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Effect of doping with Zr on the properties of the deformation-processed Cu-Fe *in-situ* composites

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Effect of doping with alloying element Zr on the structure, the electrical resistivity and the strength of deformation-processed Cu-Fe in-situ composites were studied respectively by scanning electron microscope (SEM), transmission electronic microscope (TEM), material test system (MTS) and resistance measuring apparatus. The experimental results show that the ultimate tensile strength (UTS) and the conductivity of Cu-11.5% Fe-Zr wire cold drawn to the drawing strain $\eta = 7.57$ with intermediate heat treatments were observed to be 824 MPa and 61.4% IACS respectively, and those of Cu-11.5% Fe were 752 MPa and 64.6% IACS. Doping Zr can improve the thermal stability of Cu-Fe composites. The strength of Cu-Fe-Zr wire does not drop more rapidly at higher annealing temperatures (above 300°C) than that of Cu-Fe wire.

1. Introduction

The term in-situ composite is used in the present context to describe materials where oriented fibrous microstructure is created by very heavy mechanical working as the mechanical strength increases. Among the alloys showing such behaviour it is possible to distinguish those typically containing a dendritic body centred cubic (b.c.c.) phase dispersed in a face centred cubic (f.c.c) matrix, such as Cu with Nb, Ag, Ta, Cr or Fe. The literature indicates that high strength and high conductivity Cu-X in-situ composites are widely used for applications such as lead frames and electrical connector. The Cu-Fe system is particular interest because of the relatively low cost of iron compared to the other possible components. But the relatively high solubility of iron in copper at high temperature, coupled with the slow kinetics of iron precipitation at low temperatures makes it difficult to achieve good electrical conductivity. The study on the high strength potential in drawn Cu-Fe alloys had begun several decades ago. It is reported that Hodge and his team had carried out a research programme to develop high strength and high conductivity wires for the US Army in the late 1940s [1]. They had invented a new wire with high strength and high conductivity. The alloy wire containing Cu-15%Fe-0.1%Mg, had tensile strength of 1080 MPa with conductivity of 56% IACS. The particularly attractive feature of these alloys is the combination of high strength plus high electrical conductivity. For this reason studies have employed difference mechanical and thermal treatments, for evaluating the effectiveness of various treatments at improving the strength and electrical conductivity of Cu-Fe alloys. Previous studies have been mostly directly to binary Cu-Fe alloys, with the reduction of Fe content, the conductivity is expected to increase at the expense of the strength. Verhoeven introduced proper intermediate heat treatment to the process of the deformation to promote precipitation of Fe from Cu-matrix, his experiment results shown that the electrical conductivity of alloy wires is improved [2]. Meanwhile, several investigators analyzed the strengthening mechanism [3, 4] and the relationship between the strength and the microstructure of Cu-Fe in-situ composite [5, 6]. In order to achieve higher strength and better resistance to recrystallization of Cu phases during aging treatment, small amount of third element has been added into the Cu-X alloys, such as Zr has been added into Cu-Cr alloy. It was found that the addition of the alloying element could dramatically reduces the thickness of the primary second phase at the same drawing strain, retard the dynamic recovery and recrystallization of Cu phase and lead to the banded structure in Cu. In this study the structure-property relationship in thermo- mechanically processed Cu-Fe based in-situ composites alloyed with the third alloying element Zr was examined. The purpose of this study is to investigate the effect of the third alloying element on the microstructure and physical properties of deformation processed Cu-Fe-Zr in-situ composite wires,

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TABLE I Material composition (in wt.%)

Alloys	Cu	Fe	Zr
Cu-11.5%Fe	Bal.	11.50	–
Cu-11.5%Fe-Zr	Bal.	11.50	0.200

and to examine the possible ways to improve the physical properties of Cu-Fe alloys.

2. Experimental

Two compositions were chosen for investigation, namely, Cu-11.5%Fe and Cu-11.5%Fe-0.2%Zr. The melts were prepared using electrolytic Cu with at least 99.99 wt% purity, ingot iron with at least 99.9 wt% purity and commercial Zr. The alloys were separately melted in a vacuum induction furnace using a magnesia crucible. The alloys were cast into a Cu-mould at a temperature about 1300°C. Table I shows the final compositions of the cast alloys.

Its diameter of cast samples was about 25 mm. Cylindrical ingots of 22 mm diameter were cut from the as cast samples in order to remove the oxidation layer and surface defects. The samples were produced by rotary swaging to 16 mm diameter and subsequent by rolling to 8.5 mm diameter. Then the samples were cold drawn to various strains through hard metal drawing bench dies with three intermediate heat treatments. The strains were defined by $\eta = 1\text{n}(A_0/A_f)$, where A_0 is the initial section and A_f is the final section. At last some samples were heat treatmented in a vacuum furnace. The experimental processes are shown in Fig. 1.

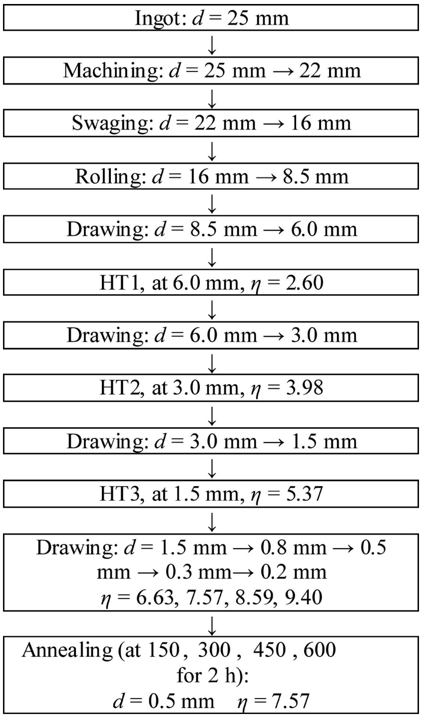

Figure 1 Processing route of Cu-Fe wires manufacture. (HT1, HT2, HT3–intermediate heat treatment, $\Delta\eta = 0.02{\sim}0.1$).

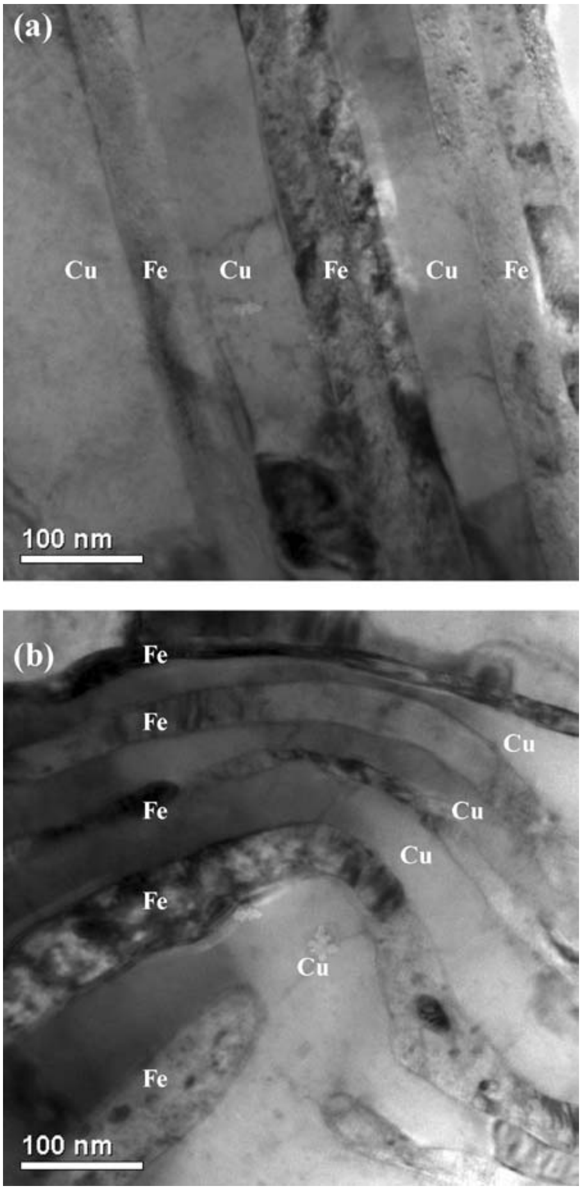

Figure 2 Longitudinal (a) and transverse section (b) TEM micrographs of the Cu-Fe in-situ composite ($\eta = 6.63$).

The microstructure of samples were investigated by transmission electron microscopy (TEM) TecnaiG^{2}20 with an accelerating voltage of 200 kV. The tensile test were carried out using material test system (MTS) at strain rate of 10^{-2} mm/s. UTS was calculated as an average for five samples with error of ±5 MPa. The fractures of the tensile specimens were examined in scanning electron microscopy (SEM) JSM-6360 with an accelerating voltage of 20 kV. The electrical resistivity was measured at room temperature with the conventional four-point method at constant current of 100 mA.

3. Results and analysis

3.1. Microstructure

Details of microstructural evolution of the as cast Cu-Fe alloys have been given elsewhere [7]. The dendrites of Fe were homogeneously distributed in the Cu-matrix. Fig. 2

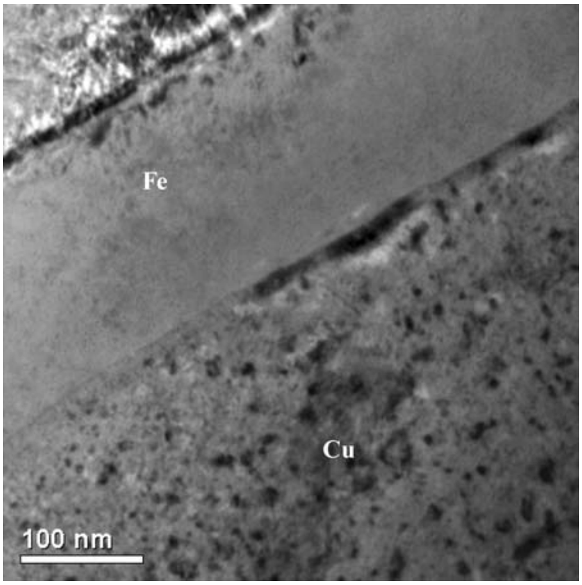

Figure 3 Longitudinal TEM micrographs of the Cu-11.5%Fe-Zr in-situ composite ($\eta = 7.57$).

shows the longitudinal and transverse sections of drawn Cu-Fe wire with three intermediate heat treatments. Since the microstructure morphology of two alloys is quite similar, only one of them is shown. On the longitudinal sections the alignment of the filaments with axis is readily apparent. The ribbonlike morphology of the filaments is clearly evident on the transverse sections. It can be see that Fe ribbons are bend on transverse section, because the Fe ribbon morphology is associated with the geometric arrangement of slip systems and the development of the ⟨011⟩ texture. The Fe ribbons tend to lie at the Cu grain boundaries. The results of the present research do not indicate any marked effect of doping with Zr on the parameters of microstructure of the investigated wires. There are many small particles on the high magnification TEM images of deformation-processed Cu-11.5%Fe-Zr in-situ composites (Φ 0.5) in Fig. 3. Some small particles are discovered on Fe filaments and Cu-matrix, whose diameters are from a couple of nm to more than 10 nm. They could be the ZrO_2 particles, according to the report about the research on Cu-Nb-Zr alloy, which found ZrO_2 precipitates of two different morphological types in Zr-doped specimens. It is evident that coarse and dispersed ZrO_2 particles are formed at different conditions. The coarse ZrO_2 particles are formed from liquid phase during crystallization due to a high thermal stability of ZrO_2 oxide, but the dispersed ZrO_2 particles are formed in the solid state [8].

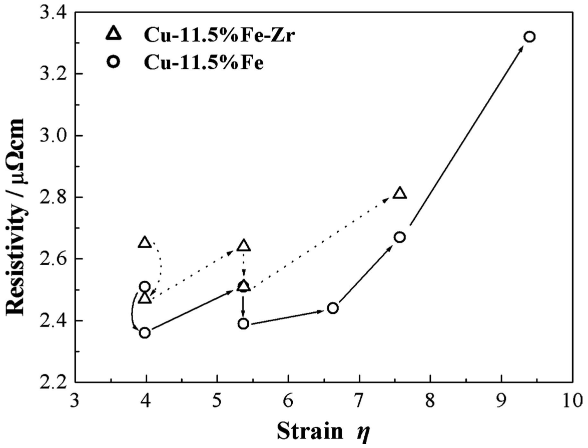

Figure 4 Effect of intermediate heat treatment and strain on the resistivity of in-situ composites.

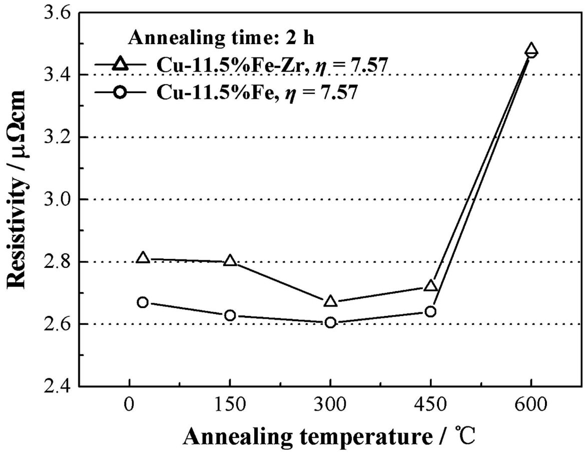

Figure 5 Effect of annealing processes on the resistivity of in-situ composites.

3.2. Electrical resistivity

The relationship between the electrical resistivity and the drawing strain of deformation-processed in-situ composites is shown as Fig. 4. It can be seen that the electrical resistivity of alloys increased as the strain increased. The addition of Zr can increase the electrical resistivity of Cu-11.5%Fe alloy about 0.15 $\mu\Omega$ cm. The variation in the value of resistance before and after the adding of Zr is almost constant with different drawing strain. The doping of Zr can reduce Fe dendrite sizes, which had been formerly discovered in Ref. [8]. The effect of Zr on the electrical resistivity may be that the addition of Zr increases impurity scattering resistivity and makes the grains finer which increases the interface scattering resitivity.

Meanwhile the result of the experiment discovered that intermediate heat treatment (HT2, HT3 for Φ 3 and Φ 1.5 wires) can decrease the resistivity of wires about 0.20 $\mu\Omega$ cm due to large dislocation density and higher temperature can promote Fe precipitation from Cu-matrix, which decreases the impurity scattering resistivity.

Fig. 5 shows the variation in electrical resistivity of Cu-Fe in-situ composites as annealing temperature. It is seen that the annealing at or lower 300°C, the electrical resistivity drops slightly, while the electrical resistivity increases sharply when the annealing temperature exceeds 450°C and the same pattern can be applied to both deformation-processed Cu-11.5%Fe and Cu-11.5%Fe-Zr in-situ com-

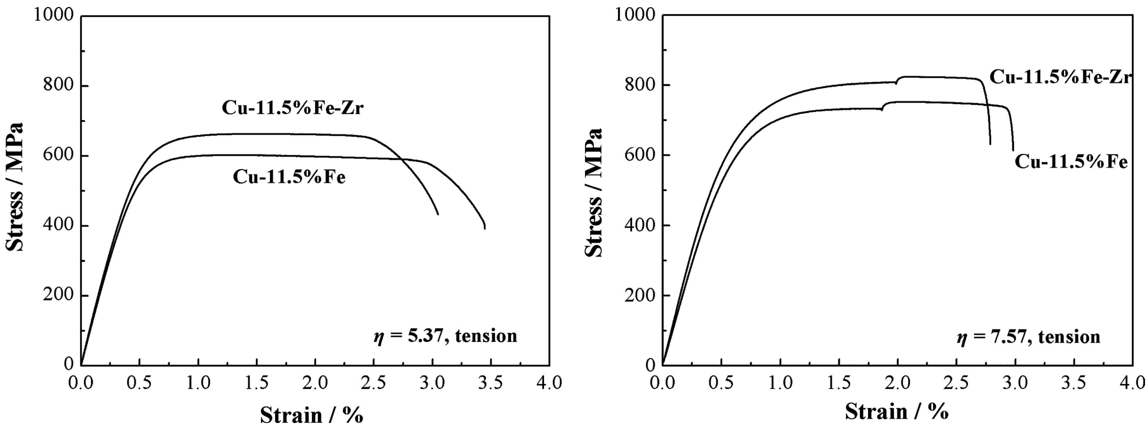

Figure 6 Stress-Strain curves of in-situ composites. (a) $\eta = 5.37$, (b) $\eta = 7.57$.

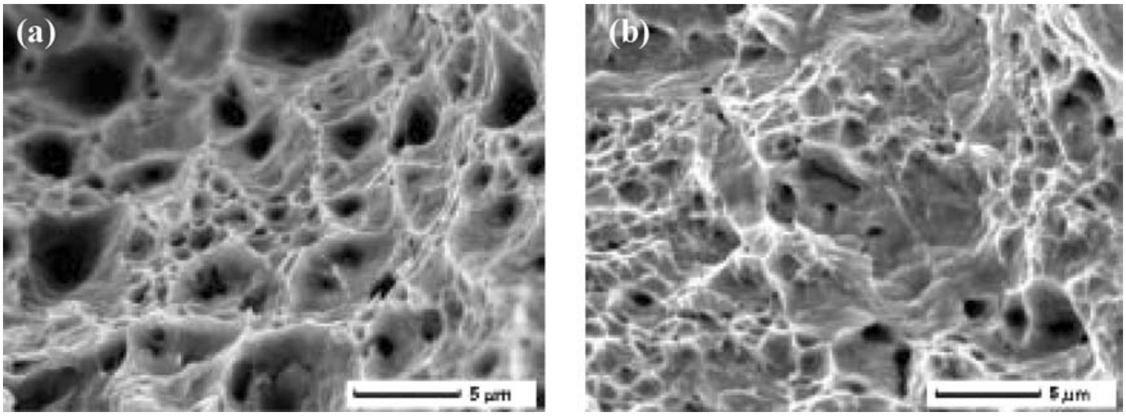

Figure 7 SEM micrographs of fracture surface for in-situ composites ($\eta = 5.37$). (a) Cu-11.5%Fe, (b) Cu-11.5%Fe-Zr.

posites. It is suggested that at or lower 300°C the Fe precipitation is promoted from the Cu-matrix, which reduces impurity scattering and consequently reduces the resistivity. When the temperature exceeds 450°C, the Fe atoms are dissolution in Cu-matrix again, which increaces the impurity scattering resistivity sharply.

3.3. Mechanical properties

Fig. 6 shows the stress-stain curves of wires at $\eta = 5.37$ and $\eta = 7.57$. It can be seen that adding a little Zr in Cu-11.5%Fe can improve the strength of alloy.

The fracture micrographs of Cu-11.5%Fe and Cu-11.5%Fe-Zr wires ($\eta = 5.37$) are shown in Fig. 7. Both alloy wires exhibited highly ductile fractures. But doping with Zr makes its contraction percentage of area drops. The contraction percentages of areas are $\psi = 64.8\%$ (Cu-11.5%Fe) and $\psi = 59.5\%$ (Cu-11.5%Fe-Zr) respectively.

The result shows that Zr enhances the strength and reduces the ductility of alloyed composites, because the ZrO_2 particles may result in the dispersion strengthening due to their small sizes and the retarding of the processes of recovery and recrystallization at intermediate heat treatment [9].

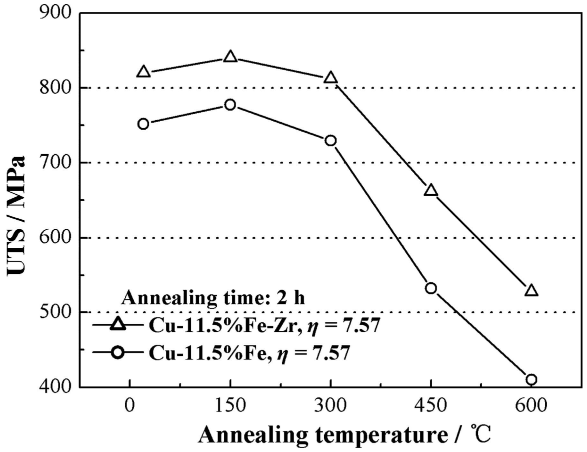

Figure 8 Relationship between strength and annealing temperature.

Fig. 8 shows the relationship between sample's UTS and the annealing temperature (Cu-11.5%Fe-Zr and Cu-11.5%Fe at $\eta = 7.57$). It is found that the UTS drops sharply with increasing annealing temperatures above 300°C, which is similar to other test results [10].

The difference of UTS between two wires after annealing at same temperature is shown in Fig. 9. We can clearly see that the adding of Zr can obviously improve the ther-

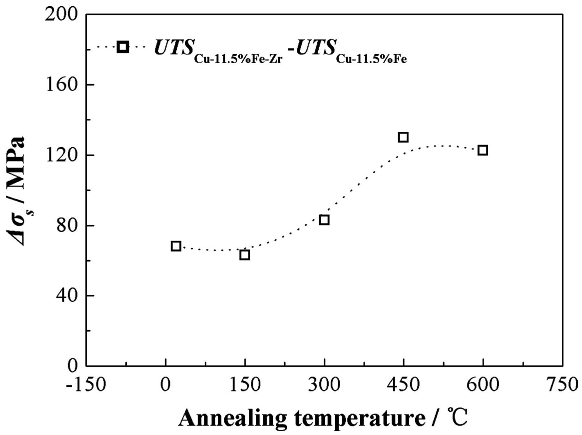

Figure 9 UTS' difference of two wires after annealing at same temperature.

mal Stability of Cu-Fe in-situ composites. The evidence is a weaker effect of annealing on the UTS of alloyed with Zr composite then unalloyed one.

4. Conclusion

Effect of doping with Zr on the structures and properties of the deformation-processed Cu-Fe in-situ composite wires has been investigated. The conclusions have been drawn as follows:

The UTS and the conductivity of Cu-11.5%Fe-Zr wire ($\eta = 7.57$) with intermediate heat treatments were observed to be 824 MPa and 61.4% IACS respectively, and those of Cu-11.5%Fe ($\eta = 7.57$) were 752 MPa and 64.6% IACS. The doping of Zr can increase the UTS about 10% with decrease somewhat the ductility and obviously improve the thermal stability of Cu-Fe in-situ composites. Because the ZrO_2 particles may result in the dispersion strengthening due to their small sizes and the retarding of the processes of recovery and recrystallization at intermediate heat treatment. However, at the same time it can slightly decrease the conductivity of the alloys, because the ZrO_2 particles can increases the impurity scattering resistivity and makes the grains finer which increases the interface scattering resistivity.

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