Einleitung

Die meisten metallischen Werkstoffe werden im polykristallinen Zustand eingesetzt, enthalten also Korngrenzen als Defekte des Kristallgitters. Korngrenzen haben einen tiefgreifenden Einfluss auf das Verformungsverhalten. Zunächst einmal begrenzen sie die Ausdehnung der Abgleitprozesse in den Körnern, also die Laufwege der Versetzungen; das erhöht die Versetzungserzeugungsrate und damit die Verfestigungsrate. Der Zwang zum Kornzusammenhalt führt dazu, dass in der Nähe der Korngrenzen lokale Anpassungsverformung erfolgen muss. Die Folge ist erhöhte Versetzungsaktivität in Korngrenzennähe und erhöhte Verfestigungsgeschwindigkeit. Diese verfestigenden Prozesse wirken sich insbesondere bei niedrigen homologen Temperaturen aus; der Hall-Petch-Effekt besagt, dass die Streckgrenze mit abnehmender Korngröße d mit $1/\sqrt{d}$ ansteigt. Bei mittleren und hohen homologen Temperaturen relaxiert die härtende Wirkung der Korngrenzen durch Korngrenzengleiten und Diffusionsfließen. Diese Mechanismen können nicht nur die Akkommodation der unterschiedlich abgleitenden Körner übernehmen, sondern auch direkt zur Verformung beitragen und im Extremfall superplastisches Verhalten erzeugen. Ultrafeinkönige (UFG) und nanokristalline (NC) Stoffe, die sich durch einen hohen Volumenanteil an Korngrenzen auszeichen, stehen als neue Stoffgruppe mit hohem Anwendungspotential im Mittelpunkt des Forschungsinteresses. Viele hilfreiche Ergebnisse zu diesem Thema finden sich in der Literatur. Jedoch ist bisher nicht geklärt, wie sich dieser Korngrenzenanteil auf den Verformungswiderstand UFG und NC Metalle auswirkt.

Das Ziel der vorliegenden Arbeit ist, den Einfluss der Korngrenze auf das Verformungsverhalten von UFG Cu hergestellt durch Equal Channel Angular Pressing (ECAP) zu untersuchen. Umfassende Kenntnis der mechanischen Eigenschaften von UFG Material hinsichtlich Verformungswiderstand und Dehnratenabhängigkeit wird angestrebt. Die Gründe des Eigenschaftenprofils werden untersucht und einige Verformungsmechanismen, die auf Verständnis der Mikrostruktur beruhen, werden vorgeschlagen.

Abschnitt 1.1 fasst die Literatur über mechanische Eigenschaften, thermische Stabilität und Herstellungstechniken von UFG Materialien zusammen. Abschnitt 1.2 schildert das Forschungsziel der vorliegenden Arbeit.

Abschnitt 2 umreißt die experimentellen Methoden, die für diese Untersuchungen notwendig sind.

Abschnitt 3 zeigt die mechanischen Eigenschaften von UFG Kupfer hinsichtlich Verformungswiderstand und Dehnratenabhängigkeit, die in einmem großen Bereich der Temperatur und Dehnrate/Spannung gemessen werden, auf. UFG und CG (coarse-grained)

Materialien werden in ihre Verformungsverhalten miteinander verglichen. Der Einfluss von Vorverformung, die durch mehrfache Druckversuche erreicht wird, auf das Verformungsverhalten von Kupfer wird auch untersucht.

Abbschnitt 4 erklärt die Ergebnisse aus den vorherigen Abschnitten basierend aus dem Verständnis der Mikrostruktur. Die vorgeschlagene Interpretation wird auch auf die Ergebnisse mit Kupfer von Dalla Torre et al. [1] und Al von Sklenička et al. [2, 3].

Abschnitt 5 fasst die Ergebnisse dieser Arbeit zusammen.

1. Introduction

Contents

Most metallic materials are applied in polycrystalline state, i.e., include grain boundaries being the defects of crystal lattice. It is well known that grain boundaries harden crystalline materials at low homologous temperatures. The Hall-Petch relationship describes the increase of flow stress with decreasing grain size. It is also known that grain boundaries may soften materials at high homologous temperatures; this is obvious from observations of superplastic behavior with fine-grained materials having a lower steady-state deformation resistance than coarse-grained (CG) materials. The effect of grain boundaries on deformation resistance is of considerable interest for ultrafine-grained (UFG) and nanocrystalline (NC) materials which have an extremely higher volume fraction of grain boundaries giving them unusual properties compared to their CG counterparts. Bulk ultrafine-grained (UFG) metals with grain size in the range of 100 nm to less than 1 μm can be successfully produced by different techniques of severe plastic deformation (SPD) [4–11]. Being viewed as "advanced structural and functional materials of the next generation of metals and alloys " [6, 12, 13], UFG materials have recently received considerable scientific attention. Today many useful results can be found in literatures. However, a database for full knowing about the mechanical properties is still not available; and the deformation mechanism remains to be understood.

In this chapter, some results documented in literatures will be reviewed in section 1.1; the plan of the current research will be outlined in section 1.2.

1.1. Literature survey

The results from literatures on UFG materials will be reviewed in sections 1.1.1 to 1.1.4 with respect to mechanical properties, thermal stability, deformation mechanism and fabrication techniques, respectively. Some remarks will be given in the last section.

1.1.1. Mechanical properties of ultrafine-grained materials

1.1.1.1. Strength and ductility

It is now generally accepted that UFG materials exhibit an extraordinary high strength compared to the CG materials, as expected from an extrapolation of the Hall–Petch relationship for CG materials [1, 14–28]. Ivanov et al. showed that ultimate tensile strength (426.5 MPa) and yield stress (415.5 MPa) of UFG Cu at room temperature exceed the corresponding values of CG Cu by approximately two and seven times, respectively [29]. Vinogradov found that the yield stress and the ultimate tensile strength increase by a factor of 3-5 when compared to those of the well-annealed counterparts [28]. Saito et al. [5] also reported that UFG Al(1100), Al-Mg(5083) and IF steel produced by Accumulative Roll-bonding, exhibit extremely high strength at ambient temperature after 8, 7, 5 Accumulative Roll-bonding cycles, respectively. It is worth to note that the statements are valid only for low (mostly ambient) temperature/high strain rate and the comparison between CG and UFG materials is limited to yield stress and ultimate tensile strength,

the comparison in steady state of deformation has not been performed so far.

Regarding the tensile ductility (elongation to failure in tension), which is very important for many shaping and forming operations and for avoiding catastrophic failure in load-bearing applications, the situation is not yet clear in detail. Vinogradov reported that the ductility of most SPD metals does not compete with that of well-annealed polycrystals [28]. Many investigations demonstrate that relative tensile elongation to failure observed for NC and UFG metals rarely exceed 5% [25, 30–33] or 10% [34], even for metals that are very ductile at conventional grain sizes. Poor ductility is also reported in [5, 14–16, 18, 19, 35]. The contradictory statement that nanostructured metals show enhanced ductility compared to their CG counterparts can also be found in literatures, see e.g., [1, 6, 36–38].

These contradictory statements can be simply explained by the difference in testing conditions, e.g., the subsequent testing T and $\dot{\epsilon}$. Wang and Ma reported three strategies to achieve uniform tensile deformation in a nanostructured metal [39]. One of these three strategies is through changing the testing conditions to obtain enhanced ductility. Höppel et al. have also found a very pronounced dependence of elongation to failure on the deformation rate in UFG Al(99.95) after 5 Accumulative Roll-bonding cycles [38]. Compared to CG Al, the tensile uniform elongation of UFG Al is increased by a factor of about 1 at $\dot{\epsilon} = 5 \cdot 10^{-4}\,\mathrm{s}^{-1}$ and 4 at $\dot{\epsilon} = 5 \cdot 10^{-5}\,\mathrm{s}^{-1}$.

The influence of temperature on ductility of UFG materials has been studied through change in T. Valiev et al. reported [40] that UFG alloy Mg-1.5%Mn-0.3%Ge displays typical superplastic properties at elevated temperature of 180°C. Since the superplastic temperature of UFG alloy decreases by 200-250°C compared to CG counterpart, we can speak of the so-called low temperature superplasticity of UFG materials. In [41], AZ91 processed by ECAP exhibited such low temperature superplastic behavior.

In addition to the influence of testing conditions, the amount of predeformation (corresponding to the number of SPD passes) has a profound influence on ductility of UFG materials. Valiev et al. [36, 42] reported a combination of high strength and high ductility in UFG Cu after 16 ECAP passes and in UFG Ti after 5 HPT resolutions. Höppel et al. [38] reported that after 1 Accumulative Roll-bonding cycle, the elongation to failure for Al is already higher than that for the cold-rolled CG counterpart; with further increasing number of Accumulative Roll-bonding cycles necking becomes less pronounced. This behavior is significant in particular for specimens with 5 and 8 Accumulative Roll-bonding cycles [38]. Similar results have also been reported for Ti-6Al-4V alloy fabricated by ECAP [43] that elongation was significantly increased with increasing ECAP straining from 4 to 8. Dalla Torre et al. have also observed an increase in the uniform elongation in UFG Cu from 4 to 16 passes of ECAP [1].

Ductility of UFG materials can also be improved by controlled annealing [25–27, 39, 44–46]; e.g., Höppel et al. [44] reported that a bimodal distribution of grain size can

be obtained during annealing of UFG Cu; they further supposed that such structure is responsible for the enhancement in fatigue life. Wang et al. [25] also showed that such bimodal structure causes only a small decrease in strength, but leads to a significant increase in plastic elongation.

1.1.1.2. Strain rate sensitivity of flow stress

Recent investigations of mechanical behavior of UFG materials have concentrated on the strain rate sensitivity m of flow stress. Many studies on UFG materials showed enhanced strain rate sensitivity [17, 36, 39, 47–54]. For example, a comparatively large $m = 0.14$ was reported by Valiev et al. [36] for UFG Cu with an average grain size of 100 nm produced by 16 passes of ECAP. Wei et al. [50] concluded from their strain rate jump tests that m was at least 0.02 for UFG Cu with average grain size of 200 nm. They also represented the grain size dependence of m in Cu by collecting literature data. Although some inconsistency existed in the absolute value, as the authors pointed out, the data indicated a substantial increase in m when d is reduced to UFG and NC regime. The d-dependence of m can also been observed from the variation of m with ECAP passes, as an increase in ECAP pass leads to an increase in the fraction of high-angle grain boundaries [1] corresponding to a decrease in d. Valiev et al. [36] reported that m was equal to 0.14 after 16 passes for ECAP Cu in contrast to $m = 0.06$ after 2 passes. Dalla Torre et al. demonstrated that m increased from 0.01 after one ECAP pass to about 0.02 after 12 passes [51]. It is necessary to note that m in UFG materials is not only d-dependent, but also varies with T and $\dot{\epsilon}$. It can been seen from the work of Wang and Ma [39] and Dalla Torre et al. [55] that m increases strongly with decreasing $\dot{\epsilon}$, and from the work of May et al. [56] that m in UFG Al99.95 varies drastically with T. Therefore, d-dependence of m makes sense only when the other factors, which influence m, are fixed.

Most of measurements of strain rate sensitivity mentioned above were limited to low temperatures and/or high strain rates [17, 26, 36, 39, 50, 51, 57]. Although the T and $\dot{\epsilon}$ dependence of deformation behavior in UFG materials has been investigated, e.g., by Wang and Ma [57], the T range (from 77 K to 298 K) and $\dot{\epsilon}$ (from $10^{-1}\,\mathrm{s}^{-1}$ to $10^{-4}\,\mathrm{s}^{-1}$) range were still limited. Wang and Ma [39, 57] also extended their measurement from $\dot{\epsilon} = 10^{-4}\,\mathrm{s}^{-1}$ to $6 \cdot 10^{-7}\,\mathrm{s}^{-1}$, however, T was limited to be at room temperature only.

The enhanced strain rate sensitivity of UFG materials is found only for fcc metals, while UFG bcc metals (e.g. Fe and Ta) showed a reduced m [50]. Similar results on the difference of d dependence of strain rate sensitivity between fcc and bcc metals have also been reported by May et al [58]. However, it is worth mentioning that such difference between fcc and bcc metals occurs only at low temperature (near room temperature). Above the athermal temperature T_a, bcc metals behave much the same as fcc metals [50]. Les et al. [59] investigated the difference of variation of m with ϵ between Ni (fcc) and α-Fe (bcc) in stages IV and V of deformation for low and high temperatures. Their measurements on m showed that the bcc metal α-Fe exhibited the same variation of m with ϵ at $T = 995$ K as fcc metals.

With regard to the strain rate sensitivity of CG materials, it is generally accepted that CG materials are rate insensitive and normally show a low value of m. Carreker and Hibbard [60] observed that m is 0.004-0.0072 for $d \geq 12$ μm. This is consistent with the result of $m = 0.006$ measured by Follansbee et al. [61].

It is worth to note that the strain rate sensitivity in CG materials is strain dependent. Early experiments by Zehetbauer and Seumer [62] showed an increase in m from 0.003 to 0.01 in Cu99.95 with increasing shear strain γ from about 0.5 to 8 by torsion at room temperature. Similarly, the results by Dalla Torre et al. showed that m for the annealed Cu increases from 0.007 to 0.0085 with increasing ϵ from about 0.06 to 0.3 [51]. The results on Al99.99 conducted by Stüwe and Les [63] also exhibited a continuous increase in m from 0.01 at $\gamma = 2$ to 0.03 at $\gamma = 12$ by torsion at room temperature. The variations of m with $\dot{\epsilon}$ and T can also be found in their work. Since the m value of 0.03 is already larger than the value of 0.014 at the same T reported by May et al. [56] for UFG Al99.95 (produced by ECAP along route B_c after 8 passes), the grain structure of Al in [63] has probably already become ultrafine at $\gamma = 12$.

1.1.1.3. Activation area

Activation volumes $b\,\Delta a$ or activation areas Δa have been used in studies of the deformation mechanisms of UFG material in attempts to identify rate-controlling mechanisms [50, 51, 64, 65]. There are two preconditions for application of the concept, namely, (i) plastic deformation must be controlled by thermally activated glide; (ii) the measurement of activation area must be performed under constant dislocation structure. These authors do not check whether these conditions are fulfilled so that the results and conclusions are dubious.

1.1.1.4. Softening in UFG materials

It is generally accepted that UFG materials have an enhanced strength compared to CG materials. However, this statement is only valid when such comparison is made within small strain. For large strains, a softening in flow stress of UFG material come out. This can be seen from the recent results on UFG Cu [47, 48, 54, 66–68] and UFG Al [56]. Dalla Torre et al. [1] have found that yield stress and ultimate tensile stress of Cu reach a maximum after 4 ECAP passes (corresponding to an cumulative strain of 4). From 4 to 16 passes the strength of the material decreases. Such softening phenomenon has also been observed by Vinogradov [28] in UFG Cu by ECAP after 16 ECAP passes.

Sklenička et al. [2, 3] observed that the creep resistance of the ECAP processed Al after one pass was markedly improved compared to unpressed material, however, successive ECAP steps resulted in a marked decrease in the creep resistance at 473 K.

1.1.2. Thermal stability of ultrafine-grained materials

For the investigation of mechanical properties of UFG materials at high temperatures, it is important to know their thermal stability. Thermal stability of UFG Cu processed by HPT was studied by Islamgaliev et al. through various techniques: transmission electron microscopy (TEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), electrical resistance and microhardness [69, 70]. Their investigation showed that the grain growth starts above 448 K. Gubicza et al. observed that the temperature of the DSC peak related to the recovery of the microstructure decreased with increasing SPD strain. For UFG Cu subjected 8 ECAP passes, the recovery of microstructure occurrs at $T > 500$ K [71]. Ivanov et al. [29] showed that grain growth in UFG Cu was not observed during annealing at 373 K for 3 hours. Korzinikov et al. [72] reported that after annealing in the temperature interval of 423-448 K the relaxation of internal stress on grain boundaries begins and moderate grain growth takes place in UFG Cu. Mechanical properties, however, have not be significantly affected. At annealing temperature above 473 K strong grain growth begins, considerable relaxation of internal stresses occurs and mechanical properties approach CG Cu. This is consistent with the result reported by Akhamadeev et al. [73] that static grain growth was only observed at 473 K. The σ-ϵ curves of UFG Cu at $T \geq 473$ K revealed gradual work hardening like CG Cu [47] indicating grain growth.

1.1.3. Deformation mechanisms of ultrafine-grained materials

The primary deformation mechanism in coarse-grained polycrystalline materials is associated with the intragranular movement of dislocations. However, when the grain size is reduced to the ultrafine or nanocrystralline level, the deformation processes are critically dependent upon the grain size of the material. As Zhu and Langdon [74] recently summarize: "in the grain size range of 100-500 nm, the deformation mechanisms are similar to those in fine-grained traditional materials; whereas for grain sizes in the range of 50-100 nm, dislocations are emitted from, and are annihilated at, grain boundaries; in the grain size range of 10-50 nm, partial dislocation emission and deformation twinning are the major deformation mechanisms; and for grain sizes below 10 nm, grain boundary sliding (GBS) is the dominant deformation mechanism". There are also many predictions about the deformation mechanisms of nanostructured materials from model and simulation. The following review focuses only on UFG materials.

The positive Hall-Petch effect in UFG materials at small strains reviewed in Section 1.1.1.1 can be simply explained by the fact that SPD processed material has been strongly predeformed; consequently, this material is in a state which is close to the steady state of deformation determined by the (final) SPD temperature and strain rate [54], i.e., a high density of dislocations already exists in UFG materials by SPD and the density quickly reaches saturation upon further deformation. Vinogradov [28] also states that this strengthening effect is expected logically from the major mechanisms, which accompany intensive cold-working-dislocation accumulation and structure (grain) refinement. Both these contributions can be combined and unified in terms of total dislocation density including

lattice dislocations , dislocations in subgrain boundaries and geometrically necessary dislocations. High strength is also explained by taking into account dislocations trapped at grain boundaries [27]. In UFG materials the specific surface of grain boundaries is high and therefore the density of dislocations trapped at grain boundaries is high as well [27, 75]. The fracture and deformation relief on the surface of samples indicate an important role of grain-boundary sliding and grain rotation as deformation mechanisms. By contrast, Valiev et al. [15] state that the high value of yield stress observed in UFG Cu cannot be explained by the dislocation pile-up approach, considering that pile-ups are not observed in TEM pictures. They interpreted the strengthening effect observed in UFG Cu by a model based on the dislocation bow-out (between grain boundaries for grain size $d < 100$ nm or dislocations for $d > 100$ nm) mechanism suggested early by Lian et al. [76].

The combination of strength and ductility in UFG materials was explained by Valiev [42] by the fact that ultrafine, equiaxed grains with high-angle grain boundaries impede the motion of dislocations and consequently enhance strength while at the same time these grains may facilitate other deformation mechanisms such as grain boundary sliding [15] which improves ductility. Valiev and coworkers experimentally observed significant grain boundary sliding in UFG Cu deformed at room temperature [15]; the contribution of grain boundary sliding to total deformation was estimated to be in the range of 10-15%. They concluded that the operation of a multitude of mechanisms, including intragranular dislocation slip, grain boundary sliding and migration, is responsible for the unique deformation behavior of UFG Cu in the steady-state flow stage. They also pointed out that the enhanced strain rate sensitivity indicated an active role of grain boundary sliding [12, 36, 42]. Chinh et al. [77] also experimentally observed indications of grain boundary sliding in UFG Al by using Atomic Force Microscopy (AFM). Together with this observation, from the obtained activation energy of UFG Al, which was similar to that anticipated for boundary diffusion in pure Al, they emphasized that at low temperatures grain boundary sliding might take place at very high strains when the fraction of grain boundaries was relatively high as in the case of fine grain sizes in materials produced by ECAP. Valiev et al. [78] checked the grain structure of superplastically deformed Ni_3Al (Ni-8.5 Al-7.8 Cr-0.6 Zr-0.02 B; in wt%) with an average grain size of 50 nm produced by HPT. Their observation showed that there are no visible distortions of the crystal lattice near the grain boundary. Additionally, TEM/HREM observations of twin boundaries in the deformed specimen showed no indication of trapped lattice dislocations, suggesting that grain boundary sliding was accommodated by diffusion, not by lattice deformation. The absence of dislocation activity may be due to the high deformation temperature (650°C) in their case. Grain boundary sliding as a significant mechanisms of UFG and NC metals can also been found in [79, 80].

Valiev in his recent paper [37] discussed why grain boundary sliding in nanostructured materials, in particular in those produced by SPD, should take place at relatively low temperature. He argued that GBS is a diffusion controlled process and usually occurs at high temperatures. A possible explanation is that diffusion may be faster in SPD-produced UFG materials with highly non-equilibrium grain boundaries [15]. So perhaps GBS is