

Growth Morphologies of Fe Nanoparticles in the Copper Alloy

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Abstract: In this paper, based on experiments, by study the nanoparticles crystallized in Cu-Fe alloy, research possibility to form situ nanoparticles dispersion in matrix of immiscible Cu-X alloy. Nanoparticles of Fe-rich dispersed in copper alloy were obtained by experimental methods. Confirmed by adding elements Fe (1-3%) and Co and by thermodynamic controlling, Fe-rich nanoparticles dispersed in matrix of the copper cast alloy can be obtained. It is proved that these Fe-rich nanoparticles and the Cu-matrix phase remains coherency relationship.

Introduction

Cu-X (X = Fe, Co, Cr, Ta, Nb, etc.) are metastable immiscible alloys [1], they have broad application prospects when the X-rich phase dispersed in the Cu-matrix when Cu is richer than X element of these alloys [2-4]. However, since the segregation structure easily formed during solidification of these alloys, their application has been limited. Phase diagrams of Cu-X metastable immiscible alloys have similarity, typical phase diagram of metastable immiscible binary alloys is shown in Fig.1. (a), below the liquids line, there is a immiscible liquid area consist of the metastable phase. When the degree of undercooling is small, the melt liquid occurs liquid-solid phase transform, but the degree of undercooling is larger, the alloy melt liquid is into the immiscible liquid area, and it forms two immiscible liquid: Cu-rich liquid phase (L₁) and X-rich liquid phase (L₂). Now, people studied Cu-X alloys especially studied Cu-Fe and Cu-Co metastable immiscible alloys [4-7], but the research work focuses on thermodynamics.

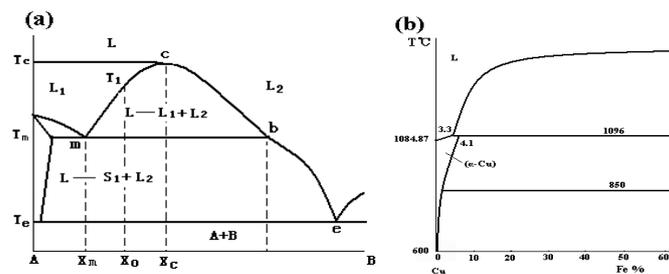


Fig.1. (a) Typical phase diagram of metastable immiscible binary alloys; (b) Cu-Fe phase diagram

In this paper, based on experiments, by study the nanoparticles crystallized in Cu-Fe alloy, research possibility to form situ nanoparticles dispersion in matrix of immiscible Cu-X alloy. Analyze changes of morphology and distribution of nanoparticles in Cu-Fe alloy when the content changes of alloying element Fe and Co and the natural convection changes in crystal process.

Nanoparticles in copper alloys

As shown in Fig.1. (b), According to Cu-Fe phase diagram under equilibrium solidification conditions [8], the solidification process of Cu-Fe (Fe < 3.3%) alloy can be described as, when the temperature of the alloy melt dropped below the liquidus line, primary α -Cu crystallized from the liquid phase. When the temperature of the alloy dropped below the solidus line, the remaining liquid would completely converted to α -Cu. As the temperature continues to drop, Fe will separate out from

α -Cu in Cu-Fe. However, quantitative number of our experiments showed that Fe particles can also crystallize from melted liquid directly, the final form of Fe is nanoparticles dispersed in the matrix of the alloy.

Experimental equipment

A vacuum induction furnace was used in the experiment, having temperature measurement, supplementary feeding, trace elements feeding and other functions. It does not destroy vacuum situation of furnace room, having filling with inert gas to furnace room to control the furnace pressure and atmosphere at the same time. Casting shapes in the experiment were quartz tubes with diameters of 3 mm and 6 mm. There is a small natural convection during solidification in 6 mm diameter quartz tube and convection is negligible when solidification in 3 mm diameter quartz tube [9]. Vacuum induction furnace is smelting equipment under vacuum or under gas protection conditions. By the action of alternating current induction, the metal furnace charge in the crucible itself heating and melting, and further the metal liquid overheating. Vacuum induction furnace main technical parameters as shown on Tab. 1.

Tab. 1. Main technical parameters of the vacuum induction furnace

Items	Parameters	Items	Parameters
capacity	10 Kg	Rated IF frequency	4000 Hz
Maximum operating temperature	1700°C	Intermediate frequency voltage	300 V
Maximum vacuum	6×10^{-3} Pa	Cooling water consumption	9 m ³ /h
Pressure rise rate	4 Pa/h	Cooling water pressure	0.3 MPa

Distribution and size of the nanoparticles in alloy

Figure 2 is TEM images of Cu-Fe cast alloys solidified in 3mm diameter quartz tube. In this condition, the diameter of quartz tube is too small, so convection is neglect [9]. As Fig. 2 (a), it is Cu-1Fe (Fe content is 1%) alloy, there are a large number of dispersed nanoparticles in the matrix, these nanoparticles can be divided into two classes, the first type nanoparticle's size is 5-10 nm (for example in the area I), dispersed in the matrix; the other type nanoparticle's size is about 25 nm (for example in the area II), dispersed in the matrix.

Figure 2 (b) compares with Fig. 2 (a), with the increase of content of Fe, particles in the matrix occurred changes on size and morphology. According to the size and shape, particles in Cu-1.5Fe alloy can be divided into three types, the first type of nanoparticle's size is 5-10 nm (for example in the area I), it dispersed in the matrix; the second type of nanoparticle's size is 50-80 nm (for example in the area II), disc-shaped and dispersed in the matrix; the third type of nanoparticle's size is about 170-300 nm (for example in the area III), petaloid and dispersed in the matrix.

Figure 2 (c) compares with Fig. 2 (b), content of Fe is increased from 1.5% to 2%, but the difference of distribution and size of the nanoparticles is very small.

Figure 2 (d) is TEM of Cu-1Fe-0.5Co (Fe content is 1%, Co content is 1.5%) cast alloy. Comparison shows, size and morphology of the particles in the matrix occurred large changes as a result of adding the element Co. As shown, there are a large number of dispersed nanoparticles on the matrix. These nanoparticles can be divide into four classes, the first class nanoparticles' size is 5-10 nm (for example in the area I), dispersed in the matrix; the second class nanoparticles' size is about 20 nm (for example in the area II), disc-shaped, and twins phenomenon began to appear (please see 2.6); the third class nanoparticles' size is about 100 nm (for example in the area III), disc-shaped dispersed in the matrix. The fourth class nanoparticles' size is greater than 150 nm (for example in the area IV), and the shape has become typical petals.

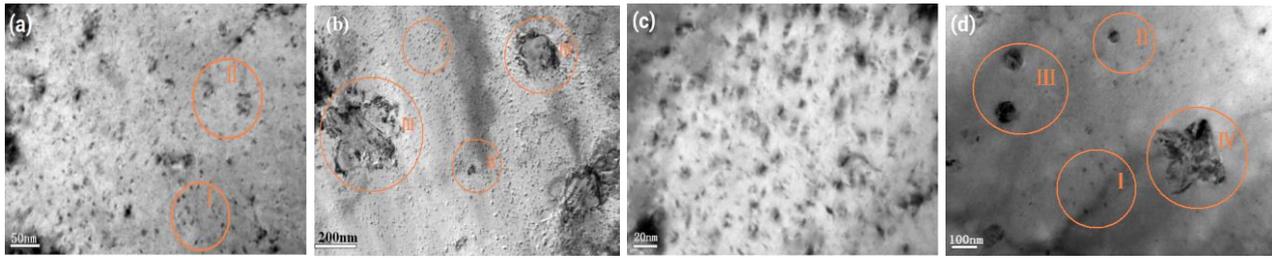


Fig.2. TEM images of Cu-Fe cast alloys solidified in 3mm diameter quartz tube (a) Cu-1Fe alloy; (b) Cu-1.5Fe alloy; (c) Cu-2Fe alloy; (d) Cu-1Fe-0.5Co alloy

Composition of the nanoparticles

As shown in Fig. 3(a) and Fig. 4(a), EDS analysis aimed a larger precipitated phase in Cu-1Fe alloy as shown in Fig. 1(a) and Cu-1Fe-0.5Co alloy as shown in Fig. 1(d). 91.48% of content of precipitated phase in Cu-1Fe alloy is element Fe, 8.52% the remainder being Cu. 60.98% of content of precipitated phase in Cu-1Fe-0.5Co alloy is element Fe, 25.95% is element Co, the remainder being Cu. Precipitated phase particles in alloys are rich in Fe, element Co and Cu are solid solution in Fe particles during solidification process. Therefore, these precipitates may be referred Fe nanoparticles.

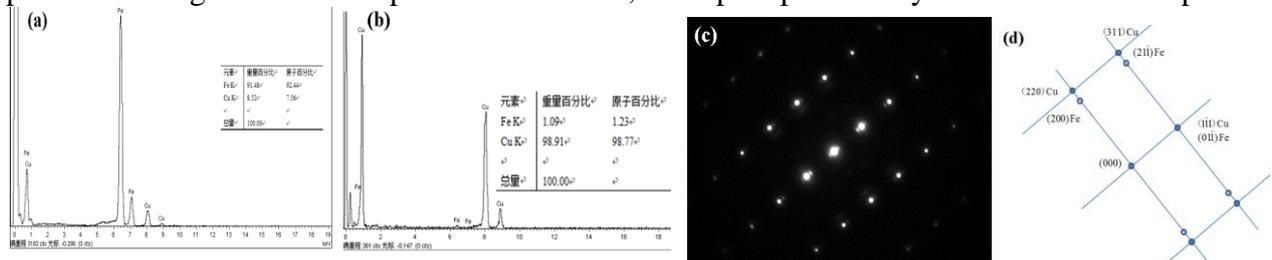


Fig. 3. EDS and diffraction pattern of Cu-1Fe alloy solidified in 3 mm diameter quartz tube (a) EDS of matrix of Cu-1Fe alloy; (b) EDS of an nanoparticle of Cu-1Fe alloy; (c), (d) Diffraction pattern and its calibration of Cu-1Fe alloy

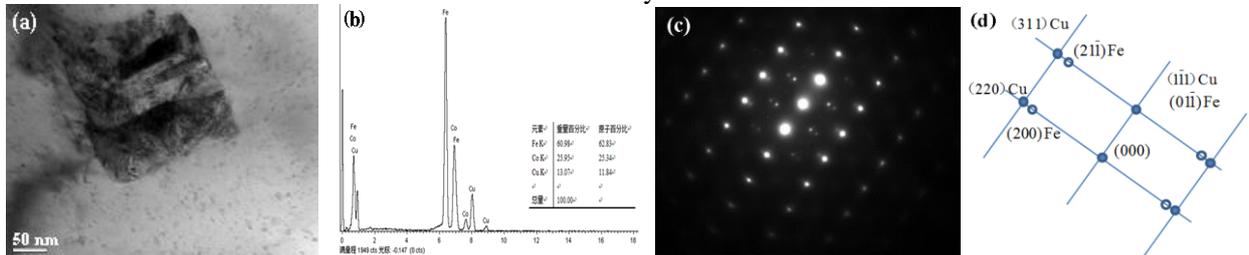


Fig. 4. EDS and diffraction pattern of Cu-1Fe-0.5Co alloy solidified in 3 mm diameter quartz tube (a) Cu-1Fe-0.5Co alloy; (b) EDS of an nanoparticle of Cu-1Fe-0.5Co alloy; (c), (d) Diffraction pattern and its calibration of Cu-1Fe-0.5Co alloy

Relationship between Fe-rich phase and the matrix phase

Diffraction pattern of area and spots in Cu-1Fe alloy is shown in Fig. 3 (b), the diffraction spots calibration is shown as Fig. 3 (c), the large, strong bright diffraction spots are the matrix of copper, the weaker spots are precipitated Fe-rich nanoparticles, because of (1-11) Cu // (01-1) Fe, so a fully coherent relationship presence between Cu-matrix and Fe-rich particles in Cu-1Fe alloy.

Diffraction pattern of area and spots in Cu-1Fe-0.5Co alloy is shown in Fig. 4 (b), the diffraction spots calibration is shown as Fig. 4(c), the large, strong bright diffraction spots are the matrix of copper, the weaker spots are precipitated Fe-rich nanoparticles, (1-11) Cu // (01-1) Fe as shown in Fig. 4(c), so a fully epitaxial relationship presence between Cu-matrix and Fe-rich particles in Cu-1Fe-0.5Co alloy too.

Morphology of the nanoparticles

Fig. 5 are TEM images of Fe-rich precipitates in Cu-2Fe alloy solidified in 3mm or in 6mm diameter quartz tubes, the size of precipitates are about 150~400nm. Compare Fig. 5 (a) and Fig. 5 (c) , when the size of precipitates is about 150nm, the boundary of the Fe-rich precipitate in Cu-2Fe alloy solidified in 3mm diameter quartz tube is relatively smooth, while the boundary of the Fe-rich precipitate in Cu-2Fe alloy solidified in 6 mm diameter quartz tube is obvious concavity (arrows Point to). When the size of precipitates is larger than 350nm, the shape of Fe-rich precipitates in Cu-2Fe

alloy solidified in 3mm diameter quartz tube become typical petaloid, as shown in Fig. 5 (b) ; and the shape of Fe-rich precipitates in Cu-2Fe alloy solidified in 6mm diameter quartz tube is also petaloid and appears fusing appearance (an arrow Points to), as shown in Fig. 5 (d) .

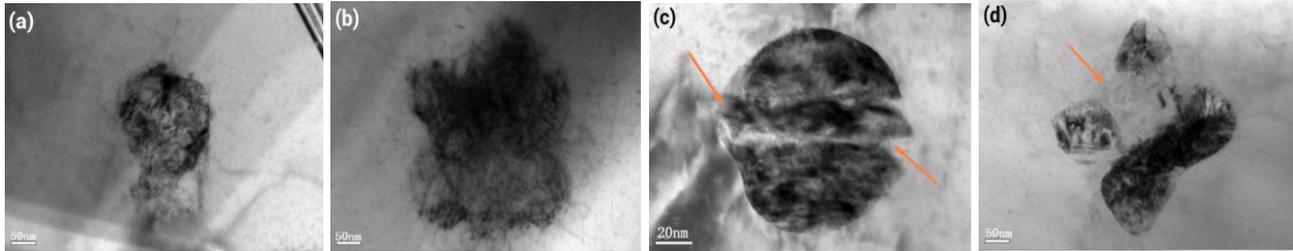


Fig. 5. TEM images of Cu-Fe cast alloys

- (a), (b) Fe-rich phase of Cu-2Fe alloy solidified in 3mm diameter quartz tube
(c), (d) Fe-rich phase of Cu-2Fe alloy solidified in 6mm diameter quartz tube

Twin structure of the nanoparticles

Figure 6 show twin crystal structure of Fe-rich phase from TEM images and diffraction spots of Fe-rich phase in Cu-1.5Fe alloy or in Cu-1.5Fe-0.5Co alloy solidified in 3mm diameter quartz tubes. By analysis of diffraction spots to the Fe-rich phase their size are about 170 nm as shown in Fig. 6(a) and Fig. 6(b). As shown in Fig. 6(c), twin plane of the Fe-rich phase of Cu-1.5Fe is (112), but in the Cu-1.5Fe-0.5Co alloy, diffraction spots of the Fe-rich phase form rings as shown in Fig. 6(d). Therefore, it is considered from diffraction spots that anisotropy of the Fe-rich phase added Co element is larger than the Fe-rich phase no added Co element.

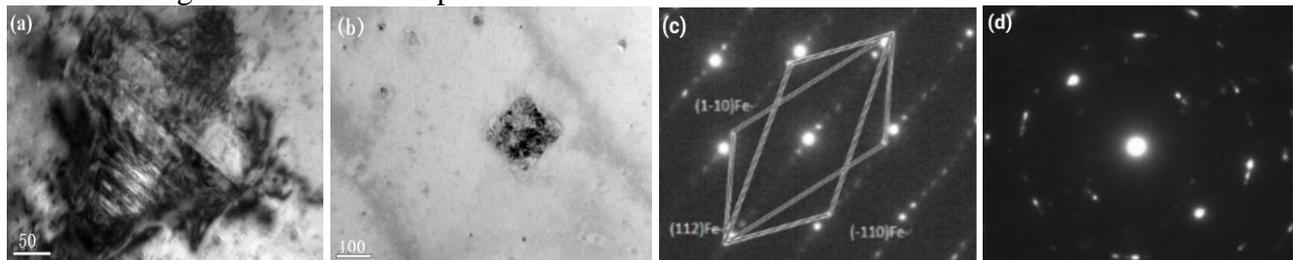


Fig. 6. The twin structure of Fe-rich phase

- (a), (c) TEM images and diffraction spots of Fe-rich phase in Cu-1.5Fe alloy
(b), (d) TEM images and diffraction spots of Fe-rich phase in Cu-1.5Fe-0.5Co alloy

Coherency relationship

Using HRTEM (High-resolution TEM image) to further study the morphology and structure of the nanoparticles. Figure 7 (a) is a HRTEM photograph of two nanoparticles, size of the larger and circular nanoparticle (arrow A Points to) is about 16nm, size of the smaller and rectangular nanoparticle (arrow B Points to) is about 6nm. Crystal plane spacing of copper matrix surrounding nanoparticles is 0.208nm, it is consistent with the crystal plane spacing of copper (-11-1). Crystal plane spacing of the nanoparticle in Fig. 7 (a) is 0.201nm equal to crystal plane spacing of iron (1-10). Fourier transformation and calibration directed to the precipitated phases in selected area, in figures, the strong brightness spots are copper matrix, the weaker brightness spots are precipitated Fe-rich phase. Mismatch between the matrix phase and the precipitated phase is calculated by the following formula with

$$\sigma = 2(d_1 - d_2) / (d_1 + d_2) \quad (1)$$

Where, σ is a mismatch between the matrix phase and the precipitated phase; d_1 and d_2 are crystal plane spacing of the Cu-matrix (-11-1) and Fe-precipitates (1-10). Calculating according to the formula (1), $\sigma = 0.034$, it falls within the range of 0-0.05 (criterion for coherent relationship), therefore, it can be considered that fully coherent relationship presence between Cu (-11-1) and Fe (1-10).

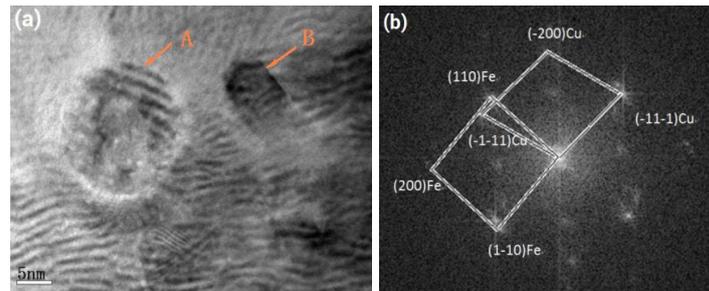


Fig.7. High-resolution TEM image and diffraction spots calibration of Fe-rich phase in Cu-1Fe alloy solidified in 3mm diameter quartz tube

Conclusion

Nanoparticles of Fe-rich dispersed in copper alloy were obtained by experimental methods. Confirmed by adding elements Fe (1-3%) and Co and by thermodynamic controlling, Fe-rich nanoparticles dispersed in matrix of the copper cast alloy can be obtained. It is proved that these Fe-rich nanoparticles and the Cu-matrix phase remains coherency relationship.

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