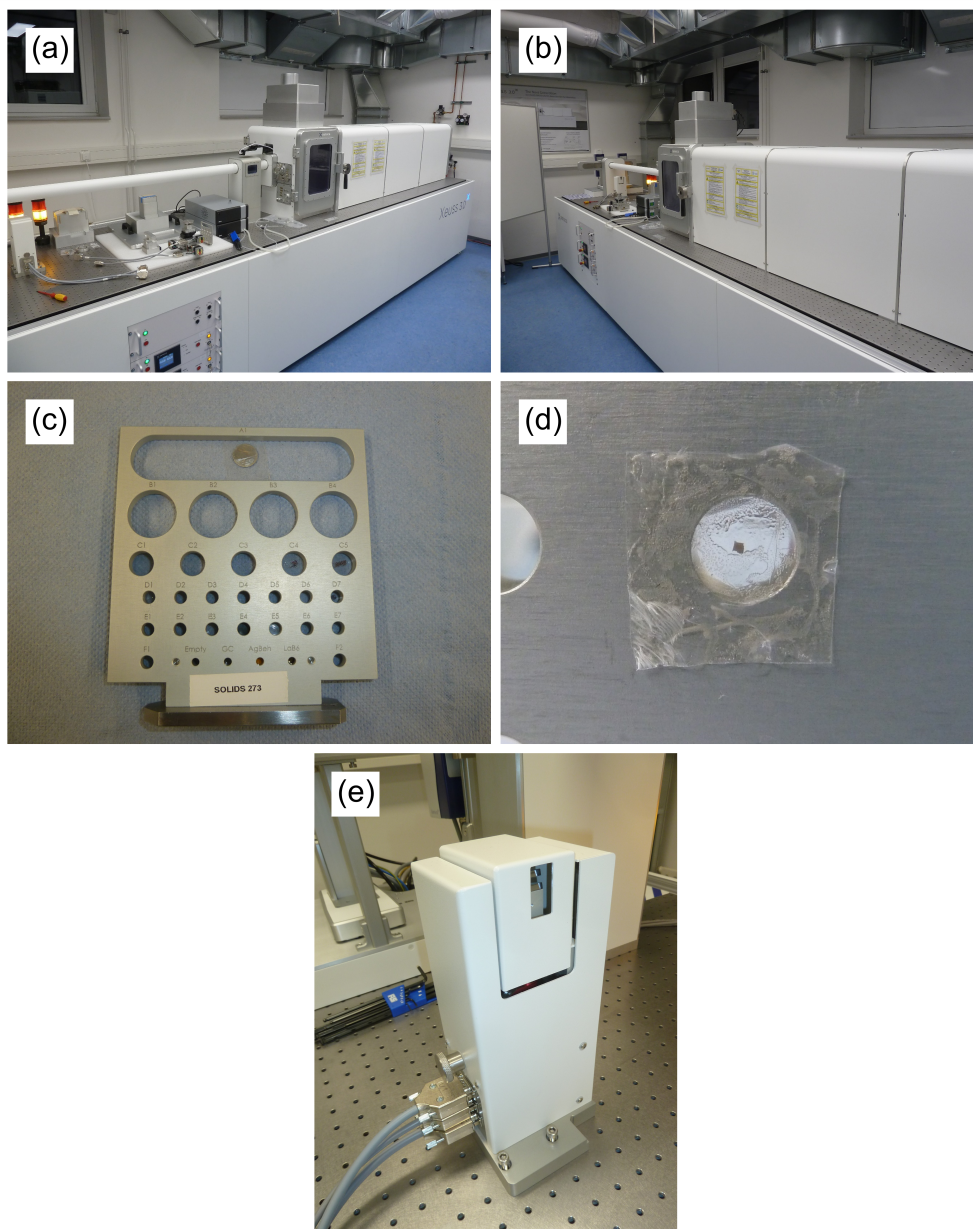


Figure 3.11: Images of the technical equipment used for small-angle X-ray scattering and ultra-small-angle X-ray scattering. (a) and (b) show the Xeuss 3.0. Molybdenum and copper X-ray sources can be seen in the rear part of image (b). The X-ray beam then passes a whitish tube before entering the sample chamber. (c) shows the solid sample holder. Samples are fixed on scotch tape which in turn is mounted on the solid sample holder. (d) shows a close-up of a NPSG sample mounted on the solid sample holder. The analyzer of the Bonse-Hart module used for ultra-small-angle X-ray scattering is shown in (e). For the execution of a USAXS measurement, the analyzer is mounted into the beamline. The analyzer crystal can be recognized in the opening in the upper part of the analyzer.

transmission and background correction. Similar to the reduction of SAXS data, the transmission correction is conducted by bringing sample and background (scotchtape) data to the same level at $q = 0$. The background correction is a simple subtraction.

Finally, the desmeared data, which is considered in a range between $q = 0.1 \text{ nm}^{-1}$ and $q = 0.003 \text{ nm}^{-1}$, is scaled to absolute units by splicing with the SAXS scattering signal between $q = 0.06 \text{ nm}^{-1}$ and $q = 0.1 \text{ nm}^{-1}$. The entire data reduction is realized with the aid of the tool USAXSGUI from XENOCES [197].

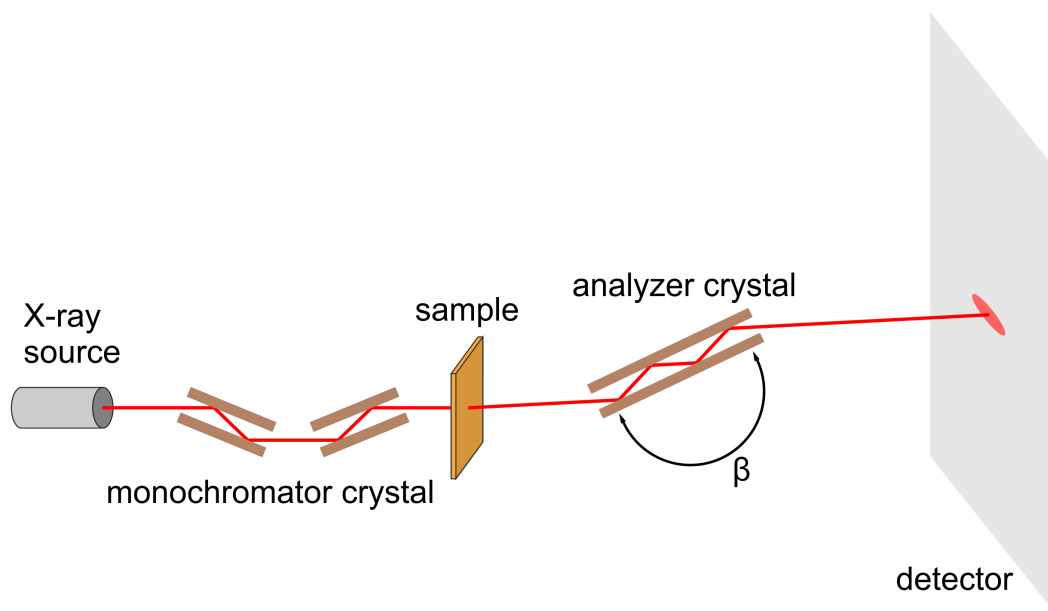


Figure 3.12: Schematic illustration of the setup used for ultra-small-angle X-ray scattering. The drawing is not true to scale. After [157].

Chapter 4

Structural analysis

4.1 Considerations with regard to the solid fraction

Summarizing the statements of the preceding chapter, synthesis variations differ from each other with regard to 5 parameters: 1. type of precursor alloy, 2. silver content after 1st dealloying $x_{\text{Ag}}^{\text{DE}}$, 3. annealing temperature T_{A} , 4. dealloying potential E_{D} and 5. number of potential cycles N_{CY} . The first two parameters, precursor alloy and $x_{\text{Ag}}^{\text{DE}}$, both influence the solid fraction after 1st dealloying. T_{A} influences the extent of coarsening during annealing, which has an impact on the ligament size of NPSG L and, correspondingly, on the upper level ligament size of HNPG L^{U} . The variation of the last two parameters, E_{D} and N_{CY} , has the purpose of adjusting the lower level ligament size L^{U} . A detailed overview of all variants, as well as of essential measured parameters, is given in Table 4.1.

Optical images of a sample in different stages of the synthesis are presented in Figure 4.1. The sample is monolithic and a size difference between NPSG (4.1(b)) and HNPG (4.1(c)) is identifiable, which is a sign of shrinkage. In some cases cracks have developed during annealing or during the 2nd dealloying. Among HNPG samples of category 2, cracks are less common than among HNPG samples of category 1. Only one synthesis variant results in the complete prevention of cracks, this is the variant with $E_{\text{D}} = 0.76 \text{ V}$.

The total solid fraction φ is derived from images such as the ones presented in Figure 4.1. By applying Equations 3.2 and 3.3, the solid fraction after 1st dealloying φ^{De} is plotted against the silver concentration $x_{\text{Ag}}^{\text{De}}$, as shown in Figure 4.2. A mean solid fraction $\varphi^{\text{De}} = 0.41 \pm 0.02$ results from a total number of $N = 25$ samples from the $\text{Ag}_{90}\text{Au}_{10}$ precursor alloy within a composition range of $x_{\text{Ag}}^{\text{DE}} = 0.73\text{--}0.77$. Decreasing the silver concentration range to $x_{\text{Ag}}^{\text{DE}} = 0.65\text{--}0.68$ lowers the solid fraction to $\varphi^{\text{De}} = 0.30 \pm 0.01$ ($N = 16$). Due to their higher initial silver content, samples from the $\text{Ag}_{93}\text{Au}_7$ precursor alloy feature a lower solid fraction in relation to $x_{\text{Ag}}^{\text{De}}$. Considering the same composition range of $x_{\text{Ag}}^{\text{DE}} = 0.73\text{--}0.77$, the solid fraction falls to $\varphi^{\text{De}} = 0.34 \pm 0.01$ ($N = 15$). This value is slightly higher than the value $\varphi^{\text{De}} = 0.31$ which is reported by [58] and which is based on samples from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy and a composition $x_{\text{Ag}}^{\text{DE}} = 0.74\text{--}0.78$. The slight discrepancy is attributed to unknown differences in the sample production.

Table 4.1: Overview of synthesis routes and compilation of measured variables. The Table covers all synthesis processes of NPSG and HNPg samples prepared for SAXS/USAXS and mechanical compression tests and specifies which of these tests is executed. Relevant synthesis parameters and measured values are tabulated. These are precursor alloy, silver content after 1st dealloying x_{Ag}^{DE} , annealing temperature T_A , dealloying potential E_D , number of potential cycles N_{CV} , ligament diameters L^L and L^U on lower and upper level, ligament spacings $\tilde{L}^L$ and $\tilde{L}^U$ on lower and upper level, total solid fraction φ , solid fraction on lower and upper level φ^L and φ^U and silver content x_{Ag}^{EDS} as determined by EDS. Error bars refer to the standard deviation. x_{Ag}^{DE} is obtained from mass values of 3–4 samples (used for compression tests) with the exception of samples made from the $Ag_{93}Au_7$ precursor alloy (category 3), where only one sample is incorporated, which prevents the indication of error bars. For the determination of x_{Ag}^{EDS} , EDS is applied on 1–2 samples with 3–8 positions on each sample. Ligament sizes L^L and L^U correspond to the samples presented in Figures 4.4–4.8. These samples are the basis of SAXS/USAXS measurements as well, except in the case of HNPg of category 1, annealed at 400 °C and dealloyed at 0.80 V or 0.83 V, where SAXS/USAXS and SEM are performed on different samples. In cases where both a SAXS and a USAXS value for $\tilde{L}^U$ are available the average is indicated. φ is based on volume and mass values of 3–4 samples, again with the exception of samples of category 3. Using an estimated value for φ^U , φ^L is determined by Equation 4.1 [61].

sample type	cate- gory	precursor	x_{Ag}^{DE} [-]	T_A [°C]	E_D [V]	N_{CV} [-]	L^L [nm]	L^U [nm]	$\tilde{L}^L$ [nm]	$\tilde{L}^U$ [nm]	φ [-]	φ^L [-]	φ^U [-]	x_{Ag}^{EDS} [-]	SAXS/ USAXS	mech. test
NPSG	1	$Ag_{90}Au_{10}$	0.75±0.01	300				57±10		162	0.40±0.01			0.78±0.02	yes	yes
			0.75±0.00	400				132±31		291	0.42±0.02			0.75±0.01	yes	yes
			0.75±0.00	500				239±56		637	0.44±0.02			0.74±0.02	yes	yes
NPSG	3	$Ag_{93}Au_7$	0.76	300				55±8		169	0.33			0.74±0.02	yes	no
			0.77	400				138±20		375	0.35			0.73±0.03	yes	no
			0.76	500				206±28		607	0.39			0.70±0.03	yes	no
HNPg	1	$Ag_{90}Au_{10}$	0.74±0.00	300	0.80	5	19±3	59±11	59	161	0.14±0.00	0.34	0.40	0.06±0.01	yes	yes
			0.75±0.01	400	0.80	5	19±3	123±25	59	287	0.15±0.00	0.35	0.42	0.04±0.01	yes	yes
			0.74±0.01	500	0.80	5	21±3	201±35	64	536	0.16±0.01	0.36	0.44	0.04±0.00	yes	yes
			0.76±0.01	400	0.76	5	29±5	125±17	107	321	0.13±0.00	0.31	0.42	0.02±0.00	yes	yes
			0.75±0.01	400	0.83	5	20±3	115±26	46	286	0.17±0.00	0.39	0.42	0.05±0.01	yes	yes
HNPg	2	$Ag_{90}Au_{10}$	0.67±0.00	300	0.90	5	15±4	69±12			0.13±0.00	0.41	0.32	0.10±0.03	no	yes
			0.66±0.01	300	0.90	60	29±6	60±8			0.14±0.01	0.43	0.32	0.02±0.01	no	yes
			0.67±0.01	400	0.90	5	15±3	130±27			0.15±0.01	0.43	0.34	0.08±0.02	no	yes
			0.67±0.01	400	0.90	60	29±6	111±20			0.14±0.01	0.42	0.34	0.02±0.01	no	yes

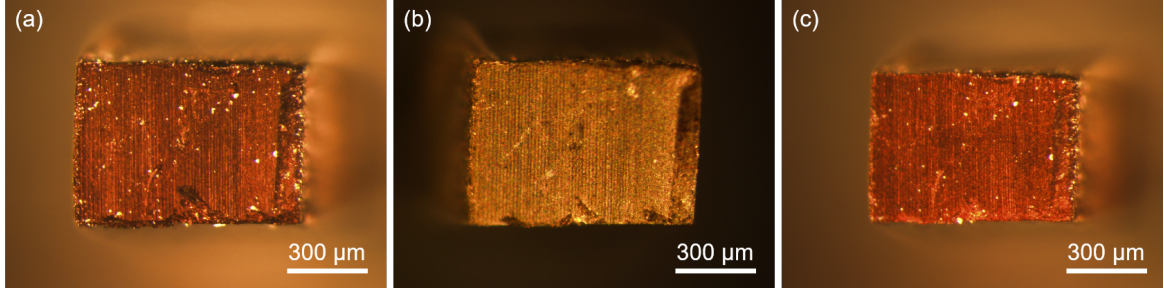


Figure 4.1: Optical microscope images of a sample in different stages of the production. (a) shows a preNPSG sample. The mass measurement yields a composition of $\text{Ag}_{75}\text{Au}_{25}$ ($x_{\text{Ag}}^{\text{DE}} = 0.75$). In (b), the sample is converted into NPSG by annealing at 400 °C. (c) presents a HNPG sample after the 2nd dealloying with a potential of $E_{\text{D}} = 0.80$ V. All images display the same side of the sample [61].

A closer look at the solid fraction data for NPSG of category 1 in Table 4.1 enables the identification of a notable effect: *Coarsening of NPSG by annealing is accompanied by shrinkage*. While annealing at 300 °C does not cause an increase of the solid fraction, annealing at 400 °C increases φ^{An} (φ in Table 4.1) from 0.40 to 0.42, while annealing at 500 °C results in an increase to 0.44. NPSG of category 3 shows the same effect, while values in general are lower. This effect, which is associated with the connectivity discussion, is observed in previous studies. It occurs during the coarsening of NPSG, as can be seen from Figure 1.4 [58], and during the coarsening of NPG, as can be seen from Figure 2.2 [79, 114].

As mentioned above, the 2nd dealloying is accompanied by a significant shrinkage. An inspection of the solid fraction data for HNPG of category 1 reveals that the solid fraction of NPSG is partially transferred to HNPG. While NPSG annealed at 300 °C, 400 °C or 500 °C exhibits solid fractions of 0.40, 0.42 or 0.44, corresponding HNPG samples feature values of 0.14, 0.15 or 0.16 when dealloyed with $E_{\text{D}} = 0.80$ V. However, changing E_{D} has a severe impact on φ^{Fn} (φ in Table 4.1). Depending on whether E_{D} is 0.76 V, 0.80 V or 0.83 V, HNPG samples types, which all emerge from NPSG with $\varphi^{\text{An}} = 0.42$, end up at $\varphi^{\text{Fn}} = 0.13$, 0.15 or 0.17. This leads to the question of how the solid fractions on the upper and the lower level can be estimated. For the sake of illustration, shrinkage can be seen as an isotropic volume contraction of a nanoporous structure. Since during the 2nd dealloying the lower hierarchy level develops and coarsens, it is likely that the shrinkage, which occurs during the 2nd dealloying, takes place entirely on the lower level. This assumption is supported by the strong influence of E_{D} on the shrinkage, since E_{D} affects the development of the lower hierarchy level. In this scenario, the cavities on the upper level shrink to the same extent as the ligaments on the upper level, and the upper level solid fraction remains constant. Following this hypothesis, the solid fraction of a NPSG sample type is identical with the upper level solid fraction φ^{U} of the respective HNPG sample type emerging therefrom. HNPG samples which emerge from, for instance, NPSG with $\varphi^{\text{An}} = 0.42$ feature an upper level solid fraction φ^{U} of 0.42. The lower level solid fraction φ^{L} is then calculated by using

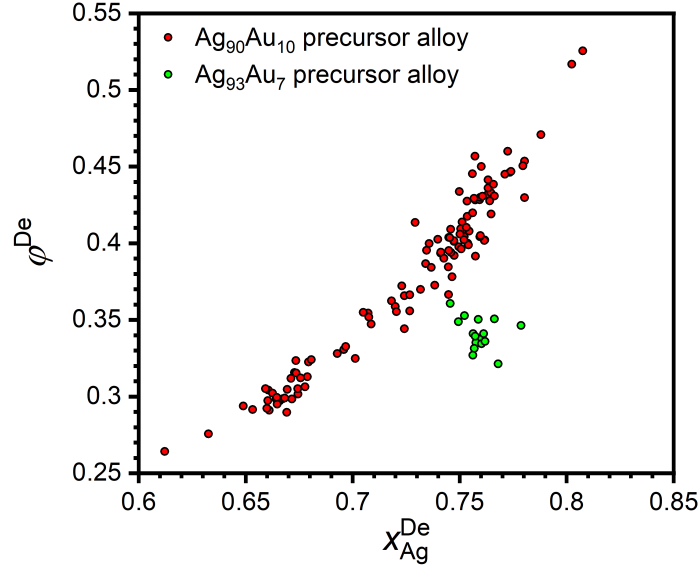


Figure 4.2: Solid fraction φ^{De} of samples after the 1st dealloying (preNPSG), as determined by the volume and mass measurement, in dependence on the silver content $x_{\text{Ag}}^{\text{De}}$, as determined by the mass measurement. Red dots indicate samples made from a $\text{Ag}_{90}\text{Au}_{10}$ precursor alloy, while green dots indicate samples made from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy. In total, measurements on 132 samples are shown.

the measured value for φ^{Fn} and the estimate for φ^{U} :

$$\varphi^{\text{L}} = \frac{\varphi^{\text{Fn}}}{\varphi^{\text{U}}} . \quad (4.1)$$

If the total volume shrinkage takes place on the upper level with constant φ^{L} and increasing φ^{U} , this would involve some bending or some thickening of upper level ligaments, which is considered unlikely. On the other side, the assumption made above results in a decrease of the upper level ligament size of HNPG L^{U} compared with the ligament size L of NPSG. It is also conceivable that upper level ligaments show additional shrinkage in transverse direction. In this case, a skeletonized version of the upper hierarchy level structure would not change, φ^{L} would increase, φ^{U} would decrease and the total volume would remain constant. Hence, macroscopic shrinkage cannot be explained.

4.2 Analysis by electron microscopy

Figure 4.3 depicts a preNPSG sample. In this stage, the ligament size L is around 10 nm. NPSG and HNPG samples of category 1 are presented in Figure 4.4. (a), (b) and (c) illustrate the adjustment of the ligament size of NPSG by the annealing temperature T_{A} . Annealing temperatures of 300 °C, 400 °C or 500 °C increase the ligament size to 60 nm, 130 nm or 240 nm. (d), (e) and (f) present corresponding HNPG samples which evolve from the NPSG sample types shown in (a), (b) and (c). They are synthesized with the same dealloying potential $E_{\text{D}} = 0.80 \text{ V}$ and their lower level ligament size is similar and amounts to $L^{\text{L}} \approx 20 \text{ nm}$. Generally, the L of NPSG is transferred to the

L^U of HNPG. In the case of the NPSG and HNPG samples with $T_A = 500^\circ\text{C}$, the L of NPSG is slightly higher than the L^U of HNPG (240 nm compared to 200 nm), while the NPSG and HNPG samples with $T_A = 300^\circ\text{C}$ and $T_A = 400^\circ\text{C}$ show a better agreement between both measured variables. In this context it is noted that the ligament size can show a variation among different samples synthesized by the same procedure.

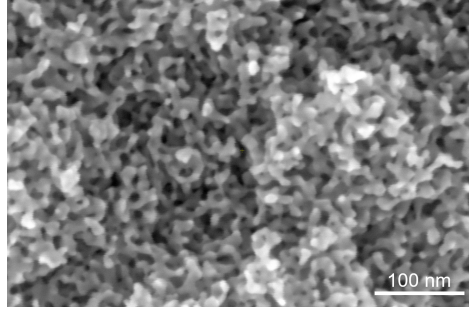


Figure 4.3: Scanning electron micrograph of a preNPSG sample. In application of Equation 3.2, the mass measurement yields a composition of $\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.77$). The image analysis with regard to the mean ligament diameter results in a value of $L = 9 \pm 2$ nm [61].

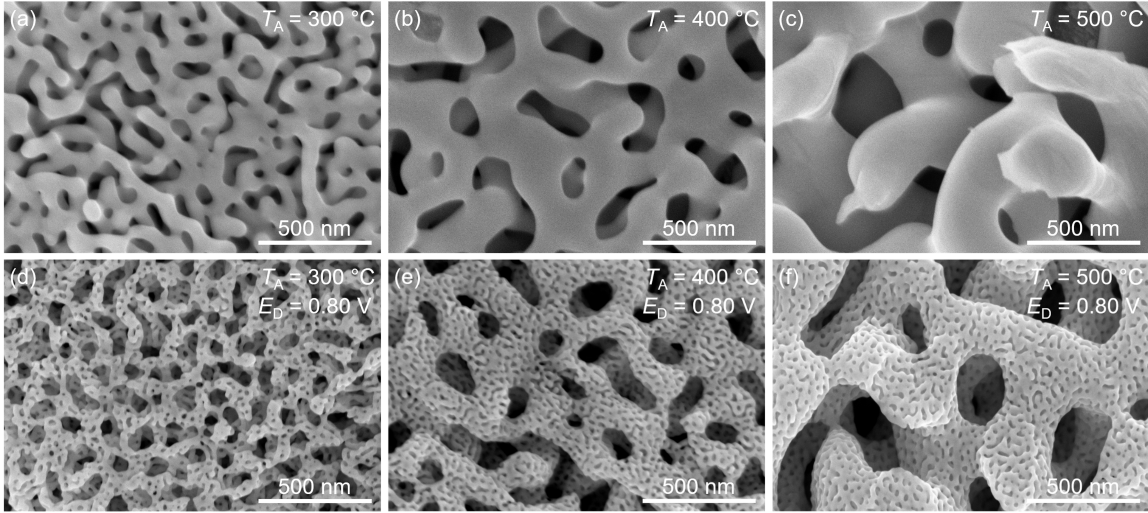


Figure 4.4: Illustration of the variation of the upper level ligament size L^U with a constant lower level ligament size L^L . (a), (b) and (c) show scanning electron micrographs of NPSG with a composition of $\text{Ag}_{73}\text{Au}_{27}$ – $\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.73$ – 0.77) which is annealed at different temperatures. (d), (e) and (f) present corresponding HNPG samples which are dealloyed at $E_D = 0.80$ V. Consequently they feature an equal L^L . Samples in the same column are annealed at the same temperature T_A which is 300°C for (a) and (d), 400°C for (b) and (e) and 500°C for (c) and (f) [61].

Figure 4.5 illustrates the adjustment of the lower level ligament size L^L by a variation of the dealloying potential E_D . All HNPG samples emerge from the NPSG sample type presented in Figure 4.4(b). Thus, T_A is 400°C and the category is 1. When E_D is increased from 0.76 V to 0.80 V, L^L falls from 29 nm to 19 nm. Another increase of E_D to 0.83 V does not lead to a further decrease of L^L . This relationship is illustrated by

Figure 4.6(a), where additional data points demonstrate that L^L shows a steplike decline at $E_D \approx 0.79$ V. Similar observations are reported in the literature in the context of the dealloying of $\text{Cu}_{75}\text{Au}_{25}$ [187] and $\text{Ag}_x\text{Au}_{1-x}$ [15], where this effect is explained by the adsorption of oxygen species for dealloying potentials above a transition potential. In another context, the role of this transition potential is noticed during the investigation of the creep of nanoporous gold [188]. For the same electrolyte, namely 1 M HClO_4 , these studies [15, 187, 188] report a transition potential similar to the value derived from Figure 4.6(a), $E_D = 0.79$ V vs. ps-Ag/AgCl = 1.30 V vs. SHE. This value is slightly higher than the half-wave potential $E_D^H = 0.75$ V vs. ps-Ag/AgCl recognizable in the current-voltage curves of the potential cycles, as presented in Figures 3.4(d), 3.5(d) and 3.6(d). With a high probability the underlying reaction is the same, whereat the exact nature of the oxygen species is not at the center of interest at this point. A striking characteristic of the variant with $E_D = 0.76$ V is the reduced height of the current maximum during the reduction of the 1st potential cycle, located at $E_D = 0.54$ V, as presented in Figure 3.5(d). The observation that oxygen adsorption in a previous step leads to an increased height of this current peak supports the assumption that the peak is related to the reduction of a superficial oxide layer [141, 185]. In any case, the oxygen species adsorbed on the surface attenuate the surface diffusion of gold, which slows down the coarsening during the 2nd dealloying. As can be seen from Figure 4.6(b) as well as from the $x_{\text{Ag}}^{\text{EDS}}$ data in Table 4.1, the residual silver content $x_{\text{Ag}}^{\text{EDS}}$ drops as L^L increases. This correlation applies to all methods for the adjustment of L^L , namely the variation of E_D as well as the variation of N_{CY} . A negative correlation between residual silver content and ligament size is characteristic for coarsening [15, 105].

Another observation derived from Figure 4.5 is the decrease of L^U with increasing E_D . Potential values E_D of 0.76 V, 0.80 V or 0.83 V result in upper level ligament sizes L^U of 125 nm, 123 nm or 115 nm. In this context the visual appearance of the ligaments shown in Figure 4.5 is of significance as well. A dealloying potential of 0.76 V leads to a more open lower level structure (Figure 4.5(a)), while a potential of 0.83 V leads to a closer, more densified lower level structure (Figure 4.5(c)). These structural characteristics go along with the lower level solid fractions predicted for the structures, which are $\varphi^L = 0.31$ for $E_D = 0.76$ V, $\varphi^L = 0.35$ for $E_D = 0.80$ V and $\varphi^L = 0.39$ for $E_D = 0.83$ V. Thereby the visual appearance of the HNPG structures confirms the assumptions made above with regard to Equation 4.1, according to which the shrinkage during the 2nd dealloying takes place on the lower level. A notable aspect is the combination of a higher degree of coarsening with less shrinkage. In that regard, the electrochemical coarsening during the 2nd dealloying is contrary to the thermal coarsening during the annealing step, where coarsening is associated with shrinkage. The shrinkage during the electrochemical coarsening is positively affected by the coverage with oxygen species, which suggests that a causal relationship exists. Parida *et al.* [142], who also observe a stronger shrinkage for higher dealloying potentials during the electrochemical dealloying in perchloric acid, speculate that surface adatoms support the formation of lattice defects, which in turn accelerate the shrinkage rate. Nevertheless, the exact nature of the mechanism remains unclear.

Scanning electron micrographs of NPSG samples of category 3, which are produced from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy, are presented in Figure 4.7. Annealing temperatures

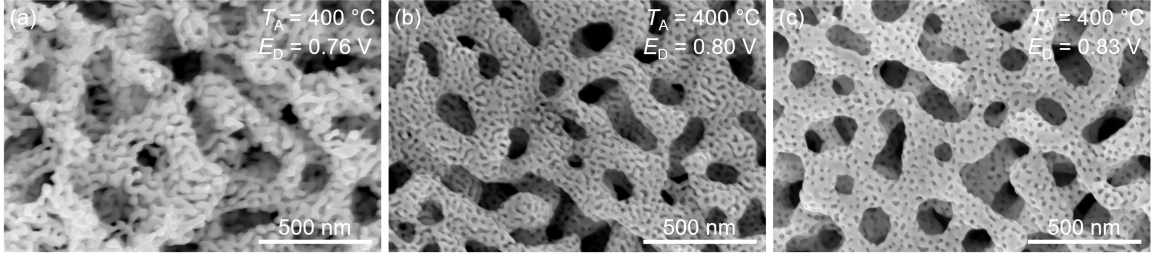


Figure 4.5: Illustration of the variation of the lower level ligament size L^L with fairly constant upper level ligament size L^U . All images show scanning electron micrographs of samples annealed at $T_A = 400\text{ }^\circ\text{C}$. For the adjustment of L^L , E_D is set to 0.76 V, 0.80 V or 0.83 V, as shown in (a), (b) and (c). All variants are produced from the NPSG structure illustrated by Figure 4.4(b) [61].

T_A of 300 °C, 400 °C and 500 °C result in ligament sizes L of 60 nm, 140 nm and 210 nm. While ligament sizes are roughly comparable to the NPSG samples of category 1 shown in Figures 4.4(a)–4.4(c), the solid fraction φ^{An} is lower and amounts to 0.33, 0.35 and 0.39, as mentioned above. HNPG of category 3 is not analyzed in this study. An astonishing observation is a divergence between $x_{\text{Ag}}^{\text{DE}}$ and $x_{\text{Ag}}^{\text{EDS}}$. The NPSG sample annealed at 400 °C features $x_{\text{Ag}}^{\text{DE}} = 0.77$ and $x_{\text{Ag}}^{\text{EDS}} = 0.73$, while for the NPSG sample annealed at 500 °C $x_{\text{Ag}}^{\text{DE}}$ is 0.76 in contrast to $x_{\text{Ag}}^{\text{EDS}} = 0.70$. For all other NPSG and preNPSG samples which are analyzed by EDS, $x_{\text{Ag}}^{\text{DE}}$ and $x_{\text{Ag}}^{\text{EDS}}$ show a maximum deviation of 0.02. Since the divergence increases with rising annealing temperature, a higher gold content at the surface of the ligaments as a result of the annealing-induced coarsening is a possible explanation [105]. This reasoning is countered by the fact that NPSG of category 1 does not show this trend. The small size of the database prevents a conclusion.

Figure 4.8 compiles SEM images of HNPG samples of category 2. As in the case of the HNPG samples presented in Figures 4.4 and 4.5, the precursor alloy is $\text{Ag}_{90}\text{Au}_{10}$. In contrast to them, their composition after 1st dealloying is $x_{\text{Ag}}^{\text{DE}} = 0.65\text{--}0.68$. Consequently, their φ^{De} is lower and amounts to 0.30, as noted in Section 4.1. Annealing increases the solid fraction to $\varphi^{\text{An}} = 0.32 \pm 0.01$ ($N=8$) for $T_A = 300\text{ }^\circ\text{C}$ or $\varphi^{\text{An}} = 0.34 \pm 0.01$ ($N=8$) for $T_A = 400\text{ }^\circ\text{C}$. These values are assumed as φ^U , as can be seen from Table 4.1. Due to the lower silver content before the 2nd dealloying, with less silver to be removed, the lower level solid fraction is higher and amounts to $\varphi^L = 0.41\text{--}0.43$. Thus, HNPG of category 2, illustrated by Figure 4.8, features a lower φ^U and a higher φ^L with comparable total solid fraction φ^{Fn} in comparison with HNPG of category 1, illustrated by Figures 4.4 and 4.5. T_A sets the upper level ligament size L^U , as seen earlier. The number of potential cycles N_{CY} is varied, which represents the method for the adjustment of L^L . $N_{\text{CY}} = 5$ results in $L^L = 15\text{ nm}$, while $N_{\text{CY}} = 60$ increases L^L to 29 nm. An adjustment of L^L by a variation of the dealloying potential E_D is not applicable to samples of category 2 because dealloying potentials of $E_D = 0.76\text{ V}$ or $E_D = 0.83\text{ V}$ result in no significant dealloying current. The higher gold content requires a dealloying potential E_D of 0.90 V, as already mentioned in Subsection 3.2.4. As can be deduced from the total solid fraction listed in Table 4.1, the additional electrochemical coarsening by an increased number of potential cycles is not accompanied by volume shrinkage. How-

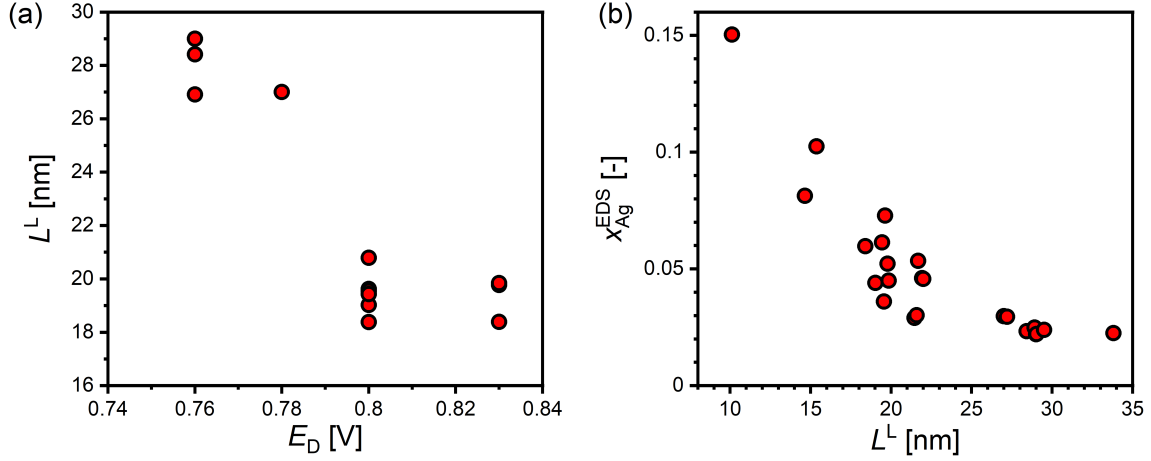


Figure 4.6: Adjustment and characteristics of the lower level ligament size L^L . (a) presents L^L in dependence on the dealloying potential E_D . For the samples whose L^L and E_D are listed in (a), the composition after 1st dealloying is always $Ag_{73}Au_{27}$ – $Ag_{77}Au_{23}$ ($x_{Ag}^{DE} = 0.73$ – 0.77). The number of potential cycles N_{CY} is 5, so that L^L is not affected by other parameters than E_D . (b) depicts the residual silver content x_{Ag}^{EDS} determined by EDS against L^L . This figure includes HNPG samples produced under a wide variety of conditions including E_D , N_{CY} and x_{Ag}^{De} . In some cases, the synthesis variant is not further reported in this thesis. Figure (b) points out that the residual silver content shows a universal decrease with increasing ligament size.

ever, L^U seems to be reduced when comparing Figures 4.8(c) and 4.8(d). A possible explanation is a shrinkage transverse to the upper level ligaments. In this case, φ^U would be even lower than assumed (0.34), while φ^L would be higher. In any case, such an effect is not considered further. NPSG with $x_{Ag}^{DE} = 0.65$ – 0.68 is not analyzed by SEM.

4.3 X-ray scattering analysis

4.3.1 Scattering signal of nanoporous silver gold and hierarchical nanoporous gold

Figure 4.9 presents scattering graphs of all samples which are subject to a X-ray scattering analysis. In Figures 4.9(a) and 4.9(b), the scattering graphs of NPSG of category 1 ($Ag_{90}Au_{10}$ precursor alloy, (a)) and NPSG of category 3 ($Ag_{93}Au_7$ precursor alloy, (b)) are presented. Corresponding SEM images are shown in Figures 4.4(a)–4.4(c) and Figure 4.7. An interference peak, which is linked to the characteristic ligament spacing of the nanoporous structure, is clearly pronounced. Higher annealing temperatures T_A , which are associated with larger ligament sizes L , shift the position of the peak to lower q -values. Without further analysis, a clear agreement between SAXS and USAXS data is evident. The lower resolution limit of SAXS is estimated to amount to $q = 0.02 \text{ nm}^{-1}$. USAXS allows the analysis of length scales which are outside the resolution limit of SAXS.

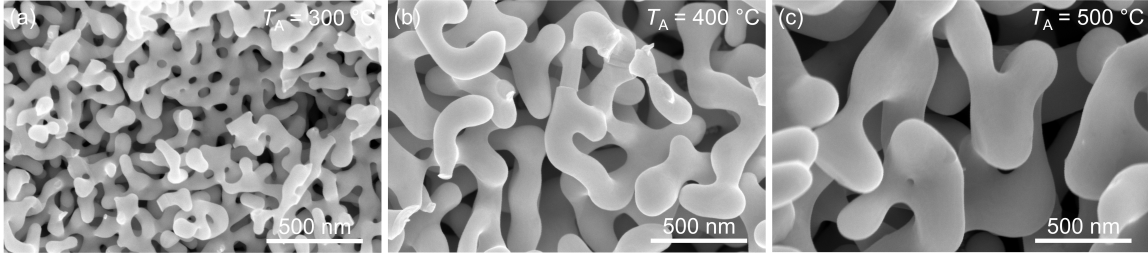


Figure 4.7: Scanning electron micrographs of NPSG produced from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy. All other scanning electron micrographs or optical microscope images presented in this thesis are acquired on samples produced from a $\text{Ag}_{90}\text{Au}_{10}$ precursor alloy. The composition of the samples presented in this figure varies in a narrow range of $\text{Ag}_{76}\text{Au}_{24}$ – $\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.76$ – 0.77). Similar to Figures 4.4(a)–4.4(c), the structures shown in (a), (b) and (c) are annealed at 300°C , 400°C or 500°C . The scale bar is slightly different from SEM images presented in Figures 4.4, 4.5 and 4.8.

HNPG scattering graphs presented in Figures 4.9(c) and 4.9(d) possess two distinct interference peaks which are associated with the two separate length scales of the structure. Figure 4.9(c) opposes scattering graphs of HNPG samples with a different annealing temperatures T_A , which are dealloyed with the identical dealloying potential $E_D = 0.80\text{ V}$. SEM images of comparable sample types can be found in Figures 4.4(d)–4.4(f). Interference peaks related to the lower level structure are located at equal q -values, which agrees with the consistent $L^\perp$ determined for these sample types. As in the case of NPSG scattering data, the wave number of the upper level peak decreases with increasing T_A . The adjustment of $L^\perp$ by the variation of E_D is illustrated by Figure 4.5. Corresponding SAXS scattering graphs presented in Figure 4.9(d) differ with regard to the position of the lower level interference peak.

4.3.2 Fitting of scattering data

A precise identification of the peak position q_{peak} is not straightforward. Subsection 2.3.3 gives a short overview. A simple method is the utilization of the data point with the highest scattering intensity $d\Sigma/d\Omega$. With regard to the SAXS scattering data shown in Figure 4.9, this method is affected by two drawbacks. In the regime of low scattering angles, interference peaks are formed by just a few data points. Furthermore, the interference peak of the lower hierarchy level takes the form of a shoulder which exhibits no intensity maximum. Welborn & Detsi [169] demonstrate that the Berk model [97, 179] is not able to reproduce the Porod regime adequately. The Berk model assumes a Gaussian distribution of q_0 as the basis of the leveled wave model, which involves a Gaussian as part of the term describing the scattering intensity. The Gaussian is however multiplied by an additional q^{-1} and supplemented by a further addition in comparison with the approach of this thesis described below [169, 179]. An alternative is the Teubner-Strey model [180] which performs a fit using an equation with three adjustable parameters A , B and C :

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{TS}} = \frac{A}{1 + Bq^2 + Cq^4}. \quad (4.2)$$

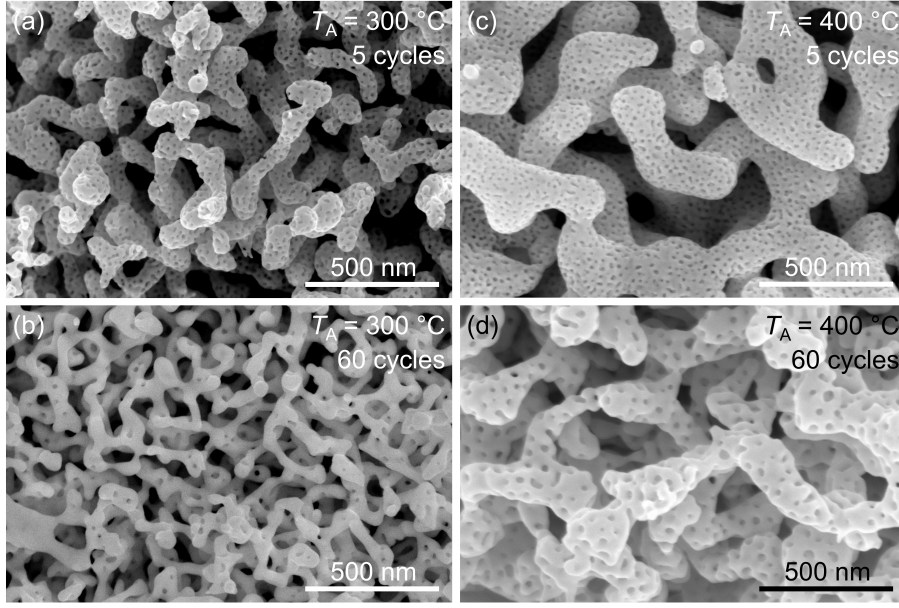


Figure 4.8: Variation of the lower level ligament size L^L by amending the number of potential cycles N_{CY} . After the 1st dealloying, the samples feature a composition of $\text{Ag}_{65}\text{Au}_{35}$ – $\text{Ag}_{68}\text{Au}_{32}$ ($x_{\text{Ag}}^{\text{DE}} = 0.65$ – 0.68). The annealing temperature T_A is $300\text{ }^\circ\text{C}$ for samples shown in the first column and $400\text{ }^\circ\text{C}$ for samples shown in the second column. For samples displayed in the first line N_{CY} is 5, while for samples displayed in the second line N_{CY} is 60. Accordingly, (a) and (c) on the one hand and (b) and (d) on the other hand feature a similar lower level ligament size L^L .

Figure 4.10(a) exemplifies the fitting of NPSG scattering data by the Teubner-Strey-model. The fit reproduces the course of the scattering curve in the Porod regime but does not reproduce the shape and height of the peak and a slight dent between peak and Porod regime. The Choi & Chen model [181] is costly in terms of effort, since it requires the formation of a spectral density function [169]. Furthermore, Welborn *et al.* [115] show that this model is not capable of replicating the shape of the interference peak of nanoporous gold. In order to ensure an adequate fitting of the scattering data, a new model is introduced, which is based on the separate consideration of the interference peak and the Porod regime. The interference peak is fitted by a Gaussian [198] which is added to a baseline. The baseline follows the course of the scattering curve in the Porod regime and transitions into a constant value in the region of the peak. For the generation of such a course, four adjustable parameters A , B , C and D are required, which control 1. the constant level A in the region of the peak, 2. the q -value where the transition into the power law takes place, 3. the abruptness of this transition and 4. the exponent of the power law (-4 in the case of the Porod regime). The resulting equation is:

$$\left(\frac{d\Sigma}{d\Omega}\right)_{\text{fit}} = \frac{A}{(1 + (Bq)^C)^D} + \frac{F}{\sigma_p\sqrt{2\pi}} \exp\left(-\frac{(q - q_{\text{peak}})^2}{2\sigma_p^2}\right). \quad (4.3)$$

In total, 7 adjustable parameters are determined. Among them, F regulates the height of the Gaussian, while σ_p is the standard deviation of the Gaussian. It is noted that

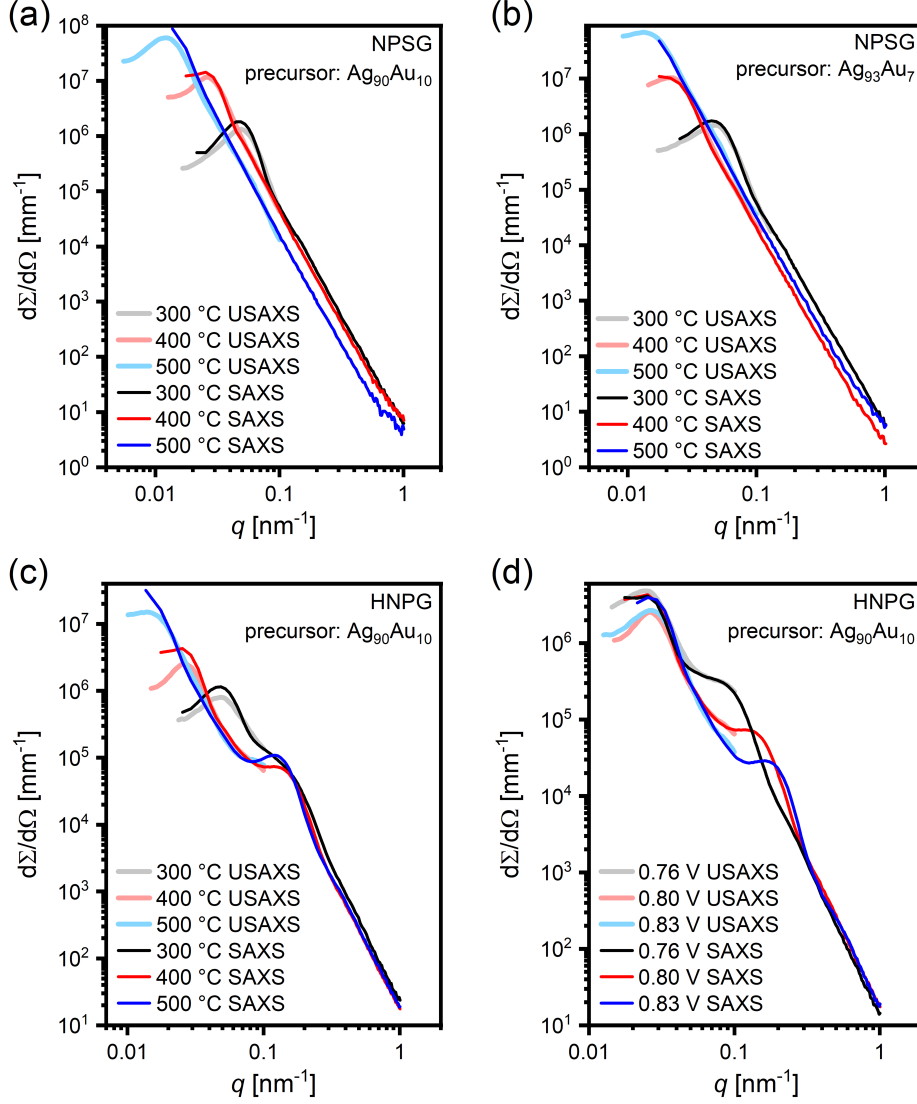


Figure 4.9: SAXS and USAXS scattering data from NPSG and HNPG samples with varied structural parameters. (a) and (b) show scattering graphs of NPSG samples which vary in their annealing temperature T_A and their precursor alloy type. (c) shows the scattering graphs of HNPG samples which vary in their T_A , while their dealloying potential E_D is 0.80 V. In (d), the dealloying potential E_D of the HNPG samples is varied, while the annealing temperature T_A is constant and amounts to 400 °C. Corresponding SEM images are presented in Figures 4.4, 4.5 and 4.7 [61].

the fit is executed in logarithmic scaling to avoid an excessive influence of data in the low q region. Equation 4.3 is converted accordingly by being prefixed by the common logarithm and by exchanging q with 10^q . Figure 4.10(b) illustrates the application of the fit to the scattering graph of NPSG annealed at 400 °C. The baseline, which is part of the entire fit, is indicated separately. The fit shows an explicit agreement with the scattering graph. For the evaluation of the scattering signal of HNPG, Equation 4.3 is duplicated, which results in two Gaussians and two baselines with 14 adjustable parameters in total. As can be seen from Figure 4.10(c), the resulting fit is able to reproduce the scattering graph of HNPG well with a slight mismatch in the region of

the lower hierarchy level interference peak. For $q \rightarrow \infty$, Equation 4.3 converges to the power law $\sim q^{-CD}$. The fit of the 11 scattering graphs yields 4.0 ± 0.1 as the value of the exponent CD . Thus, the confirmation of Porod's law leads to the conclusion that the surface of the ligaments is smooth with a sharp transition in electron density [156].

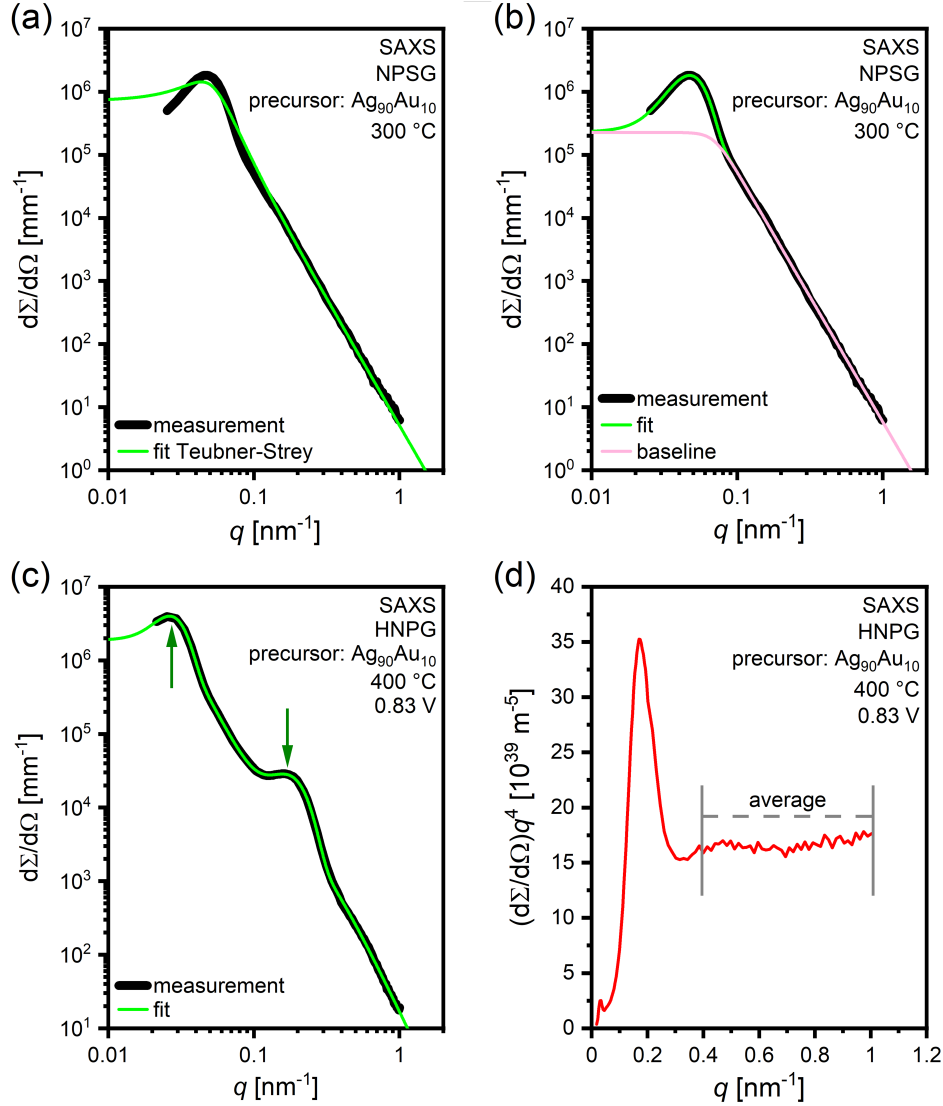


Figure 4.10: Illustration of the analysis of scattering data. In (a), (b) and (c), a fit (green line) is superimposed on the scattering curve (black line) of a selected NPSG or HNPG sample. (a) presents the fit by applying the Teubner-Strey model, Equation 4.2, while (b) presents the fit by Equation 4.3. For the purpose of illustration, the baseline (pinkish line) as part of the fit is shown separately. In (c), the fit is applied to HNPG. The peak positions as derived from the fit are indicated by arrows. (d) exemplifies the analysis of the scattering intensity in the Porod regime. The average of $(d\Sigma/d\Omega)q^4$ is calculated within the interval marked by grey lines [61].

4.3.3 Size values by SAXS/USAXS

The insertion of the peak position q_{peak} , as determined by the fit described above, into Equation 2.38 yields the ligament spacings on the upper and the lower hierarchy level, $\tilde{L}^U$ and $\tilde{L}^L$. Figure 4.11(a) presents ligament spacings of NPSG and HNPG with $E_D = 0.80$ V and varied T_A . In accordance with the SEM images compiled in Figure 4.4, the lower level ligament spacing is approximately constant and amounts to $\tilde{L}^L = 61 \pm 3$ nm. A notable deviation between the $\tilde{L}^U$ of NPSG and HNPG is observed for $T_A = 500$ °C, which is displayed by the SEM images as well. Figure 4.11(b) illustrates the variation of the dealloying potential E_D , which shows a significant influence on $\tilde{L}^L$, as already seen in Figure 4.5. A slight tendency of a decreasing $\tilde{L}^U$ with increasing E_D from $E_D = 0.76$ V to $E_D = 0.83$ V is observable as well. During the discussion of the SEM images in Figure 4.5, this effect is associated with the shrinkage during the 2nd dealloying, which is much more pronounced for $E_D = 0.83$ V than for $E_D = 0.76$ V. In this context, the shrinkage data is more significant because the database is larger. The slight decrease of $\tilde{L}^U$ seen in Figure 4.11(b) can also be attributed to a natural variation of $\tilde{L}^U$ between different samples. Figure 4.11(c) depicts ligament spacings of NPSG produced from the $\text{Ag}_{93}\text{Au}_7$ precursor alloy (category 3). SEM images that belong to these NPSG samples can be found in Figure 4.7. The general trend of an increasing $\tilde{L}^U$ with increasing T_A is present, too. As can be seen from Figures 4.11(a), 4.11(b) and 4.11(c), ligament spacings derived from SAXS and USAXS for the same $\tilde{L}^U$ show a good agreement. To be more precise, 7 ligament spacing values derived from USAXS amount to between 97% and 102% of the respective ligament spacing values derived from SAXS.

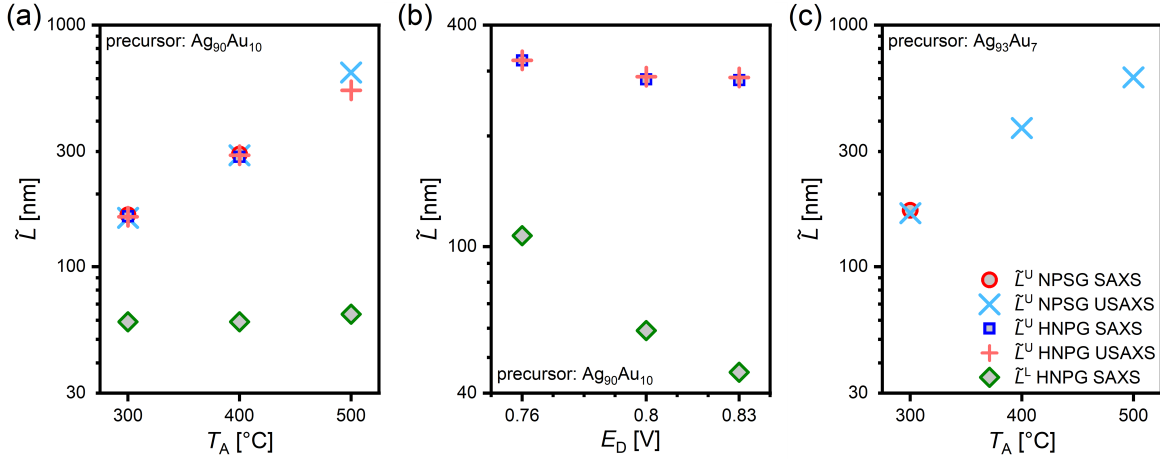


Figure 4.11: Ligament spacing $\tilde{L}$, as derived from Equations 4.3 and 2.38, for various synthesis parameters. (a) corresponds to scattering graphs shown in Figures 4.9(a) and 4.9(c), (b) corresponds to scattering graphs shown in Figure 4.9(d), and (c) corresponds to scattering graphs shown in Figure 4.9(b). Accordingly, (a) includes NPSG and HNPG with a varied annealing temperature T_A , (b) includes HNPG dealloyed with a varied dealloying potential E_D , and (c) includes NPSG produced from $\text{Ag}_{93}\text{Au}_7$ and annealed at a varied temperature T_A [61].

A comparison between the ligament spacing $\tilde{L}$ derived from SAXS/USAXS and the ligament size L derived from SEM is presented in Figure 4.12(a). All ligament

spacings $\tilde{L}$ specified in Figure 4.11, both $\tilde{L}^U$ and $\tilde{L}^L$, are incorporated into the chart. A straight-line fit through the origin yields the ratio $\tilde{L}/L = 2.8 \pm 0.01$, with the error being the standard error of the fit. Another method for the approximation of the ratio is the mean value which specifies the same value, $\tilde{L}/L = 2.8 \pm 0.4$, with the error being the standard deviation. This result is considered as a generalized ratio over the entire solid fraction range $0.3 < \varphi^{\text{lev}} < 0.5$, whereat φ^{lev} is the solid fraction φ^U or φ^L on the respective hierarchy level. A closer examination of this dependency is presented in Figure 4.12(b). $\tilde{L}/L$ displays a decreasing tendency with increasing φ^{lev} . A linear fit yields the relation

$$\tilde{L}/L = 5.60 - 7.30 \varphi^{\text{lev}}. \quad (4.4)$$

Thus, for $\varphi^{\text{lev}} = 0.30, 0.40$ and 0.50 , a mean ratio $\tilde{L}/L$ of 3.4, 2.7 and 2.0 is determined. A rough estimation arrives at the conclusion that for $\varphi^{\text{lev}} = 0.50$, when the volume fraction and the size of ligaments and pores is equal, the distance between neighboring ligaments is about twice as high as the ligament diameter [98]. This assumption is consistent with the value $\tilde{L}/L = 2.0$ estimated at this solid fraction. Lowering the solid fraction decreases the ligament diameter with constant ligament spacing, which leads to a ratio larger than 2. A similar investigation is conducted on the basis of the leveled wave model [98], where the ligament spacing $\tilde{L}$ is related to a mean ligament diameter L_G determined by granulometry [87]. For the ratio $\tilde{L}/L_G$, values of 2.2, 2.0 and 1.8 are stated at solid fractions of $\varphi = 0.30, 0.40$ and 0.50 . Since L is measured at the narrowest section of the ligaments, while L_G represents a volume averaged diameter, L_G is assumed to be larger than L . A further investigation of this interrelation, which is based on the leveled wave model as well, specifies the relation $L_G = (1.8 \pm 0.5)L$ [199]. An application of this ratio to $\tilde{L}/L_G$ results in the plot presented in Figure 4.12(c). The comparison with Equation 4.4 indicates a divergence between both approaches. At $\varphi = 0.45$, the ratio $\tilde{L}/L$ estimated by Equation 4.4 is at the lower end of the confidence interval specified by the approach using the leveled wave model. Uncertainty factors, such as a different selection of ligaments during the analysis of SEM images or factors incorporated into the confidence range specified by [199], can contribute to the divergence between both approaches. In another dataset included in Figure 4.12(c), a discrepancy is apparent as well. The study by Bapari *et al.* [200] evaluates the ligament size L on the basis of two-dimensional images of nanoporous structures which are generated by the leveled wave model. Their $\tilde{L}/L$ is consistently below the range indicated by [199], which implies that the ratio L_G/L is only slightly larger than 1.

Irrespective of the difficulty of the conversion of L into L_G , the analysis on the basis of the leveled wave model [98, 199] notices a smaller increase of $\tilde{L}/L_G$ for decreasing φ than seen in Figure 4.12(b) with regard to $\tilde{L}/L$. In other words, the slope 7.30 in Equation 4.4 is relatively high. A possible explanation is a deviation of the nanoporous structure from the leveled wave model at solid fractions $\varphi \leq 0.4$. According to this approach, at a constant φ and at a constant $\tilde{L}$, the mean ligament diameter L_G is smaller than assumed. This condition can be achieved by a uniform ligament diameter over the entire length. If a large portion of the solid volume is concentrated in large, spherical knots, which are connected by much thinner long struts, a volume averaged L_G is larger than in the case of struts of uniform thickness. The ligament size L is not part of this argumentation. Instead, an overestimation of L_G at solid fractions $\varphi \leq 0.4$ by the leveled wave model is proposed. Another possible explanation implies exactly

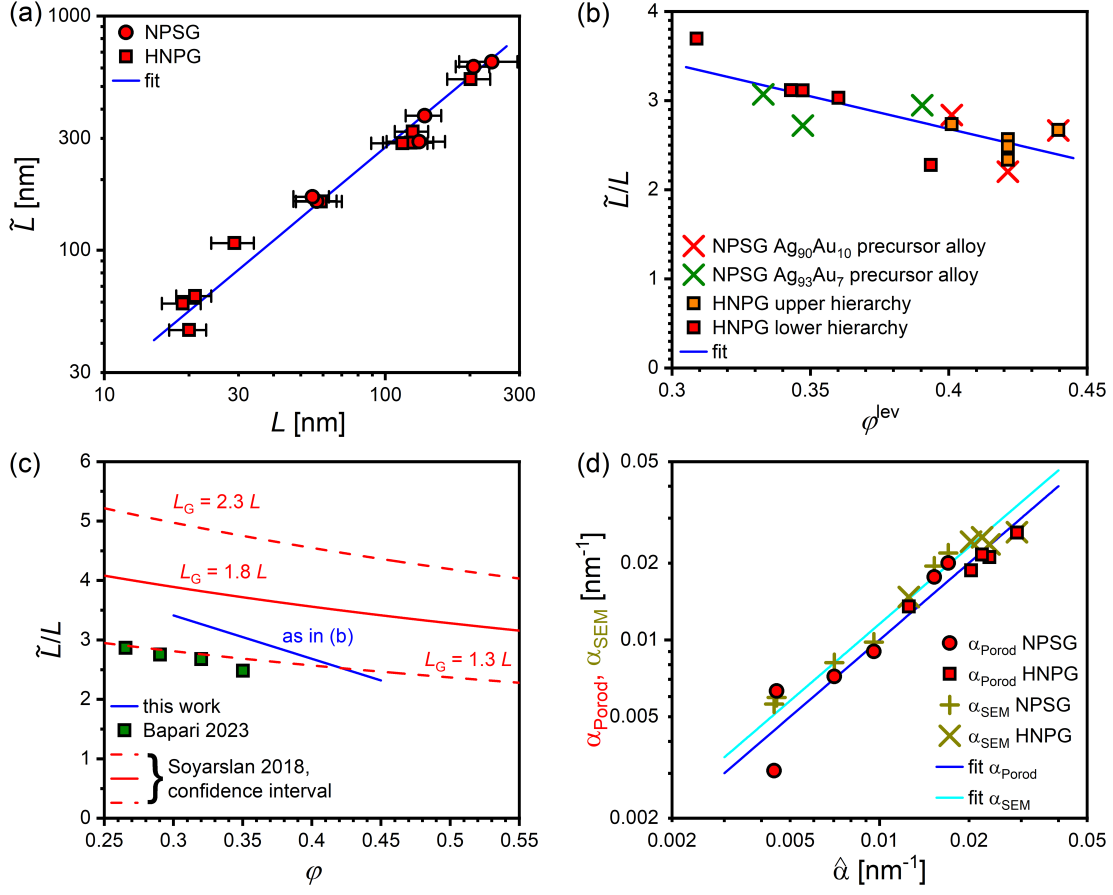


Figure 4.12: Further analysis of scattering data with regard to length scale and specific surface area. In (a), the ligament spacing $\tilde{L}$, as derived from SAXS and USAXS, is plotted against the ligament size L , as derived from SEM. In the case of ligament spacing values which are derived from SAXS and USAXS and which relate both to the same length the average is calculated. This rule applies to (b) and (d), too. The standard deviation of the ligament size L is indicated by error bars. A slope 1 (linear correlation) fit is marked by a blue line with a slope of 2.8. (b) presents the ratio $\tilde{L}/L$ against the solid fraction on the respective structural level, ϕ^{lev} . A linear correlation fit is indicated by the blue line. (c) compares the fit of (b) with literature values for $\tilde{L}/L$ [200] and with a specification of $\tilde{L}/L_G$ [98] which is converted into $\tilde{L}/L$ by using the relation $L_G = (1.8 \pm 0.5)L$ [199]. (d) illustrates a comparison between three metrics for the specific surface area: These are $\hat{\alpha}$, determined by Equations 4.7 and 4.8, using the peak position q_{peak} and applying the leveled-wave model; α_{Porod} , determined by Equations 2.36 and 2.37 and dependent on the scattering intensity in the Porod regime in relation to the total scattering intensity; and α_{SEM} , calculated by Equations 4.5 and 4.6 under usage of the ligament size L as derived from SEM. Blue and light blue lines indicate slope 1 (linear correlation) straight lines of best fit, with a slope of 1.00 (α_{Porod}) and 1.16 (α_{SEM}) [61].

the opposite. If the nanoporous structure is correctly reproduced by the leveled wave model at all solid fractions, an increase of the ratio between L and L_G at lower solid fractions can explain the higher slope seen in Equation 4.4. However, the unknown dependency of the ratio between L and L_G on the solid fraction ϕ is a substantial uncertainty factor regarding both hypotheses.

4.3.4 Determination of the specific surface area

Based on the available data, three measurands are selected for the determination of the specific surface area α (area per total volume): the ligament size L , the peak position q_{peak} and the scattering intensity in the Porod regime. With regard to the interrelation between specific surface area and ligament size, several approaches exist, such as the relation $\alpha = 4\varphi/L$ [187]. At this point, however, a different approach is chosen, which is derived from a diamond-like structure. The cylindrical ligaments have the diameter L and take the form of a tetrahedron [155]. The original equation is referred to the volume of the solid phase. Completion by an additional φ converts it into the specific surface area per total volume:

$$\alpha_{\text{SEM}} = \frac{1.63 (1.25 - \varphi) (1.89 + \varphi (0.505 + \varphi)) \varphi}{L}. \quad (4.5)$$

For hierarchical nanoporous materials, Equation 4.5 is initially written with the solid fraction of the lower level φ^{L} , but corrected by the multiplication with φ^{U} to incorporate the pores of the upper level. φ^{L} and φ^{U} subsequently unite into φ :

$$\alpha_{\text{SEM}} = \frac{1.63 (1.25 - \varphi^{\text{L}}) (1.89 + \varphi^{\text{L}} (0.505 + \varphi^{\text{L}})) \varphi}{L^{\text{L}}}. \quad (4.6)$$

For the determination of $\hat{\alpha}$ using the peak position q_{peak} , the leveled wave model is employed under the assumption that $q_0 = q_{\text{peak}}$, as already stated in Subsection 2.3.2. A direct relation between q_0 and $\hat{\alpha}$ emerges from the leveled wave model [98]:

$$\hat{\alpha} = \frac{2q_{\text{peak}}}{\pi\sqrt{3}} \exp\left(-\left(\text{erf}^{-1}(2\varphi - 1)\right)^2\right). \quad (4.7)$$

Equation 4.7 is adapted to hierarchical nanoporosity by the summation of two components. The first summand is dependent on the lower hierarchy interference peak $q_{\text{peak}}^{\text{L}}$ and refers to the structure at lower hierarchy level, whose surface area is multiplied by the upper hierarchy solid fraction φ^{U} to include the surface area reduction by the cavities of the upper level. An additional part is dependent on the upper hierarchy interference peak $q_{\text{peak}}^{\text{U}}$ and considers the surface where the lower hierarchy ligaments abut on cavities of the upper hierarchy. For the inclusion of this extra surface, the surface area of the upper level ligaments is calculated and subsequently multiplied by the lower hierarchy solid fraction φ^{L} to subtract the interface to cavities of the lower hierarchy:

$$\hat{\alpha} = \frac{2q_{\text{peak}}^{\text{L}}\varphi^{\text{U}}}{\pi\sqrt{3}} \exp\left(-\left(\text{erf}^{-1}(2\varphi^{\text{L}} - 1)\right)^2\right) + \frac{2q_{\text{peak}}^{\text{U}}\varphi^{\text{L}}}{\pi\sqrt{3}} \exp\left(-\left(\text{erf}^{-1}(2\varphi^{\text{U}} - 1)\right)^2\right). \quad (4.8)$$

A further estimate of the solid fraction is obtained by comparing the level of the straight line in the Porod regime in Figures 4.9(a)–4.9(d). In agreement with Equation 2.34, the absolute level allows a first assessment of α . In the case of HNPG, the absolute level of the scattering curve in the Porod regime is almost congruent, which indicates a similar α . In the case of NPSG, a slight inconsistency is present. Since smaller ligament sizes are associated with a higher surface area α , the level of the scattering curve is expected to decrease when T_{A} increases from 300 °C to 500 °C. NPSG of category 1 (Figure 4.9(a))

and of category 3 (Figure 4.9(b)) partially deviate from the expectation. A possible explanation is an existing uncertainty in the reduction of the scattering data. A slight deviation of the sample thickness from the value used for the data reduction cannot be ruled out, which would affect the absolute scattering intensity. With one exception, transmission values vary between 40% and 13%. The one exception is a value of 5%. The correction for transmission can contribute to the uncertainty as well. As stated in Subsection 2.3.1, a measure of the total scattering intensity is the invariant Q_S which is derived from the experimental data by integration of the scattering curve. A comparison between Q_S and Q_φ , which is derived from Equation 2.35 and which is the theoretically expected value for the invariant, allows a quantitative evaluation of the absolute scattering intensity. Indeed, Q_S amounts to $79 \pm 19\%$ of Q_φ . Thus, the experimental absolute scattering intensity is on average 21% below the theoretical expectation. The surface area calculated by Equation 2.34 is affected accordingly. Eventually, Equation 2.37, which normalizes the scattering intensity to Q_S , is used for the analysis of the intensity in the Porod regime with respect to the specific surface area α_{Porod} . For the purpose of illustration, Figure 4.10 presents the determination of $\lim_{q \rightarrow \infty} (d\Sigma/d\Omega)q^4$. The resulting value is subsequently inserted into Equation 2.37. In conformity with the power law $d\Sigma/d\Omega \sim q^{-4}$, the function $(d\Sigma/d\Omega)q^4$ displays a constant value in the Porod regime.

Summarizing the preceding paragraphs, three parameters are derived for the indication of the specific surface area: α_{SEM} , $\hat{\alpha}$ and α_{Porod} . Figure 4.12(d) presents a comparison between them. A straight line of best fit yields $\alpha_{\text{Porod}} = (1.00 \pm 0.05) \hat{\alpha}$ and $\alpha_{\text{SEM}} = (1.16 \pm 0.04) \hat{\alpha}$ with the error being the standard error of the fit. Accordingly, the fit of α_{Porod} against $\hat{\alpha}$ in Figure 4.12(d) (blue line) represents the identity of the graph. The good agreement between α_{Porod} and $\hat{\alpha}$ confirms the validity of both approaches. Since α_{Porod} and $\hat{\alpha}$ both emerge from small-angle X-ray scattering, the combination of both methods provides redundancy and permits the determination of an accurate and realistic value for the specific surface area without the requirement of a further experimental method. Furthermore, the accuracy of $\hat{\alpha}$ suggests that the leveled wave model is a realistic replication of a nanoporous structure after dealloying or coarsening. Concerning the comparison between $\hat{\alpha}$ and α_{SEM} , the result of the fit in conjunction with the narrow confidence interval demonstrates that Equation 4.5 and the underlying model of cylindrical ligaments with a diamond-like structure lead to a slight overestimation of the surface area. If the structural analysis is based on SEM images, the Equation 4.5 divided by the factor 1.16 provides an indication of the specific surface area. Uncertainties in the determination of L will also affect α_{SEM} .

4.4 Discussion

The connection of a Gaussian and a power law regime enables an accurate reproduction of the scattering data. While the utilization of a power law is based on theoretical knowledge, the fitting of the peak region by means of a Gaussian is a phenomenological approach. Equation 4.3 and their duplication, which are used for the fitting of NPSG and HNPG scattering data, also have the purpose of providing reproducibility. Several interference peaks which are located at low q -values consist of only a few data points.

Furthermore, in some cases interference peaks of the lower hierarchy level take the form of a saddle point and do not show a local maximum. In these cases, the utilization of the data point of the local maximum as the definition of the peak position q_{peak} is unprecise or not possible. The fitting by a Gaussian is a direct method for the generation of reproducibility and for the provision of an accurate fit.

What conclusion can be drawn from the observation that a Gaussian provides an accurate fit? Based on Equations 2.38 and 4.3, one conclusion is that the ligament spacing distribution takes the shape of a transformation of a Gaussian distribution. The inverse of the ligament spacing shows a normal distribution, while the ligament spacing itself shows a distribution with a steep flank at lower ligament spacings and a long descend at higher ligament spacings. From this follows that the mean $\tilde{L}$ is larger than the maximum of the ligament spacing distribution. A systematic analysis of the ligament spacing distribution and a comparison with the ligament size distribution is not performed in this thesis.

X-ray scattering experiments on nanoporous gold usually detect a distinct interference peak with recognizable intensity maximum [115, 169, 171, 174–176], with some exceptions being available [56, 84]. In several cases, nanoporous materials produced from other elements (Cu, Cu, Sb, CoPd) do not show a distinct interference peak, which indicates a broader ligament size distribution and a more heterogeneous structure [84, 169, 173]. In line with nanoporous gold in general, hierarchical nanoporous gold and nanoporous silver gold analyzed in this thesis possess clearly pronounced interference peaks. In most cases, the standard deviation of the Gaussian given by the fit amounts to 20%–30% of the peak position. Since the fit by a Gaussian is a novel approach, comparative values are not available. The existence of a Gaussian distribution alone indicates a certain degree of structural order, which confirms the representation by the leveled wave model. Another evidence of the usability of the leveled wave model is the concordance between several metrics for the specific surface area, from which $\hat{\alpha}$ is based on the leveled wave model.

As discussed in Subsection 2.3.2, the translation of the scattering intensity into the ligament spacing and vice versa is based on Equation 2.42. While the ligament diameter distribution of both as-dealloyed and coarsened nanoporous gold can be approximated by a Gaussian [85, 86], the 1st order maximum of the autocorrelation function, which represents the ligament spacing $\tilde{L}$, is asymmetrical. A clearly pronounced minimum of 1st order is opposed to a weakly pronounced minimum of 2nd order which turns into a constant value for larger correlation distances [94]. On the basis of the scattering data from this thesis an equivalent examination is possible by conversion of the differential scattering cross section into the autocorrelation function $\gamma(r)$ using Equation 2.42. It is worth considering whether the clear interference peak of NPSG also results in a distinct peak of the autocorrelation function. Furthermore, the autocorrelation function of HNPG can expand the perspective on the different distances which exist in hierarchical nanoporous metals. At this point, a further analysis on the basis of the autocorrelation function is explicitly proposed.

Chapter 5

Analysis of mechanical characteristics

Table 4.1 gives an overview of the synthesis variants which are applied for the provision of samples for compression tests. Mechanical tests are conducted on 3–4 samples of every procedure. In the Appendix, Figures A.1–A.4 present the analysis of all samples. Figures in this Chapter 5 depict the analysis of a representatively selected sample of every procedure. As can be seen from Figures A.1–A.4 in the Appendix, different samples of the same sample type show a similar behavior.

5.1 Influence of upper level ligament size

HNPG samples of category 1 ($\text{Ag}_{90}\text{Au}_{10}$ precursor alloy) emerge from NPSG samples of category 1. A transfer of ligament size effects seen in NPSG to HNPG is considered possible. Accordingly, the results of the compression test analysis are presented together in single graphs. Figure 5.1(a) depicts the Young's modulus E of HNPG and NPSG of category 1 (filled symbols) with a varied T_A (different color) and a constant dealloying potential $E_D = 0.80\text{ V}$ (in the case of HNPG). Consequently, the L^U (of HNPG) is adjusted between 60 nm and 200 nm, while the L^L remains constant and amounts to about 20 nm. Corresponding SEM images are presented in Figures 4.4(a)–4.4(f). The flow stress σ_F as a result of the analysis of the same samples is presented in Figure 5.1(b). Flow stress σ_F and Young's modulus E are determined by evaluation of the unload-load-cycles, as illustrated by Figure 3.10(b). In addition, compression test data from the study by Shi *et al.* [58] is inserted into Figure 5.1(a) (open symbols). These measurement sequences refer to NPSG and HNPG of category 3 ($\text{Ag}_{93}\text{Au}_7$ precursor alloy) with a varied T_A and, as a result, with a varied L^U and a constant L^L . The same data set is already presented in the Introduction in Figure 1.4. NPSG samples of this type are illustrated by Figure 4.7, whereat the SEM images of that figure and the compression test data in Figure 5.1(a) (open symbols) do not derive from the same work. SEM images of HNPG of category 3 (open symbols) are not presented in this thesis and must be taken from [58].

When regarding the depiction of the Young's modulus E and the flow stress σ_F against the solid fraction φ in Figures 5.1(a) and 5.1(b), a general increase of both parameters with increasing φ is apparent. While the strong relation to φ is in accor-

dance with the Gibson-Ashby- and the Roberts-Garboczi-law, deviations of stiffness and strength between different sample types at an equal φ are an indication of further factors which contribute to the mechanical response of the structure. When looking at the flow stress data of NPSG in the right half of Figure 5.1(b), a severe decrease of σ_F with increasing T_A , that is with increasing L , is identified. A possible explanation for this trend is the smaller-is-stronger-effect which is frequently observed in nanoporous metals, as presented in Subsection 2.2.3. A quantitative assessment yields an increase of σ_F by about 100%–250% when L is decreased from 240 nm to 60 nm.

In contrast to NPSG, the flow stress of different HNPG sample types, which is presented in the left half of Figure 5.1(b), converges to a similar level. The absence of the smaller-is-stronger-effect is consistent with the assumption that the lower level ligament size L^U of these sample types is nearly equal.

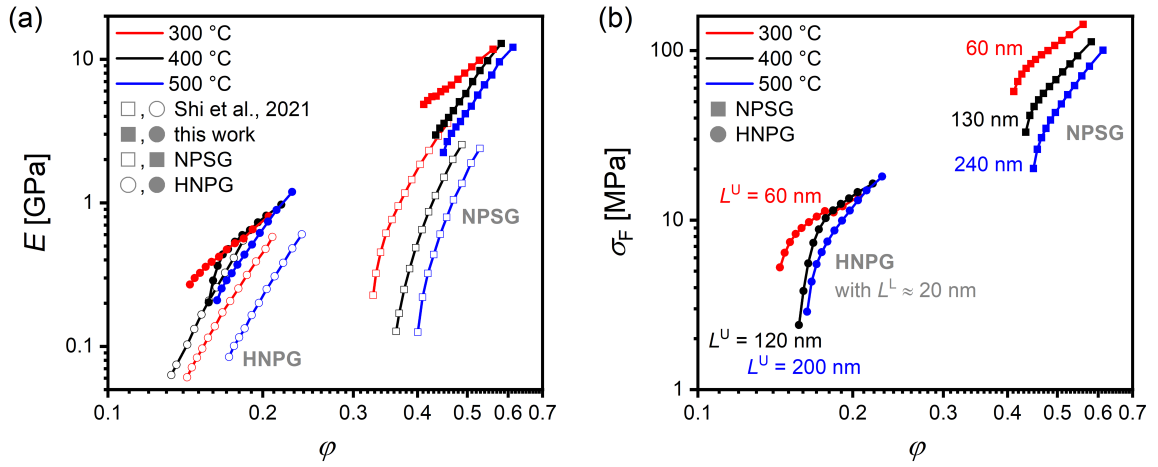


Figure 5.1: Compression test results for samples with varied L^U and constant L^L . (a) presents the Young's modulus E , while (b) presents the flow stress σ_F , each against the total solid fraction φ . Filled data points in the left half of the plots belong to HNPG illustrated by Figures 4.4(d)–4.4(f), while filled squares in the right half belong to NPSG illustrated by Figures 4.4(a)–4.4(c). Open symbols present data from [58] and refer to NPSG and HNPG produced from a $\text{Ag}_{93}\text{Au}_7$ precursor alloy. Equivalent NPSG samples are shown in Figure 4.7. Inscriptions which specify the ligament size in (b) also apply to (a). Ligament size specifications for the data from [58] can be taken from Figure 1.4.

Since the smaller-is-stronger-effect concerns the yield strength and does not affect the Young's modulus [109], differences among data sets shown in Figure 5.1(a) point to additional influencing parameters. When looking at the data series for NPSG of category 3 in the right half of Figure 5.1(a) (open symbols), which originates from the work by [58], a strong decrease of E with increasing T_A , that is with increasing L , is apparent. At $\varphi = 0.45$, a decrease of L from 180 nm to 45 nm increases E by factor 5. The same effect is already presented in Subsection 2.2.4 with reference to the data from the study by Mameka *et al.* [114] shown in Figure 2.2. A possible explanation is the decrease of the connectivity in the course of coarsening by annealing [58, 114]. In NPSG of this study (filled symbols), the same effect is still evident, but the trend is significantly weaker. In the region of an overlapping φ , a decrease of L from 240 nm to 60 nm increases E by about 50%–140%. A conceivable explanation is

provided by the dependency of the connectivity evolution during coarsening on the solid fraction. As presented in Subsection 2.2.4, coarsening is accompanied by a reduction of the connectivity when $\varphi \leq 0.27$, while a solid fraction $\varphi \geq 0.30$ involves a constant connectivity [99]. The NPG data set by Mameka *et al.* [114] noted above starts from a solid fraction $\varphi = 0.27$ before coarsening. In the case of NPSG of category 3 (open symbols), the solid fraction after 1st dealloying is 0.31 [58], while for NPSG of category 1 (filled symbols, this work) φ in this state is 0.41. The comparability with the NPG data set by Mameka *et al.* [114] is restricted by different ligament sizes and different sample compositions. On the other hand, composition and ligament size for the two NPSG data series shown in Figure 5.1(a) are similar overall. In contrast to the result by [99], a complete disappearance of the connectivity decrease during coarsening with $\varphi \approx 0.40$ is not confirmed. A closely related topic is the shrinkage during annealing, which is outlined in Section 4.1 and which can be taken from Figure 5.1(a) as well. Data series with higher T_A and thereby larger φ^{An} start at higher φ -values. The fact that coarsening involves shrinkage even for $\varphi \geq 0.40$ suggests that other factors apart from a change in connectivity play a role.

When regarding the Young's modulus E of HNPG produced from the $Ag_{93}Au_7$ precursor alloy in the left half of Figure 5.1(a) (category 3, open symbols), a different order is observed compared with the NPSG data (open symbols) in the right half of the figure. HNPG with $T_A = 400^\circ C$ exhibits a larger E than HNPG with $T_A = 300^\circ C$. The lowest stiffness is measured for HNPG with $T_A = 500^\circ C$. If basic features of the upper level structure such as the connectivity remain unchanged in the course of the 2nd dealloying, the consequence is a transfer of the dependence on the annealing temperature T_A from NPSG to HNPG. In this case, HNPG with $T_A = 300^\circ C$ is expected to exhibit a larger stiffness than HNPG with $T_A = 400^\circ C$. The fact that it is the other way round indicates the influence of an additional factor which does not affect NPSG. Shi *et al.* [58] propose the appearance of a ligament-size-ratio-effect which causes the disconnection of ligaments if the ratio between L^U and L^L falls below a certain value. A different picture emerges with regard to the Young's modulus E of HNPG produced from the $Ag_{90}Au_{10}$ precursor alloy (category 1, filled symbols). There, T_A and L^U , respectively, have a minor impact on E , and the measurement sequences of sample types with different T_A converge to the same level. If HNPG with $T_A = 300^\circ C$ is affected by a ligament-size-ratio-effect, then this effect is rather weak. For HNPG with $T_A = 300^\circ C$, ligament sizes are $L^U \approx 60$ nm and $L^L \approx 20$ nm, which results in a ligament size ratio L^U/L^L of 3. By comparison, HNPG produced from the $Ag_{93}Au_7$ precursor alloy (open symbols) features the ligament sizes $L^U \approx 45$ nm and $L^L \approx 15$ nm [58], which implies the same ligament size ratio of 3. Thus, the occurrence of a ligament-size-ratio-effect, which could explain the significant stiffness decrease seen in HNPG with $T_A = 300^\circ C$ and produced from $Ag_{93}Au_7$, is not supported.

5.2 Influence of lower level ligament size with varied lower level solid fraction

Figure 5.2 highlights the impact of a variation of E_D and accordingly L^L on the Young's modulus E (Figure 5.2(a)) and the flow stress σ_F (Figure 5.2(b)). The annealing

temperature T_A is 400 °C, and the upper level ligament size L^U is fairly constant with a minor deviation. An illustration is given in Figure 4.5. A particular feature is a significant divergence of the lower level solid fraction φ^L . For $E_D = 0.76$ V, 0.80 V and 0.83 V, φ^L is estimated to be 0.31, 0.35 and 0.39. A variation of E_D not only adjusts L^L , but has a clear influence on the lower level structure.

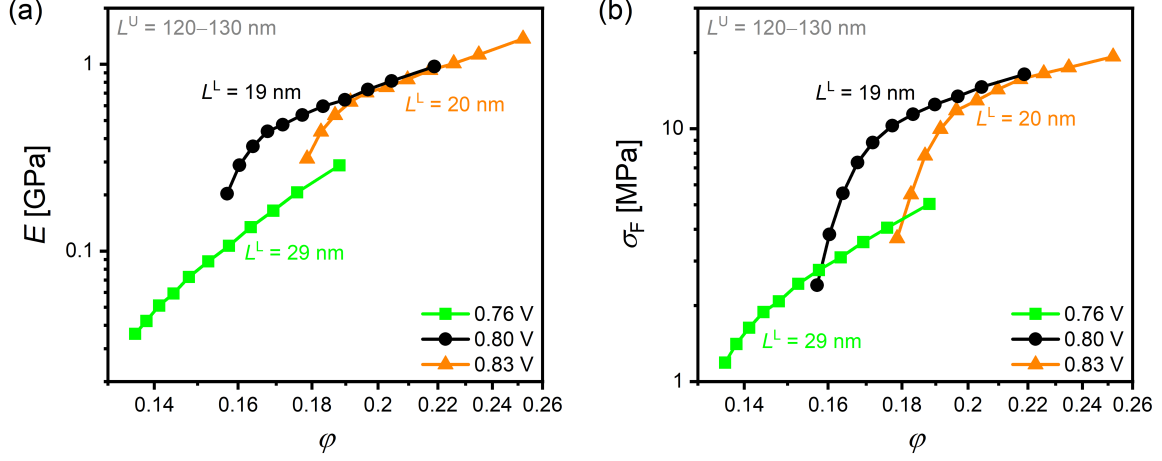


Figure 5.2: Compression test results for HNPG samples with constant L^U and varied L^L and with $\varphi^L < 0.40$. (a) presents the Young's modulus E , while (b) presents the flow stress σ_F , each against the total solid fraction φ . L^L is tuned by the variation of E_D . The annealing temperature is $T_A = 400$ °C for all samples. Corresponding SEM images are presented in Figures 4.5(a)–4.5(c).

With regard to the mechanical behavior, HNPG sample types with $E_D = 0.80$ V and with $E_D = 0.83$ V evolve in a similar way. The solid fraction at the beginning of the compression, 0.15 for $E_D = 0.80$ V and 0.17 for $E_D = 0.83$ V (see Table 4.1), is identifiable in the course of E and σ_F against φ . In the further course of the deformation, E and σ_F converge in each case to the same level. A feature which is particularly pronounced here, but which is also observed for other synthesis variants, is a higher slope of $E(\varphi)$ and $\sigma_F(\varphi)$ in the early stage of compression. After about 15% deformation, $E(\varphi)$ and $\sigma_F(\varphi)$ increase with a lower slope. A completely different behavior is observed for HNPG dealloyed with $E_D = 0.76$ V. Young's modulus E and flow stress σ_F are significantly lower. Indeed, this sample type features by far the weakest mechanical characteristics among all HNPG sample types analyzed in this study, excluding HNPG produced from $\text{Ag}_{93}\text{Au}_7$. At $\varphi = 0.17$, E amounts to 37% of the level determined for $E_D = 0.80$ V, while σ_F amounts to 45%. Lower strength values can be caused by the smaller-is-stronger-effect, since L^L is larger and amounts to about 30 nm, compared with about 20 nm for $E_D = 0.80$ V or 0.83 V. However, E is not affected by the smaller-is-stronger-effect [109]. The lower φ^L and accordingly a lower connectivity on the lower hierarchy level are a possible reason for the weak mechanical properties of HNPG with $E_D = 0.76$ V. As mentioned in the preceding section, but with respect to the upper hierarchy, coarsening is supposed to decrease the connectivity at solid fractions lower than about 0.30 [99]. The SEM image of HNPG dealloyed with $E_D = 0.76$ V, which is shown in Figure 4.5(a), is of relevance as well. In this micrograph, the lower level structure appears loose and less connected. The clear difference between HNPG with

$\varphi^L = 0.31$ and HNPG with $\varphi^L = 0.35$ on the one side and the similarity between HNPG with $\varphi^L = 0.35$ and HNPG with $\varphi^L = 0.39$ on the other side are a strong indication of a solid fraction threshold $\varphi \approx 0.32$. According to this approach, the lower level connectivity decreases during coarsening if the lower level solid fraction falls below this threshold.

A related possible explanation is based on the larger ligament size L^L of HNPG with $E_D = 0.76$ V. Accordingly, the coarsening has proceeded further. The lower stiffness of HNPG with $E_D = 0.76$ V can also be caused by a more advanced connectivity decrease during coarsening, without the occurrence of a solid fraction threshold. At least a general decrease of the connectivity during coarsening would be required. However, the very similar mechanical behavior of HNPG with $E_D = 0.80$ V and with $E_D = 0.83$ V, which also differ in their lower level ligament spacing $\tilde{L}^L$, and the significant difference to HNPG with $E_D = 0.76$ V in mechanical characteristics and in morphology are indications of the existence of a solid fraction threshold.

5.3 Influence of lower level ligament size with constant lower level solid fraction

A different method for the adjustment of L^L is the variation of the number of potential cycles, N_{CY} , between 5 and 60. In Figure 4.8, four HNPG sample types with varied N_{CY} are presented. L^U is adjusted between 60 nm–70 nm and 110 nm–130 nm by a variation of the annealing temperature T_A , while L^L varies between 15 nm and 29 nm, depending on N_{CY} . In contrast to the variation of L^L by the dealloying potential E_D , which is presented in the preceding chapter, the total solid fraction φ^{Fn} shows a minor, nonsystematic deviation. The lower level solid fraction φ^L amounts to 0.41–0.43 and shows no clear trend regarding the dependency on N_{CY} and T_A , too. Values for φ^U are 0.32–0.34.

The results of the mechanical examination are presented in Figure 5.3 with (a) showing the Young's modulus E and (b) showing the flow stress σ_F . A first examination of the influence of L^U is achievable by a comparison between HNPG with $L^U = 70$ nm (red, filled) and with $L^U = 130$ nm (black, filled), both with constant $L^L = 15$ nm. Here, an increasing L^U is accompanied by a decrease of E , especially at lower φ -values. This trend is comparable to the decrease of E with increasing T_A observed for NPSG produced from $\text{Ag}_{93}\text{Au}_7$ as presented in Figure 5.1(a) (right half, open symbols).

When looking at the effect of an increase of L^L , the result is not consistent. HNPG with $L^U = 110$ nm–130 nm features a similar stiffness which is independent of L^L . Increasing L^L from 15 nm (black, filled) to 29 nm (black, open) does not lead to a substantial change in the Young's modulus. On the other side, increasing L^L from 15 nm (red, filled) to 29 nm (red, open) clearly reduces the stiffness when L^U amounts to 60 nm–70 nm. The first observation is contrary to HNPG presented in the preceding section as well. There, an adjustment of L^L by a variation of E_D has a severe impact on E . A possible reason mentioned above is the dependency of the connectivity evolution during coarsening on the solid fraction. For the samples presented in Figure 5.3(a), φ^L is larger than 0.40. According to this approach, HNPG with $\varphi^L > 0.40$ and with

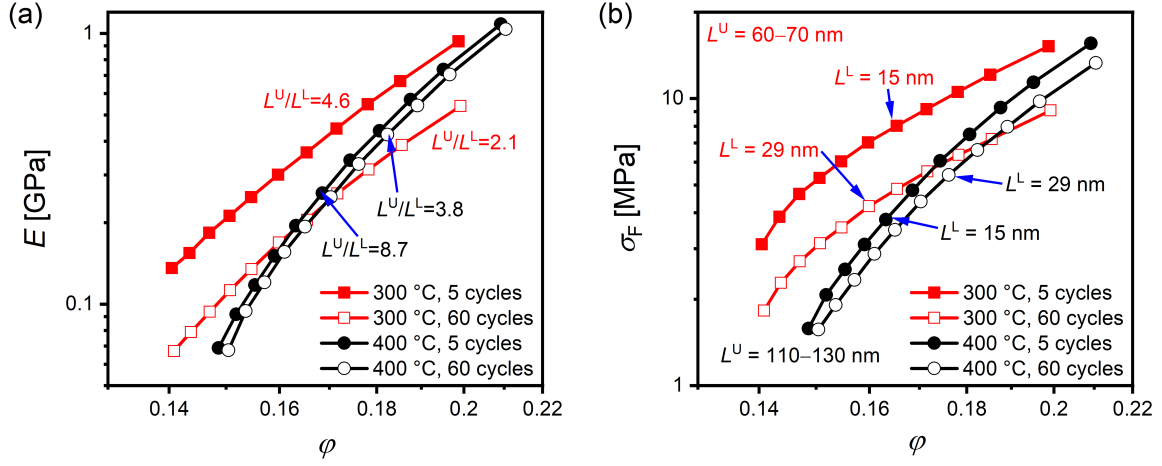


Figure 5.3: Compression test results for HNPG with varied L^U , varied L^L and with $\phi^L > 0.40$. (a) presents the Young's modulus E , while (b) presents the flow stress σ_F , each against the total solid fraction ϕ . In contrast to Figures 5.1 and 5.2, the composition after 1st dealloying is $\text{Ag}_{65}\text{Au}_{35}$ – $\text{Ag}_{68}\text{Au}_{32}$ ($x_{\text{Ag}}^{\text{DE}} = 0.65\text{--}0.68$). L^L is adjusted by the variation of the number of potential cycles N_{CY} , as indicated in the legend. Incriptions which specify the ligament size ratio or the ligament size equally apply to (a) and (b).

$L^U = 110$ nm– 130 nm (black, filled and open) does not exhibit a declining stiffness with increasing L^L because the connectivity on the lower level remains constant during coarsening.

The stiffness reduction observed for HNPG with $L^U = 60$ nm– 70 nm (red), caused by an increase of L^L , points to the emergence of a ligament-size-ratio effect. Specifications in Figure 5.3(a) report the ligament-size-ratio of the respective sample types. The ligament-size-ratio L^U/L^L is 2.1 for the data series where this effect is suspected to occur (red, open). According to this assumption, the upper level ligaments disconnect at several positions if the ratio L^U/L^L falls below a certain limit. Statistical factors also have an effect. A lower ligament-size-ratio increases the probability that the lower level structure exhibits interruptions at several positions [101]. The determination of the relationship between ligament size ratio and weakening of mechanical stiffness is the focus of a study by Wu *et al.* [101] which uses focused ion beam to cut micropillars into unimodal nanoporous gold. If the ratio between ligament size and pillar diameter falls below 20, the Young's modulus is negatively affected. A ratio of less than 5 reduces E to almost zero. These values are in contrast to the effect seen in HNPG (red), according to which a reduction of L^U/L^L from 4.6 to 2.1 lowers E by about 40%–50%. The flow stress σ_F is reduced by about 40%–45%. Thus, the ligament-size-ratio-effect is much less pronounced in HNPG than in the case of a micropillar. A possible explanation is a linkage between the upper and the lower level structure. If a pillar is cut into a nanoporous structure, the pillar, which represents the upper level structure, is a random cut into the lower level structure. In the hierarchical nanoporous structure represented by Figure 4.8(b) the lower level structure often consists of a single ligament which is parallel, and somewhat identical, to the upper level ligament. Thus, the lower level structure cannot be seen as random. Instead, with decreasing L^U/L^L , it resembles the upper level structure and retains a relatively high connectivity.

The flow stress σ_F , which is presented in Figure 5.3(b), features similar differences between the specified sample types as the Young's modulus E shown in Figure 5.3(a). Since the yield strength is additionally affected by the smaller-is-stronger-effect, the existence of this effect deserves an evaluation. When regarding the data set with $L^U = 110\text{ nm}–130\text{ nm}$ and $T_A = 400\text{ }^\circ\text{C}$, respectively, the flow stress of HNPG with $L^L = 29\text{ nm}$ (black, open) amounts to 80%–85% of the level of HNPG with $L^L = 15\text{ nm}$ (black, filled). The deduction of other factors apart from the smaller-is-stronger-effect is possible by comparing with the Young's modulus presented in Figure 5.3(a), where the E of HNPG with $L^L = 29\text{ nm}$ (black, open) amounts to about 90% of the level of HNPG with $L^L = 15\text{ nm}$ (black, filled). According to this approach, which is based on the connectivity and which is described in detail in Subsection 5.4.3, the increase of L^L from 15 nm to 29 nm reduces the strength by less than 15%. When using the power law $\sim L^{-0.61}$ [140], a ratio 15/29 is associated with a reduction to 67%. Accordingly, the smaller-is-stronger-effect is weakly pronounced in HNPG. It is noted that this argumentation, which is based on data from a single sample, is not unequivocal. Figure A.4(c) in the Appendix illustrates that the variation of σ_F between several samples of the same sample types is in the same range as the reduction to 67% stated above. Thus, the ratio between the two ligament sizes employed for analysis, 15 nm and 29 nm, is too small to yield an unambiguous result.

5.4 Discussion

5.4.1 Influence of solid fraction on upper and lower level on the Roberts-Garboczi-law

In the preceding sections, the analysis focuses mainly on a general comparison of stiffness and strength values, while the dependence on φ is not further investigated. Figure 5.4 now presents a comparison between the course of E and σ_F against φ and several approaches for scaling equations. (a) and (c) each depict the Young's modulus and the flow stress of two selected samples, while in (b) and (d) data from two other selected samples are presented. The two samples, which are compared with each other, feature the same T_A and they are both produced from $\text{Ag}_{90}\text{Au}_{10}$. Their L^U is similar, as well as their L^L , which is specified in Figures 5.4(c) and 5.4(d). Furthermore, they also feature a similar total solid fraction. Values for φ of the two respective sample types before compression, which are specified in Table 4.1, differ by 0.01. The major difference is the initial solid fraction on the upper and the lower level. Green data series in Figure 5.4 refer to HNPG samples of category 1 which are dealloyed to $\text{Ag}_{73}\text{Au}_{27}$ – $\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.73$ – 0.77) in the 1st dealloying. Consequently, their φ^U is relatively higher and amounts to 0.40–0.42, while their φ^L is relatively lower and amounts to 0.34–0.35. Blue data series in Figure 5.4 refer to HNPG samples of category 2 which are dealloyed to $\text{Ag}_{65}\text{Au}_{35}$ – $\text{Ag}_{68}\text{Au}_{32}$ ($x_{\text{Ag}}^{\text{DE}} = 0.65$ – 0.68) in the 1st dealloying. Due to the more advanced dealloying, φ^U is relatively lower and amounts to 0.32–0.34, while φ^L is relatively higher and amounts to 0.41–0.43.

The comparison between samples of category 1 and samples of category 2 reveals a different course of E and σ_F against φ . For HNPG with $\varphi^L = 0.35$ (Figure 5.4(b),

green), a kink is observed after four datapoints, that is at 5%–15% strain. A possible explanation is an effect of cracks which are closed in the early stage of the deformation. According to this hypothesis, the successive closing of the cracks leads to an increased slope of $E(\varphi)$. Another factor might be the deviation of the sample's shape from a perfect cuboid. In this case, in the early stage of the deformation just a portion of the sample contributes to the mechanical response. The first four datapoints are thereby considered defective and are ignored at this temporary state of the discussion. In the further course of the deformation the slope of E and σ_F against φ is lower in comparison with sample types with relatively higher φ^L (blue). This general difference is not affected by a variation of L^U .

A possible explanation is inspired by SEM images acquired at HNPG samples after compression. Figure 5.5 presents two respective micrographs. From Figure 5.5(a), which refers to HNPG with $T_A = 400^\circ\text{C}$ and $E_D = 0.80\text{ V}$, it is evident that the lower hierarchy level remains intact during deformation and that the voids of the upper hierarchy level are compressed. This result is first reported by Shi *et al.* [58]. A different result emerges from Figure 5.5(b) which shows HNPG with $T_A = 400^\circ\text{C}$ and with $E_D = 0.76\text{ V}$ after compression. There, the upper and the lower hierarchy are compressed, and the structure resembles a nanoporous structure with one single hierarchy level. The structure before compression is illustrated by Figure 4.5(a). For this sample type, E and σ_F are exceptionally low, as shown in Figure 5.2 (green). In Section 5.2, this observation is attributed to the relatively low φ^L and to a reduction of the connectivity on the lower level. Since the mechanical parameters show a significant deviation from other sample types, the sample type with $E_D = 0.76\text{ V}$ is considered as an exception, and the limitation of the general compression to a compression of the upper hierarchy level, as indicated by Figure 5.5(a), is regarded as the common case. Based on this presumption, it is possible to modify the scaling equations presented in Subsection 2.2.2. The orange curve plotted in Figure 1.4 assumes an equal solid fraction on the upper and the lower hierarchy level during compression, so that $\varphi^L = \varphi^U = \varphi^{0.5}$ is inserted into Equation 2.16. If, by contrast, the compression takes place on the upper level, φ^L remains constant and Equation 2.16 is modified into:

$$E = 4E_s \left(\frac{\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{2.5} \left(\frac{\varphi/\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{2.5}. \quad (5.1)$$

Resulting courses are inserted into Figures 5.4(a) and 5.4(b). The comparison between the detected Young's modulus during compression and the scaling relation represented by Equation 5.1 presupposes that the increase of the solid fraction during compression acts similar to a solid fraction increase of an undeformed hierarchical nanoporous structure. Equation 5.1 refers to an ideal hierarchical nanoporous structure and is therefore applicable to the early stage of deformation. Processes during compression, such as the strong anisotropy or internal stresses, can result in a deviation from the simple dependency on the solid fraction [155]. Taking into account the general preservation of the hierarchical nanoporous structure and the absence of cracks beyond the fracture surface, which is evident in Figure 5.5(a), the application of Equation 5.1 to deformed structures appears justifiable. This prerequisite is strengthened by previous investigations on the Young's modulus of HNPG which show that the increase of the

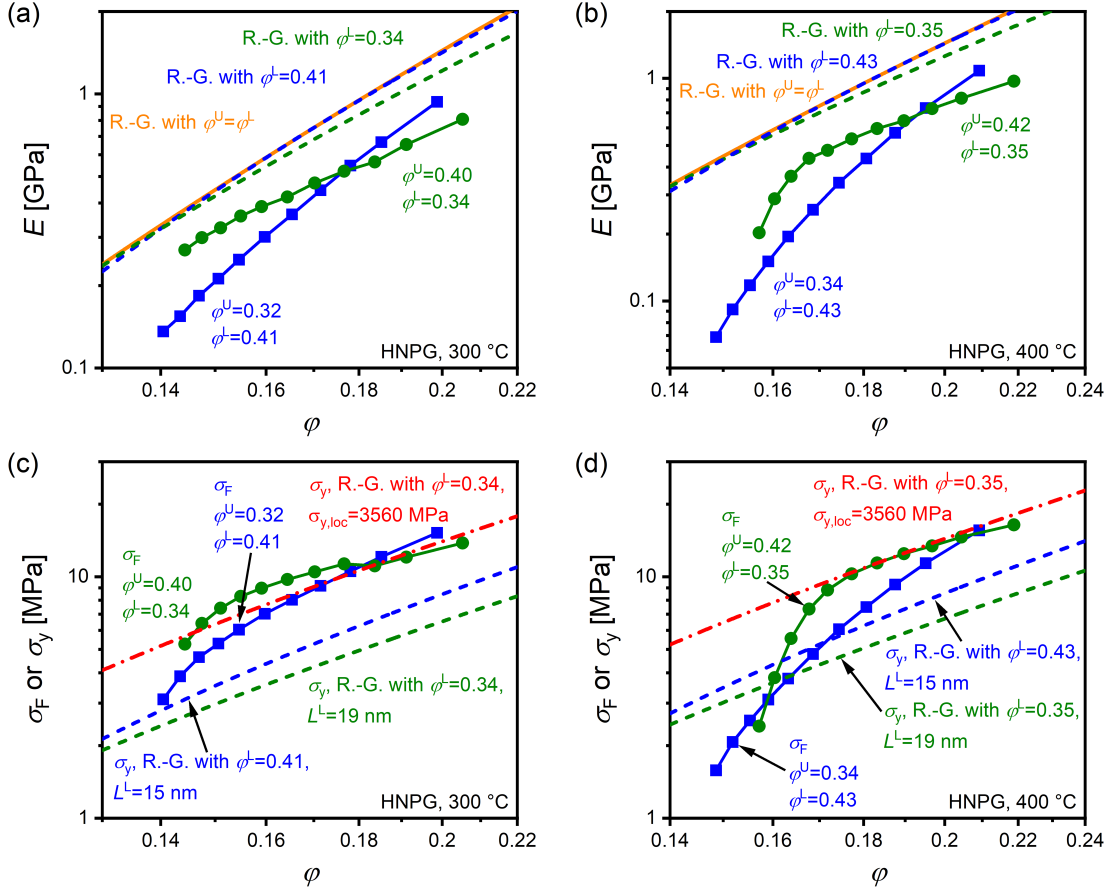


Figure 5.4: Comparison between HNPG compression test data and scaling relations. (a) and (b) present the Young's modulus E of selected samples, while (c) and (d) depict the corresponding flow stress σ_F . (a) and (c) refer to the same two HNPG samples with $T_A = 300$ °C, while (b) and (d) refer to the same two HNPG samples with $T_A = 400$ °C. The experimental data is already shown in Figures 5.1(a) and 5.1(b) and Figures 5.3(a) and 5.3(b). Both samples presented within each plot are fairly similar in their L^U , L^L and their initial ϕ and only differ in their initial ϕ^U and ϕ^L . Blue and green dashed lines represent the Young's modulus E calculated by Equation 5.1 and the yield strength σ_y calculated by Equation 5.2 and by Equation 2.21 by using $u = -0.61$ and $A = 10000 \text{ nm}^{0.61} \text{ MPa}$ [109, 140]. The ϕ^L and, with regard to σ_y , the L^L of the respective sample is inserted into the scaling relation. Dashed and dotted red lines indicate the maximum (yield) strength σ_y calculated by Equation 5.2, whereat the theoretical shear strength of gold (3.56 GPa [143]) is used as local yield strength $\sigma_{y,loc}$.

solid fraction during compression has a similar effect as the increase of the initial solid fraction [58].

Equation 5.1 replicates the characteristic according to which a relatively higher ϕ^L (blue dashed line) leads to a steeper slope of E against ϕ . A perfect reproduction of the experimental data is not observed. Measured values for E are generally lower than predicted by Equation 5.1. The lowest deviation is observed for HNPG with $T_A = 300$ °C and $\phi^L = 0.34$ in the early stage of compression (Figure 5.4(a), green), where the experimentally determined E amounts to about 75% of the expected value

according to the Equation 5.1. Another difference concerns the slope of E against φ . In the case of HNPG with $\varphi^L = 0.41$ – 0.43 (blue), Equation 5.1 predicts a lower slope than expected on the basis of the experimental data. A conceivable explanation is an error in the assessment of φ^L and φ^U . The course of E against φ for HNPG with $T_A = 300^\circ\text{C}$ and $\varphi^L = 0.41$ in Figure 5.4(a) (blue) can be reproduced by Equation 5.1, multiplied by an additional factor, when φ^L is 0.57 and φ^U is 0.23. An underlying mechanism can be an additional shrinkage on the lower level in transverse direction. This assumption is hypothetical, since φ^L can actually also be higher for the other dataset (green), where φ^L is assumed to be lower. Although the course of the Young's modulus of HNPG with $\varphi^L = 0.34$ – 0.35 (green) is approximately parallel to the expectation by Equation 5.1, this comparison is restricted by the limited applicability of Equation 5.1 to strongly deformed structures, as mentioned in the preceding paragraph. At least the influence of φ^L and φ^U on the course of E against φ must be taken into account.

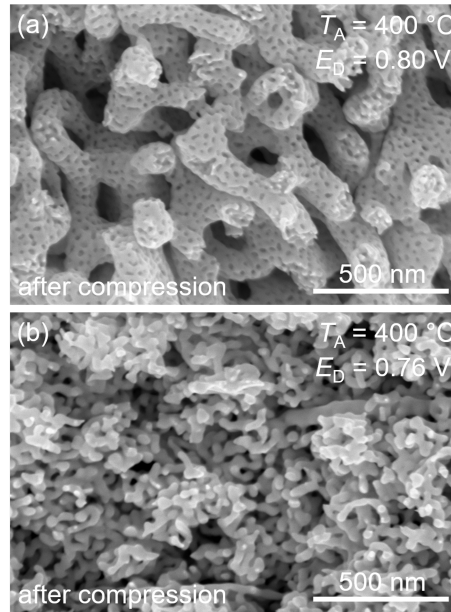


Figure 5.5: Scanning electron micrographs of HNPG after completed compression tests. Synthesis parameters are $T_A = 400^\circ\text{C}$ and $E_D = 0.80\text{ V}$ (a) or $E_D = 0.76\text{ V}$ (b). Corresponding samples before compression are presented in Figures 4.5(b) and 4.5(a).

5.4.2 Evaluation of the strength of hierarchical nanoporous gold

The quantitative evaluation of the flow stress of NPSG requires an estimation of the yield strength in gold-silver alloys. As mentioned earlier, the yield strength of gold is 55 MPa–220 MPa [139], with $\sigma_{y,s} = 200\text{ MPa}$ being frequently utilized [69, 121, 138]. The yield strength of silver is 40 MPa–55 MPa [201]. The exact determination of the $\sigma_{y,s}$ of NPSG proves to be difficult and literature values for comparison are not available. A comparison of the strength of NPSG with scaling approaches is therefore not executed. However, this does not affect the comparison of NPSG sample types with each other.

The comparability of HNPG with NPG is not precluded from the outset since the composition is similar. The combination of a constant φ^L during compression with Equation 2.17 permits a modified specification of the yield strength of hierarchical nanoporous gold:

$$\sigma_y = \frac{\sigma_{y,loc}}{4} \left(\frac{\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{15/8} \left(\frac{\varphi/\varphi^L - \varphi_0}{1 - \varphi_0} \right)^{15/8}. \quad (5.2)$$

$\sigma_{y,loc}$ is determined by Equation 2.21, whereat $u = -0.61$ and $A = 10000 \text{ nm}^{0.61} \text{ MPa}$ are inserted as the exponent or as the additional factor [109, 140]. Furthermore, the lower level ligament size L^L of the respective HNPG sample is applied. In Figures 5.4(c) and 5.4(d), dashed lines indicate the yield strength as a function of φ which derives from Equation 5.2. A comparison with the experimental data is biased, since the flow stress σ_F is not identical to the yield strength σ_y . With advanced deformation, strain hardening leads to an increase of stress values [62, 67, 140]. A deviation of measured values for the flow stress from the yield strength determined by Equation 5.2 is therefore expected. In the case of three datasets, σ_F against φ becomes roughly parallel to the estimation on the basis of Equation 5.2. One dataset, namely HNPG with $T_A = 400^\circ\text{C}$ and $\varphi^L = 0.43$ (Figure 5.4(d), blue), displays a continuous increase of the flow stress relative to the yield strength calculated by Equation 5.2, which indicates a steady strain-hardening.

Massive gold pillars exhibit a pronounced strain hardening, whereat the stress at 15% strain is more than twice as high as the yield strength [140]. Nanoporous gold features a lower strain hardening, whereat the data in literature is not consistent. Some studies observe that the stress at 20%–30% strain increases by 100% or more, compared with the yield strength [62, 67]. Other studies observe a smaller increase in strength during deformation [68, 136]. Differences in measurement methods are neglected at this point. Comparative values for HNPG can be determined from the flow stress data in Figure A.2(d). An increase of the strain from 5% to 15% is accompanied by an increase of the flow stress by a factor of 2–3. Thus, HNPG of category 1 shows a similar strain hardening rate as massive gold pillars and a higher strain hardening rate than NPG.

After completed strain hardening, the flow stress is up to about 150% larger than the yield strength predicted by Equation 5.2. When regarding the first datapoint at $\varphi = 0.144$ of HNPG with $T_A = 300^\circ\text{C}$ and $\varphi^L = 0.34$ (Figure 5.4(c), green), which is assumed to be less affected by strain hardening, the rearrangement of Equation 5.2 with regard to $\sigma_{y,loc}$ results in a ligament strength $\sigma_{y,loc}$ of 3300 MPa. From the 4th data point of the same measurement series, a maximum ligament strength $\sigma_{y,loc}$ of 4200 MPa is deduced. These values are close to the ideal theoretical yield strength of gold which is 3.56 GPa [143]. A maximum tensile strength of 3.12 GPa is detected for Au nanowires with angstrom-scaled twins. This value also applies to the yield strength of these nanowires because their mechanical behavior is very brittle [202].

By insertion of the ideal theoretical yield strength of 3.56 GPa [143] as the local yield strength $\sigma_{y,loc}$ into Equation 5.2, an ideal maximum yield strength of HNPG or an ideal maximum strength of HNPG is derived. In Figures 5.4(c) and 5.4(d), this upper limit is represented by dashed and dotted red lines. HNPG with $T_A = 300^\circ\text{C}$ and $\varphi^L = 0.34$ (Figure 5.4(c), green) reaches this limit at the beginning of the deformation and slightly surpasses it. Overall, the course of the flow stress against φ is parallel to

the ideal maximum strength. The course of the flow stress of HNPG with $T_A = 400\text{ }^\circ\text{C}$ and $\varphi^L = 0.35$ (Figure 5.4(d), green) is even more distinct. At the beginning of the deformation, the flow stress, which is roughly similar to the yield strength in this stage, is below the value calculated by Equation 5.2 (green dashed line). Subsequently, strain hardening leads to a strong increase of the flow stress relative to the yield strength until the ideal maximum strength (dashed and dotted red line) is approached. In the further course of the deformation, the flow stress is identical to the ideal maximum strength. Thus, the kink, which is observed at 5%–15% strain and which is attributed to the closing of cracks in Subsection 5.4.1, is caused by the approximation to the ideal maximum strength. HNPG of category 2 (Figures 5.4(c) and 5.4(d), blue) exhibits a lower strain hardening rate. On the other hand, strain hardening persists longer during deformation. However, HNPG of category 2 approaches the ideal maximum strength (dashed and dotted red line) as well and does not surpass it by a large margin. Differences in the course of σ_F after completed strain hardening can be attributed to the effect of φ^L , as presented in Subsection 5.4.1 with respect to the Young's modulus.

All HNPG sample types presented in Figure 5.4 reach a stage where dislocations lose their role as determining factor for the strength of the material. Accordingly, the mechanical strength is no longer affected by the generation and the movement of dislocations. Instead, the deformation is driven by the shearing of single ligaments. Based on existing approaches for the origin of the smaller-is-stronger-effect, which are presented in Subsection 2.2.3, two explanations are conceivable. The first option is an extreme increase of the dislocation density during deformation until Taylor hardening prevents any movement of dislocations [140, 150, 151]. The second explanation is a pronounced dislocation starvation [140, 148, 149]. One argument for the second hypothesis is that HNPG features a higher strain hardening rate than NPG and a similar strain hardening rate as massive gold pillars, as mentioned above. This result indicates that the hierarchical nanoporous structure positively affects the strain hardening. A relationship between the strain hardening or the smaller-is-stronger-effect and structural features above the lower level ligaments suggests that the movement of dislocations plays a decisive role. The dislocation density on the other side is assumed to be solely dependent on the lower level ligament size. The upper hierarchy exacerbates the lack of existing dislocations which strengthens the dislocation starvation. During deformation, dislocations egress from the surface [140], which is intensified by the existence of the upper hierarchy. Finally, the material reaches a "perfect dislocation starvation". As pointed out by Jin *et al.* [136], dislocations are able to overcome longer distances which exceed the size of single ligaments. The egress of a moving dislocation into a pore creates a pore channel dislocation. Jin *et al.* [136] assume that pore channel dislocations can escape from the pore. If this last process is not always ensured, then the additional upper hierarchy level represents an additional obstacle to the movement of dislocations, and the long-range migration of dislocations is negatively affected.

In the context of the scaling behavior of the strength of hierarchical nanoporous gold, results from two comparable studies are worth mentioning. Shi *et al.* [58] report that the flow stress at 10% strain of hierarchical nanoporous gold is similar to the expectation according to Equation 2.19 and Equation 2.21. In the latter one, different parameters A and u are used, which has a minor impact. The HNPG samples analyzed

by Shi *et al.* [58] are produced from $\text{Ag}_{93}\text{Au}_7$, and their mechanical behavior is generally closer to the HNPG samples of category 2 analyzed in this thesis. As can be seen from Figures 5.4(c) and 5.4(d) (blue), the strain hardening extends over a wider range in this category, and the flow stress at the beginning of the deformation, where the yield strength can be read, is close or below the dashed line. Thus, the exceptionally high yield strength of HNPG with $T_A = 300^\circ\text{C}$ and $\varphi^L = 0.34$ (Figure 5.4(c), green) does not contradict the results from the study by Shi *et al.* [58].

A different picture emerges from a study by Jeon *et al.* [62], where the mechanical behavior of HNPG is analyzed by micropillar compression tests. The stress-strain-curves which emerge from the deformation of the micropillars exhibit a distinct yield point. Jeon *et al.* [62] analyze the flow stress at 10% strain which is roughly comparable with the stress level at the yield point. The resulting yield strength is several times larger than the expectation according to Equation 2.19 and Equation 2.21. In one instance, the measured yield strength of 32 MPa and an (initial) φ of 0.20 [62] correspond to a ligament strength $\sigma_{y,\text{loc}}$ of about 7200 MPa, which is almost 6 times larger than the ligament strength determined by Equation 2.21 using the respective ligament size, 30 nm. Furthermore, the ligament strength is about twice as high as the ideal theoretical yield strength of gold which is 3.56 GPa and which is based on the theoretical shear strength [109, 143].

Another finding from the study by Jeon *et al.* [62] concerns the smaller-is-stronger-effect whose occurrence is confirmed. In Section 5.3 of this thesis, the smaller-is-stronger-effect on the lower level is found to be weakly pronounced in HNPG, whereat the analysis is affected by a high uncertainty.

5.4.3 Evolution of stiffness during coarsening

The Young's modulus of massive gold and silver amounts to 77 GPa (Au) and 74 GPa (Ag), respectively [134]. Both values are nearly identical, which is a prerequisite for the comparability between NPG and NPSG. For simplicity, 77 GPa is taken as the E_s of NPSG.

Based on this presumption, Figure 5.6 compares the Young's modulus of NPSG with the Young's modulus of NPG, as indicated in the literature [67, 70, 71, 73, 74, 79, 114, 121, 123]. This figure is similar to Figure 2.2, with the difference being the insertion of the NPSG data. The Young's modulus E of NPSG is lower than expected on the basis of the modified Roberts-Garboczi-law (Equation 2.12). Both the smallest and the largest deviation are determined at the beginning of the deformation, where the E of NPSG with $T_A = 300^\circ\text{C}$ or $T_A = 500^\circ\text{C}$ amounts to 65% or 25%, respectively, of the value determined by the modified Roberts-Garboczi-law. Concerning the relationship between an increasing ligament size by coarsening and a decreasing E , NPSG shows a clear similarity to the dataset by Mameka *et al.* [114]. Differences in material, ligament size and coarsening method prohibit a quantitative comparison, but the similarity is still sufficient to indicate that the underlying effect is the same.

As pointed out in Section 5.1 during the discussion of Figure 5.1(a), a decrease of the connectivity in the course of coarsening can be considered as a possible cause. The lower stiffness decrease observed for NPSG with an initial solid fraction of $\varphi = 0.41$ in

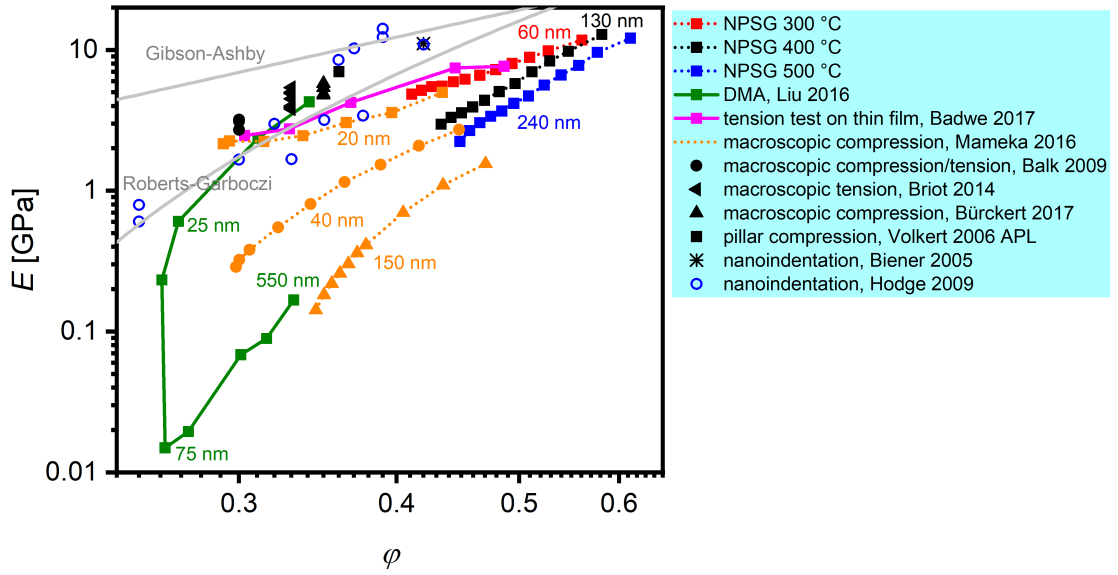


Figure 5.6: Comparison between the Young's modulus E of NPSG and literature values for the Young's modulus E of nanoporous gold [67, 70, 71, 73, 74, 79, 114, 121, 123]. Apart from the insertion of the NPSG data, this figure is almost identical to Figure 2.2. Measured values for NPSG are already presented in Figure 5.1(a).

comparison with NPSG with an initial solid fraction of $\varphi = 0.31$ [58] can be taken as an indication that the connectivity decrease during coarsening is less pronounced when the solid fraction is higher than 0.40. It must be noted that this hypothesis is not verified by any tomographic structural investigation. Instead, two tomographic studies support the theory that a connectivity decrease is not the main factor for the stiffness reduction. Hu *et al.* [86] notice no significant change in connectivity when the ligament size of NPG is increased from 26 nm to 420 nm. At the beginning of the coarsening procedure, the solid fraction is 0.30. Thereby the study by Hu *et al.* [86] is comparable with studies which observe a decline of E in the course of coarsening [58, 114]. A potential shrinkage of the sample during coarsening deserves consideration. Solid fraction data stated by Hu *et al.* [86] indicate an increase of the solid fraction from about 0.30 to about 0.35. The ideal connectivity of a leveled-wave generated structure increases by 25% when φ is changed from 0.30 to 0.35 [98]. Thus, the statement of a "constant connectivity during coarsening" results in an effective decrease of the Young's modulus when the coarsening is accompanied by shrinkage. As can be seen from Figure 1.4 and Figure 5.1(a) and as already mentioned in Section 5.1, the Young's modulus of NPSG of category 3 declines by factor 5 when the ligament size increases from 45 nm to 180 nm, which involves an increase of φ from 0.31 to 0.37 [58]. Based on Equation 2.25, this stiffness reduction correlates with a reduction of the connectivity by 50%–60%. A constant absolute connectivity during coarsening and shrinkage, which results in an effective connectivity decrease when comparing samples with different initial φ during compression, can only partially explain the stiffness reduction by factor 5. Accordingly, the contribution of the connectivity to the stiffness reduction is not completely ruled out, but other factors are assumed to occur.

The other tomographic study mentioned above combines structural investigations and mechanical tests on nanoporous niobium by liquid-metal dealloying. Sohn *et al.* [203] note that the Young's modulus is 10–60 times lower than predicted by the modified Roberts-Garboczi-law (Equation 2.12). By contrast, the connectivity g is about one third less than the value estimated on the basis of the leveled-wave model [98]. Consequently, the relatively low Young's modulus is not explained by the absolute level of the connectivity. Sohn *et al.* [203] explicitly propose an influence of the ligament size distribution on the mechanical behavior. Other explanations given by Mameka *et al.* [114] are a shear instability of the bulk [155] and a surface excess elasticity [204].

An alternative possibility refers to the grain structure in NPSG. Since the precursor alloy is not annealed after cold-rolling, grains are supposed to have a flat, layer-like structure. As a result, the area of the grain boundaries is relatively high in relation to the volume. Grain sizes of NPSG or HNPG are not analyzed in this study. Mameka *et al.* [114] state a grain size of some tens of microns for NPG. This value is used as an approximation. Cold rolling reduces the height of the precursor alloy ingot by a factor of about 5. If the ligament size is 200 nm, the ratio between ligament size and grain size parallel to the direction of compression can fall below 100. Thin film buckling tests on nanoporous gold reveal a strong decrease of the Young's modulus E with increasing ligament size, which is explained by differences in the development of the nanoporous structure between bulk and surface. A decrease of E is observed for a ratio between film thickness and ligament size lower than 10–20, whereat larger ratios remain unexplored [205, 206]. If a large portion of the volume is affected by grain boundaries, general structural characteristics of the material can change, and the total Young's modulus can decrease significantly. If the majority of the volume is not affected, it is still possible that regions next to grain boundaries act as weak points. In this case, these regions contract at the beginning of the overall deformation, which can explain a strong deviation to scaling laws at low strain values. The hypothesis of an influence of grain boundaries is however contradicted by the study by Mameka *et al.* [114, 141], where precursor alloy samples are annealed again before dealloying. A possible influence of cracks is regarded as unlikely because of the quite uniform compression behavior within a sample type (see Figure A.1).

Another hypothesis is based on the quantitative comparison between the Young's modulus E of NPSG presented in Figure 5.1(a) and the flow stress σ_F of NPSG presented in Figure 5.1(b). At first glance, the decrease of the flow stress with increasing L is an ideal example of the smaller-is-stronger-effect. At $\varphi = 0.50$ and at a ligament size of 60 nm, the flow stress is about 145% higher in comparison with a ligament size of 240 nm. Both values correspond to a factor $u = -0.65$ in Equation 2.21, which is close to the factor -0.61 proposed by [140]. This evaluation ignores a second reason for the decrease in σ_F . The combination of shrinkage and strain hardening shifts the course of σ_F to higher solid fractions. However, the downward trend of σ_F for increasing ligament sizes at the beginning of the deformation is a strong indication of the existence of the smaller-is-stronger-effect. At the same solid fraction of $\varphi = 0.50$ the Young's modulus E increases by 90% when L is reduced from 240 nm to 60 nm. Based on Equation 2.25, this indication implies that the connectivity increases by 38%. As presented in Chapter 2, the smaller-is-stronger-effect is restricted to the material's strength, while the

connectivity affects both strength and Young's modulus [109, 206]. Factors which affect E are assumed to have an impact on σ_F as well. Similar to Equation 2.25, one can assume some dependency $\sim g^{1.5}$ of σ on the connectivity. A connectivity increase by 38% consequently corresponds to an increase in strength by 62%. Other factors must contribute with an additional increase by 51% in order to achieve an increase in strength by 145%, as mentioned above. On that basis, the change in connectivity on the one hand and the smaller-is-stronger-effect as well as the shrinkage on the other hand contribute to the change in σ_F roughly equally. It appears unlikely that the decrease of σ_F during coarsening seen in NPSG is caused by several equally strong effects. Instead, the distinctness of the effect points to one dominant reason. This raises the question whether the Young's modulus is somehow affected by the material's strength. In this case, the decrease of E with increasing L is an artefact caused by the smaller-is-stronger-effect. On the basis of a schematic model, it is assumed that some ligaments, or some regions, show a classical behavior with elastic regime, yield point and strain hardening regime [134]. Other ligaments, or other regions, do not feature an elastic regime. Instead, they exhibit yielding from the beginning. Strain hardening is present and localized flow stress values are dependent on the ligament size as a result of the smaller-is-stronger-effect. At their upper ends, unload-load-cycles of stress-strain-curves such as the ones presented in Figure A.1(e) show a clearly pronounced yield point. In the model of elastic and non-elastic ligaments or regions, a yield point is expected as well. An elastic regime is existent, but the Young's modulus is reduced by the interference with the strength. This approach is similar to the concept of the early yielding in nanoporous gold which is proposed by Ngô *et al.* [155]. Accordingly, a surface-induced prestress lowers the additional external load which is required for the initiation of a plastic deformation. The prestress is presumed to have a high shear component, and several ligaments are assumed to be close to a shear instability [114, 155, 207].

In particular, the hypothesis of an early yielding of ligaments is strengthened by two arguments. Firstly, the observation that σ_F approaches the ideal maximum strength argues against a general decrease of E and σ_F by a reduced connectivity. Secondly, an overall similarity exists between the courses of E and σ_F against φ . As mentioned in Subsection 5.4.2, the approximation to the ideal maximum strength results in a kink in the course of σ_F against φ . As can be seen from the comparison between Figures 5.4(b) and 5.4(d), the Young's modulus E features a similar kink at the same stage of deformation. The higher slope of E against φ in the early stage of compression relative to scaling laws seems to be caused by the strain hardening and the impairment by the strength.

With reference to Figure 5.6, the question is raised why in some datasets an existing prestress results in an early yielding, while in other datasets the Young's modulus is not affected by this phenomenon. In this regard it is noted that the phenomenon of an exceptionally low Young's modulus as a result of coarsening with $\varphi > 0.30$ is only observed in datasets where the Young's modulus is determined on the basis of the analysis of unload-load-cycles [58, 114]. Accordingly, it is possible that the prestress is not caused by a surface-induced effect, but by the previous deformation. In this case, the Young's modulus should show some type of transition during deformation. In

Figure 5.6, the data from this thesis show a quite uniform increase of E with increasing φ . This uniform increase of E observed for NPSG contradicts the hypothesis that the prestrain is induced by the deformation and argues in favor of an inherent property of the material. A surface-induced effect on the other side is unlikely since the stiffness decrease is highest for larger ligament sizes and thereby for relatively lower surface areas [114]. An alternative possibility is the generation of prestress by shrinkage. If the shrinkage correlates with the emergence of prestress, the line of argumentation changes slightly, and the stiffness decrease in the course of coarsening originates directly from the shrinkage and not from the decrease of the strength and an impairment of the stiffness by the strength. However, the observation of a decrease in stiffness *and* in strength in the course of coarsening and shrinkage rather suggests a general impairment of the stiffness by the strength. The origin of the preexistent strain remains unknown.

In view of the stiffness reduction by the interference with the strength, the dependence of the course of E against φ on φ^L , which is discussed in Subsection 5.4.1, can also be related to a different strain hardening rate. As can be seen from Figures 5.4(c) and 5.4(d), HNPG with $\varphi^L = 0.41\text{--}0.43$ (blue) features a lower strain hardening rate than HNPG with $\varphi^L = 0.34\text{--}0.35$ (green). The observation of a relatively higher slope of E against φ for HNPG with $\varphi^L = 0.41\text{--}0.43$ (blue) in Figures 5.4(a) and 5.4(b) can be caused partly by the on-going strain hardening. In this context it is noted that the strain hardening rate correlates with the smaller-is-stronger-effect [140]. A variation of the ligament size is expected to have an influence on the yield strength as well as on the strain hardening rate. Shrinkage, on the other side, is suspected to shift the course of σ_F against φ to higher φ -values without affecting the strain hardening rate. The higher strain hardening rate of HNPG of category 1 (green) in comparison with HNPG of category 2 (blue) can therefore be related to a stronger smaller-is-stronger-effect. The influence of φ^L in conjunction with Equation 5.1 is not excluded, but it is not necessarily the only determinant. Once the flow stress has reached the maximum strength (red), strain hardening is completed, and the Young's modulus against the solid fraction is at least roughly parallel to the prediction by Equation 5.1. Thus, the modified Roberts-Garboczi-law is applicable to the determination of the Young's modulus during deformation if a general manipulation by the interaction with the strength is taken into account.

A schematic depiction of the influence of structural parameters on the mechanical behavior of HNPG is shown in Figure 5.7. This figure can also be considered as an outline of the most significant results of this chapter. The course of the flow stress σ_F against the solid fraction φ is divided into a strain hardening regime and a regime of maximum strength. The Young's modulus E is generally impaired by the flow stress σ_F as a result of the effect of an early yielding of ligaments [155]. Consequently, E is lower than the estimation on the basis of the modified Roberts-Garboczi-law. This estimate incorporates a compression on the lower hierarchy level. Accordingly, the lower level solid fraction φ^L has an influence on the mechanical behavior aside from φ . Size effects, namely the smaller-is-stronger-effect on the upper level and the combination of shrinkage and strain-hardening, affect the flow stress σ_F and thereby the Young's modulus in the strain-hardening regime. It is not clear which of the two dominates in the case of HNPG. The magnitude of the strain hardening correlates with

the smaller-is-stronger-effect [140] so that the smaller-is-stronger-effect on the upper level acts differently from shrinkage. Figure 5.7(a) reflects this difference. The smaller-is-stronger-effect on the upper level (factor 3) affects the yield strength and the strain hardening rate, while shrinkage (factor 4) shifts the flow stress to higher φ -values. In respect of the smaller-is-stronger-effect on the lower level no conclusion is provided.

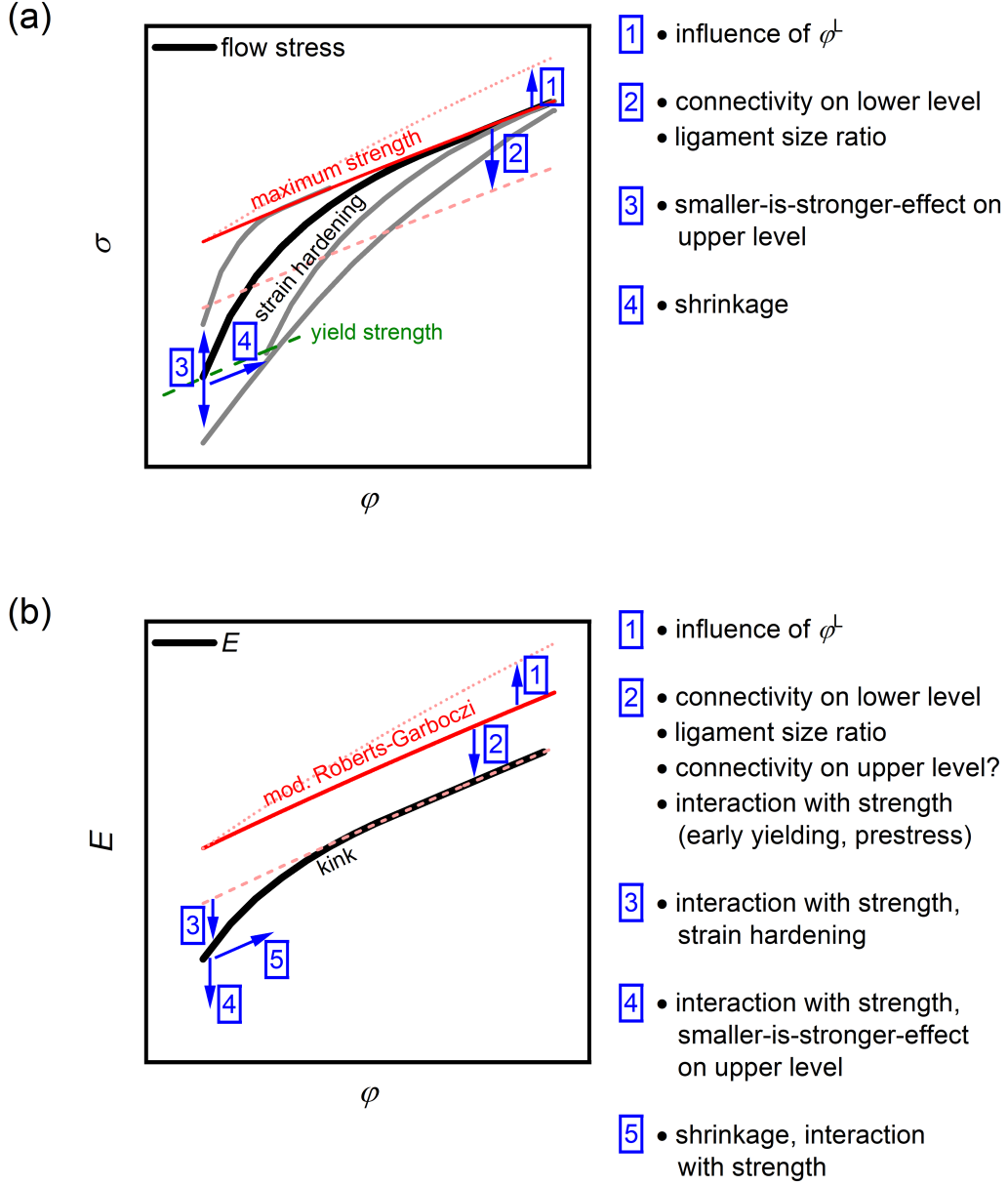


Figure 5.7: Schematic depiction of the influence of structural parameters on the mechanical behavior during compression. (a) shows the course of the flow stress σ_F against the solid fraction φ , while (b) presents the course of the Young's modulus E against the solid fraction φ . The black line represents a prototypical behavior, while grey lines indicate alternatives which result from changing structural parameters. Red and green lines express scaling laws.

The connectivity on the lower level and relatedly the ligament size ratio are structural parameters which control the general level of the course of E and σ_F . A ligament size ratio $L^U/L^L \lesssim 2.5$ and a lower level solid fraction $\varphi^L \lesssim 0.30$ are supposed

to negatively influence the lower level connectivity. The last statement is affected by uncertainty since the variant with $E_D = 0.76 \text{ V}$ represents the only sample type with $\varphi^L \approx 0.30$. The examination of a sample type with the same φ^L and φ and a relatively lower L^L is necessary to verify an effect of coarsening on the lower level. At this point, the visual appearance of the lower level structure shown in Figure 4.5(a) is emphasized again. Thus, the presumptions of a connectivity decline during coarsening with $\varphi \lesssim 0.30$ and of a constant connectivity during coarsening with $\varphi > 0.30$ seem to be more pronounced on the lower hierarchy level. Nevertheless, the influence of the connectivity remains ambiguous.

Chapter 6

Summary and Outlook

6.1 Modification of the synthesis of hierarchical nanoporous gold

The entire thesis is dedicated to the synthesis and characterization of hierarchical nanoporous gold (HNPG). Based on an existing approach [58] and starting from $\text{Ag}_{90}\text{Au}_{10}$ as the precursor alloy, macroscopic samples of HNPG in millimeter range are produced by a three-step procedure which consists of a controlled partial (1st) dealloying, coarsening by annealing and a complementary (2nd) dealloying. The synthesis route of HNPG is modified with regard to the adjustment of four structural parameters: ligament size on the upper hierarchy level, ligament size on the lower hierarchy level, solid fraction on the upper hierarchy level and solid fraction on the lower hierarchy level. Two additional parameters which are directly derived are the ratio between upper level and lower level ligament size (ligament size ratio) and the total solid fraction. Every single structural parameter is adjusted by the variation of one or several specific control variables. An adjustment of the annealing temperature results in a variation of the upper level ligament size. The lower level ligament size is influenced by two different control variables: An additional electrochemical coarsening in the final stage of the 2nd dealloying and a dependence of the lower level ligament size on the dealloying potential. Solid fractions on upper and lower level are determined on the assumption that the macroscopic shrinkage during the 2nd dealloying is restricted to the lower hierarchy level and that the upper level solid fraction is preserved. The upper and lower level solid fraction are reversely influenced by the extent of the 1st dealloying and thus the silver concentration after 1st dealloying. A lower silver concentration is accompanied by a decreased upper level solid fraction and an increased lower level solid fraction. Shrinkage is observed during the annealing step where it is closely linked to the extent of the coarsening. Furthermore, shrinkage also occurs during the 2nd dealloying where it is dependent on the dealloying potential. Solid fractions on upper and lower level are affected accordingly. Summarized, HNPG is modified in various ways, which enables the assignment of structural parameters to a specific effect on the mechanical behavior.

6.2 Characterization of nanoporous silver gold and hierarchical nanoporous gold by small- and ultra-small-angle X-ray scattering

Samples are structurally characterized by scanning electron microscopy (SEM), small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS). A novel procedure is employed for the preparation of samples for SAXS and USAXS, which involves the cutting of bulk material using plasma focused ion beam. Scattering curves of HNPG depict two distinct interference peaks, which demonstrates the existence of two well-defined length scales. In the case of unimodal nanoporous samples after the annealing/coarsening step, called nanoporous silver gold (NPSG), a single interference peak is observed. Results by SAXS and by USAXS show a good agreement, which encourages the application of USAXS for the examination of nanoporous structures whose ligament spacing is beyond the resolution limit of SAXS. Scattering data are fitted by the combination of a Gaussian and a baseline which reflects the distinct Porod regime. Ligament sizes or diameters L which result from the analysis by SEM are compared with ligament spacings or ligament distances $\tilde{L}$ which are derived from the positions of the peaks of the scattering graphs. The ratio $\tilde{L}/L$ between ligament spacing and ligament size is dependent on the solid fraction and falls from 3.4 to 2.3 when the solid fraction rises from 0.30 to 0.45. Based on this correlation, ligament sizes measured by SEM can generally be converted into a ligament spacing if the solid fraction is within the range 0.30–0.45. Finally, the specific surface area derived from the analysis of the scattering intensity in the Porod regime and the total scattering intensity is consistent with the specific surface area estimated on the basis of the peak position under application of the leveled wave model. The good agreement supports the accuracy of the combination of both methods for the determination of the specific surface area. Furthermore, the agreement between both approaches is an indication of the applicability of the leveled wave model for the representation of nanoporous metals.

6.3 Mechanical behavior of nanoporous silver gold and hierarchical nanoporous gold

The mechanical properties of HNPG and NPSG are analyzed by macroscopic compression tests. The Young's modulus E and the flow stress σ_F are determined on the basis of unload-load-cycles during compression, which results in data rows of E and σ_F against the solid fraction φ . A universally valid dependence of E on the lower level ligament size is not observed. An increase of the lower level ligament size by a factor of about 2 does not cause a recognizable change of the Young's modulus if the lower level solid fraction is larger than 0.40 and if the resulting ligament size ratio is about 4. On the other hand, an increase of the lower level ligament size reduces the Young's modulus if the resulting ligament size ratio is about 2. This finding indicates the existence of a ligament size ratio effect which occurs at a ligament size ratio lower than about 2.5. SEM images of HNPG illustrate that the lower level structure increasingly resembles a single strut parallel to the upper level ligament when the ligament size ratio converges

to 1. It is assumed that this pattern prevents a complete structural collapse which is assumed if the lower and the upper hierarchy level are completely independent from each other [101]. A coarsening on the lower level is accompanied by a strong decrease of stiffness and strength if the lower level solid fraction is about 0.30. Supported by SEM images, this observation is explained by a decline of the lower level connectivity which occurs if the lower level solid fraction is about equal or lower than 0.30. On the other side, the lower level connectivity is assumed to be constant during coarsening if the lower level solid fraction is larger than 0.35.

SEM images of HNPG after compression demonstrate that the upper hierarchy level is compressed, while the lower hierarchy level remains intact. When regarding the course of the Young's modulus against the solid fraction during compression, HNPG samples with a similar total solid fraction, but a different solid fraction on the upper and the lower level show a different pattern. This difference is replicated by the modified Roberts-Garboczi scaling law [58, 98] when the solid fractions on the upper and the lower level are included separately and when a compression on the upper level is assumed. Furthermore, for several HNPG variants the flow stress during compression reaches the theoretical shear strength of gold, referred to nanoporous structures. A possible explanation is a "perfect dislocation starvation", meaning that the upper hierarchy aggravates the lack of dislocations. After the completion of the strain hardening and the attainment of the maximum strength, the flow stress is reproduced well by the modified Roberts-Garboczi-law with respect to the absolute level and the dependence on φ .

Although differences in the course of the Young's modulus are reproduced by the modified Roberts-Garboczi-law, the measured values are generally lower than estimated from this scaling law. This observation applies to NPSG as well. The increase of the ligament size of NPSG with a solid fraction of about 0.40 leads to a reduction of stiffness and strength. A connection with a connectivity decrease during coarsening is discussed in this thesis. However, the smaller-is-stronger-effect and the combination of shrinkage and strain hardening are suggested to be responsible for the decrease in strength. The decrease of the Young's modulus is associated with the early yielding of ligaments [155]. Accordingly, the prestress level is high and several ligaments show yielding already in the elastic regime. This explanatory approach is strengthened by an overall similarity between the courses of the Young's modulus and the flow stress against the solid fraction. The flow stress σ_F transitions from a strain hardening regime to a scaling-law regime. The same pattern is observed for the course of the Young's modulus against the solid fraction, which suggests that the Young's modulus is generally affected by the strength.

6.4 Outlook

The HNPG sample type with an upper level ligament size of about 60 nm, a lower level ligament size of about 30 nm, and thereby a ligament size ratio of about 2 already represents a transition type between unimodal nanoporosity and hierarchical nanoporosity. A further raise of the lower level ligament size is possible by increasing the extent of the electrochemical coarsening in the final stage of the synthesis. In this way, the pro-

duction of a unimodal nanoporous structure with an exceptionally low solid fraction of roughly 0.15 can be possible. It would be necessary to examine if the structure retains its mechanical properties. If yes, then the resulting structure would contradict the Plateau-Rayleigh instability [109, 116, 117] and the percolation limit which actually do not permit a stable unimodal nanoporous structure with a solid fraction below the percolation limit [98].

The stiffness decrease during the thermal coarsening of NPSG is inextricably linked with the phenomenon of shrinkage. A lowering effect of shrinkage on the Young's modulus is already confirmed for nanoporous gold [75]. However, the exact mechanism of shrinkage at structural level is unclear. A structural investigation of shrinkage by means of a tomographic reconstruction is experimentally challenging. The same applies to a tomographic investigation of coarsening. Shrinkage, or the combination of coarsening and shrinkage, may result in substantial changes in network and morphology, but the experimental proof still needs to be provided. In this context, structural inhomogeneities can be investigated by the conduction of tomographic reconstructions in different regions of the macroscopic sample, including the grain boundaries. Concerning the theory of an early yielding of ligaments [155], X-ray diffraction is an option to evaluate the level of prestress [208] and to test the theory that prestress levels are sufficient to enable an early yielding of ligaments. In that regard, a contrary indication is the finding that Bragg reflection peaks of HNPG show a relatively narrow width when compared with as-dealloyed nanoporous structures [56]. The diffraction analysis needs to be based on macroscopic samples which exhibit the phenomenon of shrinkage and stiffness decrease during coarsening. In addition to that, the origin of the prestress needs to be revealed. In particular, it is of interest why this effect is observed only in certain studies [58, 114, 155], but not in others [67, 70, 71, 73, 121, 123]. Unidentified synthesis parameters, which induce an inherent prestress into the material during the production, might be the cause. A linkage with the effect of shrinkage appears possible. Apart from this, further research is needed on the effect of strain hardening, particularly with regard to the magnitude of the strain hardening, which has a direct impact on the stress values during compression. Both experimental and simulative studies can contribute to a better prediction of the extent of strain hardening.

This thesis encourages the use of small-angle X-ray scattering for the analysis of nanoporous bulk structures. The analysis of the scattering data can be refined by the conversion into an autocorrelation function. New methods for the structural characterization can be developed on the basis of the autocorrelation function. The aim would be to describe the nanoporous structure, which displays a high degree of complexity, by the lowest possible number of structural parameters, and to determine these parameters by a standard procedure based on small-angle X-ray scattering.

Apart from an enhancement of structural analysis methods for nanoporous metals in general, the objective of this thesis is to gain a better understanding of the mechanical behavior of hierarchical nanoporous metals. An application of hierarchical nanoporosity such as in catalysis or sensor technology is conceivable [5] but requires an adaptation to the desired purpose. The results of this thesis give insight into the complex mechanical behavior of hierarchical nanoporous gold and promote the comprehension of hierarchical nanoporosity in general.

Appendix

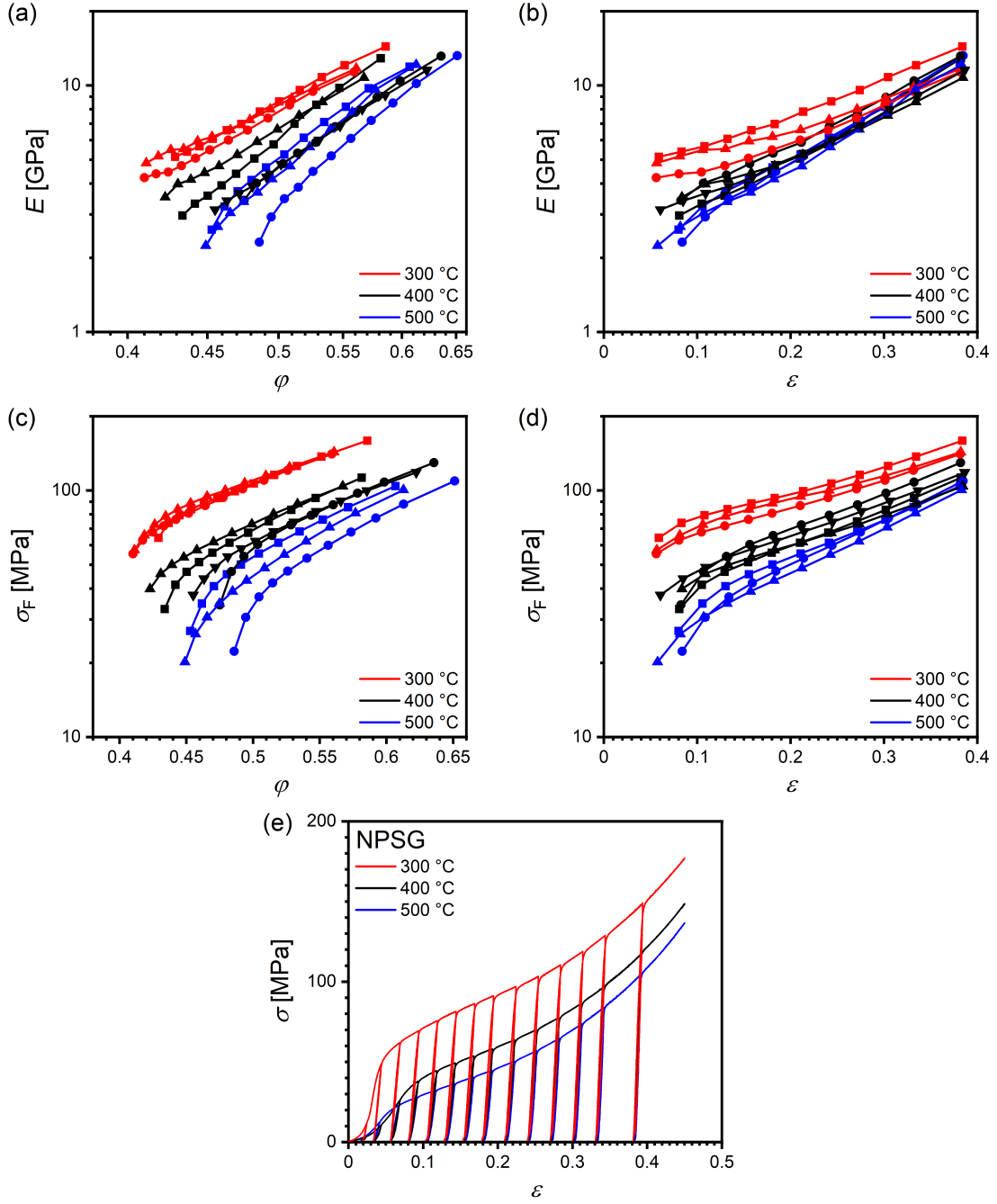


Figure A.1: Comprehensive compression test data for NPSG with varied L (category 1). In total, measurements on 10 samples with a composition of $\text{Ag}_{73}\text{Au}_{27}\text{--}\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.73\text{--}0.77$) are presented. Samples are annealed at a varied temperature T_{A} . The precursor alloy is $\text{Ag}_{90}\text{Au}_{10}$. The compilation depicts the Young's modulus E against the solid fraction ϕ (a) and against the engineering strain ϵ (b) as well as the flow stress σ_F against ϕ (c) and against ϵ (d). Selected measurement series of (a) and (c) are presented in Figures 5.1(a) and 5.1(b) in the main text. The stress-strain-curves upon which these selected measurement series are based are shown in (e).

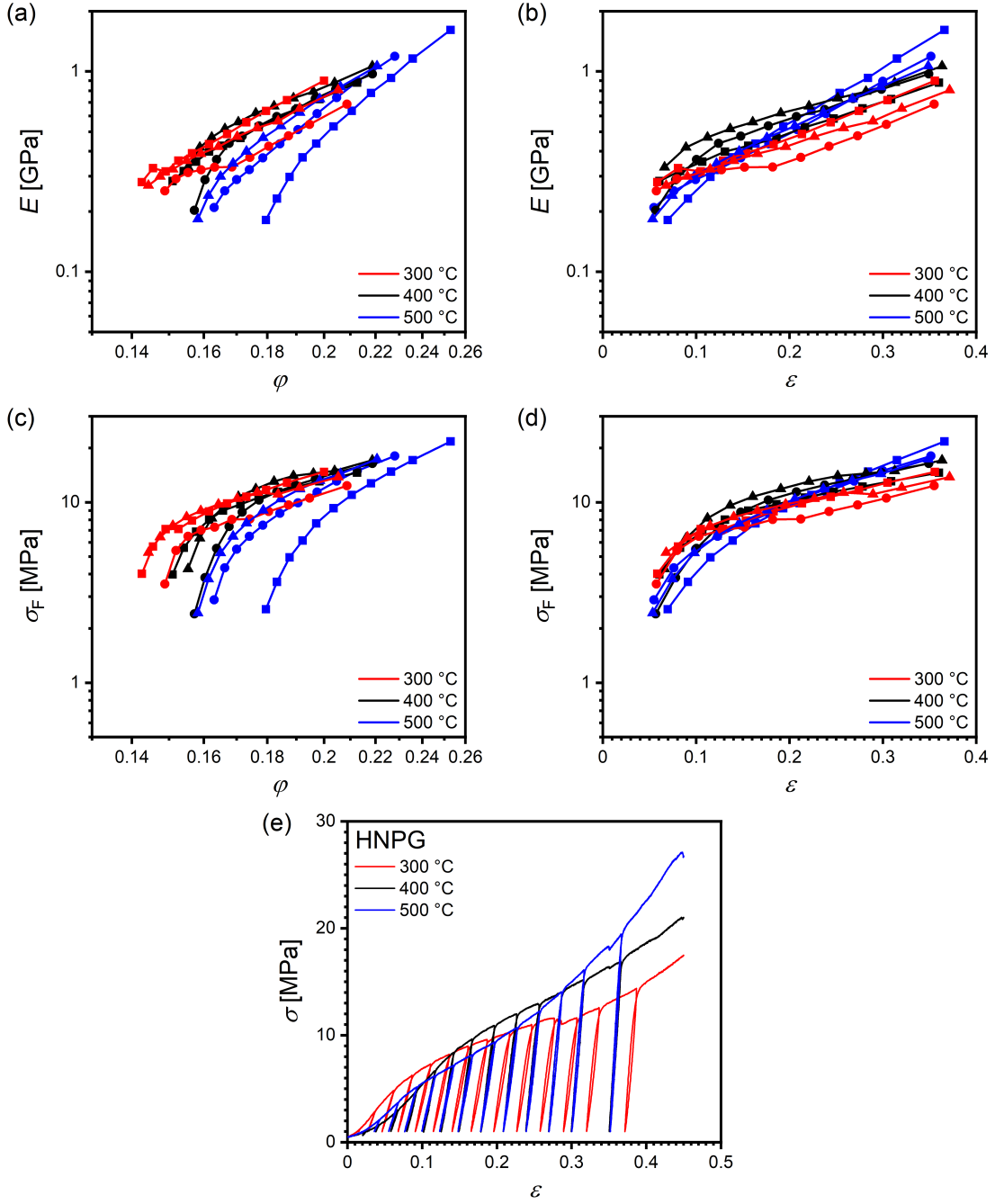


Figure A.2: Comprehensive compression test data for HNPG with varied L^U and constant L^L (category 1). In total, measurements on 9 samples with a composition after 1st dealloying of $\text{Ag}_{73}\text{Au}_{27}\text{--Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.73\text{--}0.77$) are presented. Samples are annealed at a varied temperature T_A in the annealing step and dealloyed with the same dealloying potential $E_D = 0.80$ V during the 2nd dealloying. The precursor alloy is $\text{Ag}_{90}\text{Au}_{10}$. The compilation depicts the Young's modulus E against the solid fraction ϕ (a) and against the engineering strain ϵ (b) as well as the flow stress σ_F against ϕ (c) and against ϵ (d). Selected measurement series of (a) and (c) are presented in Figures 5.1(a) and 5.1(b) in the main text. The stress-strain-curves upon which these selected measurement series are based are shown in (e). Figure 3.10 in Chapter 3 anticipates the stress-strain-curve of HNPG with $T_A = 400$ °C (black).

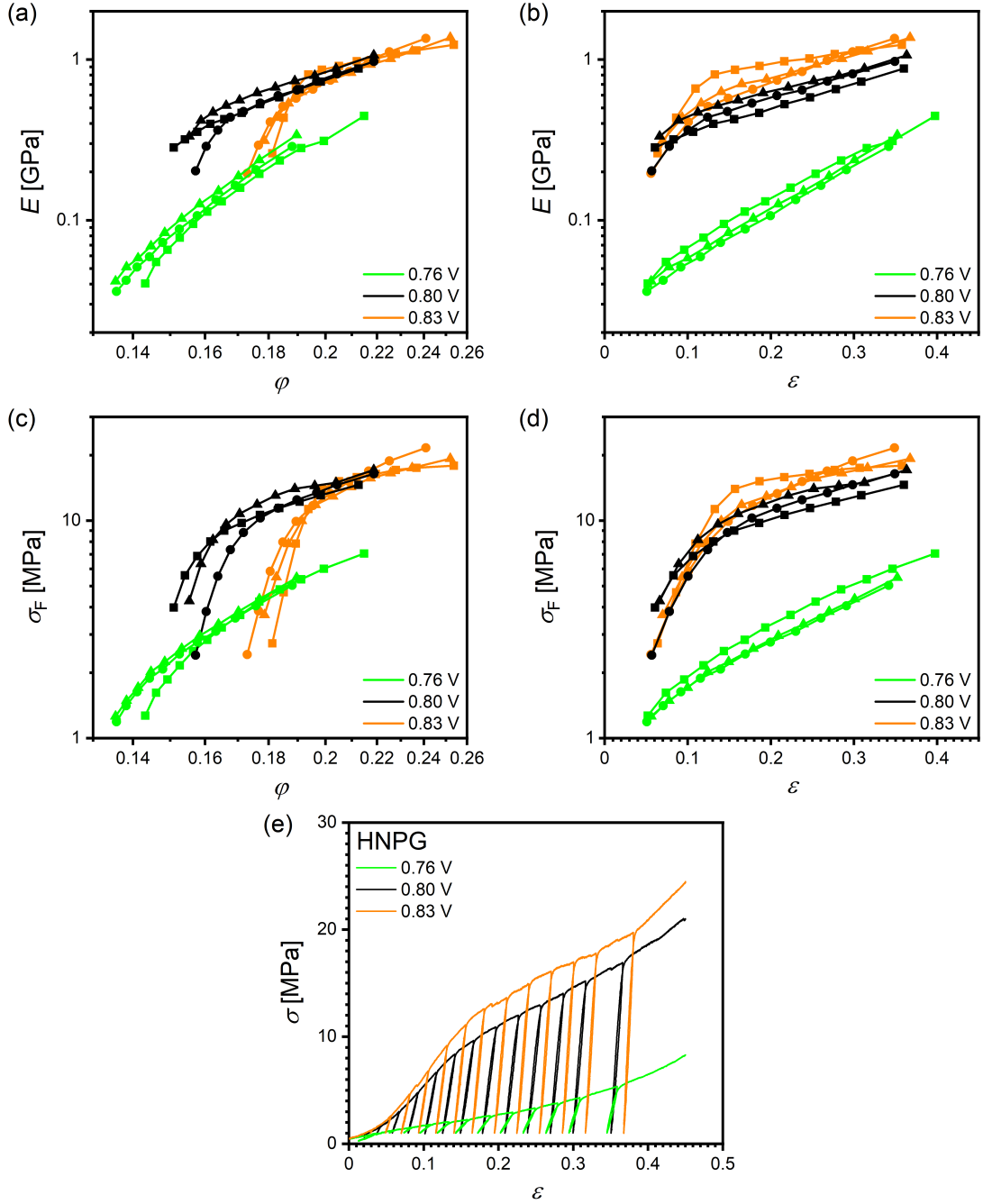


Figure A.3: Comprehensive compression test data for HNPG with constant L^U , varied L^L and with $\phi^L < 0.40$ (category 1). In total, measurements on 9 samples with a composition after 1st dealloying of $\text{Ag}_{73}\text{Au}_{27}$ – $\text{Ag}_{77}\text{Au}_{23}$ ($x_{\text{Ag}}^{\text{DE}} = 0.73$ – 0.77) are presented. Samples are annealed at $T_A = 400^\circ\text{C}$ in the annealing step and dealloyed with a varied dealloying potential E_D during the 2nd dealloying. The precursor alloy is $\text{Ag}_{90}\text{Au}_{10}$. The compilation depicts the Young's modulus E against the solid fraction ϕ (a) and against the engineering strain ϵ (b) as well as the flow stress σ_F against ϕ (c) and against ϵ (d). Selected measurement series of (a) and (c) are presented in Figures 5.2(a) and 5.2(b) in the main text. The stress-strain-curves upon which these selected measurement series are based are shown in (e). Figure 3.10 in Chapter 3 and Figure A.2(e) on the previous page depict the same stress-strain-curve of HNPG with $T_A = 400^\circ\text{C}$ and with $E_D = 0.80\text{ V}$ (black).

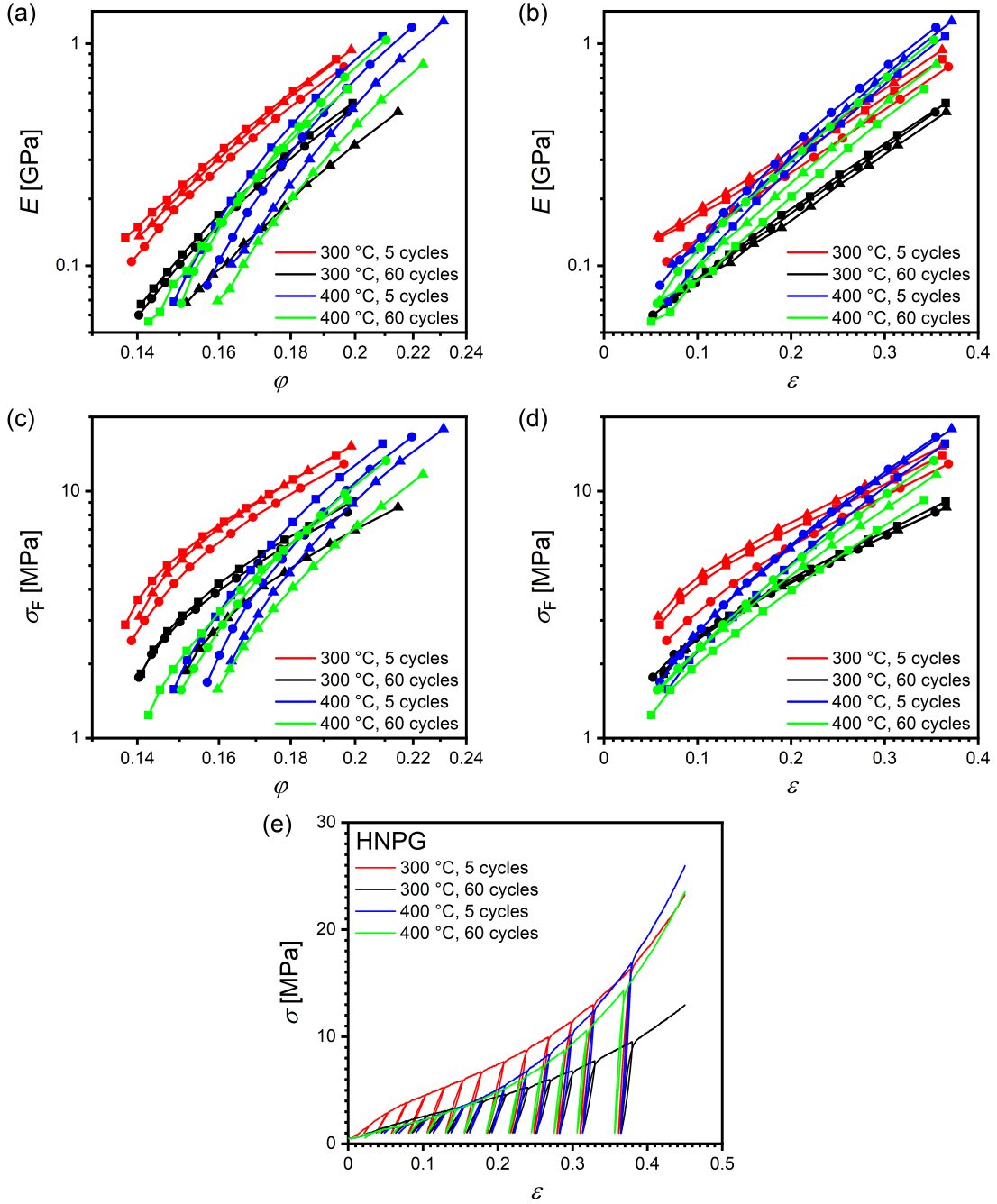


Figure A.4: Comprehensive compression test data for HNPG with varied L^U , varied L^L and with $\varphi^L > 0.40$ (category 2). In total, measurements on 12 samples with a composition after 1st dealloying of $\text{Ag}_{65}\text{Au}_{35}$ – $\text{Ag}_{68}\text{Au}_{32}$ ($x_{\text{Ag}}^{\text{DE}} = 0.65$ – 0.68) are presented. Samples are annealed at a varied temperature T_A in the annealing step and dealloyed with the same dealloying potential $E_D = 0.90$ V during the 2nd dealloying. The number of potential cycles N_{CY} , which adjusts L^L and which amounts to 5 cycles or 60 cycles, is indicated in the legend. The precursor alloy is $\text{Ag}_{90}\text{Au}_{10}$. The compilation depicts the Young's modulus E against the solid fraction φ (a) and against the engineering strain ϵ (b) as well as the flow stress σ_F against φ (c) and against ϵ (d). Selected measurement series of (a) and (c) are presented in Figures 5.3(a) and 5.3(b) in the main text. The stress-strain-curves upon which these selected measurement series are based are shown in (e).

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