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Au–Fe alloy solidification and solid-state transformations

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Abstract

In order to better understand the microstructure that forms during laser welding of an 18 carat gold and an austenitic stainless steel, solidification of the Au–Fe binary analog has been studied using thermal analysis and interrupted Bridgman experiments. For a hypoperitectic composition, the formation of the primary phase, its coarsening and the peculiar macrosegregation associated with the large density difference between the elements have been studied. Just after the peritectic phase forms around the primary dendrites, continuous and discontinuous precipitation has been shown to occur as a result of the immiscibility of the two face-centered cubic phases below the peritectic temperature. Finally, the solid-state transformations associated with the eutectoid have been characterized.

Keywords: Au–Fe; Differential thermal analysis (DTA); Peritectic solidification; Discontinuous precipitation; Coherency relationship

1. Introduction

In jewelry manufacturing, joining dissimilar materials is usually achieved by brazing. However, since this technique has several disadvantages [1,2], including undesired phase transformations and softening of the base materials during heat treatment, alternative joining methods such as laser welding are now being considered. Thanks to its high energy density and precise delivery using, for example, optical fibers, a laser beam can locally melt well-defined amounts of the base alloys located near the interface, without affecting the bulk microstructure of the parts to be joined [3]. However, this method produces an entirely new alloy in the weld trace and thus requires a thorough understanding of the microstructure that forms during solidification.

When the two alloys to be joined are multicomponent, the analysis can become quite difficult. As a first approximation, it might be useful to consider the binary system made out of the main elements constituting the base alloys to be welded. In the present study, the welding metallurgy of an austenitic stainless steel and a classical 18 carat yellow gold (Au–12.5 wt.% Ag–12.5 wt.% Cu) has been approximated by the solidification analysis of the Au–Fe system. In this binary alloy, the primary solid phase that solidifies for a Au composition between 11 and 43 at.% is austenite (γ-Fe), as can be seen on the phase diagram shown in Fig. 1. On the other side of the phase diagram, pure Au is an approximation of the Au–Ag–Cu solid solution of the 18 carat yellow gold.

Except for the establishment of the phase diagram [4–6], very few studies have been conducted on the solidification and high-temperature precipitation in the Au–Fe system. To the present authors' knowledge, all recent studies on this system have been focused on the precipitation of Fe from supersaturated face-centered cubic (fcc) Au–Fe solid solution, for compositions higher than 60 at.% Au and at temperatures lower than 600 °C. Indeed, such alloys have been shown to present interesting magnetic properties, including the giant magnetoresistive effect (GMR) [7,8].

At higher temperature, solidification of the primary phase and the peritectic reaction (γ-Fe) + liquid ↔ (Au) at 1173 °C are of primary importance for alloys containing 8–43 at.% gold, as will be shown in the present contribution. The peritectic invariant is in fact characterized by two solid phases, (γ-Fe) and (Au), which have the same fcc structure and exhibit a miscibility gap for temperatures lower than 1248 °C. Because of the existence of high-temperature equilibrium

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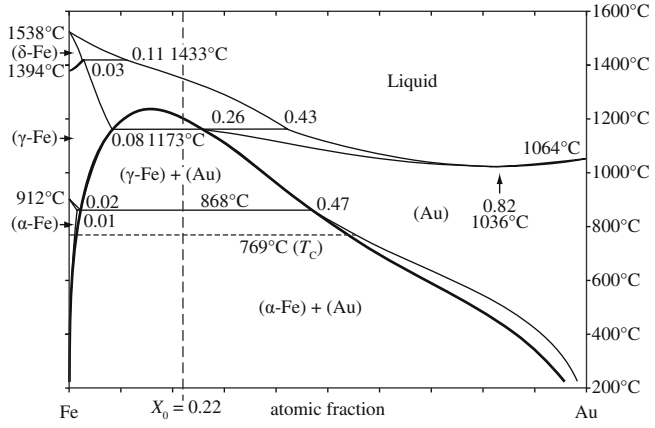

Fig. 1. Au–Fe phase diagram redrawn from Ref. [4]. The thick line represents the metastable miscibility gap of the fcc phase, calculated with the common tangent method with data from Ref. [4].

between this fcc phase and the liquid, what could have been a spinodal decomposition (see the thick line in Fig. 1) is then a peritectic reaction. This miscibility gap appears as a two-phase region with strong solvus retrogrades between the peritectic temperature and the temperature of 868 °C at which the eutectoid transformation (γ-Fe) $\leftrightarrow$ (Au) + (α-Fe) occurs. As will be shown, these retrogrades play an important role in solid-state transformations since the solubility of each element in the other phase decreases with temperature, thus inducing a continuous driving force for precipitation of (γ-Fe) from the (Au) matrix, and of (Au) from the (γ-Fe) matrix.

Below the eutectoid temperature, the solubilities of Fe in Au and of Au in Fe keep decreasing, leading to discontinuous precipitation of (α-Fe) [9–12]. According to Bosco [13], there is actually a competition between precipitation of (α-Fe) and (γ-Fe) in the (Au) matrix. The body-centered cubic (bcc) phase is stable, whereas the fcc form is metastable, but requires a lower driving force for nucleation (as the matrix is also fcc). Furthermore, the compositions of stable (α-Fe) and metastable (γ-Fe) are close to each other, as can be seen in Fig. 1. Therefore, phase selection is strongly related to defect concentration.

The aim of this study is to observe and understand the formation and evolution of microstructure during solidification and solid-state transformations of a hypoperitectic Au–Fe alloy. Differential thermal analysis (DTA) and directional solidification in a Bridgman-type furnace (DSB) have been carried out. Specimens quenched during DSB were then characterized using electron microscopy. Solidification of the primary phase, the peritectic reaction and subsequent solid-state transformations were investigated.

2. Experimental methods

2.1. Thermal analysis

Thermal analysis was conducted on a Boersma DTA, also known as heat-flux DSC (Netzsch DSC 404C Pegasus). In such a device, the sample and the reference are contained in small alumina crucibles placed over bases. Thermocouples are attached to the bases and the whole setup is placed within the same furnace, i.e. identical thermal conditions [14]. An enthalpy change associated with a phase transformation in the sample induces a small temperature difference compared to the reference. This difference can be recorded and converted into enthalpy using a suitable calibration. In the present case, the reference was an empty crucible and the Au–Fe sample weighed typically 20 mg. It was prepared by simply placing Au and Fe (99.99% purity) in the right proportion into the DTA crucible. Providing these two elements were in close contact, a first melting ensured perfect mixing of the metals by surface tension forces (Marangoni solutal convection). DTA measurements upon heating and cooling were then performed at the same rate ($\pm$10 K min^{-1}).

2.2. Interrupted Bridgman solidification

Directional solidification experiments of Au–Fe specimens were undertaken for a hypoperitectic composition of 22 at.% Au (dashed line in Fig. 1), i.e. about 50 wt.% Au. This was achieved using a high thermal gradient, vertical Bridgman furnace [15], which consisted of two parts: a hollow molybdenum susceptor heated by an induction coil and placed in a protective atmosphere for the heating stage, and a water-cooled liquid metal (LMC) bath for the cooling stage.

Taking advantage of the large density difference between Au and Fe, the specimens were prepared as follows in order to ensure a homogeneous initial composition of the sample. Fe powder (99.99% purity) was placed at the bottom of an alumina tube of 4 mm inner diameter, with the gold pellets (99.99% purity) placed above. At the beginning of the experiment, the specimen was lowered into the cold zone of the furnace. After the temperature of the furnace was raised and stabilized at 1500 °C, the crucible was slowly pulled up at 2 mm s^{-1}, allowing gold pellets to melt first. The liquid gold then seeped into, and dissolved, the iron powder. When the whole sample was liquid, the crucible was pulled down at the selected velocity (33.4 or 1.67 μm s^{-1}, which correspond to cooling rates of 0.66 and 0.034 K s^{-1}, respectively). After a certain length of solidification, the crucible was dropped suddenly into the LMC bath. This rapid quench froze the remaining liquid with a very fine microstructure, which was clearly distinct from that growing under steady-state conditions, thus allowing the latter to be observed at room temperature. The average thermal gradient measured in the mushy zone with an inserted thermocouple was around 300 K cm^{-1} (the value close to the liquidus being slightly lower, 280 K cm^{-1}) [16].

2.3. SEM-BSE image analysis of Bridgman sample

After quenching, the samples were sectioned along the longitudinal axis and hot mounted in a conductive resin