Hardening by Annealing and Softening by Deformation in Nanostructured Metals

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We observe that a nanostructured metal can be hardened by annealing and softened when subsequently deformed, which is in contrast to the typical behavior of a metal. Microstructural investigations point to an effect of the structural scale on fundamental mechanisms of dislocation-dislocation and dislocation-interface reactions, such that heat treatment reduces the generation and interaction of dislocations, leading to an increase in strength and a reduction in ductility.

A subsequent deformation step may restore the dislocation structure and facilitate the yielding process when the metal is stressed. As a consequence, the strength decreases and the ductility increases. These observations suggest that for materials such as the nanostructured aluminum studied here, deformation should be used as an optimizing procedure instead of annealing.

From the beginning of our civilization, metalworkers have known that when a metal becomes too hard—for example, when forged—it can be softened by annealing. By choosing the right combination of annealing temperature and time, a desired combination of strength and ductility can be achieved. The current focus is on nanostructured metals that have extreme strength but limited ductility and formability, which reduces their applicability. The extreme strength is obtained through a structural refinement of the grains down to nanometer dimensions, and an optimization of ductility has been sought through annealing. It has been shown (1) that when annealing under conditions that produce a structure with bimodal distribution of grain sizes from nanometer to micrometer scales, the strength of nanostructured metals decreases slightly but the deformation-induced hardening (i.e., work-hardenability) of the coarse grains in the structure gives ductility. It has been also discovered (2–4) that during annealing, it is in metals produced by inert gas condensation (2–4), electrodeposition (5, 6), and plastic deformation to very high strains (7–10). Associated with the hardening, a decrease in the tensile ductility has been reported (5, 9, 10) where tensile tests were carried out to evaluate the mechanical properties. This unusual, annealing-induced hardening has been related to changes in structural characteristics [e.g., the grain boundary structure (11)], but various hypotheses have not been verified. The present work has two objectives: to improve our understanding of the changes in properties and structure when a nanostructured metal is annealed, and to use such findings to inspire the development of new optimization processes.

We investigated annealing behavior in a fully dense, nanostructured aluminum of commercial purity (99.2%) that was prepared by a high-strain rolling deformation known as accumulative roll bonding (ARB) (12). Aluminum sheets of a final thickness of 1 mm were produced by a six-cycle ARB processing to an equivalent strain of 4.8 (13). The ARB-processed state showed a weak crystalline texture and a lamellar microstructure of dislocation boundaries and grain boundaries characteristic of high-strain rolling of metals and alloys. The lamellar boundaries are parallel to the rolling plane, with an average spacing of 180 nm. This lamellar morphology and the relatively coarse boundary spacing ensure the elimination of grain boundary sliding during tensile testing. Tensile specimens of gauge dimensions 10 mm by 5 mm were machined from the sheets and tested at room temperature. The engineering stress-strain curve of the ARB sample (Fig. 1, curve 1) shows a very high yield stress (259 MPa) and ultimate tensile stress (UTS, 334 MPa) and a reasonably good tensile ductility, as expressed by total elongation (7%) and uniform elongation (1.8%). This yield stress is nearly 10 times that of a coarse-grained material with a grain size of 50 μm (~28 MPa). When the ARB sample was annealed at 150°C for 30 min, the yield stress increased by 8.9% to 281 MPa (curve 2, Fig. 1) and the total elongation decreased markedly, making the material almost brittle. This is in contrast to behavior after annealing—a decrease and an increase in elongation or ductility.

An increase in flow stress during annealing of a deformed metal is typical if the metal contains alloying elements in solid solution that precipitate when the metal is annealed. This so-called precipitation hardening occurs in aluminum, which had a purity of 99.2%. However, other stable impurities might have dissolved during processing and reprecipitated during annealing. To prove that this was not the case, we carried out an experiment using 99.99% pure aluminum as the starting material. As with the 99.2% pure aluminum, specimens were produced by a six-cycle ARB processing to an equivalent strain of 4.8, followed by annealing at 150°C for 30 min. The samples were tested under the same conditions. The results showed that, as expected, both the yield stress and the UTS were substantially reduced relative to the 99.2% AI, but the key phenomena (i.e., the hardening by annealing and the decrease in ductility) were reproduced. For example, an increase of about 9% in the yield stress was observed after annealing. Therefore, the dissolution and reprecipitation of impurities, if it occurred, did not contribute to the annealing-induced increase in flow stress.

We used transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) to characterize the structural parameters of ARB samples before and after annealing. The initial structure (Fig. 2A) is delineated by lamellar boundaries parallel to the rolling direction (RD) and interconnecting boundaries parallel to the normal direction (ND). Table 1 shows the quantified structural parameters that are thought to contribute to the mechanical properties. Slight coarsening occurred during annealing (Fig. 2B) for both the lamellar boundary spacing D_{100} and the interconnecting boundary spacing D_{105} which produced a reduction of boundary surface area per unit volume. Statistical measurements of misorientation angles across the lamellar boundaries and interconnecting boundaries were made by Kikuchi diffraction. Misorientation angles in both samples show a bimodal distribution, with one peak located in the range below 3° and the other located between 40° and 55°. More than 60% of the boundaries were high-angle boundaries (>15°) in the ARB samples both before and after annealing. High density, in combination with the small boundary spacing, results in

Table 1. Structural parameters in samples of different conditions. f_{3°}, fraction of boundaries with misorientation angles less than 3°; f_{15°}, fraction of boundaries with misorientation angles between 3° and 15°; f_{15°}, fraction of high-angle boundaries (>15°).

<table>
<thead>
<tr>
<th>Sample</th>
<th>D_{100} (nm)</th>
<th>D_{105} (nm)</th>
<th>f_{3°} (%)</th>
<th>f_{15°} (%)</th>
<th>f_{15°} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARB</td>
<td>180</td>
<td>600</td>
<td>17.5</td>
<td>16.2</td>
<td>66.3</td>
</tr>
<tr>
<td>ARB annealed</td>
<td>225</td>
<td>640</td>
<td>12.8</td>
<td>23.3</td>
<td>63.9</td>
</tr>
<tr>
<td>at 150°C for 30 min</td>
<td></td>
<td></td>
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**Introduction**

Minimum grain size of conventional metals and alloys has been around 10 µm, though it is well known that grain refinement greatly improves the properties of metallic materials, such as strength and toughness. In the last decade, however, it has become possible to fabricate bulk metallic materials having ultrafine grained (grain sizes around 100 nm) or nanocrystalline (grain sizes around 10 nm) structures. One of the promising ways to make the grain size fine is severe plastic deformation (SPD) process illustrated in Fig.1 [1,2]. Various kinds of unique and surprising behaviors that have not yet been known in conventional metals and alloys with coarse grain sizes have been discovered in such nanostructured materials recently [3-5]. Here we observe that a nanostructured metal can be hardened by annealing and softened when subsequently deformed. Thus, the phenomena found in the present study is totally in contrast to the typical behavior of a metal.

**Experimental Methods**

We investigate the annealing behavior in a fully-dense, nanostructured aluminum of commercial purity (99.2%) that was prepared by a high strain rolling deformation, known as accumulative roll bonding (ARB) [1,6]. The ARB process was originally developed at Osaka University in 1998 [7] and is known as the only SPD process applicable to continuous production of bulky materials. The ARB process was repeated up to 6 cycles, corresponding to a total reduction of 98.4% (an equivalent strain of 4.8). These as-ARB processed samples were further subjected to various treatments including low temperature annealing at 150˚C for 30 minutes and cold rolling (CR) to 15% reduction in thickness. Tensile test at ambient temperature and the microstructural observations by electron back-scattering pattern (EBSP) analysis in a field-emission type scanning electron microscope (FE-SEM) and transmission electron microscope were carried out for the obtained specimens.

**Hardening by Annealing**

The ARB processed state showed a lamellar microstructure of dislocation boundaries and grain boundaries characteristic of high strain rolling of metals and alloys (Fig.2). The lamellar boundaries are parallel to the rolling plane with an average spacing of 180 nm. This lamellar morphology and the relatively coarse boundary spacing ensure the elimination of grain boundary sliding during tensile testing. The engineering stress-strain curve of the roll bonded sample is illustrated in Fig. 3 (curve 1), showing a very high yield stress (259 MPa) and ultimate tensile stress (UTS, 334 MPa), and a reasonably good tensile ductility expressed by the total elongation (7%) and the uniform elongation (1.8%). The yield stress is nearly 10 times higher than that (∼28 MPa) of a coarse-grained material with a grain size of 50 µm. When the ARB sample was annealed at 150°C for 30 minutes, the yield stress increased by 8.9% to 281 MPa (curve 2, Fig. 3) and the total elongation decreased dramatically. This behavior is in contrast to that expected, which is a decrease in strength and an increase in elongation or ductility. This is hardening by annealing.

Detailed characterization of structural parameters before and after annealing was made by TEM. Fig. 4 shows typical observations of the lamellar structure in the as-ARB state (A) and after annealing (B). The initial structure is delineated by lamellar boundaries parallel to the rolling direction (RD) and interconnecting boundaries parallel to the normal direction (ND). Slight coarsening occurred during annealing for both the lamellar boundary spacing, $D_{LB}$, and the interconnecting boundary spacing, $D_{ICB}$, which produced a reduction of boundary surface area per unit volume. Statistical measurements of misorientation angles across the lamellar boundaries and interconnecting boundaries were made by Kikuchi diffraction. More than 60% of the boundaries are high angle boundaries (>15°) in both the as-ARB sample and the annealed sample. 

**Fig.1** Schematic illustrations showing the principle of three representative severe plastic deformation processes. Equal channel angular extrusion (ECAE), high pressure torsion (HPT) and accumulative roll bonding (ARB).

**Fig.2** FE-SEM/EBSP orientation mapping showing the nanostructure of the ARB processed 99.2% pure aluminum. ND orientation color map (a), RD orientation color map (b) and boundary misorientation map (c).

**Fig.3** Engineering stress-strain curves for a 99.2% pure Al. Curve 1: Processed by 6 ARB cycles to an equivalent strain of 4.8. Curve 2: as 1 + annealing at 150°C for 30 minutes.
high density in combination with the small boundary spacing results in a very large area per unit volume (Sv) of high angle boundaries which can act as dislocation sinks. As an example Sv in the as-ARB sample is approximately $5.6 \times 10^6$ m$^{-1}$, which is about 100 times larger than the Sv for a typical polycrystalline material having a grain size of 50 µm. The low angle boundaries exhibit a certain width in the deformed state but they become sharper and better defined on annealing, suggesting the occurrence of a recovery process by rearrangement of dislocations in these boundaries. The most significant change observed was the decrease in the density of interior dislocations, $\rho_0$, that exist in the volume between the boundaries (Fig. 4). A determination of the interior dislocation density showed that it decreased from $1.33 \times 10^{14}$m$^{-2}$ in the deformed state to $0.53 \times 10^{14}$m$^{-2}$ after annealing.

Softening by Deformation and Repetition of Unique Behaviors

A coarsening of boundary spacing, recovery of low angle boundaries and reduction in the dislocation density in the interior, at grain boundaries and triple junctions are typical when a deformed structure is annealed at a temperature that does not cause recrystallisation. In conventional materials with medium- to large-grain sizes these changes will cause softening by a reduction in dislocation hardening and grain boundary strengthening. However the changes in the dislocation structure occurring in a nanostructured metal may play a distinct and different role. As a hypothesis it is suggested that the many dislocation sinks available in the form of closely spaced high angle boundaries will reduce the number of dislocation sources during annealing. This may lead to an increase in the yield stress in order to activate new dislocation sources during straining. Furthermore, the decrease in the density of interior dislocations which can carry the strain may efficiently reduce the elongation (2.0%). In the 15% cold rolled sample, TEM characterization shows that the dislocation configuration is very similar to that observed in the original ARB sample (Fig. 4A).

We obtained an interior dislocation density of $1.14 \times 10^{14}$m$^{-2}$ and boundaries spacings 200 nm ($D_{\text{LAB}}$) and 650 nm ($D_{\text{LAB}}$) in this sample. These parameters are close to the values measured for the as-ARB sample.

To further verify this hypothesis, further annealing and deformation experiments, and tensile tests were carried out. A repeated hardening and decrease in the elongation by low temperature annealing and softening and increase in the elongation by a low level of deformation is obtained, as shown by the curves 4 and 5 in Fig. 5. This repeated mechanical behavior, combined with the structural characterization, confirm that the removal of dislocations by annealing and their introduction by slight deformation are the cause of the changes in the mechanical properties. The deformation induced relatively small decrease in yield stress and UTS and a significant increase in the elongation greatly improves the applicability of the material.

Conclusions

The present results improve our understanding on the properties of nanostructured metals and will inspire the development of new optimization processes for nanostructured metals. The present investigation has focused on aluminum where a new strategy is suggested to optimize the mechanical properties, especially to balance strength and ductility. Instead of sample annealing as a final step, plastic deformation is proposed which will introduce dislocations which may soften the metal slightly but significantly enhance the ductility. This strategy may also apply to other metals which develop deformation microstructure similar to that of aluminum. Therefore, this strategy opens up for a research area of both fundamental and applied importance.

References