Plastic yielding in nanocrystalline Pd-Au alloys mimics universal behavior of metallic glasses

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(Dated: December 10, 2014)

Abstract

We studied solid solution effects on the mechanical properties of nanocrystalline (NC) Pd$_{100-x}$Au$_x$ alloys ($0 \leq x < 50$ at.%) at the low end of the nanoscale. Concentration has been used as control parameter to tune material properties (elastic moduli, Burgers vector, stacking fault energies) at basically unaltered microstructure (grain size $D \approx 10$ nm). In stark contrast to coarse grained fcc alloys, we observe solid solution softening for increasing Au-content. The available predictions from concepts and theories taking explicitly into account the effect of the nanoscale microstructure on shear strength have been disproved without exception. We infer that dislocation activity contributes only marginally to strength. We find a linear correlation between shear strength and shear modulus which quantitatively agrees with the universal behavior of metallic glasses discovered by Johnson and Samwer [W.L. Johnson and K. Samwer, PRL 95, 195501 (2005)].

PACS numbers: 62.20.F-, 62.25.Fg, 81.07.Bc

I. INTRODUCTION

Over the past two decades, it has been well established that decreasing the grain size $D$ of polycrystalline metals into the nanometer regime, $D < 100$ nm, results in e.g. a substantial increase of strength$^1$, improved fatigue$^2$ as well as wear resistance$^3$. Gaining insight into the physics of the underlying deformation mechanisms has motivated intense research efforts with a focus on studying microstructure-dependent deformation behavior with grain size as prominent control parameter$^4$. In particular, when decreasing the grain size to the lower end of the nanoscale $D \lesssim 10$ nm, it has been established that intragranular crystal plasticity becomes to a large proportion replaced by intergranular plasticity, i.e. deformation processes which essentially emerge in the core region of GBs. Computer simulations and experiments unraveled a variety of modes of plastic deformation that are mediated by GBs: GB slip and sliding$^5-7$, grain rotation$^8-10$ that may even lead to grain coalescence but is also an integral part of stress-driven GB migration (SGDM)$^8,11,12$ as well as of shear transformations (STs)$^{13,14}$. The latter involve shuffling or flipping of groups of atoms and may act as flow defect operating in the core region of GBs, thus playing a similar role in a disordered proximity as dislocations do in a crystalline environment. Moreover, GB facets or ledges and triple junctions act as stress concentrators thereby effectively reducing the barrier for partial dislocation nucleation and emission$^{15,16}$. Because of the complex interplay of disparate mechanisms, operating either sequentially or simultaneously, it is still under debate which role they play in responding to the intrinsic stress field and which share to overall strain propagation is carried by them.

To improve our understanding of how different plasticity mechanisms interact and contribute to strain propagation on the nanoscale, we study solid solution alloying and its effect on the strength of the material. Fortunately, the Pd-Au alloy system, which is fully miscible and has a negligibly small tendency to segregation, enables to prepare any Au-concentration at basically fixed grain size of $\approx 10$ nm. It so becomes feasible to gradually tune material parameters like lattice parameter or Burgers vector, elastic moduli, stacking fault energy and GB energy without changing the character of microstructure (grain size, texture). Particularly, the Pd-Au alloy system exhibits a high stacking fault energy $\approx 180$ mJm$^{-2}$ in the Pd-rich alloys and a low stacking fault energy $\approx 50$ mJm$^{-2}$ on the Au-rich side. Regarding deformation mechanisms, recent studies on NC Pd$_{90}$Au$_{10}$ have unraveled that plastic deformation is governed by shear shuffling (STs) at/along GBs while dislocation activity more likely plays a minor role$^{17,18}$. Nevertheless, it is an open problem whether or not an increase of Au-concentration involving a concomitant change of material parameters will lead to a change of the dominant deformation mechanism(s) operating at the nanoscale. Notably, we expect an increasing propensity for partial dislocation emission from GBs that goes in parallel with lowering stacking fault energies by increasing the Au-concentration of the NC Pd-Au alloys. To explore this scenario, we compare the evolution of strength of coarse-grained (CG) and NC Pd$_{100-x}$Au$_x$ alloys ($0 \leq x < 50$) with the predictions of available theories of solid solution strengthening.

II. SOLID SOLUTION STRENGTHENING: THEORY AND MODELS

Traditional solid solution strengthening theories rely on the idea that solute atoms, which modify the elastic energy of a dislocation, act as obstacles to dislocation motion in a crystalline environment. For the concentration dependence of flow stress or hardness different models have been suggested which all predict linear or power-law $(c^{1/2}, c^{2/3})$ increase of flow stress with concentration $c^{21-23}$. As will be shown later, solid solution strengthen-
The critical shear strength has three contributions: grain shear strength \( \Delta \tau \) is primarily a consequence of the local mismatch in shear modulus (interaction parameter \( \varepsilon_G = \frac{1}{2} \frac{\partial G}{\partial c} \)) and size \( (\varepsilon_b = \frac{1}{2} \frac{\partial \gamma}{\partial c}) \). Overall, this mismatch results in an effective barrier for dislocation glide.

Clearly, at the low end of the nanoscale the abundance of GBs, the volume fraction of which scales as \( 1/D \), has to be taken into account. Rupert et al.\(^{24}\) adapted Fleischer model to NC metals by adding two terms which allow for strength enhancement as well as softening. The first term comprises dislocation pinning at GBs and the second term renormalization of this pinning potency by considering the global changes of elastic properties and Burgers vector of the abutting crystallites which are sensed when dislocations are bowing across them. The total shear strength of NC alloys has been expressed as

\[
\Delta \tau = A \cdot G \cdot \varepsilon^{3/2} \cdot c^{1/2},
\]

where \( A \) is a material constant, \( G \) the shear modulus of the solvent, \( b \) the burgers vector of the solvent, and \( c \) the concentration of solute atoms. The increase in shear strength \( \Delta \tau \) is primarily a consequence of the local mismatch in shear modulus (interaction parameter \( \varepsilon_G = \frac{1}{2} \frac{\partial G}{\partial c} \)) and size \( (\varepsilon_b = \frac{1}{2} \frac{\partial \gamma}{\partial c}) \). Overall, this mismatch results in an effective barrier for dislocation glide.

The binary NC Pd-Au samples, with Au-concentration between 0 and 50 atomic\%, were prepared by inert gas condensation (IGC) and compaction at 1.8 GPa\(^{29}\) to obtain disc-shaped samples with a diameter of 8 mm and a thickness of about 1 mm. The composition of as prepared specimens was determined by EDX (EDAX TSL Trident system) in a SEM (JEOL F 7000). IGC-prepared samples have a random texture and lognormally distributed
equiaxed grains\textsuperscript{30,31} with a volume weighted average grain size $D_{\text{vol}} \approx 10$ nm. The latter was determined using Klug and Alexander’s\textsuperscript{32,33} modified Williamson-Hall technique applied to Bragg-peak broadening of X-ray diffraction diagrams. Lattice parameters have been determined from a Nelson-Riley\textsuperscript{34} plot of \{hkl\}-dependent Bragg peak positions. All diffraction experiments were performed on a laboratory diffractometer (PANalytical X'Pert Pro) operated in Bragg-Brentano focusing geometry and $\theta-\theta$ mode. CG Pd-Au samples were prepared by arc melting, cold deformation to a disc, and subsequent annealing at 900°C. Primary and secondary recrystallization leads to an average grain size of $\approx 100$ µm. Alternatively, we annealed NC Pd-Au specimens at 400°C to induce a curvature-driven grain-growth resulting in an average grain size of $\approx 100$ µm. Both sets of specimens are marked by blue open squares in Fig. 2 (b) and represent a consistent data set for the concentration-dependent shear modulus of the coarse grained reference state. CG samples were characterized in analogy to the NC specimen except the grain size was determined by electron backscattering diffraction (EBSD) in the SEM.

All specimens were coupled to a 20 MHz ultrasonic transducer (Panametrics V2173), capable to simultaneously transmit longitudinal and transverse waves. The ultrasonic transducer was connected to a LeCroy WaveRunner 6051 digital oscilloscope which allowed us, by applying the pulse-echo overlap method\textsuperscript{35}, to extract time-of-flight times of the waves. The velocities of longitudinal and transverse waves are given by the ratios of two times the specimen thickness over the respective time-of-flight. For a quasi-isotropic material and assuming linear elasticity, the following relations hold between the scalar shear ($G$) and Young’s ($E$) moduli and the longitudinal and transverse sound velocities, $v_l$ and $v_s$\textsuperscript{36}

\begin{equation}
G = \rho \cdot v_s^2,
\end{equation}

\begin{equation}
E = \rho \cdot v_s^2 \cdot \frac{3v_l^2 - 4v_s^2}{v_l^2 - v_s^2},
\end{equation}

where $\rho$ is the sample density. The overall density of NC-materials is reduced compared to the density of their CG counterparts. This is due to the fact that the core regions of GBs carry excess volume\textsuperscript{37,38} resulting from atomic site mismatch that is created when two differently oriented crystal lattices meet along a common interface. Nevertheless, the density of NC materials can be determined with high accuracy using the method of Archimedes in conjunction with a microbalance (reference media: air and diethyl phthalate)\textsuperscript{39}.

It remains to be addressed that Poisson’s ratio $\nu$ depends on $E$ and $G$ and assumes the following form

\begin{equation}
\nu = (E - 2G)/2G;
\end{equation}

more details on this matter can be found in\textsuperscript{40}. Vickers hardness measurements were performed on a Frank Durotest 38151 testing device applying a testing force of 980 mN (HV0.1) and averaging over 20 indents per NC sample. Following the pertinent literature, we employed the relation $HV \approx 3\sigma_y \approx 3(2\tau_y)$, and use microhardness (indent-diagonal $> 20$ µm) as measure of yield stress.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{hardness.png}
\caption{(Color online) Vickers hardness HV of nanocrystalline (black squares) and coarse grained (blue circles) Pd-Au as a function of Au-concentration. Dashed line represents the prediction from Fleischer’s model according Eq. 1.}
\end{figure}

\section*{IV. RESULTS AND DISCUSSION}

In Fig. 1 we display the Vickers hardness as a function of Au-concentration for both CG and NC Pd-Au alloys. As expected, CG Pd-Au ($D \approx 100$ µm) shows classical solid solution hardening behavior, whereas, the hardness of the NC alloys decreases with rising Au-content. Before focusing on this fundamental discrepancy, we set the benchmark for comparison by examining whether the CG alloys agree with the predictions from Fleischer’s model Eq. 1.

The needed material parameters (lattice parameter, shear modulus) are displayed in Fig. 2 together with the data for the NC alloys, which will be ensuingly addressed. Clearly, the lattice parameters follow Vegard’s rule and it is straightforward to determine $\partial b/\partial c = 13.32 (6) \cdot 10^{-2}$ pm/at.%, where it has been assumed that for full dislocations in a fcc lattice $b = a/\sqrt{2}$, and $b_p = a/\sqrt{6}$ for partial dislocations. Surprisingly, the shear modulus of the CG alloys exhibits only a weak concentration dependence $\partial G/\partial c = -0.03 (2) \cdot 10^{-2}$ GPa/at.%. With the solvent values for $b = 275, 0 (1)$ pm and $G = 44.0 (5)$ GPa taken from the pure Pd specimen and using least-squares fitting, we can verify that the Fleischer model (dashed line in Fig.1) is in good agreement with our experimental data. The parameter $A$ in Eq.1 is a material specific constant which was treated as free fit parameter and has been determined to $A = 0.029 (1)$.

To analyze the observed solution softening behavior of
Concerning this discrepancy, one could argue that the effect of dislocation motion through NC pinning points is better approximated by the grain sizes related to the alloy specimens instead of the slightly larger value of pure NC Pd. But this would even enhance the discrepancy connected with the magnitude of strength without giving rise to softening. Segregation or desegregation of solutes to/from GBs may also be invoked as a source of disagreement. However, as shown in Fig. 2 (a), the lattice parameter of CG as well as NC Pd-Au alloys follow the same Vegard rule implying that pronounced Au-segregation to GBs can be ruled out to cause softening. We are not intending to discard the model of Rupert et al., in fact, we suppose that the assumptions made in this model may properly describe the deformation behavior of NC alloys at grain sizes larger than 20 - 30 nm.

Eventually, we scrutinize the influence of stacking fault energy on the deformation behavior of NC Pd-Au alloys by referring to Asaro’s models. The material parameters shown in Fig. 2 have been used as input parameters to Eqs. 4 and 5. In Fig. 4, we display that neither the emission of partials from preexisting dislocation segments (Eq. 4) nor from stress concentrators located in/at GBs (Eq. 5) are reasonably compatible with the experimental data. When lowering the stacking fault energy, materials become increasingly susceptible to partial dislocation emission, planar slip, fault- and twin formation. Therefore, whenever dislocation activity plays a key role in enabling plasticity, we would expect that with increasing Au-concentration the experimental data and theory should rather merge than diverge.

One could yet argue that the model(s) of Asaro, which predict dislocation activity to be the dominating strain carrier, agree, even though roughly, at least with the data points of pure NC Pd and NC Pd$_{87}$Au$_{13}$. However, this reasoning is in conflict with recent detailed studies of dislocation activity in NC Pd$_{90}$Au$_{10}^{20,30}$. Even at high applied strains $\sim$ 1, partial- and full dislocation glide has been shown to only marginally contribute to overall strain. Therefore, it is implied that the rough agreement between theory and experiment is merely an accidental coincidence at low Au-concentration.

From a different perspective, Jin et al. argued, based on a universal scaling law for planar fault energy barriers, that $\Lambda$, with $0 < \Lambda = \gamma_{\text{usf}}/\gamma_{\text{int}} < 1$ (see inset Fig. 3), defines a characteristic material measure which is correlated with the tendencies to emit partial-, perfect dislocations and/or twins. The relatively large value of $\Lambda \approx 0.7$ of NC Pd$_{87}$Au$_{13}$ (Fig. 3) indicates that emission of partials is favored over twin nucleation. When $\Lambda > 0.8$, it is suggested that twinning can be basically discarded as competitive deformation mode operating along with dislocation mediated slip. But again, these ideas are in conflict with experiment. Swygenhoven et al. pointed out that the variation of $\Lambda$ with displacement has to be an integral part of any molecular dynamics (MD) simulation aiming at understanding intragranular slip in NC metals. Moreover, she argued that the high-stress/short-time restrictions inherent to MD simulations (at their present stage of development) make it impossible to determine the true rate-limiting processes of inelastic deformation.

This seems to be still a problem since Schäfer et al. found in a more recent MD simulation, focusing on the strength of NC Pd-Au alloys, pronounced solid solution hardening, irrespective of the investigated grain sizes (5, 10, 15 nm). Needless to say that deformation mechanism maps based on atomistic simulations are there-

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**FIG. 2.** (Color online) The following parameters are plotted as function of global Au-concentration: (a) Mean grain size $D_{\text{mg}}$ (black triangles) of NC Pd-Au and lattice parameter $a$ of both NC Pd-Au (black dots) and coarse-grained samples (blue circles). Dashed line connects $a_{\text{Pd}}$ and $a_{\text{Au}} = 407.9 \text{pm}^{11}$ according to Vegard’s rule. (b) Shear modulus $G$ of coarse grained (open blue squares) and NC Pd-Au (black squares). Dashed lines are linear fits to the data points. (c) Poisson’s ratio $\nu$ of CG (open blue circles) and NC samples (black dots).
fore rather misleading than useful. It remains to be summarized that either these models are imperfect or the invoked presuppositions are not met by the NC Pd-Au alloys.

In fact, the latter argument seems to be valid because detailed studies of thermal activation parameters in NC Pd$_{90}$Au$_{10}$ in conjunction with the above mentioned investigations of dislocation activity$^{20,30}$ have unraveled that dislocation scarcity makes room for GB-mediated deformation in NC metals$^{20}$. In particular, shear shuffling or STs have been identified as the major carrier of strain. In other words, in the limit of small grain sizes ($D \lesssim 10$ nm), it appears that NC metals mimic glassy behavior. In order to independently verify this idea, we are going to compare the mechanical behavior of NC Pd-Au alloys with the deformation behavior of bulk metallic glasses (BMG).

Johnson and Samwer$^{44}$ noted that the shear yield stresses $\tau_y$ of metallic glasses at room temperature exhibit universal behavior. Based on compressive yield stress $\sigma_y$ data and using $\tau_y = \sigma_y/2$, they extracted the linear correlation $\tau_y/G = 0.00267 \pm 0.002$ from mechanical testing of more than 30 different metallic glasses. Mechanistically, the elastic-to-plastic transition involves a percolation of STs in space and further deformation increments generate new STs.

A second aspect of universal behavior relates to the temperature dependence of shear yield stress. Based on a cooperative shear model, they predicted and experimentally verified that temperature dependencies of the shear yield stresses of a large number of metallic glasses fit the universal scaling law $\tau_y = \tilde{\tau} - \tau(\dot{\gamma}, T) \cdot (T/T_g)^{2/3}$ for temperatures $T \lesssim T_g$, where $T_g$ is the glass transition temperature. The athermal threshold stress $\tilde{\tau}$ represents the maximum level of shear resistance as $T \to 0$ K. The term $\tau(\dot{\gamma}, T)$, where $\dot{\gamma}$ is the prescribed strain rate, has been estimated to be very weakly temperature dependent and for typical strain rates of $10^{-2} - 10^{-4}$ s$^{-1}$ can be approximated as constant $\tau(\dot{\gamma}, T) = 0.016 \pm 0.002 G$.

A third aspect of universality of this data set has been identified by Argon$^{45}$. Introducing an appropriate normalization of the $(T/T_g)^{2/3}$ scaling relation, he demonstrated that the athermal threshold stress $\tilde{\tau} = 0.035 G$ also manifests universal character. Moreover, he pointed out that all metallic glasses that can be idealized as hard-sphere structures, regardless of their packing in various forms of short-to-medium-range order, have a rather universal plastic response in their yield behavior.

The available material parameters for the Pd-Au alloys enable to plot shear yield stress versus room-temperature shear modulus to reveal whether agreement or conflict prevails related to the universal behavior $\tau_y \approx 0.0267 G$ seen in BMGs. For comparison, we display the shear stress at yielding versus room temperature shear modulus data of a variety of metallic glasses taken from Johnson et al.$^{44}$ together with our data from CG and NC Pd-Au alloys in Fig. 5. We note that the data points of the CG specimens are certainly not related in any aspect to the metallic glasses. As shown above, the increase of shear yield stress with increasing Au-concentration agrees with Fleischer’s model and is therefore related to classical dislocation deformation physics. Metallic glasses with missing long-range order cannot sustain the formation of dislocations or other soliton-like defects. By contrast, the data points of the nanoscale microstructures ($D \approx 10$ nm) approach although not agree with the universal behavior of BMGs. A rationale that may explain this remaining discrepancy is the following.

We have recently shown$^{40}$ that the shear modulus of GBs in NC metals is reduced due to atomic site disorder by about 30% compared to the respective bulk value. It seems therefore plausible to assume that the activation of STs takes essentially place in the core region of GBs. When the shear resistance of GBs as a consequence controls the onset of yielding, it thus naturally follows that the measured shear yield stress should correlate with the shear modulus $G_{gb}$ of GBs. Based on the ray approach of ultrasound propagation and assuming that time-of-flights through crystallites and GBs are additive, we can write for the ultrasound velocity $v_{gb}$ in GBs$^{40}$

$$v_{gb} = \frac{\beta v_{nc} v_s}{(\beta - 1) v_{nc} + v_s}$$

where $v_s$ is the sound velocity in the related CG material and $v_{nc}$ is the overall ultrasound velocity in NC specimens. The parameter $\beta$ defines the length share of GBs which is proportional to $\delta/D$, where $\delta$ is the GB thickness of $\approx 1$ nm. By exciting transversal sound waves, measuring $v_s$ and $v_{nc}$ and solving for $v_{gb}$ according to Eq. 9, it is straightforward to determine $G_{gb} = \rho_{gb} v_{gb}^2$, where $\rho_{gb}$ is the GB-density. Using a rule of mixture approach, we
derive \( \rho_{nc} = (1 - \alpha)\rho_x + \alpha\rho_{gb} \), where \( \rho_{nc} \) represents the measured densities of the NC Pd-Au alloys, and \( \rho_x \) is set to the known bulk densities, respectively. The parameter \( \alpha \) represents the volume fraction of GBs and is obtained from stereology\(^{31} \). For more details, we refer to Grewer et al.\(^{40} \).

Alluding to the rationale given above, it is recommended that we correlate shear yield stresses with \( G_{gb} \) instead of \( G_{nc} \). As shown in Fig. 5, the renormalization of \( \tau_y \) with \( G_{gb} \) shifts the data points now right onto the straight line manifesting the universal behavior of BMGs. This evidence not only suggests that STs are dominant carriers of plastic strain in NC Pd-Au alloys but also implies that strain propagation dominantly takes place at/along GBs. Nevertheless, to make deformation happen in a compatible manner, other deformation mechanisms that support strain accommodation and dissipate local stress concentrations should coexist. Not least to avoid catastrophic failure appearing in the early stage of plastic material response. Likewise, using molecular dynamics simulations, Rupert\(^{46} \) found that the yield strength for a broad variety of Cu-based NC alloys with \( D = 5 \text{ nm} \) was linearly related to the Young’s modulus of those samples in agreement with experimental work on metallic glasses by Takeuchi et al.\(^ {47} \). Rupert pointed out that this behavior of NC metals manifests collective GB deformation physics reminiscent of amorphous metal deformation physics.

The conclusions given above are in line with a detailed analysis of the microstructural evolution of NC Pd\(_{90}\)Au\(_{10}\) during in situ deformation and high-energy X-ray microbeam diffraction\(^{20} \). The central evidence suggests that strain propagation in the so-called microplastic regime is solely due to linear elasticity and STs. The latter carry about 70% of the overall strain at the onset of yielding. Beyond yielding, dislocation activity and stress driven GB migration accompany STs but their respective share is on the order of 10% only, just as the share of linear elasticity. Moreover, by investigating the stress-dependence of the free energy of activation, \( \Delta G(\tau) \), related to inelastic deformation of NC Pd\(_{90}\)Au\(_{10}\) alloys, Grewer et al.\(^{20} \) found that the barrier height \( \Delta G \) exhibits universal scaling behavior \( \Delta G \propto \Delta \tau^{3/2} \), where \( \Delta \tau \) is a residual load\(^{48,49} \). They have also shown that this scaling behavior leads to a generalization of the universal \( T^{2/3} \) temperature dependence of plastic yielding in metallic glasses. From the functional form of \( \Delta G = \Delta G(\tau) \), the athermal threshold stress \( \tilde{\tau} = \tau(\Delta G = 0) = 1.2 \text{ GPa} \), representing the maximal shear resistance as \( T \to 0 \text{ K} \), has also been determined\(^{19} \). The ratio \( \tilde{\tau}/G_{nc} = 0.033 \) compares favorably with Argon’s universal relation \( \tilde{\tau} \cong 0.035 \ G \). When \( T \to 0 \text{ K} \), we expect the thermally activated GB-mediated deformation modes to become frozen out. Therefore, we use the shear modulus \( G_{nc} \) to normalize \( \tilde{\tau} \) of NC Pd\(_{90}\)Au\(_{10}\). Overall, it emerges that the yield (inelastic flow) behavior of NC Pd\(_{90}\)Au\(_{10}\) alloys in the limit of small grain sizes agrees remarkably well with the three distinct aspects of the universal yield behavior of BMGs. It remains to be verified that this is true for the whole composition range.

V. CONCLUSIONS

Studying solid solution effects on the strength of NC Pd-Au alloys, we present compelling evidence that the deformation physics of NC metals at the low end of the nanoscale (\( D \lesssim 10 \text{ nm} \)) is reminiscent of the deformation behavior of metallic glasses. In particular, it could be verified that the universal yield behavior of metallic glasses, i.e., the strictly linear relationship between shear yield stress and shear modulus, is also obeyed for NC Pd\(_{100-x}\)Au\(_x\) alloys (\( 0 \leq x < 50 \text{ at. \%} \)).

The general notion that twin- and stacking fault formation probabilities increase with decreasing ratio of intrinsic to unstable stacking fault energy, which is decreasing from 0.66 for pure Pd to 0.37 in case of pure Au, is con-
FIG. 5. (Color online) Shear strength as a function of room temperature shear modulus. Open blue circles: coarse grained Pd-Au, black squares: nanocrystalline Pd-Au normalized to the shear modulus of the nanocrystalline specimens, green stars: nanocrystalline Pd-Au related to the effective shear modulus of grain boundaries, gray diamonds: more than 30 different bulk metallic glasses from ref. 44.

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ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Deutsche Forschungsgemeinschaft (FOR714 and 385/18-1) and fruitful discussions with T.J. Rupert on solid solution strengthening in nanocrystalline materials.
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