Phase transitions in Cu-based alloys under high pressure torsion

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Severe plastic deformation not only leads to grain refinement but also accelerates mass-transfer and drives phase transformations in these Cu-based alloys. This review is devoted to the dynamic equilibrium between decomposition of (supersaturated) solid solution and dissolution of precipitates during high pressure torsion (HPT) of diluted Cu-based Cu–X alloys. The precipitation of second phase particles from a solid solution and their dissolution take place simultaneously and compete with each other. During HPT, a certain steady-state concentration \( C_m \) of a second component in a solid solution is reached, as if a sample would be annealed at a certain effective temperature \( T_{eff} \). We found that \( T_{eff} \) linearly increases with increase of activation enthalpy of bulk tracer diffusion \( H_D \). The correlation between activation enthalpy of bulk tracer diffusion \( H_D \) and melting temperature \( T_m \) of diffusing alloying component has been found for the first time. As a result, \( T_{eff} \) linearly increases with increase of melting temperature \( T_m \) of diffusing alloying component as well. The observed correlations allow one for the first time to predict the behaviour and phase transitions in the Cu-based alloys under high pressure torsion.

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1. Introduction

Severe plastic deformation (SPD) is a family of novel methods permitting metallurgists and engineers tailoring the structure and properties of materials [1]. The idea of SPD is to deform the material in a confined space. It allows an increase of the strain up to the enormous values without fracture. Since the material cannot break, the dynamic equilibrium between deformation-driven production of crystal defects and their relaxation (annihilation) is established after a certain strain value is reached. It is not astonishing that such a strong action on the material leads to various phase transformations, and nanocrystallization in the amorphous matrix [24–27].

This review paper is devoted to the decomposition of (supersaturated) solid solution and the dissolution of precipitates during SPD. Recently it has become clear that they are not independent [28]. Moreover, the precipitation of particles of a second phase from a solid solution and their dissolution take place simultaneously and compete with each other. Due to the competition between precipitation and dissolution, a certain steady-state concentration of a second component in a solid solution is reached under SPD.

Quite frequently, this steady-state concentration of a second component in a solid solution after SPD is the same as it would appear in a material after long anneal at a certain (elevated) temperature. This temperature is called effective temperature \( T_{eff} \). It has been demonstrated recently that the concept of effective temperature \( T_{eff} \) originally proposed for the materials under severe irradiation [28] is applicable also for severe plastic deformation (SPD) [29]. If the atomic movements driven by an external action (deformation or irradiation) are higher than those driven by the conventional thermal diffusion, the material is forced into a state which is equivalent to that at a certain increased (effective) temperature \( T_{eff} \). One can estimate \( T_{eff} \) if the phases in a material after SPD treatment differ from those before SPD [30]. For the

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determination of $T_{\text{eff}}$ one can use also the phase diagrams at high pressure, if they are known [21–23]. However, the SPD-treatment at ambient temperature $T_{\text{SPD}}$ usually leads to the very quick phase transformations, which is easy to understand if one considers the high density of defects, similar to that at an increased temperature. The increased pressure, oppositely, leads to a decrease of diffusivity and/or grain boundary mobility [31,32]. Some SPD-driven phase transformations need only a small shift of atoms, for other ones long-range mass transfer is needed. The results of such SPD-driven transitions cannot be explained by the bulk or even grain boundary diffusion at the SPD temperature (which usually remains slightly above ambient one). Nevertheles, during the SPD-driven mass transfer an external action forces the atoms to overcome a certain energy barrier. This energy barrier is similar to that for bulk diffusion. The measure for this barrier is the activation enthalpy of bulk diffusion $H_0$. In this review the $T_{\text{eff}}$ will be determined for various Cu-based alloys. Further, the correlation between $T_{\text{eff}}$ and activation enthalpy of bulk diffusion $H_0$ of an alloying component will be analyzed. It will be shown that $H_0$ correlates with the melting temperature $T_m$ of an alloying component in Cu-based alloys as well. In turn, $T_m$ also correlated with $T_m$. This allows on for the first time to predict $T_{\text{eff}}$ knowing the $T_m$.

2. Determination of effective temperature

External action on the material can cause an accelerated mass transfer and phase transformations. Such accelerated diffusion and unusual phase transitions were first observed under severe irradiation of materials [29]. G. Martin was first who proposed a model to describe solid solutions subjected to irradiation-induced atomic mixing [29]. His main idea was that the forced mixing induced by irradiation corresponds to the increase of entropy. As a result, the mixing was indeed found to be described by a law of corresponding states [29]. His main idea was that the forced mixing induced by irradiation corresponds to the increase of entropy. As a result, the mixing has been formulated: the equilibrium configuration of the solid under irradiation flux $\varphi$ at temperature $T$ is identical to the configuration at $\varphi = 0$ and a certain effective temperature.

$$T_{\text{eff}} = T(1 + \Delta)$$  \hspace{1cm} (1)

One can describe the irradiation-driven movements of atoms by the “ballistic” diffusion coefficient $D_{\text{ball}}$ if they are similar in amplitude to conventional diffusion jumps with conventional bulk diffusion coefficient $D_b$. In this case $\Delta = D_{\text{ball}}/D_b$, $D_b$ can be increased due to the non-equilibrium defect concentration [23]. Thus, Martin proposed to use the equilibrium phase diagram for the description of the system under irradiation. However, the phases under irradiation are identical to those at $T_{\text{eff}}$ instead of the temperature of experiment $T$. For example, the amorphous phase would appear under irradiation, if the liquid phase is present in the phase diagram at $T_{\text{eff}}$ [29,33].

To check the applicability of Martin’s law (1) to the forced diffusion driven by pure shear deformation under high pressure torsion ($D_{\text{HPT}}$) instead of irradiation ($D_{\text{ball}}$), we analyzed the experiments where HPT leads to the phase transitions. We compare the data obtained in similar straining conditions, namely those where (i) HPT was performed at 4–6 GPa with 4–6 torsions and (ii) the phases appeared after HPT are different from those present in the samples before HPT.

For the first time the HPT-driven decomposition of supersaturated solid solution was found in the Al–Zn alloys [6,7,34]. The (Al) solid solution in the as-cast Al–30 wt% Zn alloy contained about 15 wt% Zn. At room temperature (being also the HPT temperature) Zn is almost not soluble in solid Al. Therefore, the (Al) solid solution was strongly supersaturated. The as-cast Al–20 wt% Zn and Al–10 wt% Zn alloys contained, respectively, about 7 and 3 wt% Zn in the supersaturated solid solution. The HPT at room temperature produced nanograin pure Al and pure Zn particles simultaneously leading to unusual softening [6,7,34]. In all three alloys the supersaturated solid solution completely decomposed, and the lattice parameter became indistinguishable from that of pure aluminium. The respective $T_{\text{eff}} = 30{\degree}$C. The decomposition during SPD proceeds extremely quickly, already after about 0.5 rotations of the anvils, the lattice parameter becomes equal to that of Al and microhardness as well as grain sizes reach their stationary values [34].

The homogenized one-phase solid solutions in the Cu–Ni alloys with 42 and 77 wt% Ni decomposed after HPT at room temperature into Cu-rich and Ni-rich phases [8]. The composition of resulting phases permitted an estimation of $T_{\text{eff}} = 200{\degree}$C for the Cu–77 wt% Ni alloy and $T_{\text{eff}} = 270{\degree}$C for the Cu–42 wt% Ni alloy [8]. In case of Co-rich Co–Cu alloys, the as-cast Co–12 wt% Cu alloy contained the supersaturated solid solution with 8 wt% Cu in the Co matrix with fcc $\alpha$-structure [30]. After HPT, together with grain refinement, the full decomposition of supersaturated (Co) solid solution proceeds. In addition, the high-temperature fcc $\alpha$-Co transformed into low-temperaturehcp $\epsilon$-Co. The respective $T_{\text{eff}} = 400{\degree}$C for the Co–Cu system [8].

3. Effective temperature in Cu–Co, Cu–Ag, Cu–In and Cu–Sn alloys

In Cu-rich Co–Cu alloys the situation is even more interesting [28]. The Cu–4.9 wt% Co alloy has been subjected to high pressure torsion in two different states, namely with Co fully dissolved in the Cu-rich matrix (after annealing at 1060 °C for 10 h, Sample 2) and fully precipitated from the Cu matrix (after annealing at 570 °C for 840 h, Sample 1). With an increasing number of rotations, the lattice parameter of Sample 1 decreased and that of Sample 2 increased. After 5 anvil rotations the lattice parameter in both samples becomes almost undistinguishable and corresponds to the solid solution of Co in Cu with 2.5 wt%. In other words, the composition of the solid solution in the Cu–4.9 wt% Co alloy after the given HPT processing does not depend on the initial state prior to HPT. The composition of Cu-rich matrix in both alloys before and after HPT is shown in the Cu–Co phase diagram (Fig. 1). The solid solution in samples 1 and 2 after HPT contains as much Co, as if they would be annealed at $T_{\text{eff}} = 920 \pm 30{\degree}$C and $T_{\text{eff}} = 870 \pm 30{\degree}$C, respectively.

Thus, the steady-state with respect to the grain size, size of precipitates and concentration of Co in a solid solution during HPT is indeed equilibrium i.e. independent on the starting state. This term was introduced by von Bertalanffy in order to underline the analogy between equilibrium for closed systems and equilibrium for open ones [36]. Such an equilibrium has been observed also in similar experiments with Cu–8 wt% Ag alloy [37]. The effective temperature is $T_{\text{eff}} = 780 \pm 1{\degree}$C in this case.

Six Cu–In alloys with 2.3, 4, 5.8, 7, 9.5 and 13.5 at.% In have been studied in Ref. [38]. The Cu–In alloys possess the negative mixing enthalphy. The torsion torque during HPT reached a steady-state after 1–2 anvil rotations. Differently to the alloys with positive mixing enthalphy, the Cu(In) solid solution in the samples 2.3, 4, 5.8, 7, and 9.5 at.% In with did not decompose. However, the precipitates of 6-phase in the Cu–13.5 at. % In alloy partially dissolved and additionally enriched the Cu(In) solid solution. As a result, the concentration of indium in the Cu-matrix becomes at least as high as a sample annealed at $T_{\text{eff}} = 574{\degree}$C.

It has been also revealed that high pressure torsion induces phase transformations of certain Hume-Rothery phases (electron
compounds) to others [39]. High pressure torsion induces the $\zeta \rightarrow \delta + e$ reaction in copper–tin alloys with the appearance of the $\delta + e$ phase mixture as after long term annealing in the temperature range $T_{\text{eff}} = 350-589 \, ^\circ\text{C}$.

Two Cu–Al–Ni shape memory alloys (Cu–13.1 wt% Al–3.8 wt% Ni and Cu–14.4 wt% Al–4.3 wt% Ni) were studied in Ref. [40]. The as-cast alloys were annealed in the one-phase $\beta$-area of the Cu–Al–Ni phase diagram (so-called austenite area) and water quenched. As a result, one alloy was in martensitic state (mainly $\beta_2$ with a small amount of $\gamma'\gamma_3$ phase), and a second one was austenitic ($\beta_3$ phase). After HPT, both alloys became ultra-fine grained and contained mainly $\beta_2$ martensite with a certain amount of $\gamma'\gamma_3$ martensite. This is because HPT drives the precipitation of $\gamma_1$ phase in Al-poor alloy and the precipitation of $\gamma_1$-phase in the Al-rich alloy. This precipitation was followed by the characteristic martensitic transformation. We will not focus here on the details of martensitic transformations in these shape memory alloys. For this review it is important that the HPT-driven precipitation in both Cu–Al–Ni alloys is such as if they were annealed at $T_{\text{eff}} = 620 \pm 20 \, ^\circ\text{C}$.

4. Effective temperature in Cu–Hf and Cu–Cr alloys

The Cu–0.7 wt% Cr and Cu–0.9 wt% Hf alloys have been prepared from high-purity 5 N Cu, Hf and Cr by vacuum induction melting into cylindrical ingots. For HPT processing, the 0.6 mm thick discs were cut from the as-cast ingots, then ground and chemically etched. They were sealed into evacuated silica ampoules and melting into cylindrical ingots. For HPT processing, the 0.6 mm thick discs were cut from the as-cast ingots, then ground and chemically etched. They were sealed into evacuated silica ampoules and then quenched in water. The accuracy of the annealing temperature was $\pm 1 \, ^\circ\text{C}$. The annealed samples were subjected to HPT at room temperature under a pressure of 5 GPa in a Bridgman anvil-type unit (5 rotations of the anvil with the rate of 1 rpm). Samples for microstructural and X-rays investigations were cut from the HPT-processed discs at a distance of 3 mm from the sample center. The transmission electron microscopy (TEM) was performed by Tecnai G2 FEG super TWIN (200 kV) microscope equipped with an energy dispersive X-ray (EDX) spectrometer manufactured by EDAX. TEM foils were prepared by the focused ion beam (FIB) technique. Scanning electron microscopy (SEM) investigations were carried out on a Philips XL30 scanning microscope equipped with a LINK ISIS energy-dispersive X-ray spectrometer from Oxford Instruments. X-ray diffraction (XRD) data were obtained on a Pan Analytical X’Pert (Philips) diffractometer (Cu Kz radiation). Lattice parameter values were estimated using powder diffraction tool of “Fityk” software [41].

The as cast Cu–0.7 wt% Cr alloy contained elongated primary grains of Cu-based solid solution (with size about 50 × 200 µm) and fine lamellar Cu/Cr eutectic in the (Cu)/(Cu) grain boundaries (GBs). After a long anneal at 1000 °C for 384 h, the Cu–0.7 wt% Cr alloy contained large grains of Cu-based solid solution (with grain size of 100–200 µm) and few equiaxial large Cr particles with size about 3–10 µm. Cu grains also contain a lot of very fine Cr precipitates with size of 5–10 nm. The Cu–0.9 wt% Hf alloy after anneal at 550 °C for 2300 h has large equiaxial grains of (Cu) solid solution with size of about 400 µm and numerous Cu6Hf particles. The Cu6Hf particles in the bulk are almost equiaxial with size of 1–5 µm and not faceted. The Cu6Hf particles in (Cu)/(Cu) grain boundaries are elongated and sometimes form the continuous layers with thickness of 1–3 µm. This indicates complete wetting of (Cu)/(Cu) GBs by Cu6Hf that is similar to Cu6Al2Al3. The Cu6Hf precipitates are almost equiaxial with size of 1–5 µm and not faceted. The Cu6Hf particles in (Cu)/(Cu) grain boundaries are elongated and sometimes form the continuous layers with thickness of 1–3 µm. This indicates complete wetting of (Cu)/(Cu) GBs by Cu6Hf that is similar to Cu6Al2Al3. The Cu6Hf precipitates are almost equiaxial with size of 1–5 µm and not faceted. The Cu6Hf particles in (Cu)/(Cu) grain boundaries are elongated and sometimes form the continuous layers with thickness of 1–3 µm.
after annealing at 1000 °C for 384 h and 0.36172 nm after annealing at 1040 °C for 478 h. After HPT the lattice parameter of first sample increases up to 0.36172 nm and becomes equal to that of the sample annealed at 1040 °C for 478 h, and then quenched in water. Open squares mark the lattice parameter of the same samples after additional HPT. (b) Cu-rich side of Cu−Hf phase diagram [35]. Full squares show the composition of (Cu) solid solutions after annealing at 500, 550 and 1000 °C. Open squares show the composition of (Cu) solid solutions after HPT. $T_{\text{eff}} = 970 \pm 40$ °C.

0.36164 nm after annealing at 1000 °C for 384 h and 0.36172 nm after annealing at 1040 °C for 478 h. After HPT the lattice parameter of first sample increases up to 0.36172 nm and becomes equal to that of the sample annealed at 1040 °C for 478 h. It means that the fine (Cr) precipitates present in the sample after annealing at 1000 °C completely diluted in (Cu) solid solution [47]. The effective temperature for Cu−Cr alloys, therefore, can be estimated as $T_{\text{eff}} = 1040 \pm 20$ °C.

5. Correlation between $T_{\text{eff}}$, activation enthalpy of diffusion and melting temperature

In Ref. [37] a model was developed to describe the competition between dissolution and precipitation during HPT in Cu−Ag alloys. This model describes the dynamic equilibrium between dissolution and precipitation in HPT. It assumes that HPT fixes the composition at matrix-precipitate interfaces. The model shows that HPT-enhanced diffusive mass-transfer is the process controlling the observed steady-state composition in the matrix and precipitate average diameter. Using only the value of bulk diffusion coefficient $D$ one can calculate the steady-state concentration $c_{\text{ss}}$. Consequently, the usage of Cu−Ag phase diagram allows finding the temperature $T_{\text{eff}}$ where the $c_{\text{ss}}$ is equal to the solubility of Ag in Cu. $T_{\text{eff}}$ in Cu−Ag alloys (as well in other Cu-based alloy listed above) is higher than the HPT temperature $T_{\text{HPT}}$ (which is close in our experiments at room temperature). Physically, the feature that $T_{\text{eff}}$ is always higher than $T_{\text{HPT}}$ reflects the fact that the steady-state concentration of vacancies during HPT process is increased in comparison with equilibrium one at $T_{\text{HPT}}$ and can be close to that at $T_{\text{eff}}$ [48−50].

If we substitute silver in Cu-based solid solution, the diffusion coefficient $D$ would change as well. The higher diffusivity would require the lower $T_{\text{eff}}$ and visa versa. Therefore, one can expect the correlation between activation enthalpy of diffusion $H_D$ and effective temperature $T_{\text{eff}}$. Fig. 3a contains the plot showing the correlation between $T_{\text{eff}}$ and $H_D$. The values of $H_D$ were taken from the diffusion handbook [51]. The obvious linear correlation between $T_{\text{eff}}$ and $H_D$ can be seen. The increase of $H_D$ leads to the increase of $T_{\text{eff}}$. Physically, such correlation is easy to understand because the increase of $H_D$ means the increase of energy barrier for the diffusion jumps of alloying atoms in copper lattice. Increased energy barrier for diffusion jumps leads to decreased diffusivity and relaxation rate in the dynamic equilibrium during HPT. In turn, slow relaxation, increases the steady-state concentration of non-equilibrium lattice defects (vacancies). As a result, $T_{\text{eff}}$ also increases.

However, the second plot in Fig. 3 is less obvious. Fig. 3b shows the correlation between effective temperature $T_{\text{eff}}$ and melting temperature $T_m$ of alloying element in various Cu-based alloys. Similar to Fig. 3a, $T_{\text{eff}}$ monotonically increases with increasing $T_m$ of alloying element. Such a correlation would be expected if we would
It is strange that previously nobody found it, because the diffusion data for such plot are available since many dozens of years. One possible explanation is that such a correlation (opposite to that shown in Fig. 4a) has no obvious physical explanation. At the moment, we found the linear correlation between $H_D$ and melting temperature of tracer $T_m$ also for gold, silver and some other elements where enough data for tracer $H_D$ are available.

The empirical dependence between $T_{eff}$ and melting temperature $T_m$ of alloying component in copper (Fig. 3b) allows one to predict the behaviour of any Cu-based binary alloy during HPT. For this purpose one needs to know the $T_m$ value of alloying component B. Knowing $T_m$, one finds the $T_{eff}$ value for B from the $T_{eff} - T_m$ plot (Fig. 3b). Knowing $T_{eff}$, one can find the solubility $c_B(T_m)$ of B at $T_{eff}$ from the Cu–B phase diagram. The $c_B(T_m)$ value would be the steady state concentration which has to be attained during HPT. In other words, if the Cu–B would be annealed at $T > T_{eff}$ and quenched, the resulted Cu(B) solid solution would decompose during HPT, fine precipitates of B or Cu-B intermetallic compounds would form in the alloy and concentration of B atoms in Cu would decrease during HPT down to $c_B(T_{eff})$ value. Visa versa, if the Cu–B would be annealed at $T < T_m$, the particles of second phase (B or Cu-B intermetallic compounds) would dilute in the Cu matrix, and concentration of B atoms would increase during HPT up to $c_B(T_m)$ value.

The $T_{eff} - T_m$ plot in Fig. 3b is constructed for the HPT at room temperature ($RT = 300$ K). If the HPT temperature is below RT, the value of $D_b$ in Eq. (1) would decrease. On the other hand, the mechanism of HPT-driven mass transfer (described by the value of $D_{ball}$) remains more or less the same. It means that below RT the value of $D_b$ would decrease and resulting $T_{eff}$ increases. In other words, the $T_{eff} (T_m)$ lines for $T > 300$ K should be above the line shown in Fig. 3b. Visa versa, above RT the value of $D_b$ would increase and resulting $T_{eff}$ decreases. $T_{eff}$ for Cu at 0.32 nm is higher than for other metals (in comparison with $D_b$ for Cu-B intermetallic compounds) and concentration of B atoms would increase during HPT up to $c_B(T_m)$ value.

We discussed, what happens if the relaxation rate (controlled by $D_b$) changes and the rate of defects production (described by $D_{ball}$) remains the same. Can we fix $D_b$ and change $D_{ball}$? It is possible if we study the action of other SPD modes on precipitation/dissolution process in Cu-based alloy. How can we estimate the $D_{ball}$ of other SPD modes in comparison with that of HPT before direct measurements? The good possibility for rough $D_{ball}$ estimation gives the data on steady-state grain size $d_{ss}$ in pure copper which can be obtained in various SPD modes. We can suppose that if the action of other SPD mode is stronger than that of HPT and the rate of defect production is higher, than grain size would be smaller.

The steady-state grain size $d_{ss}$ for copper is $d_{ss} \approx 850$ K. Aluminium has higher self-diffusion constants ($166 \text{ m}^2\text{m}^{-3}$) in comparison with copper ($45 \text{ m}^2\text{m}^{-3}$), and respectively, higher $d_{ss}$ after ECAP (1400 nm for Al and 300 nm for Cu at 0.32 nm) [62]. Therefore, one can expect that for Al–Zn alloys would be lower than that for Cu–Zn alloys ($d_{ss} \approx 850$ K, Fig. 3b). Indeed, the HPT of Al–Zn alloys gives $T_{eff}$ close to 300 K [6,30,65]. Therefore, these examples show that $T_{eff} (T_m)$ plot...
The second component in a solid solution is reached. The solid solution torsion. If one has a CuX alloy and phase transitions in the Cu-based alloys under high pressure HPT.

Knowing the Cu concentration X, one can also estimate the respective value of T_{eff}. Knowing the Cu–X phase diagram and T_{eff}, one can estimate the concentration C_X at T_{eff}. If a Cu–X alloy has been annealed at a certain energy barrier. This energy barrier is similar to that for the bulk diffusion. The measure for this barrier is the activation enthalpy of bulk diffusion H_p. We found that T_{eff} linearly increases with increase of activation enthalpy of bulk tracer diffusion H_p. The correlation between activation enthalpy of bulk tracer diffusion H_p and melting temperature T_m of diffusing alloying component has been found for the first time. As a result, T_{eff} linearly increases also with increase of melting temperature T_m of diffusing alloying component. The observed correlations allow one for the first time to predict the behaviour and phase transitions in the Cu-based alloys under high pressure torsion.

The observed correlations allow one to predict the behaviour and phase transitions in the Cu-based alloys under high pressure torsion. If one has a Cu–X alloy and knows the melting temperature of a component X, one can also estimate the respective value of T_{eff}. Knowing the Cu–X phase diagram and T_{eff}, one can estimate the concentration C_X at T_{eff}. If a Cu–X alloy contains precipitates and the (Cu) solid solution with C < C_p, then HPT would lead to the increase of C up to C_p and dissolution of precipitates. If a Cu–X alloy contains the (Cu) solid solution with C > C_p, then HPT would lead to the decrease of C down to C_p and formation of fine precipitates.

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