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Segregation and precipitation stabilizing an ultrafine lamellar-structured Al-0.3%Cu alloy

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ABSTRACT

Understanding the coarsening mechanisms and the role of solute atoms during recovery annealing of ultrafine lamellar-structured alloys produced by high strain deformation is crucial to tailor their microstructures and mechanical properties. In the present work, a lamellar-structured Al-0.3%Cu alloy with a boundary spacing of 200 nm was prepared by cold rolling to a von Mises strain of 4.5 (a thickness reduction of 98%), featuring Cu segregation to high angle lamellar boundaries. During recovery annealing in the temperature range of 100–175 °C, precipitation of fine Al₂Cu particles occurred preferentially at lamellar boundaries. Recovery kinetics was analyzed based on measurements of lamellar boundary spacings in the annealed samples, showing an increase in the apparent activation energy from 77 kJ/mol at the beginning to 106 kJ/mol at the end of recovery. In situ observations of annealing in a transmission electron microscope revealed that the dominant coarsening process is the motion of Y-junctions formed by lamellar boundaries, which is subjected to various degrees of pinning from dislocations, dislocation boundaries and particles. Furthermore, it was found that this local pinning effect can be reinforced with the increase of misorientation angles of the attached dislocation boundaries, the coarsening of Al₂Cu particles and the combined effect of interconnecting boundaries and particles. The results underpinned the importance of alloying elements in stabilizing finely spaced lamellar structures during deformation and annealing, providing guidelines for tailoring stable ultrafine structured alloys.

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1. Introduction

After plastic deformation to high and ultra-high strain, the microstructures of metals often exhibit lamellar morphology and have lamellar boundary spacings in the sub-micrometer and nanometer range. Such ultrafine lamellar-structured metals have been investigated extensively during the past 20 years owing to their high strength [1–5]. The energy stored in this kind of deformation induced ultrafine structures is very high, providing a large driving force for recovery and recrystallization. Therefore, these ultrafine lamellar-structured metals usually lack thermal stability [6–8]. Several methods have been used to stabilize the ultrafine structure, like solid solution, boundary segregation, and precipita-

tion [9–12]. In the process of thermal treatment and during service at an elevated temperature, these stabilization factors themselves may change dynamically, such as precipitation and dissolution of second phase particles [13,14]. These changes are affected by the high densities of grain boundaries and dislocations. For example, accelerated phase transformation by grain boundary segregation has been observed in several materials with ultrafine grains [15,16]. This means that the high density of grain boundary, boundary segregation and precipitation would interact with each other during annealing, resulting in a complex annealing phenomenon.

During annealing, the ultrafine lamellar structure may coarsen continuously through the migration of Y-junctions, which are the triple junctions connecting lamellar boundaries, prior to nucleation of recrystallization [17–19]. The recovery kinetics has been modeled based on the assumption that the average boundary energy

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changes marginally and is taken as a constant during coarsening [20]. However, in materials which are stabilized by alloying elements, this assumption may not be valid during annealing. An obvious phenomenon is that the high solute concentration in the segregated grain boundary may facilitate the nucleation of phase transformation, and the boundary energy and pinning effect of the segregated alloying elements will be changed after precipitation. Therefore, further investigation on the effects of the boundary segregation and precipitation on recovery kinetics is needed to tailor the microstructure and mechanical properties of the ultrafine structured metals and alloys.

Recently, we fabricated an ultrafine lamellar-structured Al-0.3%Cu alloy [21–23] by adding 0.3wt oxygen-free high conductivity copper into a high purity (99.9996%) Al matrix and cold rolling to a thickness reduction of 98%. Our previous post mortem studies have shown that continuous coarsening of the deformed lamellar structure takes place during recovery annealing [21] and that the segregation of Cu solutes and subsequent precipitation of Al₂Cu particles preferentially occur at the lamellar boundaries [21,22]. Therefore, this alloy is an ideal model system for the present study. In this study, we carried out detailed (i) post mortem electron microscopy to quantify the lamellar boundary spacings and analyze the coarsening kinetics and (ii) in situ TEM observations to reveal the detailed pinning mechanisms of segregation and precipitation on the Y-junction motion.

2. Material and experimental procedures

The Al-0.3%Cu alloy used in this experiment was produced from 99.9996% pure Al and oxygen-free high conductivity copper. The as-cast ingot with 1.5–2 mm large grains was forged at 200 °C and then cold rolled to a von Mises strain of 4.5 (98% reduction in thickness) to obtain a 1 mm thick plate. The plate was stored in a freezer to avoid particle precipitation and structural coarsening. To study the recovery kinetics in heavily rolled Al-0.3%Cu, a number of small samples were cut from the as-rolled plate, and then subjected to isothermal annealing at temperatures of 100, 125, 150 and 175 °C over time intervals ranging from 4 min to 4096 min since our previous studies [21,23] showed that initiation of recrystallization began after annealing at 175 °C for 1 h.

The as-rolled material was inhomogeneous through the sample thickness [24], and thereby all characterizations in the present work were focused on the center layer of the samples. The microstructures and chemical compositions were analyzed by means of electron channeling contrast (ECC) imaging, transmission electron microscopy (TEM), super energy-dispersive X-ray spectroscopy (EDS) and atom probe tomography (APT). ECC observations were conducted on the longitudinal section, containing the rolling direction (RD) and the normal direction (ND), of the samples in a JEOL JSM-7800F scanning electron microscope (SEM). Samples for ECC were prepared by mechanical grinding followed by electropolishing at 20 V, -15 °C for 20 s in a solution of 90% ethanol (CH₃CH₂OH) and 10% perchloric acid (HClO₄). Thin foils for TEM were prepared by twin-jet electropolishing using the same solution at -20 °C.

APT was performed in a CAMECA LEAP 4000 HR type local electrode atom probe at a temperature of 50 K with a pulse fraction of 15%, a pulse rate of 200 kHz and a detector efficiency of 36%. Needle-shaped samples for APT were prepared by a standard two-stage electropolishing technique. Reconstruction and quantitative analysis of the APT data were performed using the IVAS™ 3.6.12 software. EDS detections were performed in an FEI Titan G² 60-300 ChemiSTEM with a super EDS system.

TEM characterizations were carried out in a JEOL JEM-2100 electron microscope operated at 200 kV. An online Kikuchi-line analysis system was used to determine the misorientation angles of grain boundaries with a misorientation resolution of 0.3° [25].

In situ observations of recovery annealing were performed inside a transmission electron microscope. TEM foils of the deformed state were mounted in a double-tilt heating holder. After the deformed structure was characterized, the foil was heated to 150 °C in ~10 min, and then held for a period of ~25 min. Other areas of the foil annealed at 150 °C were also investigated after cooling to room temperature. Afterward, the foil was re-heated to 150 °C followed by heating to 250 °C. Likewise, the microstructure after annealing at 250 °C for 25 min was characterized in detail. During both heating and holding periods, the microstructural changes were recorded by a TVIPS Fast Scan camera with a maximum frame rate of 12 fps at full resolution. In situ observations with different target temperatures were carried out for a few samples to better characterize the microstructural evolution during recovery.

3. Results

3.1. As-deformed state

The microstructure of the deformed state has a strong influence on the recovery and recrystallization behavior during subsequent annealing treatments [26,27]. Therefore, a comprehensive characterization of the cold-rolled sample is essential in understanding the annealing phenomena.

3.1.1. Lamellar structure

The deformed microstructure produced by cold rolling to a large strain shows a typical lamellar morphology in the longitudinal section (RD-ND plane). The boundaries in the lamellar structure fall into two categories, which are extended lamellar boundaries along the RD named geometrically necessary boundaries (GNBs) and short incidental dislocation boundaries (IDBs) interconnecting the lamellar boundaries. Most of the misorientation angles across the GNBs are characterized as high angles (>15°), and the average boundary spacing along the direction perpendicular to the GNBs has been measured to be 200 nm. Meanwhile, the IDBs consist of low angle boundaries with an average misorientation angle of 3.6° and an average spacing of 780 nm. A more detailed description of the deformed structure can be found in [21].

3.1.2. Cu distribution

Distribution of Cu atoms at boundaries in the deformed structure has been investigated by using ChemiSTEM-EDS and APT. According to our previous work [22], the vast majority of the lamellar structure is free of particles, although a few small particles can be observed lying at the lamellar boundaries. Here, a new example of Cu distribution in the deformed sample combining EDS mapping and TEM characterization is presented in Fig. 1. It can be seen that all the lamellar boundaries with strong Cu segregation are characterized as high angle boundaries in this example.

More results coupling EDS spectroscopy and boundary misorientation measurement have been counted and plotted in Fig. 2. There are 88 lamellar boundaries analyzed in total. The result indicates a strong correlation between Cu segregation and boundary misorientation. Cu segregation occurs at most of lamellae boundaries with misorientation angles higher than 15°, whereas there is a small fraction of low angle (<15°) boundaries having segregation. This observation suggests that Cu atoms prefer to segregate at high angle boundaries, in good agreement with the literature [28–30]. Meanwhile, it should be emphasized that all the observed low angle boundaries with Cu segregation belong to lamellar boundaries, which are parallel to the RD. Furthermore, no extensive segregation at IDBs was observed in all the EDS spectroscopies.

To further understand the distribution of Cu at the segregated lamellar boundaries, detailed APT analyses were performed. Fig. 3

Fig. 1. Microstructure and Cu segregation at boundaries in the 98% cold rolled Al-0.3%Cu sample. (a) TEM image with misorientation angles of lamellar boundaries indicated. The position used to measure misorientation is marked by a red line. Misorientation angles of lamellar boundaries with and without strong Cu segregation are marked by yellow and white numbers, respectively. (b) EDS mapping from the same area.

Fig. 2. The misorientation dependence of Cu segregation at lamellar boundaries.

shows two typical examples of reconstructed atom probe images. Strong enrichment of Cu at lamellar boundaries can be observed both in Figs. 3a and 3c, in agreement with the EDS results. Meanwhile, analyses of the same data in Figs. 3b and 3d reveal some Cu atom clusters larger than 10 atoms (average distance between each atom less than 0.8 nm) in the boundaries, indicating that Cu atoms are unevenly distributed in the boundaries. It is noteworthy that both the concentration of Cu and the density of Cu cluster at different segments of the same boundary are not uniform as shown in Fig. 3d. The solid solubility of Cu in Al matrix at room temperature is 0.1–0.2 wt.%, and it could be higher in nanostructured Al matrix because of the high density of crystallographic defects. Thus, most of the Cu atoms in the deformed sample are present in solid solution, in accordance with both the ECC and TEM results, where only a few small particles are located at lamellar boundaries and triple junctions. The APT data show that the Cu concentration in the matrix is about 0.2 wt.% for the as-deformed sample.

Fig. 3. APT characterizations of Cu segregation at lamellar boundaries in the deformed sample. (a) and (c) Distribution of Cu in two regions; (b) and (d) Cu clusters in the two regions.

3.2. Recovery

3.2.1. Post mortem observations

Fig. 4 presents the microstructural evolution of the samples annealed at 100 °C for different times. It is clear that the lamellar structure shows a continuous coarsening while retaining a lamellar morphology with increasing annealing time, although a few equiaxed grains were observed within the lamellar structure when the annealing time was up to 4096 min. Compared to the initial deformation structure, recovery annealing gradually transformed the structure into a more equiaxed pattern owing to the increase in the average lamellar boundary spacing (i.e. lamella thickness) and the decrease of the length of some lamellae, both resulted from triple junction motion in the rolling plane. Meanwhile, second phase particles (Al_2Cu) were also observed by ECC, appearing as bright spots in Fig. 4. At the beginning of annealing as shown

Fig. 4. ECC images showing microstructural evolution in the samples isothermally annealed at 100 °C for (a) 4 min, (b) 16 min, (c) 32 min, (d) 64 min, (e) 128 min, (f) 256 min, (g) 1024 min, (h) 4096 min. The particles appear as bright spots.

in Fig. 4a and 4b, the number of Al_2Cu particles was quite small. More particles precipitated at lamellar boundaries after annealing for 32 min (Fig. 4c). There was a steady growth in the number of particles with increasing annealing time. A vast number of particles were observed in the sample annealed for 256 min (Fig. 4f), and there was a slight increase as the annealing time was up to

4096 min. The majority of the second phase particles were located at lamellar boundaries, and a small part of particles precipitated in the interior of some lamellae. It is worth noting that some of the interior particles are lying in line along the rolling direction, which is highly likely due to precipitation at lamellar boundaries followed

Fig. 5. Variation of Al_2Cu particle density (number per unit area) during isothermal annealing at different temperatures.

by removal of these boundaries through triple junction migration during annealing.

ECC observations of the samples annealed isothermally at 125, 150 and 175 °C showed similar microstructural coarsening and precipitation behavior to the 100 °C annealed samples. In addition, faster coarsening of the lamellar structure and earlier precipitation of particles were observed for higher annealing temperatures. For example, some equiaxed grains were observed after annealing at 150 °C for 1024 min, and similar features can be observed after annealing at 175 °C for only 60 min. Similarly, annealing at 125 °C for 16 min and annealing at 175 °C for 4 min showed a similar number of particles precipitated in the lamellar structure. The amount of the precipitated particles during annealing at different conditions was quantified by the number density of particles (the number of particles per unit area) counted from the ECC images.

The number density variation with annealing time at different temperatures is shown in Fig. 5. It can be seen that the number density of Al_2Cu particles increased continuously and then reached a steady level with little changes with further increasing annealing time. More rapid precipitation occurred at higher annealing temperatures according to the rough slope of the plotted lines in Fig. 5, which indicates that precipitation of Al_2Cu particle is highly sensitive to the annealing temperature. The number density of particles during annealing at 175 °C showed a rapid increase in the first 4 min followed by a slow increase, possibly due to more coarsening of particles at this temperature, i.e. a larger particle size.

3.2.2. Coarsening kinetics

Borelius and co-workers [31] have suggested a rate equation for recovery as

$$\frac{dP}{dt} = -K_0 P \exp\left(-\frac{Q_0 - \beta P}{RT}\right) \quad (1)$$

where P is the stored energy decreasing during annealing, t is the annealing time, R is the universal gas constant, T is the absolute temperature, Q_0 is the apparent activation energy at the end of recovery, and the three fitting parameters K_0 , Q_0 , and β are associated with the operative recovery mechanisms. This recovery rate equation allows the apparent activation energy to vary during recovery depending on the remaining stored energy, in agreement with Kuhlmann's original suggestion and experimental data [32].

Recently, a unified coarsening model for deformation microstructures was proposed based on Eq. (1) by correlating the stored energy P with the boundary spacing D of the coarsening microstructure and assuming the average boundary energy as a

Fig. 6. Variation of the average lamellar boundary spacing during isothermal annealing at different temperatures.

constant during coarsening [20]. The stored energy is expressed as [27,33]

$$P = \frac{\gamma\alpha}{D} \quad (2)$$

where γ is the average boundary energy, α is a geometrical constant depending on the morphology. The rate equation for recovery can be transformed to

$$\frac{dD}{dt} = k_1 D \exp\left(\frac{k_2}{DT}\right) \quad (3)$$

$$k_1 = K_0 \exp\left(-\frac{Q_0}{RT}\right) \quad (4)$$

$$k_2 = \frac{\alpha\beta\gamma}{R} \quad (5)$$

where k_1 is temperature dependent and k_2 is a constant.

With the aid of exponential integrals, the integrated form can be expressed as

$$\text{Ei}\left(-\frac{k_2}{D_0 T}\right) - \text{Ei}\left(-\frac{k_2}{DT}\right) = k_1 t \quad (6)$$

where Ei is the exponential integral function.

Subsequently the apparent activation energy at any stage of coarsening can be obtained as

$$Q = Q_0 - \frac{k_2 R}{D} \quad (7)$$

Eq. (6) describes the continuous coarsening of a deformation structure during isothermal annealing. By a two-step fitting procedure [20,34], the apparent activation energies at different stages of coarsening can be estimated.

In the present study, the structural evolution in heavily rolled Al-0.3%Cu during isothermal annealing at temperatures of 100, 125, 150 and 175 °C covering a time span from 4 min to 4096 min has been characterized by ECC. The lamellar boundary spacing D of each annealed sample has been measured by the line-intercept method along the ND based on a number of ECC images, as plotted in Fig. 6, which serves as the input to study the coarsening kinetics based on the above coarsening model. After fitting the data based on Eq. (6), the average value of k_2 was calculated as 0.0007 m·K. The corresponding coarsening curves fitted collectively for different temperatures are drawn in Fig. 6, showing a good fitting with the experimental data.

In order to determine the apparent activation energy, it is reasonable to assume that the same recovery mechanisms operate at

Fig. 7. The dependence of apparent activation energy on the lamellar boundary spacing during coarsening. The inset shows the determination of Q_0 .

different annealing temperatures at a specified coarsening stage (i.e. the same apparent activation energy at a given grain size independent of temperature). According to Eq. (4), the temperature dependence of the model parameter k_1 is an Arrhenius-type relationship, which was plotted in Fig. 7 by using the values of k_1 at different temperatures obtained from the previous fitting. Thus, the apparent activation energy at the end of coarsening (i.e. Q_0) was calculated as 106 kJ/mol from the slope of the linear fitting in Fig. 7, in a good agreement with the result reported in our previous paper based on hardness analysis [23]. The detailed dependence of the apparent activation energy on the boundary spacing based on Eq. (7) was drawn in Fig. 7. It can be seen that the apparent activation energy increased as recovery proceeded and it increased rapidly at the beginning of recovery and slowly at later stages. At the beginning of recovery ($D = D_0$), the apparent activation energy was calculated as 77 kJ/mol.

3.2.3. In situ observations

In order to investigate the structural coarsening and its interaction with dislocations, boundaries and particles in real-time,

we performed in-situ annealing inside a transmission electron microscope. Little changes were observed during long temperature-holding periods, indicating a weak time dependence of recovery, in agreement with the literature [18,35]. Thus, the focus was on the temperature-rising period and the temperature-reached moment of the in-situ annealing. Fig. 8 provides a panoramic view of the microstructural evolution after reaching the target temperatures. Compared to the deformed state (Fig. 8a), significant changes can be observed after the annealing temperature has reached 150 °C (Fig. 8b). Besides a decrease in the density of loose dislocations, there was a reduction in the number of lamellae as a result of the migration of triple junctions (each connecting three lamellar boundaries) along the RD, leading to widening of the lamellar structure along the ND, accompanied by the precipitation of a considerable quantity of particles, most of which lay at grain boundaries. When the annealing temperature was further increased to 250 °C (Fig. 8c), a coarser and clearer structure with fewer particles was formed by fast migration of triple junctions along the RD and re-dissolution of many particles. At the same time, a few larger particles were observed both at grain boundaries and inside grains. It is a remarkable fact that a string of particles was distributed along the RD in the interior of a widened lamella (in Fig. 8c), following the removal of a lamellar boundary (Fig. 8b), where the particles originally precipitated, consistent with the result of furnace annealing of bulk samples.

Besides the global coarsening through triple junction motion, the evolution of individual lamellae and triple junctions during recovery were also characterized. Fig. 9 shows an example in a lamellar structure during annealing up to 150 °C. In Fig. 9a, a Y-junction (pointed by an orange arrow) in the as-deformed structure can be seen on the bottom left of the micrograph. This Y-junction was pinned on the right side by an adjoining interconnecting boundary with a misorientation of 0.5°. A few particles were located at the upper two lamellar boundaries constituting the Y-junction. When the annealing time was longer than 105 s, the Y-junction started to adjust the morphology a little and migrated along the RD. With the increase of the temperature, the junction unpinned from the interconnecting boundary after 40 s and was in the position shown in Fig. 9b. Afterwards the Y-junction rapidly went through a few small particles and attached dislocations on

Fig. 8. A gradual evolution of the lamellar microstructure in the same position of the TEM foil during in situ annealing. (a) Cold-rolled state; (b) at 150 °C for about 25 min; (c) at 250 °C for about 25 min; (d) sketch marked as (1), (2) and (3) corresponding to the areas enclosed by the dashed lines in (a), (b) and (c), respectively. Some triple junctions (i.e. Y-junctions) in (a) are marked by orange arrows.

Fig. 9. In situ TEM observations of Y-junction motion in Al-0.3%Cu during annealing at temperatures changing from 20 °C to 150 °C. The annealing times are given on each micrograph. The positions of the Y-junction pointed by the orange arrow in (a)–(h) is traced and corresponds to the positions marked by A–H in (i). Two IDBs in the neighboring lamellae are also traced and their misorientation angles are shown. The migration direction of Y-junction is shown by the black arrow. Some particles are shown by black dots.

the way (Fig. 9c). Stronger pinning occurred when the junction met a group of particles originally existed at the lamellar boundaries (Fig. 9d and e). The junction took ~3 min to pass the particle group completely, as shown in Fig. 9f. After a short while, the junction met another dislocation boundary (Fig. 9g), whose misorientation angle was measured as 0.8°, and moved only a little in the following 90 s before the temperature was stabilized, owing to a large dragging force provided by the newly encountered dislocation boundary. Later, the junction also migrated only a little under the pinning of the boundary after keeping at 150 °C for 25 min, as shown in Fig. 9h.

Subsequent in-situ investigation focusing on the migrated Y-junction shown in Fig. 9 was performed with a target temperature of 250 °C. The subsequent motion of the Y-junction and the

evolution of the surrounding structure are presented in Fig. 10. Compared to the junction after annealing at 150 °C, the observed morphology of the junction before further heating changed slightly as a consequence of the movement and tilting of the foil. After the temperature was increased to 190 °C, the corresponding microstructure is shown in Fig. 10a. No changes in morphology and no movement of boundaries occurred, apart from the redissolution of some particles both at grain boundaries and inside grains. Thus, the microstructure as shown in Fig. 10a was considered as the initial microstructure for the second step of heating. With further increasing temperature, this Y-junction migrated again. It took 153 s for the Y-junction to get unpinned from the dislocation boundary on the right side (Fig. 10b). Afterwards, the Y-junction interacted with loose dislocations on its left side and got

Fig. 10. In situ TEM observations of Y-junction motion in Al-0.3%Cu during annealing at temperatures changing from 150 °C to 250 °C. The annealing times are given on each micrograph. The positions of the Y-junction pointed by the orange arrow in (a)–(e) are traced in (a–e). Two IDBs in the neighboring lamellae are also traced and their misorientation angles are shown. The migration direction of Y-junction is shown by the bold black arrow. The structural evolution in (e)–(g) is traced in (e–g). The black dashed line corresponds to the former microstructure. The black arrow indicates the migration direction of the corresponding lamella. Some particles are shown by black dots.

unpinned after 1 s. The Y-junction was then pinned strongly by a large particle and a new interconnecting boundary with a misorientation angle of 2.4° on its right side, as shown in Fig. 10c. There were little changes except for some minor adjustments in morphology in the next 4 s (Fig. 10d). This configuration was rather stable in the following 6 min owing to the larger pinning force from both the interconnecting boundary and the particle, although the particle tended to shrink slowly (Fig. 10e). It can also be observed from Fig. 10d to Fig. 10e that the lamella on the left side of the investigated Y-junction became wider in that period of time as a result of the migration of neighboring triple junctions along the RD. In the following time of less than 1 s (from Fig. 10e to Fig. 10f), migration of another Y-junction (outside the viewing area) from

the upper-right direction led to the shortening of the widened lamella on the left side of the first Y-junction. It is worth noting that this new junction also stopped when it was very close to the same particle, as shown in Fig. 10f. At that point, the lamellar boundary between those two junctions transformed to be perpendicular to the RD, resembling the morphology of an interconnecting boundary. That configuration remained stable both in the following limited temperature-rising period and at 250 °C for 25 min even though the particle re-dissolved completely (Fig. 10g), indicating a strong stabilizing effect through local rearrangement of lamellar and interconnecting boundaries.

More observations of Y-junction motion during in situ annealing were counted and plotted in Fig. 11. Almost all recorded Y-

Fig. 11. Statistics of Y-junctions interacted with particles in Al-0.3%Cu during in situ annealing at different temperatures.

junctions moved during annealing, indicating the universality of this coarsening mechanism. The disappearance of most Y-junctions occurred at the early stage of coarsening, leading to the removal of the corresponding lamellae, most of which were thinner than the average. For annealing starting from 20 °C, most of the disappeared Y-junctions were free from particle pinning; most of those moved but retained Y-junctions, experienced different levels of pinning from particles during migration. After annealing, these retained Y-junctions typically rested in positions pinned by particles and/or interconnecting boundaries. During further annealing starting from 150 °C, many retained Y-junctions unpinned from particles and disappeared due to the high annealing temperature.

During the migration of a Y-junction, dislocations and dislocation boundaries in neighboring lamellae also interacted with the junction, retarding its migration. Fig. 12a shows an example, where some dislocations seemed to be dragged out from an interconnecting dislocation boundary, and glided following the motion of the Y-junction. This Y-junction at the resting position was further

pinned by another interconnecting boundary. This kind of pinning, referred to as structural pinning [18], was common in the recovered Al-0.3%Cu, both in the bulk samples and in situ annealed foil samples. Moreover, the pinning from interconnecting boundaries was superimposed by Al₂Cu particle pinning since particles were frequently observed next to those interconnecting boundaries, pinning the same Y-junctions, as shown in Fig. 12b. This combined pinning by both particles and interconnecting boundaries greatly stabilized the microstructure.

In order to further reveal the effect of particle and interconnecting boundary on Y-junction motion, the positions of Y-junctions at different annealing times were recorded and the migration distances of Y-junctions at the corresponding times were measured based on in situ observations of annealing. Fig. 13a shows the variation of migration distance of the Y-junction investigated in Figs. 9 and 10 with the annealing time. This Y-junction quickly moved 840 nm in the first three minutes and then slowed down significantly due to the pinning from particles (corresponding to the position D in Fig. 9). After passing through this set of particles, the IDB pinning (corresponding to the position G in Fig. 9) reduced the migration rate again and only migrated slightly during subsequent annealing. As the annealing temperature was further increased, this Y-junction was unpinned from the interconnecting boundary and moved about 500 nm. Then a combined pinning from a particle and an interconnecting boundary reduced the migration rate close to zero. The variations of migration distances of other Y-junctions with annealing time at different temperatures were plotted in Fig. 13b, which is consistent with Fig. 13a, showing significant decreases in the migration rate when a Y-junction met particles and/or interconnecting boundaries.

4. Discussion

4.1. Effect of solute Cu on deformation microstructure

It has been suggested that solute atoms play a crucial role in fabricating ultra-fine grained or nanostructured alloys [36–40]. In the present work, a lamellar structure with a boundary spacing of 200 nm is prepared in Al-0.3%Cu by cold-rolling to a strain of 4.5. This is much smaller than the boundary spacing in commercial purity aluminum AA1050 (0.25 wt.% Fe and 0.15 wt.% Si as major im-

Fig. 12. Structural pinning of Y-junction motion by (a) neighboring dislocations and dislocation boundaries assisted by (b) particle pinning in Al-0.3%Cu after in situ annealing.

Fig. 13. Variations of migration distances of Y-junctions in Al-0.3%Cu during coarsening. (a) The Y-junction investigated in Figs. 9 and 10; (b) other Y-junctions. The pinning of Y-junction motion by particles and dislocation boundaries is pointed by blue and red arrows, respectively. t_0 is the starting time of Y-junction motion.

purities) produced by ARB to a strain of 4.8, where the boundary spacing is 400 nm [41]. In these two Al alloys, Cu is mainly dissolved in the Al matrix and strongly segregated at lamellar boundaries, whereas Fe and Si are mainly present in particles. Therefore, this high concentration of Cu atoms at lamellar boundaries appears to be the key cause of the finer microstructure in Al-0.3%Cu, where strong Cu segregation leads to stable lamellar boundaries during deformation.

It has been suggested that Y-junction migration during deformation is mechanically assisted—enhanced by a dynamic environment with a high concentration of excess vacancies, a high density of gliding dislocations and high internal stresses [42]. However, Cu atoms may still significantly reduce the mobility of lamellar boundaries and Y-junctions in this dynamic environment through their strong binding with the boundaries/junctions and sluggish long-range diffusion [43,44]. The result is in agreement with previous work on Al-4wt.%Cu alloy processed by surface mechanical grinding treatment at liquid nitrogen temperature [45], where grain boundary segregation of Cu was reported in the gradient nanostructured surface layer.

4.2. Effect of solute Cu on microstructural coarsening

The addition of solutes not only promotes the structural refinement during deformation but also stabilizes the deformed microstructure during annealing [12,27,37,46]. Recrystallization was remarkably delayed (annealing at 225 °C for 1 h is needed to get a fully recrystallized structure) with the help of a small concentration of Cu solutes in the current study as compared to high purity Al (99.9996%) [47]. An increase in recrystallization temperature was also reported in heavily cold-rolled Al-1%Si (1 wt.% Si) alloy [48] and commercial purity aluminum AA1050 [49]. Full recrystallization was obtained after annealing at 250 °C for 1 h for the former and at 300 °C for 2 h for the latter. The stabilizing effect of solutes during annealing is closely related to the activation energy for their diffusion. The coarsening kinetics of the deformed Al-0.3%Cu during annealing has been analyzed based on the unified coarsening model proposed by Yu and Hansen [20], and the apparent activation energy for continuous coarsening of the deformed lamellar structure has been estimated. The low activation energy (77 kJ/mol) at the early stage of structural coarsening may be attributed to the high stored energy manifested in a high density of crystallographic defects in the ultrafine scaled structure, indicating a weak solute drag or short-circuit diffusion of solutes [50,51]. The relatively low activation energy led to a rapid coarsening of the lamellar structure as shown in Fig. 6. As structural coarsening proceeded, the apparent activation energy increased gradually and was up to 106 kJ/mol at the end of the process. This estimated

activation energy, is between that for grain boundary diffusion of Cu in Al (89 kJ/mol) and that for lattice diffusion of Cu in Al (134 kJ/mol) [52,53], indicating the importance of both solute drag and short circuit diffusion [54,55]. Despite a higher solute concentration of Cu compared to Fe in the Al matrix, the lower activation energy for diffusion and the higher diffusivity of Cu compared to Fe in Al led to a lower thermal stability (i.e. lower recrystallization temperature) of Al-0.3%Cu than commercial purity aluminum AA1050, where the apparent activation energy at the end of uniform coarsening was reported to be 240 kJ/mol [51,52]. The result therefore indicates the importance of the type of solutes in stabilizing the deformation microstructure during annealing; solutes with a high activation energy for diffusion and a low diffusivity at the annealing temperatures are preferred.

The above results reveal that there may be a trade-off between the finest lamellar structure that can be reached and the thermal stability of the lamellar structure by a single alloying element in Al. For example, Cu as a solute element leads to a finer deformation microstructure, whereas Fe leads to a higher thermal stability. The results point to the importance of using multiple alloying elements in order to obtain fine microstructures with a high thermal stability. One successful example is commercial purity aluminum AA1100 [56,57], which contains both Cu and Fe solutes. Its deformation microstructure is as fine as Al-0.3%Cu and the recrystallization temperature is as high as AA1050 [49]. However, further research is needed to better understand the effect of different solutes and their interaction.

4.3. Particle pinning of Y-junction motion

Thermally activated Y-junction motion was found to be the dominant mechanism for uniform coarsening of the heavily cold-rolled Al-0.3%Cu, in agreement with previous observations in Al, Fe and Ni alloys of lamellar microstructures [19,20]. The structural coarsening in Al-0.3%Cu was accompanied by the precipitation of Al_2Cu particles, resulting in the interaction of Y-junction motion with Al_2Cu particles, as presented in Figs. 9b-f and 10c-f. This interaction provided a pinning effect on Y-junction motion and retarded microstructural coarsening.

The pinning efficiencies can be determined from the migration rate of Y-junction revealed in Fig. 13 (i.e. the slope of the plotted curve). Small particles have a limited pinning effect, as the interaction times for small particles in Fig. 9b-d were very short and the corresponding migration rates for those Y-junctions in Fig. 13 were virtually unaffected. The weak pinning from small particles may be understood from three aspects. Firstly, the volume fraction of small particles was relatively low, which in principle favors boundary passage [58]. Then, the pinning force of individual particle is

Fig. 14. Schematic drawing showing the particle (solid dot) pinning of (a) normal boundary migration; (b) Y-junction motion; (c) Y-junction motion by at least two particles. The arrows indicate the directions of normal boundary migration and Y-junction motion.

proportional to the radius of the particle according to the Zener pinning equation [59,60] and thus is small. In addition, these small particles were distributed along lamellar boundaries so that they were passed one by one without much synergy—boundary migration only occurs in the vicinity of the moving Y-junction and interacts with small particles one by one. In contrast, large particles were difficult to be passed as shown in Fig. 9d–f, reflected by the fact that the migration rate of Y-junctions decreased significantly after encountering these large particles—each particle alone exerted a large local pinning force.

However, compared to the pinning of normal boundary migration, the pinning effect of a single particle on Y-junction motion is rather limited. In the case of the pinning of normal boundary migration in 2D, as sketched in Fig. 14a, a negative boundary curvature is formed and the moving boundary may be completely pinned by the particle [61,62]. In the case of the pinning of Y-junction motion in 2D (Fig. 14b), the curvature near the particle is always positive, although it decreases continuously as the two receding boundaries migrate towards each other. In other words, a single particle cannot completely stop a Y-junction—the driving force provided by the curvature cannot be reduced to zero. To further reduce the driving force, at least two closely-spaced big particles are needed to simultaneously pin a Y-junction, as shown in Fig. 9d–e and sketched in Fig. 14c. In 3D, similar pinning requires two arrays of big particles interacting simultaneously with one Y-junction. It is therefore expected that a limited volume fraction of particles cannot pin Y-junction motion completely although they can retard the motion by reducing the driving force.

4.4. Structural pinning of Y-junction motion

Another important observation of in situ annealing is the interaction of Y-junction motion with dislocations/dislocation boundaries in neighboring lamellae. The reduction of migration rate of Y-junction after interacting with interconnecting boundaries is shown in Fig. 13, which can be interpreted as structural pinning from interconnecting boundaries (Figs. 9g and 12a). Y-junction motion leads to the bowing and extending of interconnecting boundaries attached to the receding lamella boundary; interconnecting boundaries resist extending and drag the moving Y-junctions. Thus, extra energy is required to overcome the pinning force to unpin Y-junction from the interconnecting boundary.

Many parameters of dislocation boundaries can affect the pinning force and the most important parameter is the misorientation angle, which, to a large extent, determines the boundary energy [63]. An interconnecting boundary with a high misorientation angle may provide a large pinning force owing to the high boundary energy, leading to a low Y-junction migration rate as experimen-

Fig. 15. Misorientation angle distributions for the IDBs that show pinning of Y-junctions and no pinning of Y-junctions in the bulk sample annealed at 150°C for 1 h.

tally observed (Fig. 13). In addition, based on the EBSD data of the bulk sample annealed at 150°C for 1 h, misorientation angle distributions of IDBs pinning Y-junctions and not pinning Y-junctions are plotted in Fig. 15. It is shown that the fraction of IDBs pinning Y-junctions increases significantly with increasing misorientation angle. This result indicates that IDB with a larger misorientation angle can exert a stronger force, i.e. the retained Y-junctions after annealing tend to stop at IDBs with larger misorientation angles. Moreover, the misorientation angle has an influential effect on solute segregation at low angle grain boundary [28,64]. Segregation of more solutes at interconnecting boundaries as a result of the increase of misorientation angle may reinforce the pinning. Compared to the strong pinning effect of interconnecting boundaries, loose dislocations have a much weaker effect, since it is much easier to drag one dislocation than an interconnecting boundary (just like it is easier to unpin one particle than an array of particles).

Structural pinning of Y-junction motion from interconnecting boundaries may be reinforced by Al_2Cu particle, as sketched in Fig. 16b. Compared to the pinning of an interconnecting boundary (Fig. 16a), the addition of a particle or an array of particles stabilizes both the interconnecting boundary and lamellar boundary, leading to a more stable configuration, which is frequently observed, e.g. in Fig. 12b.

Another kind of structural pinning is from an attached lamellar boundary, which can be observed in Fig. 10e–f and is sketched in Fig. 16c–d. When two adjacent Y-junctions migrate towards each

Fig. 16. Schematic drawing showing the structural pinning of Y-junction motion. (a) By an interconnecting boundary; (b) by an interconnecting boundary assisted by particle pinning (solid dot); (c) and (d) by a shared lamellar boundary between two Y-junctions; (e) by a shared lamellar boundary assisted by particle pinning. The arrows indicate the directions of Y-junction motion.

other, the shared lamellar boundary between two Y-junctions will shorten continuously and transform to be perpendicular to the RD, resembling the morphology of an interconnecting boundary. Such a configuration greatly reduces the driving force for Y-junction migration and stabilizes the microstructure. When combined with particle pinning, an even more stable configuration may be produced, as sketched in Fig. 16e. The combination of structural pinning and particle pinning plays a curial role in stabilizing the lamellar structure during annealing of heavily rolled Al–0.3%Cu.

5. Conclusions

The coarsening kinetics and the role of solute atoms during recovery annealing of an ultrafine lamellar-structured Al–0.3%Cu alloy produced by 98% cold rolling have been studied by SEM-ECC characterizations of bulk samples and in situ TEM observations of foil samples. The pinning from dislocations, dislocation boundaries and particles on Y-junction motion have been analyzed. The following conclusions can be drawn.

- 1) Segregation of solute Cu at most of high angle lamellar boundaries is observed in the deformed sample, which reduces the overall energy of the structure and the mobility of lamellar boundaries and Y-junctions, leading to an ultra fine lamellar structure with a high density of dislocations.
- 2) Y-junction motion dominates the uniform coarsening of the deformed lamellar microstructure during recovery annealing. The apparent activation energy for Y-junction motion is calculated to increase from 77 kJ/mol at the beginning to 106 kJ/mol at the end of recovery, which is the main cause of a significant decrease in the coarsening rate at later stages of coarsening.
- 3) The pinning from dislocations, dislocation boundaries and particles on moving Y-junctions reduces the rate of Y-junction motion and delays the removal of thin lamellae. The local pinning effect can be reinforced by the increase of misorientation angles of the attached dislocation boundaries, the coarsening of particles and the combination of interconnecting boundaries and particles.
- 4) A comparison with the results reported for commercial purity Al containing impurity element Fe shows that Cu is more effective than Fe in retarding dynamic recovery due to its higher concentration at lamellar boundaries, whereas Fe is more effective than Cu in retarding microstructural coarsening during annealing due to its higher activation energy for diffusion in Al.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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