Effect of Chemical Composition on Structure and Properties of Ultrafine Grained Cu-Cr-Zr Alloys Produced by Equal-Channel Angular Pressing

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The properties of multi-functional CuCr and CuCrZr alloys with ultra fine grains (UFG) produced by equal-channel angular pressing (ECAP) have been investigated in dependence of concentration of alloying elements. A special attention is paid to optimization of fatigue performance together with strength, thermal and electric properties after ECAP and subsequent aging. Substantial improvement of fatigue life is evidenced in ECAP-fabricated alloys when compared with conventional tempers.

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1. Introduction

Equal-channel angular pressing (ECAP)¹⁻³⁾ is a cold-working technique utilizing intensive simple shear for structure refinement and enhancement of physical and mechanical properties in a broad variety of materials. Many engineering applications require a rather sophisticated combination of materials characteristics. Copper alloys are widely used when a good electrical conductivity is required in combination with high tensile and cyclic strength and thermal stability.⁴⁾ For example, it has been demonstrated recently that CuCrZr alloys can be effectively used in high-speed railways where progressing train speed imposes increasingly severe demands to the strength of the contact wire.⁵⁾ In the latter case it is particularly important to obtain a superb endurance limit in the high-cyclic fatigue (HCF) together with a good resistance to short time periodic overloads in the low-cyclic fatigue (LCF) regime. The requirement of having the electric conductivity exceeding at least 75% IACS (international annealed copper standard) limits the possibility of strengthening the materials for electro-mechanical applications by impurities which concentration should be kept as low as possible for satisfactory electric performance. At the same time, the ECAP technique seems to be most efficient for strengthening of less alloyed systems when the potential of Hall-Petch hardening can be fully realized while the solid solution and precipitation hardening can mask the effect of grain refinement. Therefore, as long as the complex multifunctional properties are of major concern, the material should be carefully designed to meet practical requirements. The effect of ECAP on enhancement of properties of Cu-0.44Cr-0.21Zr alloy has been discussed in detail⁶⁾ and the significance of the number

of ECA-pressings as well as of the post-ECAP aging has been demonstrated for the remarkably improved mechanical properties. However, the role of chemical composition has not been explored so far. Therefore, in the present work we report on experimental findings concerning the multi-functional properties of CuCrZr alloys having different concentrations of components. Special attention is paid to the properties of main interest-tensile and fatigue strength, thermal stability and electric conductivity.

2. Experimental Procedure

The following chemical compositions have been chosen for the present study: Cu-0.36Cr, Cu-0.44Cr-0.21Zr and Cu-0.8Cr-0.05Zr (in mass%). Before ECAP the billets of 14 mm × 15 mm × 175 mm dimensions were solution treated at 1040°C for 30 min and quenched in a 5% water solution of NaCl. Eight ECA-pressings have been performed through 90° die-set with 0.4 mm/s velocity at room temperature via the so-called “route Bc” when the sample was rotated through 90° clockwise about working axis between subsequent passes.

The samples for mechanical testing were shaped by spark erosion to have a nearly square cross-section of 2 × 2 mm² and a gauge length of 10 mm and 3 mm for tensile and fatigue tests respectively. The specimen axis was aligned with the extrusion direction. All specimens were mechanically and electrolytically polished before testing. The LCF experiments were carried out on an Instron hydraulic frame under plastic strain control in fully-reversed tension-compression at constant plastic strain amplitudes, $\varepsilon_{pl} = \Delta\varepsilon_{pl}/2$, ranged from 5×10^{-4} to 1×10^{-2} and at the average cyclic strain rate of $1 \times 10^{-2} \text{ s}^{-1}$ in ambient air at room temperature. The constant stress amplitude was applied in the course of HCF tests. The tensile tests were performed on the same testing machine with a constant strain rate of 10^{-3} s^{-1} .

To obtain maximum strength after ECAP and to satisfy the requirements of electric conductivity, the specimens were

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subjected to isothermal aging at different temperatures using the infra-red furnace allowing rapid heating and precise temperature control in vacuum. Differential scanning calorimetry (DSC, Rigaku 8230) helped to evaluate the thermal stability of ECAP structure and to monitor the phase transformations under linear heating with a constant heating rate of 20 K/min. The Vickers microhardness was measured on the plane perpendicular to the extrusion direction in the as fabricated ECAP state after different heat treatments. The applied load was 500 g, and the loading time was of 15 s. The average values of at least five successive measurements were calculated. The electric conductivity prior to and after annealing was measured relative to the IACS.

A 200 kV transmission electron microscope JEOL 2000FX equipped with an energy dispersive X-ray spectrometer (EDS) was used to characterize the structure after ECAP and subsequent aging. The thin foils were prepared from the flow plane of the billet.

3. Results

3.1 Structure

The structure of Cu-0.44Cr-0.2Zr alloy after ECAP and subsequent aging has been reported in Ref. 6) in some details. Here let us illustrate the typical features of ultrafine structures for CuCrZr alloys by TEM micrographs for the Cu-0.8Cr-0.05Zr specimen, as shown in Fig. 1. The TEM photographs were taken from the billet's flow plane. One can see a rather

uniform structure with nearly equiaxed grains of 200 nm size in average. The grain boundaries are significantly curved and contain numerous offsets. Many grain boundaries are not clearly visible because of a high dislocation density in their intimate vicinity. Although a large number of high-angle grain boundaries exist in the ECAP structure, the significant fraction of low-angle boundaries is also apparent. The extinction contours perpendicular to the grain boundaries indicate the presence of strong elastic stresses in the grain interior, which most likely have been produced by severely distorted grain boundaries. After aging the structure remain fine without appreciable grain coarsening, Figs. 1(c), (d). However, the grain boundaries become more clearly visible, *i.e.* some recovery occurred in the grain boundaries and their vicinity. The narrow annealing twins can be found in the fine structure after aging, Fig. 1(c). Cr-rich precipitates are visible along the grain boundaries primarily, Fig. 1(d), although the EDS analysis identifies precipitates in the grain bodies as well.

3.2 Thermal stability, electric conductivity and aging conditions

The importance of aging for deformation-processed Cu-based alloys, including those fabricated by ECAP, has been well understood for optimization of properties of interest-strength and electrical conductivity.⁷⁾ The DSC measurements, Fig. 2, reveal a multistage character of structural transformations in CuCrZr alloys upon heating. The onset of

Fig. 1 Typical TEM micrographs showing the fine structure of Cu-0.8Cr-0.05Zr alloy after ECAP (a) and (b) and subsequent aging at 450°C for 1 h (c) and (d).

Fig. 2 The enthalpy release rate during linear heating of the ultrafine grain Cu-Cr-Zr alloys.

the first exothermal reaction in Cu-0.44Cr-0.21Zr is noticed about 220°C and the first DSC peak arises around 350°C. The second strong maximum is achieved near 440°C. A similar behavior is noticed in the Cu-0.8Cr-0.05Zr alloy. The precipitation kinetics in ternary alloys is more complex than that of binary ones; however, the peak around 440°C, which is associated with Cr precipitation, appears most pronounced for all alloys investigated. These findings are in line with former detailed investigations of precipitation kinetics in binary CuCr, CuZr and ternary CuCrZr alloys,⁸⁾ where it was found that in the as-quenched specimens Cr precipitates appeared first at about 440°C and then Cu₃Zr precipitation occurred separately at about 520°C. In the cold-worked specimens, the order of precipitation was reversed, that is, Cu₃Zr and Cr appeared at about 370°C and 425°C, respectively. Two precipitation temperatures observed in the ternary alloy agreed well with those of the respective binary alloys in the above cited paper.⁸⁾

The dependence of H_V on aging temperature is illustrated in Fig. 3(a) for all specimens. The temperature, at which the maximum H_V magnitude is achieved, depends on the amount of impurities. Since we are interested in the highest achievable strength, the peak aging conditions, *i.e.* 375, 425 and 500°C, were chosen for further testing of Cu-0.36Cr, Cu-0.44Cr-0.21Zr and Cu-0.8Cr-0.05Zr alloys, respectively. At the same conditions, the satisfactory electric properties have been obtained as illustrated in Fig. 3(b) and Table 1. To meet the industrial needs, the Cu-based alloys for electro-mechanical applications must possess the electric conductivity σ_{el} better than 75–80% IACS.^{5,9)} As shown in Fig. 3(b), the electric conductivity of as-fabricated ECAP samples is

Fig. 3 Vickers microhardness H_V (a) and electric conductivity (b) of ultrafine grain Cu-Cr-Zr alloys as a function of aging temperature (aging time is of 1 h).

very poor, σ_{el} of 25–30% IACS, which is not acceptable. The post-ECAP peak aging improves this property up to affordable magnitudes. Vinogradov *et al.*⁶⁾ have demonstrated that grain growth in the ECAP Cu-0.44Cr-0.21Zr becomes appreciable at temperatures higher than 550°C, *i.e.* the former results as well as the present DCS data show that a good thermal stability is achieved in the UFG state of Cu-based alloys subjected to severe plastic deformation.

3.3 Mechanical behavior

Tensile stress-strain curves for the peak aged samples are shown in Fig. 4. The results of mechanical testing of an ordinary commercial Cu-(0.9–1.3)Cr alloy produced by Yamaha Corp. (Japan) are plotted for comparison. One can see that despite notably lower concentration of Cr, the ECAP Cu-0.36Cr alloy reveals the same yield stress $\sigma_y \approx 390 \pm 20$ MPa as the cold-drawn Cu-(0.9–1.3)Cr. It is not surprising that the ternary Zr-containing alloys exhibit higher strength than the binary CuCr alloys. The highest strength of 710 MPa

Table 1 Properties of Cu-Cr-Zr alloys.

	Cu-0.31Cr-0.07Zr		Cu-(0.9-1.3)Cr (Yamaha Corp)	ECAP followed by peak aging		
	Wire ⁵⁾	Rod ⁵⁾		Cu-0.36Cr	Cu-0.8Cr-0.05Zr	Cu-0.44Cr-0.21Zr
H_V (MPa)	160	170	150 ± 14	162 ± 8	202 ± 5	230 ± 12
σ_{UTS} (MPa)	609	555	460 ± 5	445 ± 5	595 ± 5	710 ± 7
δ (%)	6.2	6.2	19 ± 2	23 ± 3	14 ± 2	12 ± 2
σ_f (MPa)	—	120	110	210 ± 7	240 ± 6	280 ± 8
IACS (%)	80.7	78	90	77	78	76

Fig. 4 Tensile stress-strain curves of the peak aged ECAP Cu-0.44Cr-0.21Zr, Cu-0.8Cr-0.05Zr and Cu-0.36Cr alloys. The tensile stress-strain curve for the commercial Cu-Cr alloy produced by Yamaha Corp. (Japan) is shown for comparison.

is reached in the Cu-0.44Cr-0.21Zr alloy which appears to be markedly higher than the results typically reported for commercially available CuCrZr alloys such as C18150 alloy (Cu-1Cr-0.15Zr, $\sigma_{UTS} = 425$ MPa)¹⁰ (see also Table 1 for other examples). It is worth noticing that all UFG ECAP-fabricated alloys reveal significantly higher ductility than their ordinarily produced counterparts. It turns out that the addition of Zr is particularly significant for the strength of UFG ECAP alloys: Cu-0.44Cr-0.21Zr possesses higher strength than Cu-0.8Cr-0.05Zr although the latter contains a greater total amount of solutes than the former.

As we have stated in Introduction, the HCF resistance of Cu-based alloys can be a property of particular engineering interest. The results of HCF testing are shown in Fig. 5. One can see that ECAP CuCrZr does not have an apparent endurance limit in the range of number of cycles up to 10^7 .

Fig. 5 Wöhler plots for ECAP Cu-Cr-Zr alloys in comparison with conventionally produced Cu-based tempers.

Fig. 6 Cyclic response of ECAP Cu-Cr-Zr alloys peak aged and tested under constant plastic strain amplitude $\Delta\epsilon_{pl}/2 = 1 \times 10^{-3}$.

There is no any pronounced knee or trend to leveling on the S-N (stress versus number of cycles to failure) curve. This is, however, typical of Cu-based alloys. It is worth noticing that HCF life of ECAP CuCrZr is much longer than that of its conventionally produced counterparts. As can be seen in Fig. 6, the fatigue limit σ_f defined on the basis of 10^7 cycles in ECAP Cu-0.44Cr-0.21Zr is of 285 MPa which is considerably higher than that for Cu-0.8Cr-0.07Zr ($\sigma_y \approx 100$ MPa, $\sigma_f \approx 120$ MPa),⁵ Cu-1.98Ni-0.32Be beryllium bronze ($\sigma_y \approx 700$ MPa, $\sigma_f \leq 250$ MPa) or binary Cu-0.75Cr ($\sigma_y \approx 310$ MPa, $\sigma_f \leq 100$ MPa).¹⁰⁻¹² Furthermore, Table 1 shows that the mechanical properties including fatigue limit of the ECAP CuCrZr alloys are remarkably higher than those of the cold-drawn peak aged Cu-0.31Cr-0.07Zr proposed in⁵ as a potent candidate to be used as the contact wire for high-speed railways.

The cyclic response of all ECAP CuCrZr alloys is qualitatively similar as shown in Fig. 6. Intensive cyclic softening is observed in aged specimens. As has been demonstrated, cyclic softening in ECAP CuCrZr can be caused by dislocations cutting through fine precipitates.⁶ Thus, cyclic softening should be dependent on the size, amount and distribution of precipitates. In line with these trivial expectations, Fig. 6 shows that the rate of softening differs for materials with different chemical compositions under the same testing conditions. Since the susceptibility to softening is very sensitive to the thermo-mechanical history of the specimens and, possibly, to the texture formed during processing, it seems plausible to suppose that cyclic softening is strain-path dependent. Detailed investigation of this issue is currently in progress and will be reported elsewhere. One can notice that the higher softening rate is observed in the peak-aged binary ECAP Cu-0.36Cr while the ternary Cu-0.44Cr-0.21Zr reveals slower softening and longer fatigue life despite somewhat lower tensile ductility of the latter alloy (see Table 1 and Fig. 4). It has long been recognized from the strain-based representation of fatigue life¹³ that in the low-cyclic regime at fairly large strains, the plastic strain amplitude is dominant and fatigue life is controlled by ductility. However, it is apparent that the correlation between tensile ductility and crack propagation resistance associated with LCF properties is not straightforward particularly in

dispersion hardened materials where the degradation of properties under LCF depends on a large number of factors including the particle size, distribution and the interaction of particles with moving dislocations. To the contrast, the HCF performance is governed by the elastic portion of the strain range, as would be logically expected from the correlation between the fatigue performance and yield properties or ultimate strength, Table 1.

4. Summary and Conclusions

The ultrafine grain CuCr and CuCrZr dilute alloys with different concentrations of alloying elements have been fabricated by ECAP followed by heat treatment. The post-ECAP aging makes the precipitation hardened ultrafine grain structure rather stable under both thermal and mechanical influence. Optimal aging conditions are found to ensure the best high-cyclic fatigue performance in combination with good electric conductivity, strength and ductility. The significant improvement of tensile and HCF properties is observed together with improvement in ductility if compared to ordinary CuCrZr alloys fabricated by cold working and heat treatment. In combination with proven high thermal stability⁶⁾ and good electric conductivity, the superior mechanical properties and fatigue resistance of ECAP CuCrZr open new perspectives for potential applications if the key obstacles associated with the production cost and scaling will be overcome. Both issues may find their resolution if, for example, the so-called CONFORM (“continuous forming”) process¹⁴⁾ is realized industrially instead of multiple pressings of short billets. It seems clear that, the Cu-based alloys with a broad diversity of properties can be manufactured by ECAP (or similar techniques involving severe plastic deformation) to meet industrial demands by varying chemical compositions, amount of strain and aging conditions.

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