Phases formed during crystallization of amorphous Al$_{84}$Y$_{9}$Ni$_{5}$Co$_{2}$ alloy

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Abstract

Understanding crystallization of amorphous metals is essential for the production of amorphous ribbons and powders and for the production of larger bodies by means of consolidation of an amorphous alloy powder. In this paper, we describe the evolution of the crystalline phases that form upon crystallization of amorphous Al$_{84}$Y$_{9}$Ni$_{5}$Co$_{2}$ ribbons during heating in a differential scanning calorimeter. X-ray diffraction and transmission electron microscopy (TEM) with energy dispersive spectroscopy were used to determine the phases formed. Crystallization occurs in three stages: (1) primary crystallization of α-Al, (2) formation of an unknown phase, and (3) formation of Al$_{3}$Y, Al$_{6}$Co$_{2}$ and ‘Al$_{16}$Ni$_{3}$Y’ needles.

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1. Introduction

In 1988, Masumoto et al. [1] and, in an independent study, Poon et al. [2–5] reported that some Al–Y–Ni compositions could be cooled by melt spinning to form Al-based amorphous alloys with high strengths and 180° bending ductility indicating that they might have some intrinsic ductility. The amorphous phase was formed over a composition range encompassing 3–22 at.% Y and 4–33 at.% Ni. In 1989, Inoue et al. [6] reported that additions of Co to an Al–Y–Ni alloy increased mechanical strength with no detriment to the bend ductility. The alloy Al$_{85}$Ni$_{5}$Y$_{8}$Co$_{2}$ (at.%) is a glass former, resulting in an increase in the maximum ribbon thickness that is completely amorphous single phase material from 120 µm for the ternary Al–Y–Ni alloy to 720 µm for the quaternary alloy Al–Y–Ni–Co. In addition, the latter alloy had tensile fracture strength of 1250 MPa. For some compositions, the ‘amorphous’ ribbons contained a dispersion of α-Al particles; these partially crystalline ribbons had greater fracture tensile strengths and hardness than those of the fully amorphous alloys of the same compositions and similar bending ductility [7,8]. The volume fraction of crystalline particles was controlled by the cooling rate (i.e. ribbon thickness) either by changing the rotation speed of the copper wheel or by varying the superheat temperature of the molten alloy prior to the melt spinning. Amorphous powders of these alloys with particle diameters <25 µm were also produced by high-pressure gas atomization and then extruded above the crystallization temperature [9]. For the composition Al$_{85}$Ni$_{5}$Y$_{8}$Co$_{2}$ a crystalline alloy compact [9] was produced which had greater fracture strength than those of aluminum alloys produced by conventional powder metallurgy routes.

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Based on the number of processing routes available for these amorphous and partially amorphous alloys, we note that an understanding of their crystallization is of both technological and scientific importance in our opinion. This information is essential for the production of amorphous ribbons and powders and for the production of larger bodies by means of consolidation of amorphous alloy powder.

Studies on the quaternary Al–Y–Ni–Co amorphous alloys were reported by Masumoto et al. [6] and their studies on the crystallization process of Al85Ni5Y5Co2, Al85Ni2.5Y10Co2.5 and Al83.3Ni4.9Y9.8Co2 amorphous ribbons were limited to the first stage, in which the formation of fcc-Al phase has been observed by transmission electron microscopy (TEM). The crystallization of Al87Y8Ni3Co2 amorphous ribbon was studied by Lloyd et al. [10]. They reported that three stages of crystallization have been identified by differential scanning calorimetry (DSC) analysis, where X-ray diffractometry (XRD) analysis showed that the first stage was the precipitation of fcc-Al from the amorphous phase; the second stage was formation of an unidentified crystalline phase from the remaining amorphous matrix by a eutectic crystallization. The third stage was a crystallographic transition of the intermetallic phase with little change in the fcc-Al phase. Kokoszkiewicz et al. [11,12] studied two compositions of this quaternary alloy, Al90Y5Ni1Co4 and Al90Y5Ni2Co2.5. They reported that the amorphous ribbons of both alloys had a two-stage crystallization process. While the authors did not compare their results with other studies, we note that the Y + Ni contents in both of their alloys are less than those in the other studies [6,10]. Based only on XRD analysis, the crystallization stages were: first the precipitation of spherical fcc-Al crystal with diameters on the order of 10 nm from amorphous matrix and then precipitation of Al3Y(Ni, Co)-like crystalline phase from the remaining amorphous matrix. The diverging results concerning the number of crystallization stages we attribute to the sensitivity of the differential scanning calorimetry technique to heating rate, sample amount and calibration. This can lead to a superposition of two sequential transformations under only one peak in the thermogram which is possible. There have been only a few papers in the literature reporting the crystallization of amorphous alloys in this system and none that presents a detailed description of the phases formed during the devitrification process.

This paper reports the results of determining the phases formed during the crystallization of amorphous Al84Y9Ni5Co2 melt spun ribbons by using a combination of TEM with energy dispersive spectra (EDS) and XRD analysis.

2. Experimental

Amorphous Al84Y9Ni5Co2 (at.%) alloy ribbons were produced using a single roll melt spinner with a copper wheel at a speed of 35 ms⁻¹ in an Ar atmosphere. The resulting ribbons were typically 70 µm thick by 3 mm wide. 3 mm diameter disks were punched and crystallized by heating to temperatures in the range of 572 and 833 K and cooling to room temperature by using a differential scanning calorimetry (DSC) (Netzsch GmbH, mod.404). The heating and cooling rate were 20 and 40 K/min, respectively. The crystallization temperatures were selected to be within each of three stages of crystallization for the alloy (572, 613 and 684 K). Thermal and kinetic analysis of the crystallization process for this alloy was published elsewhere [13]. Microstructure of the as-quenched and crystallized samples was done by standard X-ray powder diffractometry (Philips APD 3720) and by transmission electron microscopy (Philips EM420). The TEM specimens were prepared by twin-jet electropolishing in a 5% perchloric acid, 15% nitric acid and 80% methanol solution at 243 K.

3. Results

Fig. 1 shows the XRD traces from the Al84Y9Ni5Co2 ribbon in the as-quenched condition and after crystallization at various temperatures from 572 to 833 K. The XRD of as-quenched specimen had diffuse maxima typical of an amorphous material. An XRD scan from a
specimen heated to 572 K (first crystallization peak in the DSC) had diffraction peaks corresponding to the $\alpha$-Al phase and the diffuse peaks from the remaining amorphous matrix. The identification of the $\alpha$-Al and the crystalline phases, described below, was accomplished by comparison with the JCPDS data. An XRD scan from a specimen heated to 613 K (second crystallization peak in the DSC) appeared somewhat similar to the first peak and contained larger amplitude $\alpha$-Al peaks and three smaller unidentified peaks. An XRD scan from specimens heated to 684 K (third crystallization peak in the DSC) consisted of peaks identified as coming from $\alpha$-Al, Al$_3$Y, Al$_9$Co$_2$ and a set of unidentified peaks. An XRD scan from specimens heated to 833 K (temperature above the third crystallization peak in the DSC) contained many diffraction peaks, including those observed for the specimen heated to 684 K, along with secondary peaks of the compounds already described and several unidentified peaks.

Fig. 1. XRD traces from Al$_{84}$Y$_{9}$Ni$_5$Co$_2$ ribbon, as quenched and heated to various temperatures from 572 to 833 K.

Fig. 2. Bright-field micrograph of a specimen heated to 572 K (first crystallization peak). The micro diffraction was taken from one of the crystallites with $B = [011]$.

Fig. 3. Bright-field micrograph and a corresponding SADP showing the phase observed together with $\alpha$-Al and amorphous phases in the specimen heated to 613 K (second crystallization peak). This phase, indicated by the arrow, is unknown in comparison with current crystallographic data [18].
The structure of the specimen heated to 572 K (first crystallization peak) had a ‘dendritic’ morphology of $\alpha$-Al on the order of 100 nm inside an amorphous matrix (Fig. 2). The presence of $\alpha$-Al was confirmed by micro-diffraction and the amorphous phase by noting the diffuse ring was present in both patterns. Similar ‘dendritic’ $\alpha$-Al was reported by Cantor et al. [14] for the ternary Al–Ni–Y alloy.

TEM analysis of ribbons heated to 613 K (second crystallization peak) detected $\alpha$-Al and another phase (Fig. 3). The selected area diffraction pattern (SADP) from this second phase could not be indexed based on any of the reported phases [15] in this system and we assumed it to be a new metastable phase. EDS analysis taken from this particle in the TEM indicated that it is probably a quaternary Al–Ni–Y–Co phase, with a larger yttrium to nickel ratio (Fig. 4) than the other phases. Work is in progress to determine the crystal structure of this phase.

For the specimen heated to 684 K (third crystallization peak), the SAD analysis detected $\alpha$-Al, Al$_3$Y and Al$_6$Co$_2$ (Fig. 5). EDS analysis indicated the presence of Ni substitution for Co in Al$_6$Co$_2$ (Fig. 4). A fourth needle-like phase with a $d$ spacing $\sim$2.7 nm was observed and appeared to fit the Al$_{16}$Ni$_3$Y crystal structure reported by Rykha [16]. However, EDS analysis indicated that the composition of this phase is inconsistent with the Al$_{16}$Ni$_3$Y stoichiometry assuming that Co substitutes for Ni. Thus, further work is needed to determine the structure and composition of this phase.

4. Discussion

The XRD data indicates that the crystallization occurred in three stages: (1) precipitation of $\alpha$-Al from the amorphous phase, (2) formation of more and larger $\alpha$-Al particles and an unidentified phase(s) from the remaining amorphous phase, and (3) formation of Al$_3$Y, Al$_6$Co$_2$ and one or more unidentified compounds from the remaining amorphous phase. The presence of unidentified diffraction peaks was also reported for other Al–Y–Ni–Co alloy compositions [10–12] but no fur-
ther information was presented. We note that the unknown phase observed after heating to the second crystallization peak was not observed after the third crystallization peak, which indicates that it is a metastable phase. This observation is consistent with the enthalpy involved in the second stage of crystalization (smallest of the three stages) [17].

This second stage of crystallization and the formation of this unknown phase may be due to the larger Y content because it can be overcome by decreasing the Y content, as reported by Masumoto et al. [6].

TEM analysis indicated that the unidentified phase observed in XRD analysis of ribbous heated to 684 K correspond to a needle-like phase that appeared to fit the Al16Ni3Y crystal structure which composition is inconsistent with the Al16Ni3Y stoichiometry. Thus, the final microstructure consisted of α-Al, Al3Y, Al9Co2 and this unidentified compound.

5. Conclusions

Crystallization of amorphous Al84Y9Ni5Co2 melt-spun ribbons occurs in three stages: (1) primary crystallization of α-Al; (2) formation of an unknown phase, and (3) formation of Al1Y, Al3Co2 and ‘Al16Ni3Y’ needles. The morphology, EDS and diffraction analysis indicated that the two unknown phases from the second and third peaks are different and that both are quaternary compounds.

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