Einführung

Polykristalle mit Korngrößen im Submikometer-Bereich stellen eine aussichtsreiche Materialklasse für strukturelle Anwendungen dar. Insbesondere bei niedriger homologer Temperatur $T_{\mathrm{hom}} = T/T_{\mathrm{M}}$ (mit T: absoluter Temperatur und T_{M}: Schmelzpunkt) zeigen sie, verglichen mit konventioneller Korngröße (cg), verbesserte mechanische Eigenschaften [1]. Veröffentlichte Festigkeitssteigerungen beziehen sich zum Großteil auf den Beginn plastischer Verformung. Hansen [2] sowie Meyers und Mitarbeiter [3] zeigten, dass die erhöhte Festigkeit entlang der Fließkurve erhalten bleibt. Für Rein-Cu (OFHC) stellten Blum *et al.* [4] die jeweils bei Raumtemperatur in Druckversuchen gemesse Fließspannung und mittels Nanoindentierung gemessene Härte für den Korngrößenbereich 0.10 μm $\leq d \leq$ 50 μm zusammen. Die Daten zeigen, dass eine Hall-Petch Beziehung sogar für bzw. nahe am Zustand stationärer Verformung gilt, d.h. die Fließspannung und Härte nimmt mit abnehmender Korngröße zu. Somit verfestigen Großwinkl-Korngrenzen dieses Material bei Raumtemperatur. Allerdings findet sich für hochverformtes Cu mit ultrafeinen Körnern der Größe 0.35 μm bei erhöhter Temperatur und/oder geringen Dehnraten, dass die stationäre Fließspannung unter derjenigen bei konventieller Korngröße liegt [5–8]. Dieses Phänomen wurde durch beschleunigte Versetzungsannihilation an Korngrenzen erklärt [5]. Der Zustand stationärer Verformung – mit gleichbleibender Fließspannung und Dehnrate bei konstanter Temperatur – ist dabei durch ein dynamisches Gleichgewicht der Evolution der Versetzungsstruktur gekennzeichnet.

Man nimmt an, dass Plastizität auch in nanokristallinen Stoffen bis in den Bereich von d $\approx$ 30 nm durch die Gleitung von Gitterversetzungen dominiert wird [9]. Ferner wird vermutet, dass der Verformungswiderstand von (ultra)feinkörnigen Materialien stark durch die überproportionale Anreicherung von Versetzungen an Korngrenzen beeinflusst ist [5, 9, 10]. Unter dieser Annahme spielen die Deposition und Annihilation von Korngrenzversetzungen eine entscheidende Rolle. Ersteres erzeugt eine Festigkeitssteigerung während Letzteres eine entfestigende Tendenz erklären kann. Zur Zeit existiert noch kein schlüssiges Modell, welches auf Basis von Ratengleichungen für die Erzeugung und Vernichtung von Korngrenzversetzungen die beobachteten Phänomene einer durch hohen Anteil von Großwinkel-Korngrenzen verursachte Ver- und Entfestigung zu erklären vermag. In der vorliegenden Arbeit wird versucht ein einfaches statistisches Versetzungsmodell zu entwickeln, das in der Lage ist die entscheidenden Einflüsse der Korngröße auf den stationären Verformungswiderstand wiederzugeben. Die Ableitung von Mechanismen zur Versetzungsstrukturevolution steht dabei im Vordergrund.

Am Beispiel von Cu mit Korngrößen 0.10 μm $\leq d \leq$ 100 μm werden ausführliche Simulationen des Modells durchgeführt. Der resultierende stationäre Verformungswiderstand wird unter zwei Gesichtspunkten analysiert. Zum Einen wird dessen Abhängigkeit von Dehnrate und Temperatur für eine Reihe fester Korngrößen untersucht. Zum Anderen der Einfluss der Korngröße bei gegebenen Verformungsbedingungen studiert. Anhand des Vergleichs mit experimentellen Ergebnissen wird das Modell kritisch diskutiert.

1 Introduction

Contents

From the point of view of structural application, the continuing scientific interest in polycrystalline materials with grain sizes from sub-micron to nanometer is mainly due to their improved mechanical behavior, especially at low homologous temperatures $T_{\mathrm{hom}} = T/T_{\mathrm{M}}$ (where T and T_{M} are (absolute) temperature and melting temperature, respectively), compared to material of conventional grain size (cg) [1]. To a large extent, reported strengthening concerns the onset of plasticity. Hansen [2] and Meyers *et al.* [3] pointed out that such improved mechanical behavior also holds beyond plastic yielding [2, 3]. Recently, for pure Cu[1] of various grain sizes 10 nm $\leq d \leq$ 50 μm the flow stress from uniaxial compression and the hardness from nanoindentation at ambient temperature were compiled [4]. These data indicate that a Hall-Petch relation holds at room temperature even near or in the steady state of deformation, *i.e.*, flow stress increases with decreasing grain size. That suggests that the material is hardened by high-angle grain boundaries at ambient temperature. However, at elevated temperatures and/or low strain rates, for severely plastically deformed Cu with ultrafine grains of 0.35 μm, the steady state flow stress becomes smaller than that of cg material [5–8]. This phenomenon has been attributed to fast dislocation annihilation within high-angle grain boundaries, meaning that high-angle grain boundaries soften the material at elevated temperatures [5]. The term steady state deformation is defined as the state of dynamic equilibrium of the dislocation structure consisting of free dislocations (not incorporated in dislocation networks constituting low-angle grain boundaries) and low-angle boundaries, where both flow stress σ and strain rate $\dot{\epsilon}$ do not change any more with strain ϵ at constant temperature T. In the present work, attempts will be made on microstructural basis to model the role of high-angle grain boundaries in the deformation of pure Cu in a wide range of grain sizes and temperatures.

In this section we shall start with demonstrating the phenomena of grain boundary hardening as well as softening found in Cu with grain size range of $0.01 < \mathrm{d}\ /\mu\mathrm{m} < 50$ in the interval $298 \leq T/\mathrm{K} \leq 470$ corresponding to $0.22 \leq T_{\mathrm{hom}} \leq 0.35$. The deformation mechanisms of relevance will be briefly reviewed in section 1.2. The detailed scope of the current work will be presented in section 1.3.

1.1 Phenomena of grain boundary hardening and softening

Figure 1.1 combines published data of the maximum deformation resistances (maximum stress σ at constant strain rate $\dot{\epsilon}$ and minimum $\dot{\epsilon}$ at constant σ) of Cu of different initial grain sizes in a wide range of temperatures and strain rates [4]. The normalization of the ordinate was done as proposed by Kocks and Mecking [11] by $k_{\mathrm{B}}T/(G\,b^3)\,\ln(\dot{\epsilon}/\dot{\epsilon}_0)$, where k_{B} is Boltzmann constant, G is the shear modulus, b is the length of Burgers vector, and $\dot{\epsilon}_0 = 10^7\ \mathrm{s}^{-1}$. The values of G and b were taken from [12] (also see Table 3.1). This normalization successfully serves the purpose to combine data measured at different temperatures in a narrow band. Grain size varies over a large range from 0.01 μm up

[1] oxygen-free high-conductivity grade

to the dimensions of the single crystalline specimen. The circles stem from tests on bulk specimens with conventional grain size of 50 μm and ultrafine grain (ufg) size of 0.35 μm [13]. The ufg material originally came from the same batch as the cg one and achieved its fine structure by SPD through 12 passes of equal channel angular pressing (ECAP) on route C at room temperature. The tests were performed in uniaxial compression in a temperature range extending from ambient temperature up to $T_{\mathrm{hom}} = 0.33$. For details it is referred to [5, 8]. The triangles stem from hardness H measured in nanoindentation at ambient temperature (see [14]). The materials with small sizes subjected to nanoindentation were prepared in several ways, such as magnetron sputtering ($d \leq 0.031$ μm), mechanical attrition ($d = 0.042$ μm) and ECAP ($d = 0.19$ μm) (see [14] for details). The flow stresses were calculated as $\sigma = H/3$ from the hardnesses H [4].

1.1.1 Grain boundary hardening at low homologous temperature

Comparison of the data from nanoindentation to uniaxial compression tests at a normalized strain rate of about -0.13 shows that the flow stress increases significantly with decreasing d (see Fig. 1.1)[2]. Fig. 1.2 shows the room temperature data from Fig. 1.1 as function of $d^{-0.5}$. Within scatter the data for room temperature are well described by a straight line in agreement with the Hall-Petch relation:

$$\sigma = \sigma_0 + k_{\mathrm{HP}}\, d^{-0.5}\,, \tag{1.1}$$

where σ_0 is the overall resistance of the crystal lattice to dislocation movement and k_{HP} represents the relative hardening contribution of the grain boundaries.

1.1.2 Grain boundary softening at elevated homologous temperature

For elevated temperature of 418 K, the trend is reversed in Fig. 1.2 compared to room temperature, as the maximum flow stress decreases with decreasing d. This decrease is related with increase of the strain rate sensitivity $m = \mathrm{d}\log\sigma/\mathrm{d}\log\dot{\epsilon}$ observed to occur for ufg Cu in Fig. 1.1. The significant difference in strain rate sensitivities causes a crossover in the saturation stresses of ufg and cg Cu at a normalized strain rate of 0.17. This means that ufg Cu becomes softer than the cg variant for normalized strain rates < -0.17 (see Fig. 1.1). There is thus a transition from hardening at low T_{hom} and high strain rate $\dot{\epsilon}$ to softening at elevated T_{hom} and low $\dot{\epsilon}$ in ufg Cu compared to cg Cu. Note that the softening relates to the steady state of deformation, but not to the yield stress which is lower for cg Cu compared to ufg Cu even at elevated temperatures [8].

Breakdown of the Hall-Petch relation has frequently been reported to occur even at low temperature, where yield stress decreases with grain refinement once the grain size is

[2] The fact that the flow stresses for $d = 50$ μm are distinctly higher than those for $d = 23$ μm is not unexpected, as in the first case stresses have been extrapolated to be the steady-state stresses corresponding to $\epsilon \approx 2$ [15] from the values measured at $\epsilon \approx 0.35$, while in the latter case the stresses were measured only at about $\epsilon \approx 0.15$.

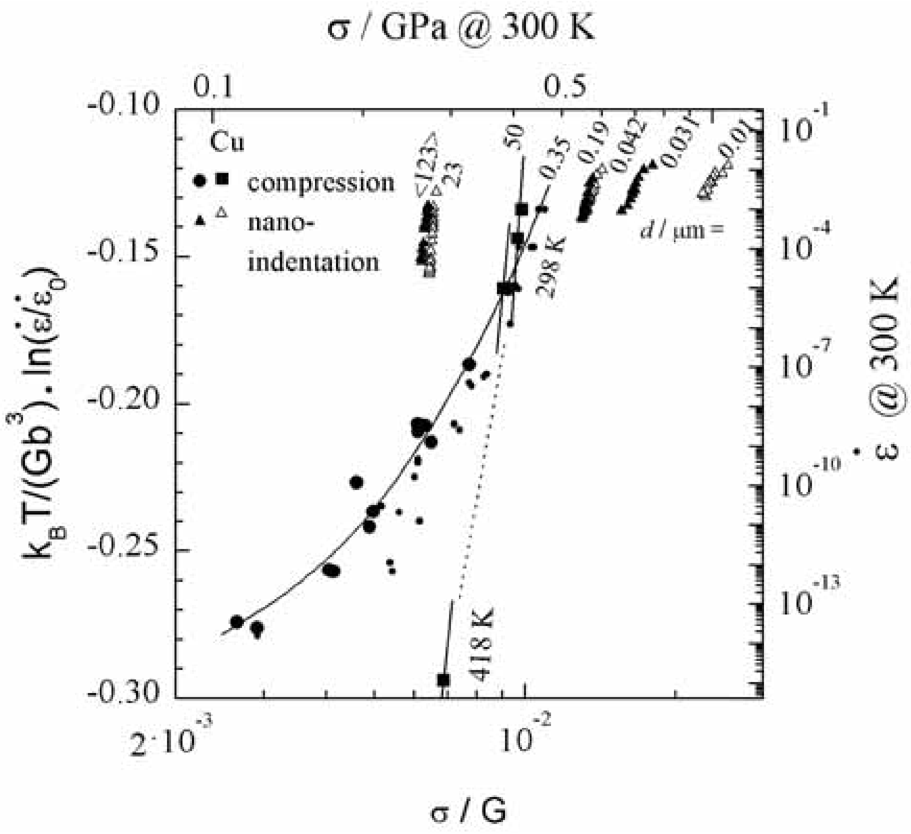

Figure 1.1: Temperature normalized strain rate as function of shear modulus normalized flow stress for Cu with different grain sizes d and a ⟨123⟩-oriented Cu single crystal from nanoindentation at ambient temperature ($T_{\text{hom}} = 0.22$) [4, 14] and uniaxial compression from room temperature up to 448 K ($T_{\text{hom}} = 0.35$) [5, 8, 15]. Large symbols: saturation stress (or steady-state deformation resistances); small symbols: maximum deformation resistance (the flow stress or creep rate measured at the end of a test). Right ordinate axis: strain rate at 300 K.

reduced below a critical value [16–20]. However, as stated by Meyers *et al.* in their recent review paper, "Though researchers have debated the existence of the negative Hall Petch effect, there is insufficient information to validate the existence of this effect" [1].

1.2 Review on deformation mechanisms for grain boundary hardening and softening

This section briefly reviews some relevant deformation mechanisms responsible for hardening/softening by grain boundaries.

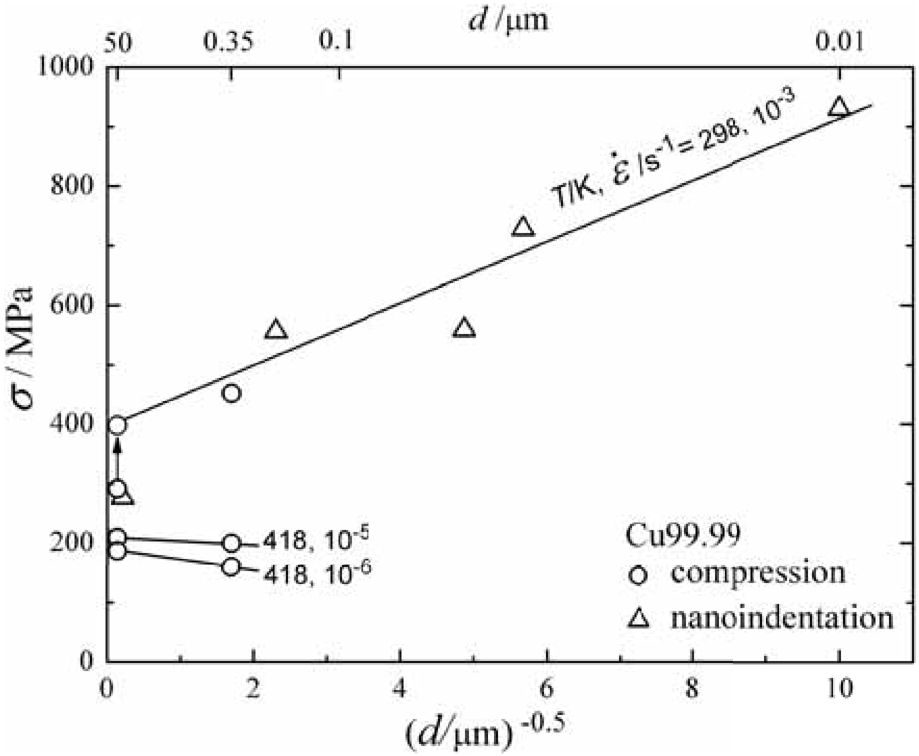

Figure 1.2: Variation of flow stress with inverse square root of grain size d with different T and $\dot{\epsilon}$. The arrow pointing to the saturated flow stress (400±50) MPa of cg Cu with $d = 50$ µm [4]. Data from Fig. 1.1.

1.2.1 Hall-Petch relation and explanation

As stated above, the Hall-Petch relation (1.1) describes not only the yield stress, but also the flow stresses beyond plastic yielding and the hardnesses derived from indentation testing [2–4]. Many theoretical studies have been conducted to understand this relation [21–26]. In the following some of them will be briefly reviewed.

1.2.1.1 Pile up theories

The original mechanism proposed by Hall [21] and Petch [22] involves a pile-up of dislocations against grain boundaries. The grain boundaries act as obstacles, hindering the dislocation glide along the slip planes. When subsequent dislocations move along the same slip plane, the dislocations pile up at the grain boundaries. The dislocations repel each other, so that the stress on the grain boundary increases with increasing number of dislocations in the pile-up. If there are n dislocations in the pile-up, the stress at the grain boundary will be $n\,\sigma$ where σ is applied stress. In order to propagate the plastic deformation, dislocations are needed to be emitted into the neighboring grain. If the critical stress required at a grain boundary for the emission of a dislocation is σ_c, then there needs to be a stress of σ_c/n applied to the sample. In a larger grain there will be more dislocations within the grain, so there will be more dislocations in the pile-up. Therefore a lower applied stress is required to produce a local stress which is sufficiently large to cause emissions of dislocations.

Many researchers have theoretically studied various kinds of pile-ups. These include single-layer single-ended pileups in homogeneous, heterogeneous, and anisotropic media, single-layer double-ended pileups, circular pileups, and multiple-layer pileups. Excellent reviews were presented by Li and Chou [26] and Hirth and Lothe [27].

Several considerations stemming from experimental observations lead one to question the general applicability of the pile-up theories. The first is the lack of direct observation of pile-ups in pure metals. Secondly, Worthington and Smith [28] found that in Fe-3%Si, dislocations are emitted from grain boundaries at stresses much below the yield stress without the help of pile-ups and that these stresses do not seem to depend on grain size. According to the pile-up model, the function of the pile-up is to create a stress concentration at the grain boundary to activate dislocation sources. If these dislocation sources can be activated without a pile-up and at stresses below the yield stress, the necessity for pile-ups is no longer existing. Also, as the number of pile-up dislocations is reduced with grain size, the multiplication effect is lost when the dislocation spacing becomes comparable to the grain size in the nanocrystalline (nano) regime.

Motivated by these considerations, theories without the use of pile-ups have been proposed, *e.g.*, work hardening theories, grain boundary source theories and a theory based on geometrically-necessary dislocations (GNDs).

1.2.1.2 Work hardening theories

In this class of theories the athermal stress component, which is inversely proportional to the average dislocation spacing $\rho^{-0.5}$, serves as a hardening term [24, 29]:

$$\sigma = \sigma_0 + \alpha\, M\, G\, b\, \sqrt{\rho}\,. \tag{1.2}$$

σ_0 is a lattice friction stress. To arrive at the Hall-Petch relation, ρ needs to be inversely proportional to d. The essential assumption of the work hardening theories is that the mean free path of dislocations, Λ, is limited by the grain size d (not by the dislocation structure) so that $\Lambda = \beta\, d$ where β is a constant. Dislocations with a density of ρ gliding a distance L produce a plastic shear strain $\gamma = \rho\, b\, L$, so that $\rho = \gamma/(b\,\Lambda) = \gamma/(b\,\beta\, d)$ with $L = \Lambda$. Inserting the expression into Eq. (1.2) yields (1.1) with

$$k_{\mathrm{HP}} = \alpha\, M\, G\, \sqrt{\gamma}/\sqrt{b\,\beta}\,. \tag{1.3}$$

Supporting evidence for this model was found by Conrad *et al.* [29] who showed that flow stress of niobium (columbium) is linear with the square root of strain as required by Eqs. (1.3) and (1.1) However, as ρ is not generally linearly dependent on ϵ and σ is not generally a parabolic function of ϵ as derived in Eq. (1.3), this treatment is not generally valid.