EFFECT OF QUASI-HYDROSTATIC EXTRUSION ON MICROHARDNESS IN CuCrZr ALLOY

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Effect of quasi-hydrostatic extrusion at liquid nitrogen (77 K) and room (300 K) temperatures on the microhardness in high-strength CuCrZr alloy has been investigated. It is shown that the combination of equalchannel angular compression (ECAP) and quasi-hydrostatic extrusion (QHE) allows raising microhardness of CuCrZr alloy especially in the case of the low-temperature (77 K) QHE treatment.

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INTRODUCTION

Copper and copper alloys are widely used because of their excellent thermal conductivity, outstanding resistance to corrosion, ease of fabrication as well as good strength and fatigue resistance. The high-strength copper materials take the special place in the contemporary physical experiments [1]. They are perspective for the resistance spot welding. Optimization of the technology of such kind of alloys is in progress today. Hot hardness is the key property for such application. In this case the main scientific problem consists in the necessity to have maximum percent of Cr precipitations in the copper melt while retaining its high electro and thermal conductivities with the stabilization of all physical characteristics.

During the past ten years the ternary Cu-Cr-Zr system has been widely investigated because of excellent combination of mechanical strength and electrical (thermal) conductivity.

Our previous paper [2, 3] has been devoted to complex investigations of the effect of the structure and size of grains on changes in the microrelief and optical characteristics of CuCrZr alloys with substantially different grain size.

The aim of the present communication is mainly to study the microstructure and precipitates distribution of the high-strength Cu-Cr-Zr alloy, in order to get a better understanding of the strength mechanism and the composition of the precipitates.

1. MATERIALS AND EXPERIMENTAL PROCEDURE

The starting material investigated in the present study was a recently developed precipitation-strengthened by ECAP light ternary high-strength commercial Cu-Cr-Zr alloy [2, 3].

Later the starting material was treated by quasi-hydrostatic extrusion (QHE) at room and cryogenic temperatures [4].

In the initial state, the starting material was a bar with a diameter of 20 mm. Cylindrical preforms ~ 4.3 mm in diameter and a length of about 20 mm have been cut into the longitudinal sections relative to the axis of the starting bar for subsequent QHE treatment. Later in the text this direction will be labeled as Lg – the longitudinal section.

Later these cylindrical preforms were subjected to QHE at 300 and 77 K. In the text such kind of treatments are labeled as "QHE300" and "QHE77", correspondingly. Then the extrudates were cut into specimens of ~1×2.5×16 mm along the extrudates axis. Specimens were prepared using standard mechanical and electrochemical polishing methods to get a high optical mirror quality. In summary there were the two specimens for investigation: N1 − (LgQHE300), N2 − (LgQHE77).

To remove the possible contaminants and the surface oxides layers after mechanical treatment, the specimens were cleaned using ions of deuterium plasma ($E_i \approx 60$ eV/ion; fluence ~2.5×10^{23} ion/m^2). The specimens were sputtered with ions of deuterium plasma having a wide energy distribution ($\langle U \rangle = -600$ V; $j = 2.8$ mA/cm^2; each exposure, 10 min) [2, 3]. Electron cyclotron resonance discharge was used for plasma production in deuterium. In summary one cleaning step and five sputtering steps were performed.

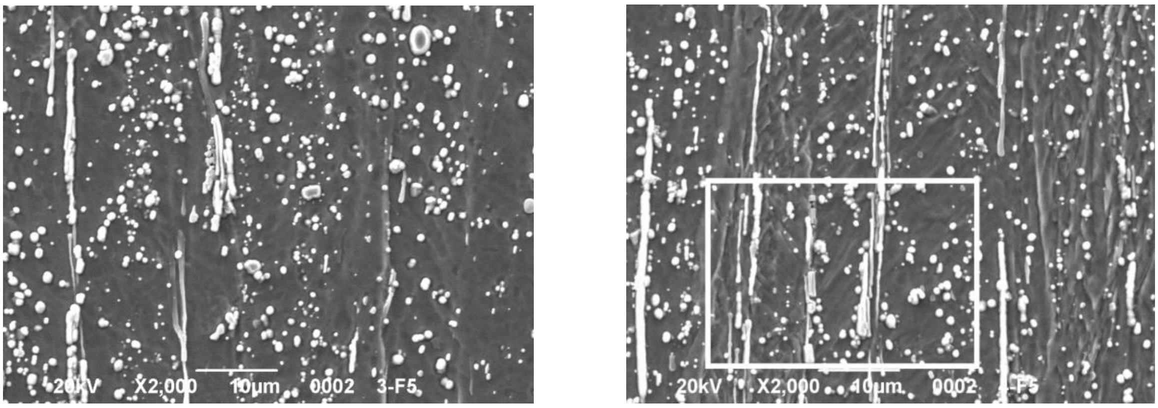
The microstructures of CuCrZr alloy were examined by the interferometry and scanning electron microscopy (SEM). Precipitates in CuCrZr alloy were analyzed by a JSM-6390LV(JEOL Ltd., Japan) scanning electron microscope (SEM), equipped with energy dispersive X-ray spectroscopy (EDXS). Micro-interferometric setup based on an MII-4 microinterferometer [5] and multifunctional optic complex [6] were used to investigate the specimen surface relief.

The standard microhardness tester with load 1H was used for microhardness analyzing.

2. EXPERIMENTAL RESULTS

The dominating feature of the microstructure of the CuCrZr alloy after the first sputtering step was the presence of a relatively high density of Cr-rich precipitates. After each subsequent sputtering step the number of precipitates grew. The saturation has been reached up to fifth sputtering. It means that the sputtered film eroded by mechanical treatment was taken off.

Fig. 1 reproduces the general feature of the precipitate microstructure for the two samples after the fifth sputtering: dots and elongated precipitates (fibers).



a b

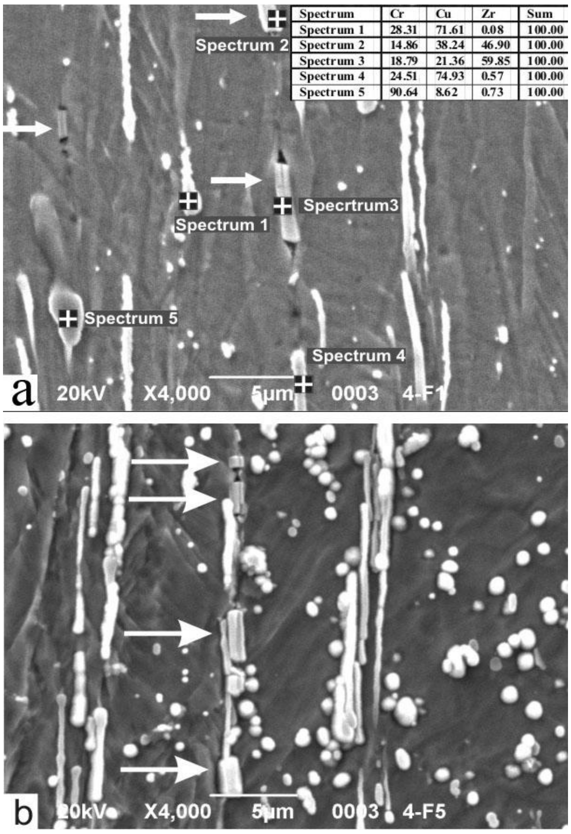
Fig. 1. SEM micrograph showing precipitates microstructure of the CuCrZr alloy after the fifth sputtering: (*a*) *LgQHE300* (*N1*) *and* (*b*) *LgQHE77* (*N2*)

Quasi-hydrostatic extrusion at 77 K leads to more high dispersive and homogeneous distribution compared with similar treatment at 300 K (Figs. 1,a,b). That ensures high precipitate density. As a result, there are more precipitates in LgQHE77 samples and they are smaller. This is connected with that the nucleation centers can not grow through the uniform compression forces, but there are many precipitates of such kind.

Fig. 2 shows the precipitates distribution and results of EDXS analysis for a few areas of samples (see Fig. 2,a). After the fifth sputtering the precipitates with Cr and Zr enrichments are detected. Analysis of the matrix shows that it is CuCrZr alloy. The alloy composition over the sample area is very heterogeneous (spectrums - insertion to Fig. 2,a). Near Cr clusters the Cu content reduction takes place in matrix (see Fig. 2,a spectrum 5) in comparison with distant area.

It should be noted to the special features, connected with the formation of Zr precipitates. Their number is much smaller than Cr. The large scale micrograph (Fig. 2,b) shows fragment of the LgQHE77 sample surface. The Zr precipitates are marked by the white arrows. First it is important to note that they look like parallelepiped in the “crack” of the cooper matrix, which is attributed to significant distortions of the crystal lattice. A careful observation of the image (see Fig. 2,b) revealed some kinds of contrasts associated to Zr precipitates. One can see the black boundaries of the crack on the top and from the bottom of the white parallelepiped - Zr precipitate (see Fig. 2,b). Evidently, Zr localization in the copper matrix induces large local lattice distortions of matrix. Specific reason of the crack formation associated with Zr precipitates remains unknown to us at present.

Fig. 2,b shows the large scale fragment marked by the white frame in Fig. 1,b. Zr-rich precipitates which look like the fibers are indicated by the white arrows. One can see this image as a line of fibers (or one but long). For longitudinal samples (both for LgQHE300, and for LgQHE77) there are large Zr precipitates which look like elongated precipitates (fibers) having the lengths ranging from 5 to 50 μm (data not shown here). It should be noted that the elongated precipitates (fibers) were formed under ECAP treatment.

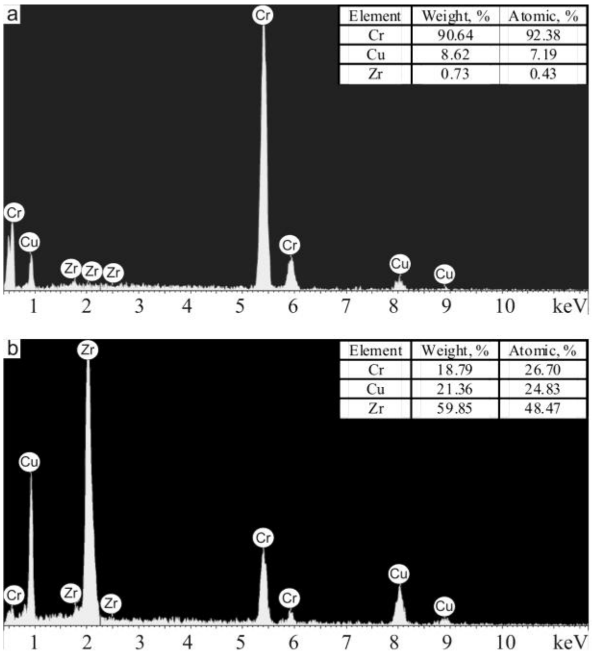


Spectrum	Cr	Cu	Zr	Sum
Spectrum 1	28.31	71.61	0.08	100.00
Spectrum 2	14.86	38.24	46.90	100.00
Spectrum 3	18.79	21.36	59.85	100.00
Spectrum 4	24.51	74.93	0.57	100.00
Spectrum 5	90.64	8.62	0.73	100.00

Fig. 2. A typical SEM of a large scale micrograph of the LgQHE77 surface fragment (a); Zr precipitates for sample LgQHE77 after the fifth sputtering (a large scale micrograph of the surface fragment marked by the white frame in Fig. 1,b) (b). Insertions: EDXS analyzes of the second phases in the areas marked by “+” (wt%)

There are the three phases in the alloy: copper matrix, Cr-rich phase and Zr-rich phase. A typical EDXS qualitative analysis spectrum of the Cr-rich phase is shown in Fig. 3, a (spectrum 5 in the insertion to Fig. 2,a). There are Cu and Zr peaks besides the Cr peaks in the spectrum. The EDXS qualitative analysis results in spectrum 5 (the insertion to Fig. 2,a) shows that the Cr content of the particle was up to 90.64 wt.%, so we can suppose that the Cr-rich phase is pure chromium. Most of the Cr-rich phase is distributed as little globular particles in a copper matrix. But a few is distributed as coarse particles (see Fig. 2,a, spectrum 5).

A typical EDXS qualitative analysis spectrum of Zr-rich phase is shown in Fig. 3 (see Fig. 2,a, spectrum 3). There are copper, chromium and zirconium peaks. The zirconium content of the particle was up to 59.85 wt.%. Almost all of the zirconium-rich phase is distributed as coarse particles, as precipitates in Fig. 2,a. One should note that in the present study, Zr precipitates were not found homogeneously distributed in the matrix.



Element	Weight, %	Atomic, %
Cr	90.64	92.38
Cu	8.62	7.19
Zr	0.73	0.43

Element	Weight, %	Atomic, %
Cr	18.79	26.70
Cu	21.36	24.83
Zr	59.85	48.47

Fig. 3. A typical EDXS qualitative analysis spectrum in the areas marked by "+" in Fig. 2,a of: (a) chromium-rich phase (spectrum 5) and (b) zirconium-rich phase (spectrum 3). Insertions: EDXS analyzes of the second phase in the areas marked by "+" in Fig. 2,a

Microhardness of the copper alloy before ECAP, after ECAP, after QHE300 and QHE77 treatments

Treatment stage	H_v, MPa
Before ECAP	1600±30
After ECAP	1820±40
After QHE300	2100±30
After QHE77	2310±30

The microhardness data for the two samples are displayed in the Table. Provided data are the average of at least 20 measurements. The Vickers microhardness (H_v) values ranging from 1600 up to 2310 MPa are rather large. The data in the Table reflect the effectiveness of QHE treatment. It is remarkable that QHE77 treatment ensure higher microhardness in comparison with the same treatment at 300 K. We have found that the precipitate density for QHE300 samples is significantly lower in comparison with QHE77 samples.

3. DISCUSSIONS

The analysis of the experimental data shows that the nature of the CuCrZr alloy microstructure is connected with the Cr and Zr precipitates distribution and their sizes. As described above, there are three phases in the alloy, Cu matrix, Cr-rich and Zr-rich phases.

The dominating feature of microstructure as revealed by the SEM investigation is the presence of a relatively high density of chromium-rich precipitates. It is concluded that the coarse precipitates mainly consist of pure chromium. The SEM results indicate that the precipitate is likely to be pure chromium, with sizes ranging from 150…700 nm. The average chromuim precipitate size in the CuCrZr alloy was found to be 460 nm. The content of zirconium in the alloy is reduced to 0.1 wt.% or less. The possibility visualizing the microstructure of the alloy under the sputtering process is based on the fact that the sputtering yields for precipitates are lower than for the cooper matrix [7]. In the delivery state the heterogeneous mechanism of precipitation takes place.

In the present paper at the first time the influence of the successive employment QHE at liquid nitrogen (77 K) and room (300 K) temperatures to precipitates distribution in the prior precipitation-strengthened by ECAP CuCrZr alloy was investigated. The physical mechanisms of precipitates distribution in the precipitation-strengthened CuCrZr alloy after ECAP and QHE are determined. It is shown that the combination of ECAP and QHE leads to subsequent grain refinement, to the alloy structure homogenization and the reduction of its precipitates size. QHE77 treatment after ECAP leads to the maximum grain refinement and more homogeneous distribution of the precipitation compared with QHE300, which is connected with retardation of the diffusion process and recrystallisation for the second time at low temperature.

As it is shown above in the Table the QHE77 treatment ensures higher microhardness (~2300 MPa) in comparison with the same treatment at 300 K. This fact reflects the precipitates density in the samples. It is higher for QHE77 in comparison with the QHE300 treatment. This result is correlated with microstructure data which is connected with the homogeneous distribution of Cr precipitates.

The spatial distribution of the precipitates was found to be fairly homogeneous throughout the whole volume and there were no significant variations in the size and density of precipitates over the surface. The precipitate density increasing is connected with the stress growth. The crack formation is a result of this process. Along these cracks through the high stress the precipitates dots transform into the elongation strips with high density. The density of inclusions became so high that many combined with adjacent ones, forming a system of oblong curved hillock-type defects. It is lead to local inhomogeneity on the sample surface.

As a consequence, one may conclude the following. If the cooper matrix grains are much larger than the size of the second phase particles, precipitates Cr and Zr are localized prior over the grain boundaries. It is shown that the grain boundaries are the most effective concentrators for precipitators at the grain size ~30…40 μm [2, 3]. The result of the present paper shows, that the grain size of cooper matrix is much less than the precipitate size. In this case the nucleation center of the Cr and Zr precipitates are determined by the defects and dislocations in the samples. As a result of QHE grain size is <100 nm and the homogeneous distribution of precipitates takes place: precipitate distribution is determined only by the dislocations and other defects. The later distribution determines the topography and the surface roughness. It is noteworthy that the combination of equal-channel angular compression (ECAP) and quasi-hydrostatic extrusion (QHE) allows raising microhardness of CuCrZr alloy especially in the case of the QHE77 treatment.

CONCLUSIONS

Effect of quasi-hydrostatic extrusion at liquid nitrogen (77 K) and room (300 K) temperatures on the structure formation of preliminary dispersion-strengthened CuCrZr alloy has been investigated in this communication. The sputtering process with deuterium ions was chosen as an instrument for examining the alloy structure. The main peculiarity of microstructure is connected with the high density of small chromium precipitates. It is shown that the combination of equal-channel angular compression (ECAP) and quasi-hydrostatic extrusion (QHE) allows raising micro hardness of CuCrZr alloy especially under low-temperature QHE77 treatment up to 2300 MPa.

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ВЛИЯНИЕ КВАЗИГИДРОЭКСТРУЗИИ НА МИКРОТВЕРДОСТЬ СПЛАВА CuCrZr

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Исследовано влияние квазигидроэкструзии при температуре жидкого азота (77 K) и комнатной температуре (300 K) на микротвердость жаропрочного CuCrZr-сплава. Выявлено, что комбинация равноканального углового прессования (РКУП) и квазигидроэкструзии (КГЭ) приводит к увеличению микротвердости CuCrZr-сплава, особенно в случае низкотемпературной (77 K) КГЭ-обработки.

ВПЛИВ КВАЗІГІДРОЕКСТРУЗІЇ НА МІКРОТВЕРДІСТЬ СПЛАВУ CuCrZr

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Досліджено вплив квазігідроекструзії при температурі рідкого азоту (77 K) та кімнатній температурі (300 K) на мікротвердість жароміцного CuCrZr-сплаву. Визначено, що комбінація рівноканального кутового пресування (РККП) та квазігідроекструзії (КГЕ) призводить до підвищення мікротвердості CuCrZr-сплаву, особливо у випадку низькотемпературної (77 K) КГЕ-обробки.