Grain refinement of coarse grained gold by combined thermo-mechanical process of severe plastic deformation and low temperature annealing

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Abstract. A high purity gold composed of coarse grains (d = 1.7 mm) was repeatedly thermo-mechanically processed by multi directional forging (MDF) at room temperature and annealing at warm temperature range. The effects of small addition of Ca (180 at. ppm) to Au on the static recrystallization (SRX) behavior and ultrafine grain evolution were investigated. Extensive SRX was observed in the MDFed Au sample to cumulative strain of $\Sigma \Delta \varepsilon = 1.2$ even at 453 K. After 2 cycles of the repeated TMP, fine grains of about $d = 10 \mu m$ was obtained in the Au sample. The Au-Ca alloy MDFed to $\Sigma \Delta \varepsilon = 1.2$, however, was hardly SRXed even by annealing at 543 K. Subsequently, the fine-grained Au and Au-Ca alloy were further MDFed to $\Sigma \Delta \varepsilon = 8.0$ at maximum at room temperature. By the prolonged MDF, average (sub)grain size of about 200 nm was achieved in the Au sample. The hardness increased with increasing cumulative strain. Although the tensile strength was also raised with cumulative strain, large loss of ductility did not appear.

1. Introduction
Recently, special attention is paid to fabrication of ultrafine grained (UFGed) structure by severe plastic deformation (SPD). It is because the grain refinement induces both of strengthening and formability of metallic materials. The former effect is brought by reduction of mean-free path of dislocations by high density of grain boundaries, which is well-known as Hall-Petch relation.

By SPD, multidirectional forging (MDF) [1-3], equal channel angular pressing (ECAP) [4] and accumulative roll-bonding (ARB) [5], UFGs from 20 to 200 nm in diameter were easily and homogeneously evolved. Actually, such UFGed structures evolved by MDF were revealed to possess quite high tensile strength, i.e., 920 MPa and 2.2 GPa for Cu-Zn alloy [2] and SUS316 stainless steel [3], respectively. However, such UFGed metallic materials obtained by SPD tend to possess poor ductility. Even though the above MDFed alloys exhibited superior ductility of about 20% in nominal strain, most of the SPD alloys show quite poor ductility, less than 10%, in nominal strain [5].

It is known traditionally that Au and its alloys possess superior nature of extensive deformability. For example, deep drawing to fabricate Au wire of 20 $\mu m$ in diameter is industrially common technique. The Au wire is composed of ultrafine fiber structure, where the direction is parallel to the drawing axis [6]. However, studies about the mechanical behavior of the UFGed Au and Au alloys processed by SPD are quite few as far as the authors know. The purpose of the present study is to investigate the evolution UFGs in Au and Au alloys during MDF and to reveal their mechanical properties.

2. Experimental
Hot extruded high purity Au (99.999%) and Au-180 at. ppm Ca alloy were cut into rectangular shaped samples of dimensions of $9.8 \times 7.8 \times 6.5 \text{ mm}^3$. Hereafter, these samples are referred as 5N-Au and Au-Ca, respectively. The initial grain size of the as-hot extruded samples was so coarse (1.7 mm and 1.2 mm, respectively) that MDF to obtain UFGs is not efficient, they were preliminary fine grained by repeated cycles of combined thermo mechanical process (CTMP) of MDF to $\Sigma \Delta \varepsilon = 1.2$ and low temperature annealing. This is because that grain refinement during MDF is more accelerated when the initial grain size is smaller [1]. In the MDF method, the samples were pressed with changing loading direction 90 degrees pass by pass (i.e. z to x to y to z …). A pass strain of $\Delta \varepsilon = 0.4$ and strain rate of $3.0 \times 10^{-3} \text{ s}^{-1}$ were employed for MDF.
After the sufficient grain refinement by CMTP, the samples were further MDFed up to cumulative strain of $\Sigma \Delta \varepsilon = 8$ at maximum (i.e., 20 passes) at room temperature. The evolved microstructure was examined by optical microscopy (OM) and transmission electron microscopy (TEM). The grain size was estimated by the line-intercept method. Mechanical properties were investigated by micro Vickers hardness test and tensile test. Tensile test was carried out on an Instron-type mechanical testing machine at an initial strain rate of $2.5 \times 10^{-3}$ s$^{-1}$ at room temperature. The dimensions of the gage size of the tensile samples were $3 \times 3 \times 0.8$ mm$^3$.

3 Results and discussion

3.1. Grain refinement of coarse grained initial microstructure

The true stress-cumulative strain curves obtained during MDF of the coarse grained as-hot extruded 5N-Au are shown in Fig. 1. The rapid work hardening occurred at the first pass of forging. The work hardening appears to be gradually saturated with increasing cumulative strain. This would be closely related to the saturation of dislocation density, but not to evolution of UFGs. For the UFG evolution by MDF, much higher cumulative strain more than $\Sigma \Delta \varepsilon = 3$ is required [1-3].

The above MDFed 5N-Au to $\Sigma \Delta \varepsilon = 1.2$ was subsequently annealed at warm temperature range. Figure 2 summarized the results of hardness change during annealing. The hardness decreases with increasing annealing time. The softening appears more rapid as the temperature becomes higher. The softening was induced mainly by occurrence of static recrystallization (SRX), as will be shown later. In contrast, softening did not appeared in the MDFed Au-Ca alloy even at 483 K, while the result is not shown here. The low temperature annealing of the MDFed Au-Ca was, therefore, carried out at 543 K. This result indicates that addition of quite small amount of Ca to Au causes drastic improvement of thermal stability.

After the first cycle of CTMP, the samples were further processed by the secondary cycle of CTMP. Figure 3 summarized the grain size change during low temperature annealing after secondary MDF. The grain size of 5N-Au reduced down to about 900 μm after the first cycle of CTMP, and then, it became to be about $d = 10.5$ μm at minimum after second CTMP (Fig. 3 (a)). When compared Figures 2 and 3 (a), it is evident that the time to onset SRX was much shortened. This is because that density of grain boundaries, where...
heterogeneous deformation microstructure can evolve along them to raise stored energy, affects much on the SRX behavior. That is, SRX was much stimulated by the reduction of grain size from 1.7 mm to 900 μm. Actually, it is known that ultra grain refinement by SPD is accompanied with loss of thermal stability [2]. It should be also noted that SRX took place at relatively low temperature around 433 K; 0.32 Tm, where Tm the melting temperature. Such low SRX temperature in 5N-Au should be caused by the effects of high purity and high energy stored by MDF. On the other hand, the minimum grain size of Au-Ca obtained after 2 cycles of CTMP was 260 μm (Fig. 3 (b)). The coarser grain size of Au-Ca obtained was induced by relatively higher annealing temperature compared with that of 5N-Au.

3.2. Multi directional forging and the evolved microstructure
The fine-grained 5N-Au and Au-Ca by 2 cycles of CTMP were further MDFed at room temperature to cumulative strain of ΣΔε = 8.4 at maximum, while the grain sizes were largely different (10.5 μm and 260 μm). The microstructural change was observed by OM and the typical photographs are exhibited in Fig. 4. It can be seen in Fig. 4 that, with increasing cumulative strain, the initial straight grain boundaries having sharp contrast gradually curved and became unclear accompanied with evolution of substructures in grain interiors. After MDF to ΣΔε = 6.0 (ΣΔε_total = 8.4), it is difficult to identify the initial grain boundaries among the evolved granular-look structure.

Figure 5 shows the TEM microstructure of 5N-Au MDFed to ΣΔε = 6.0. It is evident that the 5N-Au was already composed of fine (sub)grains ranging from 100 to 400 nm. Suzuki et al. estimated the grain sizes in Au and Au-Ag alloy ECAPed from the surface morphology to be 200 to 400 nm [7]. The above grain sizes are almost comparable with that observed at the cross section of deeply drawn Au wire [6]. Belyakov et al. have revealed that UFG evolution during MDF is more accelerated with decreasing initial grain size [1]. It can be estimate, therefore, the grain size in Au-Ca must be much coarser than that in 5N-Au. Sakai et al. proposed a mechanism of UFG evolution during MDF as low temperature dynamic recrystallization [8]. In this mechanism, introduced dislocations form dislocation walls at first and, then, their misorientation gradually increase to evolve high angle boundaries with increasing cumulative strain. Therefore, the microstructure obtained by MDF inevitably contains a certain fraction of low angle boundaries.

3.3. Mechanical properties of the multi directional forged Au and Au-Ca alloy
Figure 6 represents the hardness changes during MDF. The higher hardness of Au-Ca before MDF is resulted mainly by higher dislocation density because of incomplete occurrence of SRX. It is apparent that the hardness of both samples gradually increased with cumulative strain and looked saturated at high cumulative strain region.
The lower hardness even though the expected finer grain size in 5N-Au may be affected by recovery at ambient temperature [9]. Suzuki et al. measured the hardness of 4N purity Au ECAPed to equivalent strain of 4 by route Bc and reported it to be about 940 MPa [7]. The results obtained by MDF in the present study seem to be comparable or slightly lower than that by ECAP, although the purity is much different.

The MDFed 5N-Au and Au-Ca samples were tensile tested and the true stress vs. nominal strain curves are shown in Fig. 7. It can be seen that the ultimate tensile strength (UTS) was gradually raised with increasing cumulative strain. The UTS of 330 MPa was achieved in the 5N-Au sample. The slightly higher value of the UTS in the MDFed 5N-Au than that of the ECAPed 4N-Au (245 MPa) [7] would be resulted from more uniform evolution of UFGs. The increment of UTS of the Au-Ca is rather smaller than that of the 5N-Au and it looked soon saturated over $\Sigma \Delta \varepsilon = 1.2$. This difference would be resulted from much delayed evolution of UFGs owing to the coarse initial grains in Au-Ca. It is also notable in Fig. 7 that ductility was not so reduced, more than 40 %, even at high cumulative strain region around $\Sigma \Delta \varepsilon = 6.0$. Similar tendency of such large ductility of the ECAPed Au and Au alloys was reported [7]. UFGed metallic materials fabricated by SPD process tends to lose its ductility [5]. The observed large ductility of Au and Au-Ca even after MDF should be due to the inherent nature of extended ductility in Au.

4. Summary

Combined thermo mechanical process (CTMP) of multi directional forging (MDF) and low temperature annealing was applied to high purity Au (5N-Au) and Au-Ca alloy composed of coarse grains. Uniform evolution of fine grains of about 10.5 µm was obtained in 5N-Au after 2 cycles of CTMP. Addition of small amount of Ca to Au improved thermal stability, and therefore, recrystallization temperature was much raised. The higher thermal stability resulted coarser grain size of the Au-Ca alloy even after 2 cycles of CTMP. Ultrafine (sub)grains (UFGs) were almost uniformly evolved by the prolonged MDF of the above fine grained 5N-Au. The UFGed 5N-Au exhibited quite high ultimate tensile strength (UTS) and ductility. The excellent balance of mechanical properties of the UFGed 5N-Au must be related with the inherent nature of Au. In contrast, the coarse grained Au-Ca alloy showed comparably lower UTS even though MDFed to higher cumulative strain. This was assumed that initially coarser grain affected to retard UFG evolution.

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