Phase transitions in metallic alloys driven by the high pressure torsion

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\textbf{A B S T R A C T}

Severe plastic deformation can lead to the phase transformations in the materials. Even the severe plastic deformation at ambient temperature is frequently equivalent to the heat treatment at a certain elevated temperature (effective temperature). However, if the real annealing at the elevated temperature leads to the grain growth, the severe plastic deformation leads to strong grain refinement. In this review the methods of determination of effective temperature after high-pressure torsion of metallic alloys are discussed.

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\textbf{1. Introduction}

Severe plastic deformation (SPD) frequently leads to the phase transformations in the materials. Even the SPD-treatment at ambient temperature $T_{SPD} = 300 \, K$ is frequently equivalent to the heat treatment at a certain elevated temperature $T_{eff} > 300 \, K$. It has been demonstrated recently that concept of effective temperature $T_{eff}$ originally proposed for the materials under severe irradiation [1] is applicable also for severe plastic deformation (SPD) [2]. If the atomic movements driven by an external action (deformation or irradiation) are higher in comparison with the conventional thermal diffusion, the material is forced to undergo 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 [2]. This method is quite productive since SPD frequently leads to the phase transformations [3] e.g. the formation [4–12] or decomposition [13–15] of a supersaturated solid solution, dissolution of phases [16–28], disordering of ordered phases [19–31], amorphization of crystalline phases [32–40], synthesis of the low-temperature [21,28], high-temperature [41–43] or high-pressure [44–52] allotropic modifications, and nanocrystallization in the amorphous matrix [53–61]. For the determination of $T_{eff}$ one can use also the phase diagrams at high pressures, if they are known [44–52]. However, the SPD-treatment at ambient temperature $T_{SPD}$ usually leads to the very quick phase transformations, which is easy to understand if one considers the high density of defects, similar to an increased temperature. The increased pressure, oppositely, leads to the decrease of diffusivity and/or grain boundary mobility [62,63]. Some SPD-driven phase transformation needs only a small shift of atoms, for other...
ones the 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). In this review the methods of $T_{\text{eff}}$ determination of metallic alloys after high-pressure torsion are discussed. For the determination of $T_{\text{eff}}$ we choose the alloys where the phases after HPT strongly differ from the ones before HPT. The alloys studied have also well investigated and unambiguously known equilibrium phase diagrams. These phase diagrams (in coordinates “temperature-composition” and/or “temperature-pressure”) allowed us the easy comparison with observed phases after SPD and, therefore, easy and reliable determination of $T_{\text{eff}}$.

2. Experimental

The Al–Zn, Al–Zn–Mg, Cu–Ni, Co–Cu, Ni–Y–Nb and Zr–Nb alloy systems of various compositions were investigated. The alloys were prepared of high purity components by the vacuum induction melting. The melts were poured in the water-cooled cylindrical copper crucible of 10 mm diameter. After sawing, grinding, and chemical etching, the 0.7 mm thick disks cut from the as cast cylinders were subjected to HPT in a Bridgman anvil type unit (room temperature, pressure 5 GPa, 5 torsions, 1 rotation-per-minute). After HPT, the central (low-deformed) part of each disk (about 3 mm in diameter) was excluded from further investigations. The samples for structural investigations and calorimetry were cut from the deformed disks at a distance of 4–5 mm from the sample centre. At this distance the shear strain is $\sim 6$. The 2 mm thick slices were also cut from the cylindrical ingots, then divided into four parts. After quenching, samples were embedded in resin and then mechanically ground and polished, using 1 µm diamond paste in the last polishing step, for the metallographic study. After etching, samples were investigated by means of the light microscopy (LM) and by scanning electron microscopy (SEM). SEM investigations have been carried out in a Tescan Vega TS5130 MM microscope equipped with the LINK energy-dispersive spectrometer and on a Philips XL30 scanning microscope equipped with a LINK ISIS energy-dispersive spectrometer produced by Oxford Instruments. LM has been performed using a Neophot-32 light microscope equipped with a 10 Mpix Canon Digital Rebel XT camera. The samples for TEM investigations were prepared by ion milling on the PIPS machine. TEM investigations were carried out on a Tecnai F2 electron microscope with acceleration voltage of 200 kV. The dark field image was taken in the most bright reflection to which contribute both $\alpha$ and $\omega$ phases. X-ray diffraction (XRD) data were obtained on a Siemens diffractometer (CoK$\alpha$ radiation). Grain size was estimated by the XRD line broadening and using the Scherer formula. Both the as-cast coarse-grained CG and fine-grained HPT-samples were studied with the aid of differential scanning calorimetry (DSC) using the NETZSCH Pegasus 404C and TA Instruments (models 910 and 1600) calorimeters in the dry argon atmosphere, $Al_2O_3$ crucibles and at the cooling and heating rates of 10 and 20 K/min.

3. Results and discussion

Usually, the high applied pressure decreases the diffusivity and grain boundary mobility [62,63]. However, the atom movements caused by strong external forces can drive both accelerated diffusion and phase transformations in the material [64]. Historically, such unusual behaviour was first observed in materials under severe irradiation [1]. Martin proposed a simplified mean-field description of solid solutions subjected to irradiation-induced atomic mixing [1]. His main idea was that the forced mixing induced by irradiation emulates the increase of entropy and changes the thermodynamic potentials in the alloy. In a simple case of regular solution in the Bragg-Williams approximation, a law of corresponding states was 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

$$T_{\text{eff}} = T(1 + \Delta). \quad (1)$$

If the irradiation-driven movements of atoms are similar in amplitude to conventional diffusion jumps, they can be described by the “ballistic” diffusion coefficient $D_{\text{ball}}$ and $\Delta = D_{\text{ball}}/D_{\text{sp}}$ where $D_{\text{sp}}$ is conventional bulk diffusion coefficient, possibly increased due to the non-equilibrium defect concentration [1]. It means that one can use the equilibrium phase diagram for the description of the system under irradiation, but at $T_{\text{eff}}$ instead of the actual temperature $T$. For example, if the liquid phase is present in the phase diagram at $T_{\text{eff}}$, the amorphous phase would appear under irradiation [1,65].

To check the applicability of the Martin’s law (1) to the forced diffusion driven by pure shear deformation ($D_{\text{HPT}}$) instead of irradiation ($D_{\text{ball}}$), experiments where HPT leads to the phase transformations have to be analysed. We have chosen for the comparison the data where (i) the HPT-driven atomic movements are comparable with each other, i.e. HPT was performed at 4–6 GPa with 4–6 torsions and (ii) the phases appeared after HPT can be easily localized in the phase diagrams and are different from those present in the samples before HPT.

The composition of the phases after SPD allows to localize those phases in the respective equilibrium phase diagram and to estimate the effective temperature $T_{\text{eff}}$. Such a schematic diagram is shown in Fig. 1. In this figure the dashed vertical lines denote compositions of the various studied alloys. Figurative points corresponding to the effective temperature of the alloys are indicated by an open circle and numbered. Each star with a letter indicates the composition and temperature of an alloy’s treatment (normal cooling, SPD or rapid quenching).

The supersaturated solid solution in the as-cast Al–30 wt % Zn alloy contained about 15 wt% Zn (Fig. 2) [13,14,67]. It corresponds to the point $b$ in Fig. 1. The as-cast Al–20 wt% Zn and Al–10 wt% Zn alloy contained about 7 and 3 wt% Zn in the supersaturated solid solution (Fig. 2). The HPT at room temperature (point $a$ in Fig. 3) produced nanogranulated pure Al (point $1$) and pure Zn particles simultaneously leading to unusual softening [13,14]. In other two as-cast alloys the
supersaturated solid solution also completely decomposed, and the lattice spacing in all three alloys became indistinguishable from that of pure aluminium (Fig. 3). The decomposition during SPD proceeds extremely quick, already after about 0.5 rotations of anvils the lattice spacing becomes equal to that of Al–30 wt% Zn alloy (Fig. 4) and microhardness reaches its stationary value (Fig. 5) [67].

The homogenized one-phase solid solutions in the Cu–Ni alloys with 42 and 77 wt% Ni (point 3) decomposed after HPT at room temperature (point a) into Cu-rich and Ni-rich phases (Fig. 6) [15]. The composition of resulting phases permitted an estimation of \( T_{\text{eff}} = 200 \, ^\circ\text{C} \) for the Cu–77 mass% Ni alloy and \( T_{\text{eff}} = 270 \, ^\circ\text{C} \) for the Cu–42 wt% Ni alloy (Fig. 6) [15].
The results of the work on HPT of Co–Cu alloys are schematically shown by the points a, b and 2 (Fig. 1) [2]. The composition of the supersaturated solid solution of the component B in γ-phase of A corresponds to the point b. This undercooled supersaturated solid solution in the metastable γ-phase is HPT-treated in the point a. After HPT the almost pure α-phase of A is formed as a consequence of the γ→α transition. It corresponds to the point 2. In case of Co–Cu alloys, the as-cast Co–12 wt% Cu alloy contains the supersaturated solid solution with 8 wt% Cu in the Co matrix with fcc α-structure (Fig. 7). After HPT, together with grain refinement, the full decomposition of supersaturated (Co) solid solution proceeds. In addition, the high-temperature fcc α-Co transformed into low-temperature hcp ε-Co (Fig. 7). The respective \( T_{\text{eff}} = 400 \, ^\circ\text{C} \) for the Co–Cu system (Fig. 7) [2].

The Fe–20 wt% (Nd, Pr)–5 mass% B–1.5 wt% Cu alloy containing crystalline phases \([Nd\text{Pr}2]Fé14B\) and Pr-rich phase transforms after HPT (point c) into a mixture of the amorphous phase and \((Nd\text{Pr}2)Fé14B\) nanograins [16]. According to the Martin’s model this means that the \( T_{\text{eff}} \) is so high that the configurative point for the treated alloy is in the two-phase area where both solid and liquid phases are present (point 4, Fig. 1). The melt appears in the Nd–Fe–B system above eutectic temperature \( T_{\text{e}} = 665 \, ^\circ\text{C} \) [17]. It means that the effective temperature is slightly above \( T_{\text{e}} = 665 \, ^\circ\text{C} \) and can be estimated as \( T_{\text{eff}} = 700 \, ^\circ\text{C} \).

The coarse-grained as-cast Ni–20 wt% Nb–30 wt% Y and Ni–18 wt% Nb–22 wt% Y alloys contained before HPT the NiY, NbNi4, Nb2Y, Ni2Y2 and Ni3Y phases (point g, Fig. 3) (Fig. 8a) [36,39]. After HPT these alloys transformed into a mixture of two nanocrystalline NiY and Nb3Ni2 phases and two different amorphous phases (one was Y-rich and another Nb-rich) (point 6, Fig. 3). The Ni–Nb–Y phase diagram contains two immiscible melts above \( 1440 \, ^\circ\text{C} \) [66]. Therefore, the effective temperature is slightly above \( T_{\text{e}} = 1440 \, ^\circ\text{C} \) and can be estimated as \( T_{\text{eff}} = 1450 \, ^\circ\text{C} \) (Fig. 8a). It is remarkable that the rapid solidification of these alloys from the liquid state (point f, Fig. 1) also allows obtaining the mixture of two amorphous phases.

Especially valuable data on the effective temperature of SPD can be extracted from the work on HPT of Ti–48.5 at% Ni, Ti–50.0 at% Ni and Ti–50.7 at% Ni alloys [33]. The HPT of equiatomic Ti–50.0 at% Ni alloy at room temperature (point e, Fig. 1) resulted in the fully amorphous state (point 5, Fig. 1, \( T_{\text{eff}} = 1350 \, ^\circ\text{C} \), respectively). The HPT of the non-equiatomic Ti–48.5 at% Ni alloy at 270 °C (point h) produced the mixture of amorphous and nanocrystalline phases (point 7, \( T_{\text{eff}} = 1050 \, ^\circ\text{C} \)). When the HPT temperature of the Ti–48.5 at% Ni alloy increased up to 350 °C (point i), only the mixture of nanocrystalline phases formed, without amorphous phase. It means that the corresponding point moved from the position 7 in the 6+L region into position 8 in the two-phase δ+γ region and the effective temperature decreased to \( T_{\text{eff}} = 950 \, ^\circ\text{C} \). The HPT of another non-equiatomic Ti–50.7 at% Ni alloy at 200 °C (point j) produced the mixture of amorphous and nanocrystalline phases (point 9, \( T_{\text{eff}} = 1250 \, ^\circ\text{C} \)). When the HPT temperature of the Ti–50.7 at% Ni alloy increased up to 250 °C (point k), only the mixture of nanocrystalline phases formed, without amorphous phase. It means that the corresponding point moved from the position 9 in the 6+L region into position 10 in the two-phase δ+β region and the effective temperature decreased to \( T_{\text{eff}} = 1100 \, ^\circ\text{C} \). Therefore, it can be clearly seen from the data obtained by Prokoskhi et al. [33] that the increase of the HPT treatment temperature leads to the decrease of \( T_{\text{eff}} \). It is in full accordance with Eq. (1) because the increase of \( T \) leads to increase of \( D_\text{HPT} \) and at the same time the amount of deformation-driven atomic movements characterized by \( D_\text{HPT} \) remains unchanged.
The values of $T_{\text{eff}}$ can also be extracted from the experiments on the so-called nanocrystallization. The rapid solidification of these alloys from the liquid state (point d, Fig. 1) produces the fully amorphous phase. Afterwards the amorphous phase was subjected to the HPT at room temperature (point c, Fig. 1). HPT led to the formation of crystalline nanoparticles in the amorphous matrix (point 4, Fig. 1). The position of point 4 in a respective phase diagram slightly above the $T_e$ permits to estimate $T_{\text{eff}}$ for the nanocrystallized Ni-$29$ wt% Fe-$15$ wt% Co-$10$ wt% B-$2$ wt% Si alloy [53] our estimation gives $T_{\text{eff}}=1000$ °C. For the nanocrystallized Cu-$20$ wt% Zr-$20$ wt% Ti alloy [54] $T_{\text{eff}}=700$ °C. For the nanocrystallized Al-$8$ wt% Ce-$5$ wt% Ni-$2$ wt% Co alloy [55] $T_{\text{eff}}=400$ °C. For the nanocrystallized Fe-$6$ wt% Si-$13$ wt% B alloy [56] $T_{\text{eff}}=1100$ °C. For the nanocrystallized Zr-$5$ wt% Ti-$20$ wt% Cu-$10$ wt% Al-$8$ wt% Ni alloy [57] $T_{\text{eff}}=1100$ °C. We have to underline again that the effective temperatures determined in this way are much higher than the macroscopic temperature of the SPD-treatment which is usually only slightly above the ambient one. From this point of view HPT strongly differs for example from friction stir processing where the part being processed is really “lightening” during the treatment [70–72].

It is rather easy to estimate the $T_{\text{eff}}$ if one can find the phases existing in a material before and after SPD in an equilibrium “temperature–composition” phase diagram. But it becomes a real challenge if the high-pressure phases appear during SPD. A good subject for such experiments is the titanium group of elements (Ti, Zr, and Hf). Ti, Zr, and Hf all have the hcp crystal structure ($\alpha$-phase) at room temperature and zero pressure. At high temperature and zero pressure they transform to the bcc structure ($\beta$-phase) before reaching the melting temperature. At room temperature and under pressure they undergo a crystallographic phase change into the so-called $\omega$-structure. At even higher pressures both Zr and Hf have been observed to transform to the bcc structure ($\beta$-phase) (see [73] and references therein).

The as-cast Zr-$2.5$ wt% Nb and Zr-$8$ wt% Nb alloys contain mainly $\alpha$Zr with hexagonal closely-packed lattice [73]. The Nb-rich body-centred cubic phase is absent. Small amount of $\beta$-Zr is present in the CG as-cast alloys. Nb-poor $\beta$Zr has a body-centered cubic lattice and is isomorphous to the Nb-rich bcc-phase. After HPT both fine-grained Zr-Nb alloys contain mainly the $\omega$-Zr phase [73]. The $\omega$-Zr phase possesses the hexagonal C32 structure [74]. The Nb-rich ($\beta$-Nb-phase) is absent both after and before HPT. The HPT-treatment of Zr-$2.5$ wt% Nb and Zr-$8$ wt% Nb alloys at 5 GPa produced the $\omega$-Zr high-pressure allotrope [73]. Therefore, the usage of equilibrium “temperature–composition” diagrams (like in Figs. 3, 6–8) is not enough to estimate the effective temperature of SPD. As we already mentioned above, high pressure always decreases the diffusivity and grain boundary mobility [62,63]. It means that in order to explain the increased atomic fluxes during SPD we need the increased $T_{\text{eff}}$ and we have to search for the respective phases in the “temperature–pressure” or even the “temperature–pressure–composition” phase diagrams.

In Fig. 9 the conditions of HPT (small full symbols) and the estimated values of effective temperatures (large open symbols) are shown for Ti, Zr and Hf. The starting $\alpha$-phase in 99.8 wt% pure Zr [46] and commercially pure Zr [48] transforms into a $\omega$/$\beta$ mixture after HPT with 1 rpm and 5 rotations at 3 and 6 GPa (full squares, Fig. 7b) [46,48]. This fact permits to estimate the $T_{\text{eff}}$ at the $\omega$/$\beta$ equilibrium line as 650 °C (open square). After HPT at 1 GPa [46,48,75], 2 GPa [46,50], 3 and 4 GPa [46] the $\alpha$-phase does not transform in other phase(s). It does not permit to estimate the effective temperature of HPT process. The HPT at 6, 14, 22, 30 and 40 GPa with 1 rpm and 5 rotations (small full pentagons) transforms the starting $\alpha$-phase into $\omega$-phase [50,77].
However, the \( \omega \)-phase is in equilibrium at room temperature above 3.4 GPa (star) [76]. Therefore, one cannot estimate the effective temperature using these results. The HPT of an Zr–2.5 wt% Nb alloy at 0.25, 0.5 and 5 GPa with 0.2 rpm and 5 rotations (full circles) permits to transform the starting \( \alpha \)-phase into a \( \alpha+\beta+\omega \) phase mixture [44]. This mixture can be found in the \( \alpha+\beta+\omega \) triple point at 670 °C (large open circle). In our work the HPT of Zr–2.5 wt% Nb and Zr–8 wt% Nb finishes in the \( \beta+\omega \) mixture, almost without any \( \alpha \)-phase. Also, the addition of Nb decreases the temperature of \( \alpha \)-\( \beta \) transition at ambient pressure (see also phase diagram in Fig. 3). One can suppose that the temperature of \( \alpha \)-\( \beta \) (and \( \omega \)-\( \beta \)) transition decreases in Zr–Nb alloys also at high pressures. The dashed lines starting in stars at 0.1 MPa show this shift for 2.5 and 8 wt% Nb. The respective effective temperatures are shown by large open squares and are \( T_{\text{eff}}=620 \) °C for Zr–2.5 wt% Nb and \( T_{\text{eff}}=550 \) °C for Zr–8 wt% Nb.

Analysing and comparing all these results, one can conclude that the original idea of Martin [1] is applicable, in its developed form, also to the SPD-driven phase transformations. We can draw this conclusion despite the fact that in the model of Martin it is supposed that the irradiation-driven movements of atoms are similar to the diffusion jumps. This is, obviously, not completely true for the case of SPD-driven movements of atoms. Nevertheless, the general tendency (1) is quite similar. In this work we have compared the alloys deformed by HPT in comparable conditions \( (T_{\text{SPD}}=300 \text{ K, } \sim 5 \text{ GPa, } \sim 1 \text{ rpm, } \sim 5 \text{ torsions}) \) with each other. One can suppose that the SPD-driven atomic movements are comparable in all systems under consideration. On the other hand, the “natural” diffusion movements of the atoms are quite different due to the difference of melting temperature \( T_m \) of the considered materials. Since the \( T_{\text{SPD}}=300 \text{ K} \) is almost the same, the “natural” diffusion coefficients are low for the materials with high \( T_m \). In this case the SPD-driven atomic movements are large in comparison with diffusion jumps, and \( T_{\text{eff}} \) is high (as predicted by Martin, see Eq. (1)). In the opposite case of low \( T_m \) (like in the Al-based alloys), the \( T_{\text{eff}} \) is low and can be close to the ambient temperature of \( T_{\text{SPD}} [13,14,67] \).

4. Conclusions

Severe plastic deformation by HPT leads to the phase transitions and strong grain refinement in several metallic alloys. SPD-treatment at ambient temperature \( T_{\text{SPD}} \) is frequently equivalent to the heat treatment at a certain elevated (effective) temperature \( T_{\text{eff}} \). If the condition of SPD-treatment is similar, the materials with high melting temperature \( T_m \) also yield high \( T_{\text{eff}} \) values. The materials with low \( T_m \) have low \( T_{\text{eff}} \). Contrary to the effect of increasing temperature, the increasing pressure slows down the diffusion and grain boundary migration. Therefore, the forced atomic movement during HPT produces the states equivalent to higher temperature, but not to the higher pressure.

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