ENHANCED MECHANICAL AND SERVICE PROPERTIES OF ULTRAFINE-GRAINED COPPER-BASED ALLOYS WITH Cr, Zr, AND Hf ADDITIVES

МЕХАНИЧЕСКИЕ И ЭКСПЛУАТАЦИОННЫЕ СВОЙСТВА УЛЬТРАМЕЛКОЗЕРНИСТЫХ МЕДНЫХ СПЛАВОВ, ЛЕГИРОВАННЫХ Cr, Zr И Hf

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Abstract: *Structure and properties of low-alloyed copper-based alloys with Cr, Zr and Hf after severe plastic deformation (SPD) using techniques of high pressure torsion (HPT) and equal channel angular pressing (ECAP) have been studied. SPD significantly increases strength of the alloys by formation of ultrafine-grained structure. Cu_5Zr and Cu_5Hf particles suppress the grain growth in ultrafine-grained (UFG) structure more effectively than the Cr particles and provide additional hardening during aging. Moreover, it was found that the application of additional aging after SPD significantly improves service properties of the alloys (fatigue limit, wear resistance and electrical conductivity). This combination of properties results in a high durability of electrodes for resistance spot welding produced from UFG Cu-based alloys.*

***KEYWORDS**: SEVERE PLASTIC DEFORMATION, ULTRAFINE-GRAINED STRUCTURE, COPPER ALLOYS, ELECTRICAL CONDUCTIVITY, STRENGTH, WEAR RESISTANCE, FATIGUE LIFE, RESISTANCE SPOT WELDING ELECTRODES*

1. *Introduction*

Low-alloyed chromium, zirconium, and chromium-zirconium alloys are widely used in electrotechnical industry as resistance spot welding electrodes due to a good combination of strength and electrical conductivity. Traditional treatment including quenching, deformation, and aging provides a high electrical conductivity, due to decomposition of supersaturated solid solution and a high strength caused by the precipitation of dispersed chromium and the Cu_5Zr particles. Application of severe plastic deformation (SPD) to such bronzes leads to significant grain refinement of Cu-based solid solution and strengthening particles [1]. Previous studies showed possibility of the formation of submicrocrystalline structure in Cr, Zr, and CrZr bronzes by SPD methods such as equal channel angular pressing (ECAP) [2–15] and high pressure torsion (HPT) [16–23]. Along with strength increase in ultrafine-grained (UFG) low-alloyed bronzes, SPD allows to improve some functional properties such as wear resistance [13,15], electrical conductivity [2,4,12–14,19–23], fatigue life [2–4,6] etc. However, in terms of electrotechnical applications, the most important is the combination of high strength and electrical conductivity provided by high thermal stability. Thus, the alloying of chromium bronzes with Hf is promising since Hf may better enhance thermal stability, because the solubility of Hf in Cu at eutectic temperature is higher than that of Zr. Therefore, the higher hardening effect can be expected after deformation and aging due to the larger amount of strengthening particles. The main aim of this study is to investigate the structure, mechanical and service properties of low-alloyed copper-based alloys with Cr, Zr and Hf after severe plastic deformation.

2. *Materials and methods*

The Cu-0.7%Cr, Cu-0.18%Zr, Cu-0.9%Hf, Cu-0.5%Cr-0.08%Zr and Cu-0.7%Cr-0.9%Hf (in wt %) alloys were selected for the study. The alloys were prepared by vacuum arc melting and subjected to hot forging with subsequent water quenching from a temperature of 1000 °C (2 h) for the Cu-0.7% Cr and Cu-0.5%Cr-0.08%Zr alloys and water quenching from a temperature of 900 °C (2 h) for the Cu-0.18%Zr, Cu-0.9%Hf and Cu-0.7%Cr-0.9%Hf alloys.

HPT was carried out on the samples with 10 mm diameter and 0.6 mm in thickness at room temperature with 1 rpm rotation speed under 4 GPa pressure for 5 revolutions. The deformation was performed in a “groove” with 0.2 mm depth.

ECAP was conducted on the samples of 10 mm diameter and 70 mm length using Bc route, in which the sample was rotated between passes successively around its axis by an angle of 90°. The number of passes was 10. Deformation was performed at room temperature with direct channels intersection angle.

The Vickers microhardness was measured with a 402 MVD Instron Wolpert Wilson Instruments tester after holding for 10 s at a load of 50 g. The electrical resistivity was measured with a BSZ-010-2 micro-ohmmeter at room temperature on the basis of four-point method on flat samples. The resistivity was calculated and transformed into electrical conductivity according to International Annealed Copper Standards (IACS). The microstructure was observed using JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Thin foils for electron microscopy were prepared by ion polishing with a GATAN 600 unit. Uniaxial tensile tests were conducted at room temperature with an «INSTRON 3382» testing machine on flat samples with a gage zone of 5.75x2x1 mm and a total length of 14mm. Two samples were used for each regime.

The high-cycle fatigue (HCF) tests were carried out on Cu-0.7%Cr-0.9%Hf alloy under repeated tension conditions on an ElectroPuls™ E3000 machine at 30 Hz testing frequency and a stress ratio $R = 0.1$. Scheme of the specimen for fatigue test is shown in Figure 1.

The tribological properties were studied for the Cu-0.7%Cr-0.07%Zr alloy after warm extrusion and HPT at ambient temperature under 6 GPa pressure for 15 revolutions on samples with 20 mm diameter.

The wear tests were conducted using a computer controlled UTS Tribometer T30M-HT test machine with reciprocating ball-on-disc contact in unlubricated conditions at ambient temperature with sliding distance of 200 m and 6 mm diameter Al_2O_3 ball as a counter-face. The applied normal load was systematically changed in the range of 5–20 N with a constant sliding speed of 0.1 ms^{-1}. The wear resistance was determined primarily by measuring the weight loss.

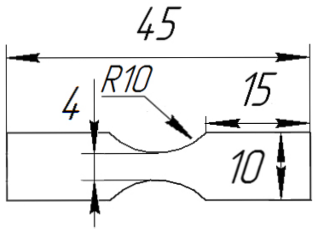


Fig. 1. *Scheme of the specimen for fatigue test*

3. *Results and discussion*

HPT leads to significant strengthening of low-alloyed Cu-based alloys. The microhardness of the alloys after HPT rises in the following row: Cu-0.7%Cr, Cu-0.18%Zr, Cu-0.9%Hf, Cu-0.5%Cr-0.08%Zr, and Cu-0.7%Cr-0.9%Hf alloys from 1.7 to 2.4 GPa (Fig. 2a) while the grain size decreases from 209 to 108 nm (Fig. 3).

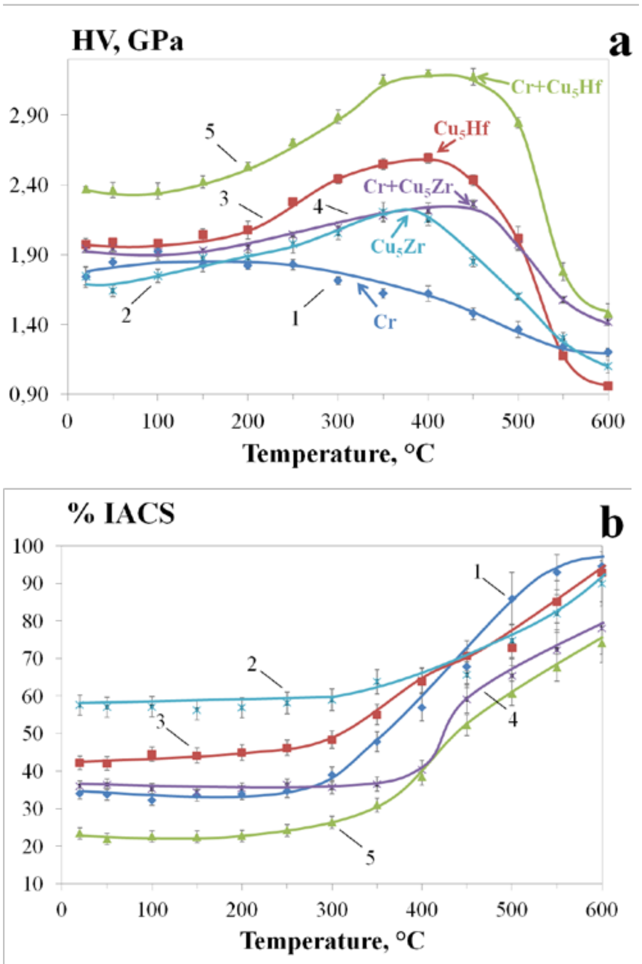
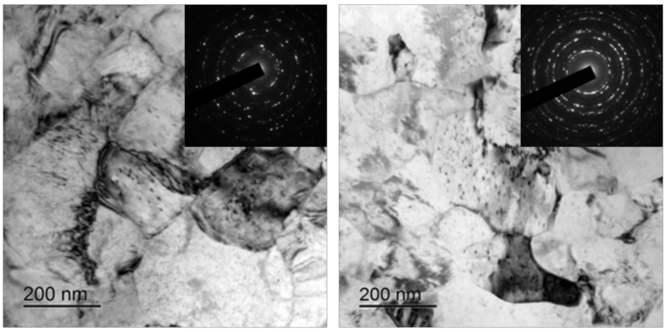


Fig. 2. *Vickers microhardness (a) and electrical conductivity (b) of Cu-0.7%Cr (1), Cu-0.18%Zr (2), Cu-0.9%Hf (3), Cu-0.5%Cr-0.08%Zr (4), and Cu-0.7%Cr-0.9%Hf (5) alloys as a function of aging temperature (annealing time 1 h)*

The electrical conductivity of the alloys after HPT increases noticeably with the aging temperature, which gives an evidence of precipitation from the solid solution (Fig. 2b). However, in the case of Cu-0.7%Cr alloy hardening is thermally stable only up to 300°C because of low efficiency of Cr particles for the stabilization of UFG structure during heating. In binary Cu-0.18%Zr and Cu-0.9%Hf alloys allocation of Cu_5Zr and Cu_5Hf particles suppress the grain growth in UFG structure more effectively than the Cr particles and provide additional hardening during aging (Fig. 2). It should be noted that the Cu-0.9%Hf alloy possesses a higher microhardness and thermal stability as compared with the Cu-0.18%Zr alloy. Additional alloying of binary Cu-Zr and Cu-Hf alloys with Cr can further improve their thermal stability and strength.



(a) (b)

Fig.3. *Structure of Cu-0.7% Cr (a) and Cu-0.7%Cr-0.9%Hf (b) alloys after quenching and HPT*

The results obtained on the alloys after HPT are in good agreement with data on the alloys after ECAP. Thus, the ECAP significantly increases strength of the Cu-0.7%Cr-0.9%Hf alloy by formation of UFG structure with a grain/subgrain size of 220 nm. Yield stress and ultimate tensile strength are 5 and 2 times higher (465 and 571 MPa), respectively, in comparison to initial coarse grained state (Table 1). The alloy after ECAP possesses a relatively high elongation at fracture (10.4%) and low electrical conductivity (35%IACS).

Table 1. *Mechanical and fatigue properties of Cu-0.7%Cr-0.9%Hf alloy (YS = yield stress, UTS = ultimate tensile strength, EL = plastic elongation at fracture, σ_f = fatigue limit)*

Treatment	YS, MPa	UTS, MPa	EL, %	σ_f, MPa (10^7 cycles)
Quenching	89	272	49	185
Quenching + 450 ºC (3.5 ч)	120	306	35.5	215
ECAP	465	571	10.4	310
ECAP + 450 ºC (2.5 ч)	496	605	11.4	375

Subsequent aging leads to a further increase in strength properties due to Cr and Cu_5Hf precipitation, wherein elongation is practically unchanged and electrical conductivity reaches 78%IACS.

ECAP increases the fatigue limit of Cu-0.7%Cr-0.9%Hf alloy from 185 to 310 MPa in comparison to quenched state (Fig.4).

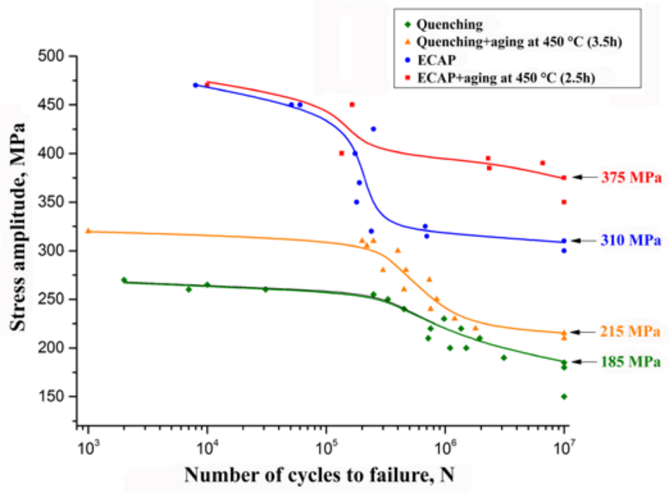


Fig.4. *Stress amplitude versus number of cycles to failure (S–N curves) of Cu-0.7%Cr-0.9%Hf alloy after different treatments*

Fatigue ratio 0.54 in the alloy after ECAP indicates a high resistance to fatigue failure. Additional aging at 450°C for 2.5 hours further increases fatigue limit up to 375 MPa.

Also, considerably enhanced wear resistance under dry conditions is shown in the Cu-0.5%Cr-0.08%Zr alloy after HPT and aging at 450 °C (1h): weight loss decreases by a factor of 8.5 (Table 2).

Table 2 *Weight loss (mg) of Cu-0.5%Cr-0.08%Zr alloy after wear tests under different normal loads*

Treatment	Normal load, N		
	5	**10**	**20**
Warm extrusion	1.10±0.10	3.50±0.20	5.10±0.20
Warm extrusion + 450 °C (1h)	0.50±0.08	1.30±0.10	2.40±0.15
HPT	0.25±0.05	0.90±0.04	1.25±0.05
HPT + 450 °C (1h)	0.35±0.05	0.45±0.05	0.60±0.10

This combination of high wear resistance, mechanical and fatigue properties results in a high durability of electrodes for resistance spot welding. Composite electrode which consists of inexpensive alloy having good electrical conductivity as a holder and UFG Cu-0.7%Cr-0.9%Hf alloy also having good electrical conductivity and in addition good strength for the insert tip was produced (Fig.5). 1000 and 2000 welding cycles were performed under 5,8-7,4 kA current and 0.4 sec. pulse duration.

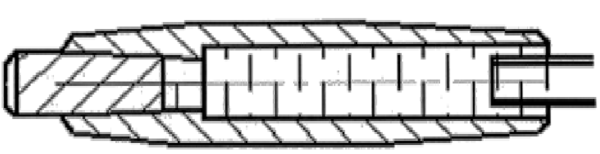


Fig. 5. *Sectional view of an resistance welding composite electrode with an insert tip.*

Studies have shown that the working surface wear of the electrode from the UFG Cu-0.7%Cr-0.9%Hf alloy after 2000 welding cycles is smaller by a factor of 5, relative to a commercial coarse-grained alloy (Table 3).

Table 3 *Relative widening of the electrodes working surface after different number of welding cycles*

Alloy	Number of welding cycles	Relative widening of the working surface), %
Indusrtial alloy Cu-Cr	1000	6.84
	2000	7.24
UFG Cu-0.7%Cr-0.9%Hf alloy after ECAP	1000	1.38
	2000	1.4

4. Conclusions

1. The microhardness of the alloys after HPT rises in the following row: Cu-0.7%Cr, Cu-0.18%Zr, Cu-0.9%Hf, Cu-0.5%Cr-0.08%Zr, and Cu-0.7%Cr-0.9%Hf alloys from 1.7 to 2.4 GPa while the grain size decreases from 209 to 108 nm.
2. Cu_5Zr and Cu_5Hf particles suppress the grain growth in ultrafine-grained structure more effectively than the Cr particles and provide additional hardening during aging.
3. The application of SPD and subsequent aging leads to simultaneously high electrical conductivity, strength, wear resistance and fatigue properties in low-alloyed Cu - based alloys.

5. Acknowledgements

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