Graphical Abstract

Breakdown of Varvenne scaling in $(AuNiPdPt)_{1-x}Cu_x$ high-entropy alloys

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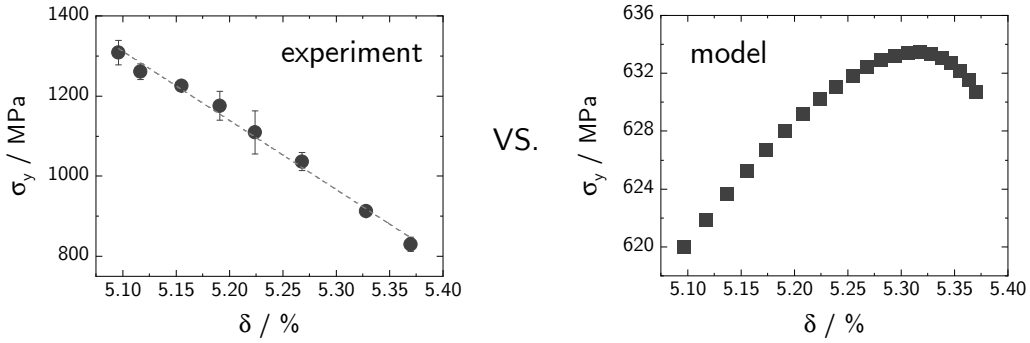

Highlights

Breakdown of Varvenne scaling in $(AuNiPdPt)_{1-x}Cu_x$ high-entropy alloys

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- $(AuNiPdPt)_{1-x}Cu_x$ forms a homogeneous solid solution with deliberately adjusted Cu concentration making it an ideal candidate to investigate concentration-dependent solid solution strengthening in concentrated solid solutions.
- The yield strength of $(AuNiPdPt)_{1-x}Cu_x$ decreases linearly with x, while the opposite trend and non-linear scaling is expected from theory.
- The absolute values as well as the range across the Cu concentration of the experimental yield strength is higher and much more pronounced when compared to the theoretical prediction.

Breakdown of Varvenne scaling in $(AuNiPdPt)_{1-x}Cu_x$ high-entropy alloys

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Abstract

The compositional dependence of the yield strength σ_y has been studied for a series of polycrystalline $(AuNiPdPt)_{1-x}Cu_x$ alloys by means of compression tests. σ_y is found to decrease linearly with increasing Cu concentration. This behaviour is in contradiction to the generalised theory for solid solution strengthening in concentrated solid solutions provided by Varvenne et al. [1]. A breakdown of the scaling behaviour is found as σ_y should be non-linear and slightly increasing when modifying the composition from AuNiPdPt to AuCuNiPdPt.

Keywords: high-entropy alloys, noble metals, mechanical properties, solution strengthening, yield stress predictions

In the past decade, a new class of materials possessing advanced properties has attracted much interest in the field of physical metallurgy. These materials are the result of an alternative design strategy; while conventional

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alloy design is based on one main element, there is no main element in multicomponent alloys which are called high-entropy alloys (HEA). The class of HEA has stimulated research since its discovery back in 2004 [2, 3]. Besides superior properties that are addressed with the HEAs in particular, the phenomenon of solid solution strengthening is still under investigation [4, 5]. Nowadays and in what follows here, only those multi-component alloys which are single-phase are called HEAs [6].

Up to now, there is no wholistic model to assess the effect of solid solution strengthening in HEAs. The development of such a model is challenging, since it would need to consider contributions to the strength arising from (i) lattice distortions, (ii) variations of the shear modulus as well as (iii) variations of the stacking fault energy. However, the latter has been proven to have only minor influence on the strength [7, 8]. So far, the most comprehensive model applied for the assessment of the solid solution strengthening in HEAs is that one derived by Varvenne et al. [1, 9]. This model represents an extension of the Labusch-type weak-pinning model [7, 1]. It clearly identifies which material parameters play the major role for strengthening, i.e. (i) the strength does not directly depend on the number of elements in the alloy, (ii) the shear modulus or the concentration-weighted mean-square misfit volume quantity are the key parameters for the determination of the strength. Although being widely applied, this model bears significant drawbacks. The theory assumes a random distribution of the components on the lattice site, which is presumably not the case. Local chemical environments as e.g. segregations, structural disorder and short-range order represent additional contributions to the strength of HEAs which are not addressed in

the model, as recently stressed in [10].

AuCuNiPdPt represents a HEA, that was designed upon a combination of elements whose binary phase diagrams show solubility within the entire concentration range [11, 12]. Besides the quinary alloy, any quaternary combination of Au, Cu, Ni, Pd and Pt has been proven to form a homogeneous solid solution [11]. As a consequence, this system represents an ideal candidate to investigate composition-dependent solid solution strengthening in concentrated solid solutions.

In the present article, the scaling behaviour of the yield strength σ_y and the microhardness have been investigated for a series of $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$ high-entropy alloys. Moreover, the yield strengths of this series of alloys were calculated according to Refs. [1, 9] and compared to the experimental results. The mentioned series has been chosen in accordance to the model of solid solution strengthening with respect to the corresponding increase of the strength originating from the parelastic interaction.

Polycrystalline samples of $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$(x $= 0, 1, 3, 5, 7, 10, 15, 20$ at.%) were prepared from pure elements by arc melting. For this purpose, x Cu was added in stoichiometry to a previously prepared master alloy with the nominal composition AuNiPdPt. For improving the sample homogeneity, the samples were turned-over and re-melted four times prior to suction casting into a water-cooled copper mould with 4 mm in diameter and 75 mm in length. The as-cast alloys were homogenised at 1100 °C to 1200 °C depending on the composition for 20 h with subsequent water-quenching. The proper homogenisation temperature T_h of any individual alloy has been determined previously by differential scanning calorimetry and set to be at least

$T_\mathrm{h} \simeq 0.9\, T_\mathrm{m}$, with T_m being the melting temperature of the alloy. Annealing was performed in sealed fused silica ampoules under protective Ar atmosphere. The homogenised samples were cold worked by rotary swaging at room temperature up to a deformation strain of $\varphi = 0.6$ and afterwards heat treated at the same temperatures mentioned above for 1 h in order to obtain a fully recrystallised microstructure. Phase purity has been investigated by means of X-ray diffraction (XRD) in Debye-Scherrer geometry on samples with a thickness of $\leq 30\ \mu$m utilising a STOE STADI P diffractometer with $\mathrm{MoK}_{\alpha 1}$ radiation.

For microstructural analysis and microhardness tests, the samples were prepared by a conventional metallographic procedure as described in Ref. [12]. Microstructural characterisation was carried out by scanning electron microscopy (SEM) using a FEI Helios 600i operating at 10 kV and 1.4 nA. Microhardness measurements were performed with a Shimadzu HMV-2 hardness tester operating at a load of 1.98 N. Mechanical tests were performed in compression utilising an electro-mechanical Instron 8562 testing machine on samples with an initial diameter d_0 of 3 mm and a height h_0 of $\lesssim$ 6mm. Tests were stopped when the aspect ratio approached $\mathrm{h_0/d_0} = 1$. An initial engineering strain rate of $\dot{\varepsilon} = 1 \cdot 10^{-3}\ \mathrm{s}^{-1}$ was applied.

Calculation of the yield strength as a result of solid solution strengthening has been performed according to the Varvenne model [1, 9] assuming that it can be described by an effective average matrix ("solvent") with all atoms being embedded "solute" atoms. Here, the average matrix represents the mean properties of the HEA, while the embedded solutes account for the local chemical fluctuations [1, 13, 14]. The model has been simplified considering

only for elastic contributions, i.e. Eqs. 1-3 are used to evaluate the critical shear stress for dislocation slip τ_{y} as function of temperature T and strain rate $\dot{\varepsilon}$:

$$\tau_{\mathrm{y}}\left(T,\dot{\varepsilon}\right)=\tau_{\mathrm{y0}}\left[1-\left(\frac{k_{\mathrm{B}}T}{\Delta E_{\mathrm{b}}}\ln\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}}\right)^{\frac{2}{3}}\right],\text{with} \tag{1}$$

$$\tau_{\mathrm{y0}}=0.01785\alpha^{-\frac{1}{3}}\bar{G}\left(\frac{1+\bar{\nu}}{1-\bar{\nu}}\right)^{\frac{4}{3}}\left[\frac{\sum_n c_n\Delta V_n^2}{b^6}\right]^{\frac{2}{3}},\text{and} \tag{2}$$

$$\Delta E_{\mathrm{b}}=1.56318\alpha^{\frac{1}{3}}\bar{G}b^3\left(\frac{1+\bar{\nu}}{1-\bar{\nu}}\right)^{\frac{2}{3}}\left[\frac{\sum_n c_n\Delta V_n^2}{b^6}\right]^{\frac{1}{3}}, \tag{3}$$

with $\bar{G}$: average shear modulus of the matrix as calculated upon the linear rule of mixture, $\bar{\nu}$: Poisson's ratio, c_n: concentration of the alloying element n, $\Delta V_n = V_n - \bar{V}$: misfit volume, b: length of the Burgers vector, k_{B}: Boltzmann constant. The input data is provided in Tab. 1 and the following parameters have been used: $\alpha = 0.123$, $\dot{\varepsilon} = 10^{-3}\mathrm{s}^{-1}$, $\dot{\varepsilon}_0 = 10^4\mathrm{s}^{-1}$ in accordance with Ref. [1]. $\sum_n c_n\Delta V_n^2$ is the key misfit parameter. In the present case all elements crystallise in the same crystal structure, a homogeneous solid solution is observed and Vegard's law can be applied. Therefore, in accordance to Ref. [15] this misfit parameter can be related to:

$$\delta=\sqrt{2\sum_n c_n\Delta V_n^2/9b^6}. \tag{4}$$

δ can also be obtained from the misfit of the lattice parameters, which would yield approximately the same result. However, this consideration [1, 15] was made for alloys where the corresponding elements have similar lattice parameters, which is not the case for the Au-Cu-Ni-Pd-Pt system. Hence, the two δ values are different but qualitatively yield the same results for the present alloy and the misfit parameter calculated on the basis of the volume

(c.f. Eq. 4) is used for the following discussion. Using a Taylor factor of 3.06, τ_{y} provides the yield strength $\sigma_{\mathrm{y}}^{\mathrm{theo}}$.

All recrystallised $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$ alloys are single-phase and crystallise in a face-centered cubic structure (fcc, Cu-type). The corresponding XRD patterns show no evidence of secondary phases as can be seen exemplarily for the $(\mathrm{AuNiPdPt})_{97}\mathrm{Cu}_3$ alloy in Fig. 1. This figure also depicts the microstructure of the recrystallised alloys utilising SEM with backscattered electron (BSE) imaging. The images reveal no indications of secondary phases and an average grain size of 40 µm to 60 µm.

Rietveld refinements of the XRD patterns were utilised to determine the lattice parameter a of the $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$ alloys. As can be seen from Fig. 2, the lattice parameter scales linearly with the Cu content. This behaviour is not unexpected, since the applicability of Vegard's law has already been observed for the lattice parameter of the four- and five-component equimolar alloys within the Au-Cu-Ni-Pd-Pt-system [11]. This linear dependency of the lattice parameter is a direct evidence for preserving the single-phase fcc crystal structure throughout the entire compositional range. Additionally, the scaling of the misfit parameter δ upon the composition is shown in Fig. 2, which obviously is non-linear. It should be noted, that this also holds for the dependency between δ and a. The lattice parameter of AuNiPdPt ($a = 0.3875$ nm) is slightly higher than the value obtained from the rule of mixture of the constituent elements [11, 15]. These small differences do not change the predictions enough to account for the experimental results.

Fig. 3 shows the interrelation of hardness and yield strength with the

composition of the $(AuNiPdPt)_{1-x}Cu_x$ alloys. Both measures are not related to each other. Nevertheless, the hardness is typically related to the flow stress at a true plastic strain of 0.07 by a factor of ~ 3[16]. The corresponding flow stresses are also shown in Fig. 3, while selected true stress-strain curves are provided in the supplementary. Summarising, the depicted values show the same trend, i.e. a decrease with increasing Cu content. In particular, the strength of this series apparently scales linearly with the concentration. Furthermore, this linear scaling is also seen in dependence of the lattice parameter (not shown here). The yield strength of AuNiPdPt amounts to 1308 MPa. This value is perplexingly high for a homogeneous solid solution and would not have been expected when considering standard noble metal based alloys as e.g. typically applied in jewellery.

Amongst the possible strengthening mechanisms in single-phase alloys, the main contribution in this alloy series stems from solid solution strengthening ($\Delta\tau_{c,ss}$). This is because all samples are tested in a comparably coarse-grained recrystallised state with low dislocation density. Therefore, Hall-Petch-type strengthening ($\Delta\tau_{c,HP}$) as well as strain hardening ($\Delta\tau_{c,\rho}$) contribute with a constant but low value to the total strength. In particular, the contribution of grain boundary strengthening in AuCuNiPdPt amounts to $\Delta\tau_{c,HP} = 23-33$ MPa for grain sizes ranging from 40 to 60 μm [12]. With the plausible assumption that the Hall-Petch coefficient and the dislocation density are similar for all alloys, the corresponding strengthening mechanism do not affect the scaling behaviour significantly. In addition, no evidence of long-range ordering was observed from transmission electron microscopy utilising selected area electron diffraction for numerous zone axes (cf. supple-

mentary). Nevertheless, short-range ordering cannot be excluded from the present experimental results.

Although, the yield strength is not supposed to show a linear scaling with the misfit parameter, as shown in Fig. 4, the experimentally observed behaviour cannot be explained exclusively by the misfit parameter as commonly seen for high-entropy alloys [17, 18, 19].

In particular, Varvenne et al. used their model in a reduced form, that accounts only for elastic contributions to predict the yield strength of (noble) high-entropy alloys, while the chemical contribution and solute/stacking fault interaction energy is not considered [15]. The theory is valid if the dislocation dissociation width $d > 6.5b$, and this depends on elastic constants and stacking fault energy. This prerequisite might be violated in the Cu-lean alloys due to the rather high stacking fault energies of the remaining elements. A serious problem to experimentally prove these predictions lies within the efforts to be done to obtain single-phase solid solutions from most of these systems. Especially, those high-entropy alloys containing Ag turn out to be difficult or even impossible to obtain single-phase. Other systems possess miscibility gaps that might also be hard to overcome.

The most obvious contradiction between the experimental behaviour of the yield strength and the corresponding calculations is the trend of the data. While the yield strength is found to decrease with increasing Cu content (and even with increasing misfit parameter) a non-linear increase of σ_y would be expected from the model. Furthermore, it should be emphasised that the absolute values as well as the spread across the Cu concentration of the experimental yield strength are higher when compared to the theoretical

prediction with the exception of the AuCuNiPdPt alloy. It should be noted, that the experimental values contain the friction stress ($\tau_0 \approx 39$ MPa) and the contributions to the strength arising from grain boundaries ($\Delta\tau_{c,HP} \approx 23$ MPa) [12]. Considering the Taylor factor and the calculated $\Delta\tau_{c,ss}$ of the AuCuNiPdPt alloy, the critical shear stress of $\tau_y = 268$ MPa (equivalent to a yield strength of $\sigma_y = 820$ MPa) is well reproduced, i.e. $\tau_y = \tau_0 + \Delta\tau_{c,HP} + \Delta\tau_{c,ss}$.

The calculations based on the proposed model for solid solution strengthening [1, 15] yield a maximum difference of only 14 MPa in strength for all investigated alloys. Taking typical standard deviations for proof stresses into account, the verification of this change is demanding and the change itself can be considered negligible. In contrast, the mechanical tests performed reveal a maximum yield strength of 1308 MPa in the case of AuNiPdPt and an almost linear decrease of about 500 MPa towards AuNiCuPdPt. As the breakdown of the scaling behaviour is obvious, the model might not be applicable with the commonly applied simplifications being made. Furthermore, the experimentally observed reduction in σ_y across the series of $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$ is large when compared to a slight variation of the calculated σ_y.

Recent experimental data on the room temperature hardness and yield strength of single-phase, fcc $(\mathrm{AuNiPdPt})_{1-x}\mathrm{Cu}_x$ alloys were evaluated against the model for solid solution strengthening in fcc high-entropy alloys [1, 9]. There is an obvious discrepancy between the experimental data and the model as the strength decreases with increasing Cu content, while the model predicts a slight increase. The observed difference cannot be rationalised in terms of both absolute strength values and trend of strength with increasing

Cu content. While long range order could not be observed utilising TEM (cf. supplementary), we cannot rule out short range order at present. It seems, however, not likely because such an increase in strength can be observed for some noble metals being optimised in strength by long range order [20] but the strength increase of short range oder is expected to be lower. Otherwise, the model assumes that the shear modulus of the alloys can be calculated upon the rule of mixture, which might not be true. Further investigations are required to resolve these open questions. For now, it is questionable whether the model that assumes a random matrix and additional solutes involving solely an averaged shear modulus is capable of accurately describing solid solution strengthening in the present case. The evaluation of further high-entropy alloy series and the stacking fault energy variation within the present system are required to address this open question.

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Table 1: Input data of the properties for the pure elements contained in the HEA taken from the "Springer Handbook of Materials Data". a_0 is the fcc lattice constant, E the Young's modulus, and G the shear modulus.

Element	a_0/Å	G/GPa	E/GPa
Au	4.0784	26	78
Cu	3.6149	46.8	128.8
Ni	3.5241	78.5	220
Pd	3.8901	43.5	121
Pt	3.9233	60.9	170

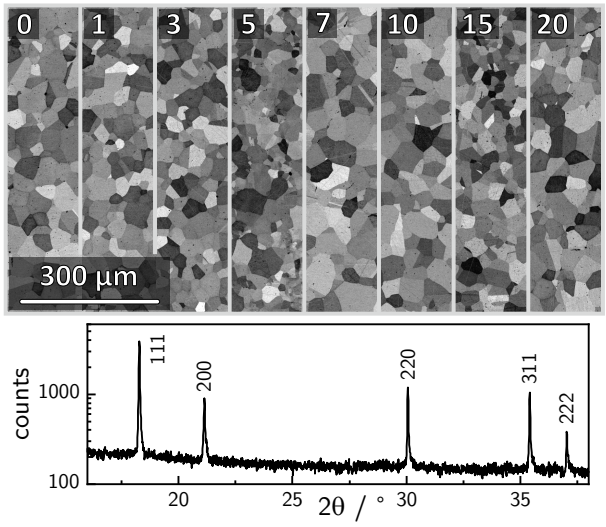

Figure 1: Microstructure of $(AuNiPdPt)_{1-x}Cu_x$ alloys in the recrystallised state. The scaling bar accounts for all micrographs and the depicted number accounts for the Cu content. The lower part of the image shows the XRD pattern for $x = 3$ as a representative example of this series.

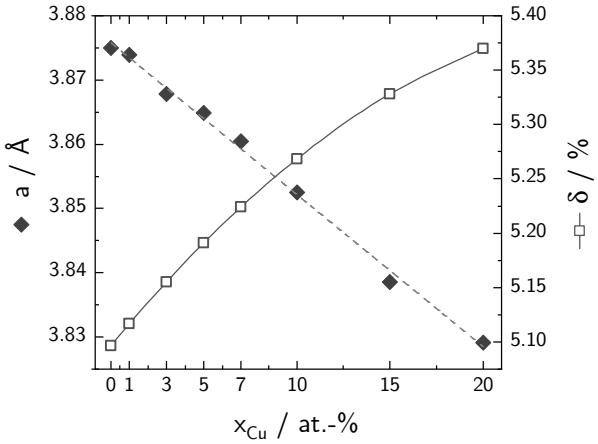

Figure 2: Lattice parameter of $(AuNiPdPt)_{1-x}Cu_x$ alloys (closed symbols, linear trend) as well as misfit parameter δ (open symbols, non-linear trend) in dependence of the Cu content. The lines are guides to the eye, only.

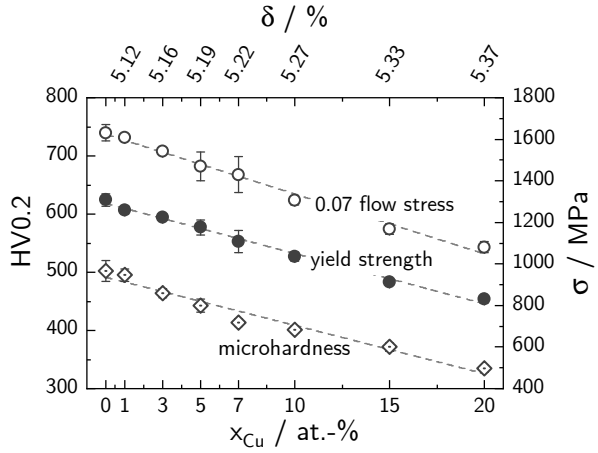

Figure 3: Vickers microhardness (◇), yield strength (●) and flow stress at 0.07 plastic strain (○) of $(AuNiPdPt)_{1-x}Cu_x$ alloys in dependence of the Cu content. The upper labels refer to the misfit parameter δ for the depicted composition. The dashed lines represent linear fits to the data.

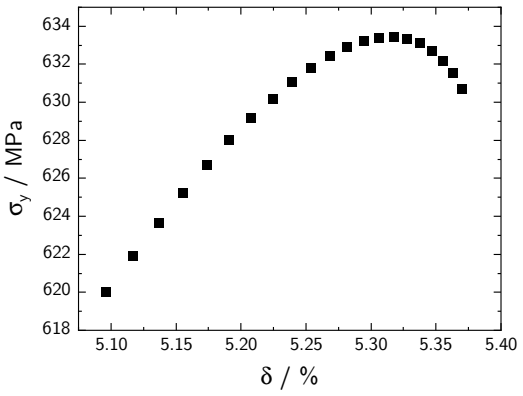

Figure 4: Calculated yield strength as a function of the misfit parameter in accordance to the Varvenne model [1].