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The mechanical properties of OFHC copper and CuCrZr alloys after asymmetric rolling at ambient and cryogenic temperatures

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Abstract: This work deals with comparing the mechanical properties of OFHC copper and CuCrZr alloys processed by asymmetric ambient rolling (ASaR) and asymmetric cryo-rolling (AScR). The conditions for asymmetrical rolling were ensured by different diameters of the main rolls. The thickness of samples was reduced about 20% - 70% at ambient temperature and at a temperature of liquid nitrogen. Mechanical properties such as yield strength, tensile strength, reduction of area and microhardness were determined for all rolled samples. Rolling at cryogenic temperatures provide about 50-60 MPa more tensile strength for Cu and 60-80 MPa for CuCrZr alloys when rolling at ambient temperature. After AScR of CuCrZr alloys, a start of precipitation was shifted at the temperature of 434°C and recrystallization was a part of the precipitation peak. According to the results, plastic deformation through shear bands is the dominant mechanism in materials with lower stacking fault energy (CuCrZr) treated under cryogenic conditions.

Keywords: cryo-rolling, asymmetric rolling, mechanical properties, microstructure, differential scanning calorimetry

1 Introduction

Many modern engineering applications mostly require a high material strength; but, on the other hand properties as ductility, reduction of area, electro conductivity and others have an opposite tendency. Nowadays, scientific research has been intensively focused on enhancing the mechanical properties through mechanical strengthening of the internal structures using unconventional plastic deformation processes, entitled to a severe plastic deformation (SPD). SPD provides significant grain size refinement below 1 μm ; thereby, forming the ultrafine-grained structure (UFG). SPD methods such as equal channel angular pressing (ECAP) [1–4], high-pressure torsion (HPT) [5] and their modifications are very popular nowadays. The main disadvantage of this is producing relatively small samples. To produce UFG materials with unlimited length, there were designed methods such as accumulative roll-bonding (ABR) [6], equal channel angular rolling (ECAR) [7–10], asymmetric rolling (ASR) [11–14] and cryo-rolling (CR) [16–18]. At the present time, asymmetric rolling has become a subject of intensive scientific research due to the simplicity of equipment configuration and promising results. Asymmetric rolling could be assured by a different diameter of the rolls [11], rotating at different velocities [12] or different friction conditions between rolls [13]. A number of studies [14, 15] focused on the comparison of ASR and symmetric rolling (SR) confirmed that asymmetric rolling imposes intense shear deformation throughout the sheet thickness. Hence, the effective plastic strains reached by ASR are larger than those obtained with SR at the same rolling reduction. This was also confirmed by FEM [11, 13, 19]. The plastic deformation temperature plays a crucial role in forming the ultrafine-grained microstructure because materials such as Al, Cu, Ag can recover dynamically and recrystallize already at ambient temperatures. It was found that, cryodeformations carried out in liquid nitrogen (LN2) as cryo-rolling (CR), cryoforging (CF) [20] or other cryogenic tech-

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nologies [21] produce a fine-grained structure in materials. Suppressing the dynamic recovery causes a constant increase of dislocation density that re-arrange to the subgrains after dislocation saturation. It was shown that twinning activity is sensitive to the processing temperature and deformation twinning is more pronounced when the temperature is less than 100 K [22–24]. Another highly unique characteristic of twinning, firstly pointed out by Armstrong and Worthington, is the larger grain size dependence on the twinning stress as compared with the slip stress [23, 25]. The Hall–Petch slope for twinning in copper is larger than that for slip, i.e. $k_{twin} = 21.6 \text{ MPa mm}^{1/2}$ and $k_{slip} = 5.4 \text{ MPa mm}^{1/2}$, respectively [23]. For FCC metals, it is well-known that the twinning stress increases with increasing of the stacking-fault energy (SFE). Substitution also often have a pronounced effect on reduction of the stacking-fault energy. The stacking-fault energy of pure copper is 78 mJ/m^2 ; while the presence of 30 wt.% Zn reduces to 14 mJ/m^2 [25].

The aim of this study it is to compare the mechanical properties and microstructure evolution in Oxygen free High Conductivity copper (OFHC) and CuCrZr alloy after asymmetric rolling and cryo-rolling. Asymmetric rolling was ensured by different diameters of the rolls. Thermally activated processes such as recovery and precipitation for CuCrZr were studied using differential scanning calorimetry.

2 Materials and methods

The materials used in this study were OFHC copper with a purity of 99.99% and a precipitation-hardened Cu-0.96%Cr-0.06%Zr alloy supplied as a plate with a thickness of 5 mm. Before asymmetric rolling, samples were given an annealing treatment under the following conditions: $600^\circ\text{C}/120 \text{ min}$ and air cooled for OFHC copper, $1020^\circ\text{C}/30 \text{ min}$ and water quenched for CuCrZr. Asymmetric rolling was assured using different roll diameters with the ratio of 2.4. The samples were rolled under the same deformation conditions at room temperature and at cryogenic temperature (77 K) in LN₂. The specimens were kept in LN₂ for 5 minutes before and after rolling. The samples were rolled several times to ensure deformations of 60 – 70 %, approximately reduction in thickness (RT) of 20% was given to the sample through one pass. For investigations, the samples were taken after deformations of 20, 40, 60 and 70 %, gradually. The samples were artificially aged for 30 minutes at 430°C and 480°C , followed by cooling in the air. The static tensile tests were carried out using

a Tinius Olsen machine of 300kN capacity according to the EN ISO 6892-1. Vickers microhardness was measured on the samples with a polished surface under a load of 4.91N for 5 seconds using Struers apparatus. The initial microhardness values before processing were 63 HV0.5 for Cu and 58 HV0.5 for CuCrZr. Microstructural observations were carried out by optical microscopy (Zeiss AxioVert A1), samples were etched in a solution of 10g FeCl₃, 60 ml HCl and 70 ml methanol for 1-2 seconds. Some samples were selected for measuring by a thermos-analytical technique using differential scanning calorimetry (DSC) on Netzsch STA 499 F1 Jupiter machine. For DSC measuring, samples were prepared on a diamond wire cutting machine with a weight about 30 mg. DSC experiments were carried out in the N₂ atmosphere with a heating rate of 30 K/min (up to 400°C for Cu and 680°C for CuCrZr). The measurement method was focused on the investigation of heat-irreversible effects such as structural recovery and precipitation.

3 Results and discussion

On Cu and CuCrZr samples, after asymmetric rolling at room temperature (ASaR) and asymmetric cryo-rolling (AScR), mechanical properties were determined by tensile tests and Vickers microhardness. In Figure 1a, the progress in mechanical properties of copper after ASaR and AScR for a particular specimen processed at room and cryogenic temperature are compared. It is obvious that, the yield strength (YS) and ultimate tensile strength (UTS) increased with increase in the % RT. On the other hand, a corresponding reduction of area (RA) had an opposite progress. After AScR, YS and UTS increased uniformly up to 60% deformation (slope of curve $K_{UTS} = 2.7$) at 375 MPa and 404 MPa, respectively. Nevertheless, after ASaR, YS and UTS were lower about 50 – 60 MPa (slope of curve $K_{UTS} = 1.7$) at 351 MPa and 286 MPa, respectively. Compared to Dasharath et al. [18], it seems that AScR is more effective than cryosymmetric rolling (ScR) as UTS was just $411 \pm 2.5 \text{ MPa}$ after 90% deformation within RT. It implies that shear strain is more intensive within AScR compared to ScR processing. The progress in mechanical properties after ASaR and AScR processing for CuCrZr is shown in the Fig. 1b. Slope of curve was higher for AScR ($K_{UTS} = 3.8$) than that for ASaR ($K_{UTS} = 2.6$). The difference in YS and UTS is approximately 60 – 80 MPa.

According to the obtained data, it is clear that deformation at cryogenic temperature results in higher strength properties (where $\Delta\text{UTS} \approx 50 - 80 \text{ MPa}$), meanwhile

plastic properties remain conserved. Different curves of strengthening ($\Delta K_{UTS} \approx 1$) imply that the process of plastic deformation at cryogenic temperature is more intense.

The optical microstructures of Cu after asymmetric rolling at room and cryogenic temperature are shown in Fig. 2. In both cases, in elongated grains, it is possible to observe the shear bands with parallel strips, which are differently oriented. The highest density of the shear bands was achieved after cryo-rolling. According to Wei, shear bands are the result of clustered deformation twins, this phenomenon was also found in Cu-Al alloys subjected to cryogenic SPD [28].

Intensive plastic deformation at cryogenic temperature is also recognized from DSC measurements. Fig. 3, shows the heat flux for Cu samples after ASaR and ASrR of 70% RT where the exothermic peak represents a process of recovery. The microstructure after annealing does not provide any exothermic reactions. Cryo-rolling results in 2.5 times greater stored energy compared with ambient rolling, with 0.84 J/g for cryo-rolling and 0.33 J/g for ambient rolling. A recovery process is shifted at the temperature of 190°C. It means, Cu strength properties are not stable under elevated thermal conditions (up to 190°C); because, recovery of the deformed-strengthened microstructure happens.

The microstructure of the CuCrZr after ASaR and ASrR (40% RT) is given in Fig. 4c-d. In the microstructure after ambient rolling, there was not recognized any shear bands were not recognized; While ASrR, there were a lot of visible shear bands.

Comparing with the microstructure of pure copper after ASrR (60% RT), it is seen that the shear band is a dominant process of plastic deformation at a cryogenic temperature in materials with lower stacking fault energy (as a CuCrZr alloy).

DSC curves showing enthalpy release rate within the linear heating of CuCrZr after annealing, ASaR and ASrR are given in Fig. 5. For annealed materials, two peaks on the DSC curve were recognized. The first peak can be associated with Cu_3Zr or Cu_5Zr precipitation in the range of 471 – 539°C. According to the study [26, 28], the second peak (in the range of 563 – 584°C) can be associated with recrystallization. After ASrR, a double peak is seen on the DSC curve and a start of precipitation is shifted to the temperature of 434°C and recrystallization is a part of the precipitation peak. According to the DSC, there were specified temperatures for artificial aging of 480°C and 430°C for ASaR and ASrR, respectively. In the temperature range of 250 – 300°C, it is observed that the exothermic peak is related to the recovery of the severely deformed structure.

Figure 1: Mechanical properties after ASaR and ASrR: a) Cu, b) Cu-CrZr alloy.

According to the DSC measurement, intensive plastic deformation has got a positive impact on recovery processes in the alloy as it moves the recovery at lower temperatures

Figure 2: Optical micrographs of Cu after: a) ASaR – 70% RA; b) ASaR – 60% RA.

Figure 3: DSC curves of Cu after processing by annealing, ASaR and ASaR.

Figure 4: Optical micrographs of CuCrZr after: a) ASaR – 40% RA; b) ASaR – 40% RA; c) ASaR – 40% RA + HT 480°C; d) ASaR – 40% RA + HT 430°C.

resulting in processing expenses. Nevertheless, when the recovery temperature is reached, the effect of precipitation strengthening is lost.

In Fig. 6a, microhardness across the sample thickness for CuCrZr after ASaR and ASaR (20% RT) at room temperature (in RT) is compared. In both cases, shear deformation is greater at the bottom of the sample, because, the diameter of the lower roll is higher. This was also confirmed by

Figure 5: DSC curves of CuCrZr after processing by annealing, ASaR and ASaR.

Y.H. Ji et al. [19] through finite element simulation (FEM) methods. Fig. 6b shows changes in the microhardness for CuCrZr alloys after ASaR and ASaR which were annealed at a temperature of 480°C and 430°C, respectively.

Microhardness of CuCrZr after rolling in the N₂ is about 20 HV0.5 higher compared to ASaR, but this trend was not visible after the ageing process (480°C/30 min.). The microstructure after the ageing process (Fig. 2e) revealed deformation and temperature twins. This is due to highly-deformed microstructure providing a greater stored energy which shifts precipitation and recrystallization to lower temperatures.

Figure 6: Microhardness of CuCrZr: a) across the sample of thickness and b) microhardness after rolling and ageing.

A gap between the end of precipitation and the start of recrystallization is narrow having an impact on the process of partial recrystallization. Ageing at 430°C for 30 minutes causes the increase of microhardness to 190

HV0.5 whereby temperature twins were not revealed in the microstructure (Fig. 2f).

4 Conclusions

In this study, experimental asymmetric rolling at low temperature was carried out to ensure enhanced mechanical properties in pure Cu and CuCrZr alloy. According to the experimental results, it can be concluded that:

- The following higher mechanical properties were obtained after cryo-deformation for copper and CuCrZr alloy:
 - Cu: $YS_{ASaR} = 286$ MPa, $YS_{AScR} = 375$ MPa
 - CuCrZr: $YS_{ASaR} = 339$ MPa, $YS_{AScR} = 393$ MPa
- at cryogenic temperatures, the shear band is a dominant mechanism of plastic deformation particularly in materials with lower stacking-fault energy
- after 70% of deformation at cryogenic temperature, the stored energy of copper is 0.87 J/g.
- after ASaR for CuCrZr alloy, where a start of precipitation is shifted to the temperature of 434°C and recrystallization is likely to be a part of the precipitation peak
- the maximal microhardness value of CuCrZr alloy HV0.5 = 188 is obtained after ageing (430°C/30min.).

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