Icosahedral quasicrystal-enhanced nucleation of the fcc phase in liquid gold alloys

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Abstract

Although the grain refinement of yellow gold alloys with Ir has been used in industry and known for nearly half a century, the basic mechanism is still unknown. The present contribution shows that the mechanism is the same as that evidenced recently in Al–Zn alloys, when small amounts of Cr (1000 ppm) are added to the melt (Kurtuldu et al., 2013). The reduced face-centered cubic (fcc) crystal size, the abnormal fraction of twin, or near-twin, grain boundaries and the 5-fold symmetry crystallographic orientation of multiple nearest-neighbor grains reproduce the symmetry of icosahedral quasicrystals (iQCs) with the following heteroepitaxial relationships: $\{111\}_{fcc}/\langle110\rangle_{fcc}\perp$ 3-fold/2-fold symmetry axes of iQCs. While iQCs and the approximant stable $Al_{45}Cr_7$ phase, which contains several 5-fold symmetry building blocks in its unit cell, are known to exist in Al–Cr alloys, no such phases have been reported for yellow gold +Ir. Nevertheless, when minute amounts of Ir ($\lesssim 200$ ppm) are added to the gold alloy melt, it is shown that the grain refinement from 248 to 30 μm is accompanied by a spectacular increase in the fraction of twinned grain boundaries, i.e. from less than 1% without Ir to 11% with 200 ppm Ir. Furthermore, up to 9 grains have been shown to reproduce the six 5-fold symmetry axes of the icosahedron, while many other grain configurations exhibit this heteroepitaxial relationship with the icosahedron or interlocked icosahedron. This confirms that fcc crystals can form in a supercooled liquid by heteroepitaxial growth from an iQC template.

1. Introduction

In order to explain the large supercoolings of metallic liquids observed by Turnbull [1], Frank [2] suggested in 1952 that atoms in metallic liquids develop short-range icosahedral order when the temperature is reduced below the equilibrium freezing point. Molecular dynamics simulations [3,4] and small-angle scattering in various metallic liquids [5–8] confirmed this conjecture. More recently, Shechtman et al. [9] discovered quasicrystals (QCs) in a rapidly solidified Al–Mn alloy, thus changing our view on crystallography. While exhibiting long-range order and 5-fold symmetry, QCs do not possess translational order. Although metastable Al–Mn QCs were shown to remain stable for 1 h up to 350 °C, they transformed into the approximant Al_6Mn phase above this temperature. After this discovery, for which Shechtman won the Nobel prize in 2011, thermodynamically stable QCs were found in binary [10,11] and ternary alloys [12–14], and were grown into grains several millimeters in size.

Interestingly, Shechtman et al. [9] had already noticed that crystalline films of face-centered cubic (fcc) Al formed around nodular shaped QCs, which is expected for such a peritectic system, but did not investigate further if there

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were some crystallographic relationships between these films and QCs. Singh and Tsai [15] demonstrated that epitaxial crystallographic relationships exist between the α-Mg phase and Mg–Zn–Y QCs, as well as between Pb, Bi and Sn particles embedded in an icosahedral Al–Cu–Fe matrix. Crystallographic relationships were also found between QCs and approximant intermetallic phases [16–18], in particular in rapidly solidified Al–Cr alloys. In vapor-deposited Al films on Al–Pd–Mn icosahedral QC (iQC), an epitaxial relationship between the fcc phase and QCs was observed, with the $\langle 1 1 1 \rangle_{fcc}$ direction parallel to one of the 3-fold symmetry axes of the icosahedron [19,20].

We have recently shown that iQCs can also play a role in the nucleation of the fcc Al phase during solidification of an Al–20 wt.%Zn alloy [21]. Small additions of Cr (1000 ppm) in the liquid metal drastically decrease the size of the fcc grains and induce an abnormally high fraction of twin or near-twin grain boundaries (> 2%). By careful analysis of the orientation of nearest-neighbor fcc grains, we also found several configurations where multiple-twinned grains exhibited a symmetry which could be explained only if they were assumed to form on a single regular or interlocked icosahedron with the epitaxial relationship: $\langle 1 1 1 \rangle_{fcc} \| $ 3-fold symmetry iQC axes, and $\langle 1 1 0 \rangle_{fcc} \perp$ 2-fold symmetry iQC axes. This provided compelling evidence supporting the concept that fcc grains could nucleate from an icosahedral template, known to be present as iQCs in the supercooled liquid or as building blocks of the crystalline structure of the approximant $Al_{45}Cr_7$ phase [22,23]. The phase initiated from a melt can be the one that is closest in free energy to the liquid, not the thermodynamically most stable one [24]. Metastable iQC in supercooled metallic liquid is the most likely candidate to form initially due to its low interfacial energy [25,26]. Indeed, Kelton et al. [27] have demonstrated that the icosahedral short-range order first grows into a metastable iQC phase, then transforms into a more stable crystalline phase in a supercooled $Ti_{39.5}Zr_{39.5}Ni_{21}$ liquid.

This iQC-induced nucleation is schematically summarized in Fig. 1. In Fig. 1a, Al and Zn atoms (in blue) tend to arrange around Cr atoms (in red) in Frank's configuration. The liquidus temperature of the approximant $Al_{45}Cr_7$ being above that of the fcc phase in this alloy, iQCs (or the approximant phase itself) form at some undercooling (Fig. 1b). As the Al–Cr system is peritectic, the liquid layer ahead of the iQC is depleted in Cr, thus favoring the formation of the fcc (Al–Zn) phase, with epitaxial relationships (Fig. 1c). Upon further solidification and cooling, the iQC disappears while the fcc phase grows with multiple twin or near-twin relationships between the various grains, as indicated in Fig. 1d. Once the fcc phase reaches a critical radius, the solid–liquid interface is destabilized, thus leading to the formation of twinned dendrites [28,29,21], a morphology known in industrial direct chill-cast Al alloys for more than 60 years and whose origin could not be explained before this nucleation mechanism was demonstrated.
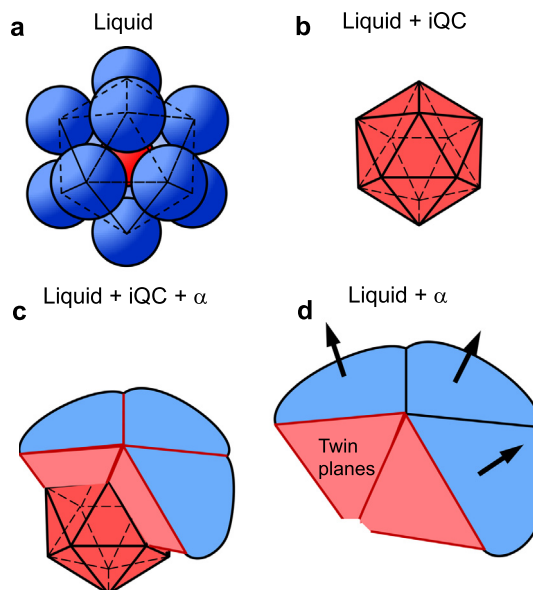

Fig. 1. Nucleation mechanism assisted by iQC formation: (a) Frank's icosahedral short-range order of atoms in the liquid (red: Cr atoms; blue: Al or Zn atoms); (b) formation of iQC in the liquid; (c) heteroepitaxy of the α-fcc phase on the iQC facets, with twin planes in between the various α nuclei; (d) growth of the fcc phase and dissolution of the iQC during cooling due to the peritectic nature of the phase diagram. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this paper, the same nucleation mechanism is shown to operate in yellow gold alloys (Au–12.5 wt.%Cu–12.5 wt.%Ag or Au–28.4 at.%Cu–16.7 at.%Ag) when minute amounts of Ir (5–200 wt. ppm) are added to the melt. "Inoculation" of such alloys with Ir is a grain-refining technique currently used in industry and known for nearly half a century [30–32]. However, although the effect of Ir on grain size is well established, there has been no investigation on the basic mechanism responsible of such grain refinement.

2. Experimental methods

Ingots of 700 g of Au–28.4 at.%Cu–16.7 at.%Ag alloys (purity Au, Ag, Cu: 99.99%) with a suitable amount of Ir (in the form of Cu–0.67 at.%Ir) were prepared in a vacuum induction furnace under an argon atmosphere. The mixed elements were heated in a graphite crucible. The temperature was brought up to 1300 °C for 5 min and then reduced to 1100 °C, where it stabilized for another 5 min. The ingots were cast at 1100 °C into copper molds $(20 \times 20 \times 100 \text{ mm}^3)$ at room temperature. Samples were cut at about two-thirds from the top of the ingot and prepared for electron backscattered diffraction (EBSD) analysis by polishing with 0.5 μm alumina suspension (OPS) and by subsequent etching with KCN. Optical and electron microscopy as well as EBSD observations were made on yellow gold specimens containing 5, 10, 20, 30, 50, 100 and 200 wt. ppm Ir. A Phillips XLF-30 FEG SEM with