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Heterogeneous nucleation effect of in situ iron-rich nanoparticles on grain refinement of copper alloy

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ABSTRACT

Grain refinement of casting Cu–10Sn–2Zn–(1–3)Fe–0.5Co (wt%) alloys were characterized under the heterogeneous nucleation effect of in situ iron-rich nanoparticles. Grain size of the alloys decreases sharply with an increase of Fe content (Fe ≤ 1.5 wt%), but levels off with a further increase of Fe content (Fe > 1.5 wt%). The heterogeneous nucleation effect is correlated with wettability, spatial distribution and size distribution of the nanoparticles and limited by recalescence of the melt. This work offers a potential pathway for fabricating bulk nanostructured alloys to realize excellent properties by investigating the heterogeneous nucleation effect of in situ precipitation nanoparticles.

1. Introduction

Nanoparticle strengthening has been presented for steel, copper alloy and Mo alloy, through which dispersion-strengthened materials possess high strength without sacrificing their ductility [1–7]. Except by aging treatment [5] and powder metallurgy [1,6,7], nanoparticles fabricated in copper alloys during solidification process [3,4] is extremely noticeable. As summarized in Fig. 1, cast nanostructured Cu alloy with numerous in situ iron-rich nanoparticles well dispersed in refined micrometer-sized grains achieve the unprecedented properties, i.e. simultaneous high strength and extraordinary ductility, comparisons with previously reported pure Cu or Cu alloys, including dendrite [3,4], bimodal [8] coarse-grained [8] or nanocrystal [8–11] copper alloys which possess either low strength or low ductility. Refined grains in the nanostructured Cu alloys are supposed to be correlated with the heterogeneous nucleation effect of iron-rich nanoparticles. As known, much work has been carried out to study the precipitation of iron-rich nanoparticles in Cu–Fe or Cu–Fe–Co alloys [3,4,12–17]. People mainly focus on characterization and strengthening effects of the nanoparticles, but systematic studies have rarely been carried out to investigate their heterogeneous nucleation effect in copper alloys. Actually, heterogeneous nucleation during solidification can result in significantly smaller grain sizes [18] and markedly improved yield strength according to the Hall–Petch relationship without ductility decrease [19,20]. Therefore, it is significant to investigate heterogeneous nucleation effect of the nanoparticles.

The wettability or crystallographic matching with metal matrix are key factors for the particles to be active nucleation sites [18,21,22] and the spatial distribution of the particles determines the final as-solidified grain structure [18,23]. However, comely used exotic ceramic particles especially nano-sized ones in liquid metals are extremely difficult to obtain uniform dispersion due to high viscosity, poor wettability in the metal matrix, and a large surface-to-volume ratio [24]. Hereby, such exotic ceramic particles poor in the properties will hardly be potent substrates and cannot be effective in heterogeneous nucleation of copper matrix. Besides, effective refinement requires not only heterogeneous nucleation but growth restriction. In a solidifying system, the remaining melt can be sufficiently undercooled to guarantee the nucleation occurring only if there is some solute in the melt to restrict the growth of the solid [22]. Due to these demands, the aim of this work was to carry out a detailed investigation on the heterogeneous nucleation effect of in situ iron-rich nanoparticles.

2. Experimental

Virgin Cu–10Sn–2Zn (wt%) alloy and a set of Cu–10Sn–2Zn–(1.0, 1.5, 2.0, 3.0)Fe–0.5Co (wt%) alloys were melted and cast into

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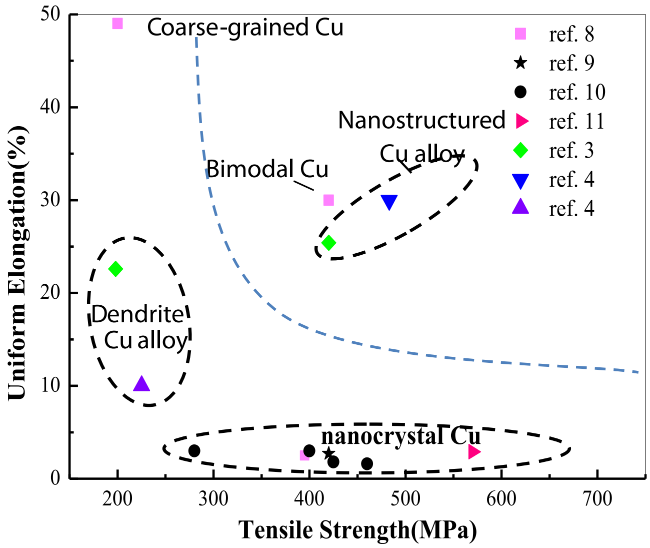

Fig. 1. Tensile strength versus uniform elongation of nanostructured Cu alloys with minor Fe, Co in comparison with available literature data. Figure reproduced from Ref. [3].

rod samples ($\Phi 20 \times 140$ mm). The main processing steps have been described [3]. It is noted that Co were added with Fe to the melt at 1350 °C and held for 30 min. The difference of density between iron and copper is not too large, 7.8×10^3 kg m^{-3} for Fe and 8.9×10^3 kg m^{-3} for Cu, respectively, and the melt of the alloys has been stirred in the middle frequency furnace during the melting process. This can effectively to modify the particle size and distribution in the melt. Then, the melt was poured into the graphite mold at 1200 °C on a centrifugal disc, which was rotated at the velocity of 300 rpm. As illustrated in [4], centrifugal pressure condition is beneficial for maintaining the nano-sized scale of iron-rich phase. The microstructures of the alloys were examined with a LEO1450 Scanning Electron Microscope (SEM) and a 9XB-PC optical microscope (OM). The mean linear intercept technique was used to quantify grain size. The morphology and composition of the nanoparticles was characterized by transmission electron microscopy (TEM) on a JEOL JEM-2100 TEM operated at 120 kV and spherical aberration corrected scanning transmission electron microscope (Cs-corrected STEM) with a JEOL-ARM (200F) 200kV FEG-STEM/TEM.

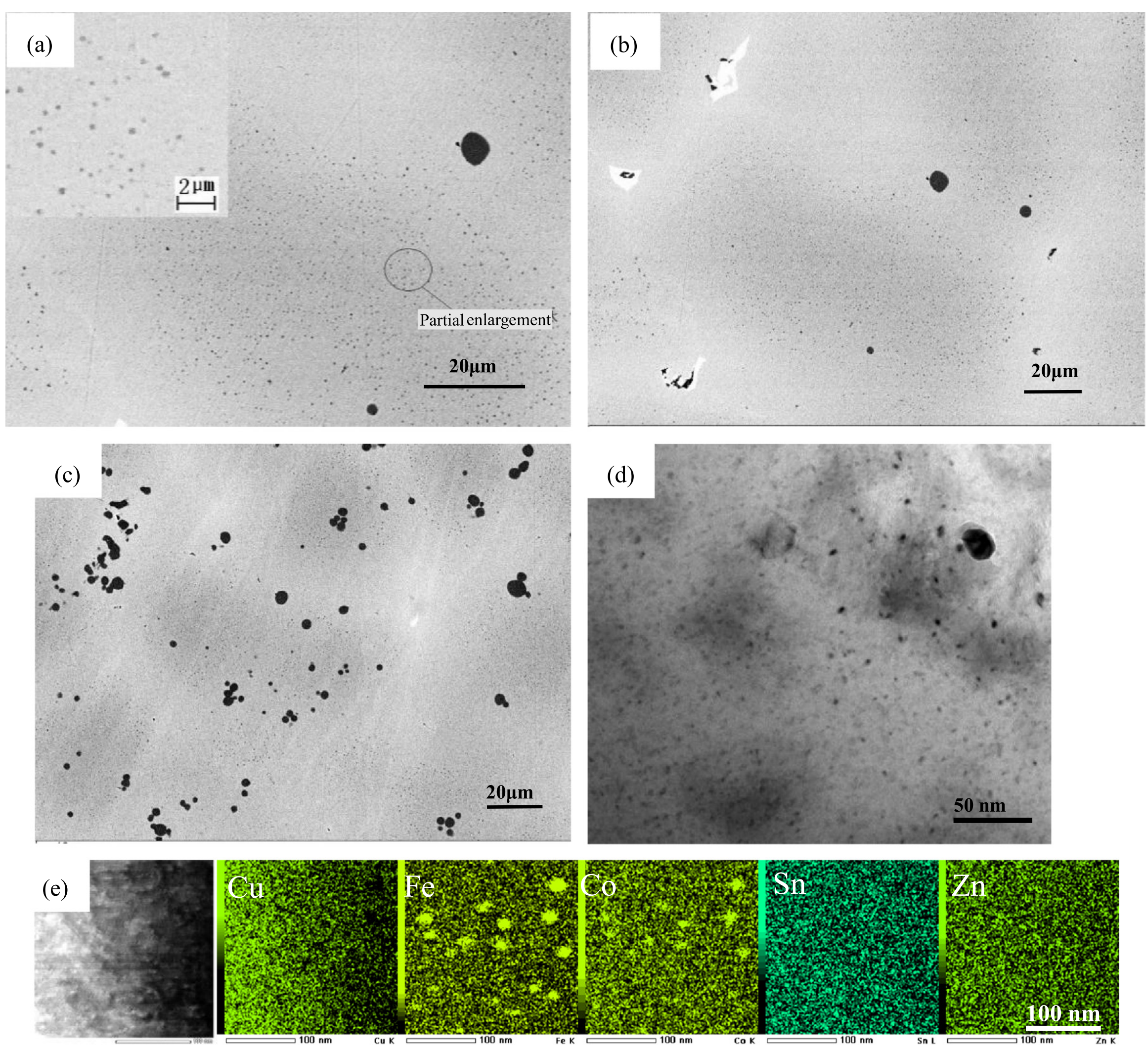

Fig. 2. SEM micrographs of uniformly distributed iron-rich nanoparticles in (a) Cu–10Sn–2Zn–1.5Fe–0.5Co, (b) Cu–10Sn–2Zn–2Fe–0.5Co, (c) Cu–10Sn–2Zn–3Fe–0.5Co (wt%) alloys; (d) TEM image of iron-rich nanoparticles in Cu–10Sn–2Zn–1.5Fe–0.5Co (wt%) alloy; (e) STEM image of the nanoparticles in Cu–10Sn–2Zn–1.5Fe–0.5Co (wt%) alloy and its elemental maps.