Materials Science Forum Vols. 539-543 (2007) pp. 1917-1920
online at http://www.scientific.net

Crystallization Behavior of $Al_{87}Ni_5La_7Zr_1$ Metallic Glass

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Keywords: Aluminium based melt-spun ribbons, crystallization, Transmission electron microscopy (TEM), Three dimensional - Atom Probe (3D-AP)

Abstract: Nano-crystalline-amorphous Al based alloys with minor additions of rare earth elements and transition metals are of technical interest, because of their extraordinary high mechanical strength. This strengthening effect depends strongly on the alloy composition and the pathway of crystallisation. The crystallisation behaviour of $Al_{87}Ni_6La_7$ and of $Al_{87}Ni_5La_7Zr$ metallic glass was studied with complementary methods such as XRD, TEM and 3D-AP. The amorphous matrix of the Zr-containing glass shows fluctuations of all minor elements on the nanometer scale. It is suggested, that these fluctuations act as nucleation zones for the crystallization of the glass during annealing.

Introduction

Nanocrystalline Al-based alloys with additions of less than 20 at.% rare earth elements (RE) and transition metals (TM) obtained by crystallisation of fully amorphous metallic glasses have considerably larger strengths than comparable conventional polycrystalline materials [1,2]. Strengthening in such nanocrystalline alloys is caused by a very high fraction of fcc α-Al precipitates dispersed in an amorphous matrix. This α-phase crystallises first although crystallisation of the RE- and TM–rich intermetallic phases should be thermodynamically favoured. Crystallisation of Al-Ni-La alloys and the influence of the La content on the pathways of crystallisation were recently investigated [3]. It has been suggested that separation within the glassy phase could be a possible precursor stage to Al nanocrystallization [4]. In order to investigate this picture 1% La in the $Al_{87}Ni_7La_6$ alloy was replaced by Zr. Zirconium has a strong negative heat of mixing (ΔH^{mix}/ kj mol^{-1}) with Ni and Al (Zr-Ni = –49, Zr-Al= –44) but a positive heat of mixing with La (Zr-La= +13) [5] which could lead to a change in local order within the glassy phase. The crystallisation sequence of $Al_{87}Ni_7La_5Zr$ which differs only slightly from the alloy studied in the present work has been investigated by XRD [4]. In both cases [3,4] crystallisation starts with the formation of Al-rich phases. In the present study the Ni-content of alloy $Al_{87}Ni_6La_7$ was reduced in favour of Zr, whereas the La content was kept constant. In order to study the crystallisation behaviour of $Al_{87}Ni_6La_7$ and $Al_{87}Ni_5La_7Zr$ metallic glasses the microstructure of the as-melt spun material and of the material in the early stages of crystallisation is analysed by complementary microanalysis methods such as XRD, TEM and 3D-AP.

Experimental

The metallic glasses $Al_{87}Ni_6La_7$ and $Al_{87}Ni_5La_7Zr$ were produced by melt spinning with a wheel velocity of about 40 m/s. The resulting ribbons were about 30 μm thick and 1-2 mm wide. The

$Al_{87}Ni_5La_7Zr$ ribbons were annealed for 2 h both at 210°C and 245°C. TEM samples were prepared electrochemically by jet polishing the ribbon material at 240 K and 20 V, using a solution of 3 parts of CH_3COOH and 1 part of HNO_3 and subsequently thinning by ion beam milling. A Philips CM30 TEM microscope operating at 300 kV was used for the analysis. Specimens for TAP were thinned mechanically to prisms 0.03x0.03x10 mm^3 in size, after which one end was electropolished in a solution of 5% $HClO_4$ in butoxyethanol at room temperature with 10 V DC. TAP analyses were performed in ultra-high vacuum (10^{-8} Pa) with a pulse repetition frequency of 1000 Hz. The fraction of pulse voltage to the standing tip voltage was 0.2. The tip temperature was about 60 K. The XRD analysis were performed using Cu-Kα radiation.

Results and discussions

The results of the XRD analysis of the $Al_{87}Ni_6La_7$ and $Al_{87}Ni_5La_7Zr$ melt-spun ribbons are shown in figure 1. For $Al_{87}Ni_6La_7$ the typical broad diffraction maxima of the amorphous phase are visible. On the contrary, the Zr containing ribbons show Bragg patterns arising from crystalline phases superimposed on the broad diffraction signal of the amorphous phase. The primary crystals giving rise to Bragg peaks in figure 1 were further examined by TEM. Figure 2 shows a large crystalline agglomerate of a dendritic morphology consisting of many small crystals embedded in an amorphous matrix. The size of agglomerates is about 4 μm. Their number density is low. The TEM studies revealed that the large agglomerates are homogeneously distributed in the amorphous matrix which is indicated by the diffuse rings of SAED pattern typical for glasses (not shown here). A TEM/EDX analysis of the crystal agglomerates reveals phases with varying compositions. The dark areas in figure 2 are Zr-La-rich crystals of the $Al_7(Zr,La)_3$ type. Next to these La-rich crystals of the $Al_{11}La_3$ type can be identified. Some Al-rich crystals with contens up to 92 at.% Al were observed by TEM, although no Bragg peaks of such phase appear in figure 1, indicating that the amount of such crystals is very small.

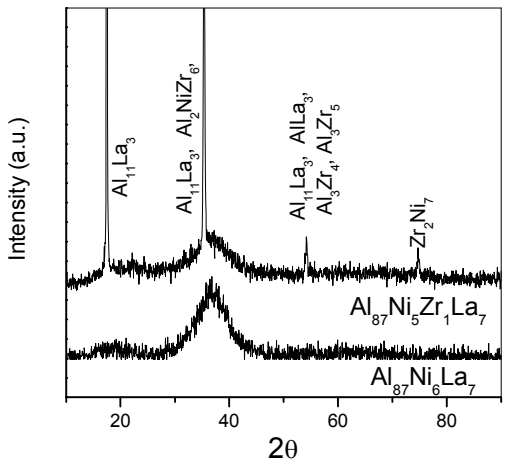


Fig. 1 XRD patterns of amorphous $Al_{87}Ni_6La_7$ and partially amorphous $Al_{87}Ni_5La_7Zr_1$ melt-spun ribbons.

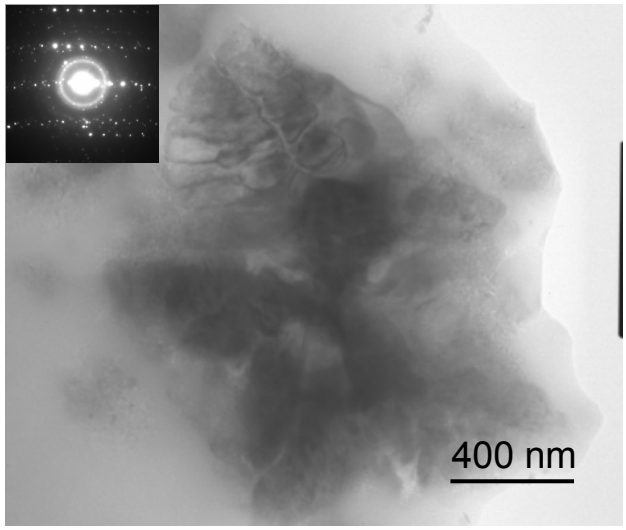


Fig. 2 BF TEM image of large crystal embedded in amorphous matrix of the as-quenched $Al_{87}Ni_5La_7Zr_1$ alloy. The corresponding SAED pattern image is given in the inset.

The amorphous matrix of the as-quenched $Al_{87}Ni_5La_7Zr$ ribbons was also investigated by TAP. A representative result of the element distribution is shown in figure 3.

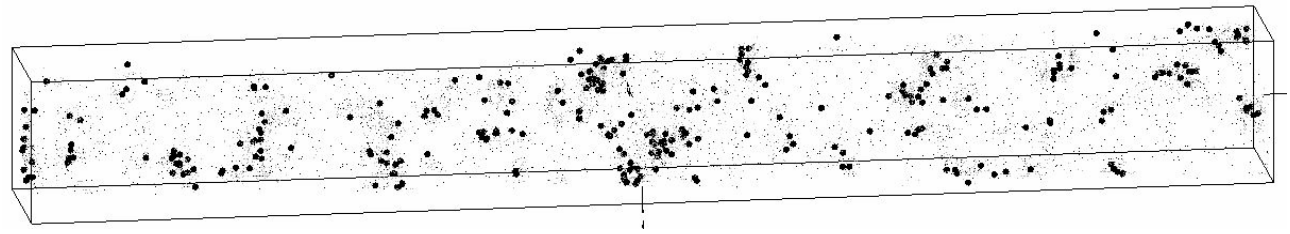


Fig. 3 Three dimensional reconstruction of Zr atom positions in an 8x8x69 nm^3 volume of as-quenched $Al_{87}Ni_5La_7Zr$ ribbon analysed by TAP. Additionally Zr-rich cluster position are indicated too. The distribution of all other elements looks similar.

Small Zr-enriched clusters containing more than 6 at.% of Zr - i.e. 6 times the nominal content - are shown in figure 3. The heterogeneous fluctuations were identified using a cluster-identification module developed by the Groupe de Physique des Matériaux in Rouen [6]. Like Zr, all other elements are also heterogeneously distributed and form clusters. The mean chemical composition of the various clusters (in at.%) is: Zr-rich clusters: **6.2 Zr**–6 La–2.9 Ni–84.9 Al; La-rich clusters: 1.2 Zr-**11.6 La**-2.9 Ni–84.3 Al and Ni-rich clusters: 0.9 Zr–5.3 La–**11.5 Ni**-82.3 Al. All these clusters enriched in one element exist separately as can be seen in the small volume shown below in figure 4.

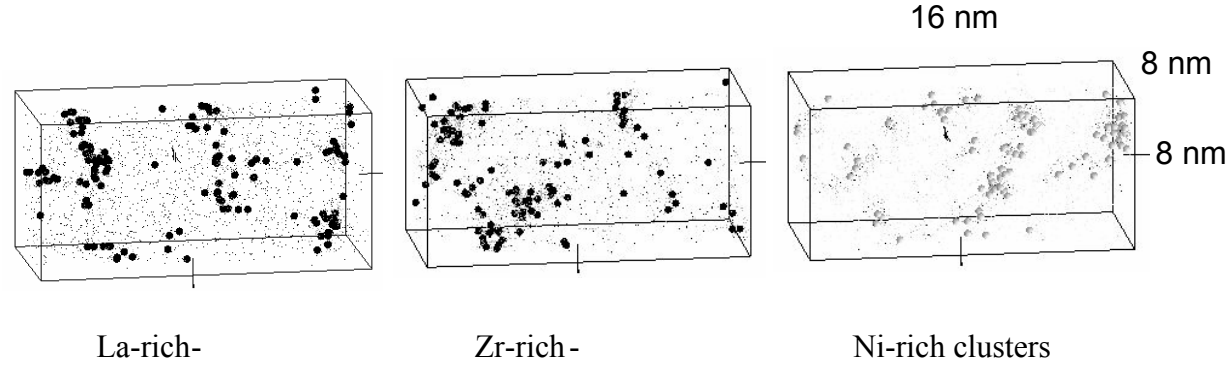
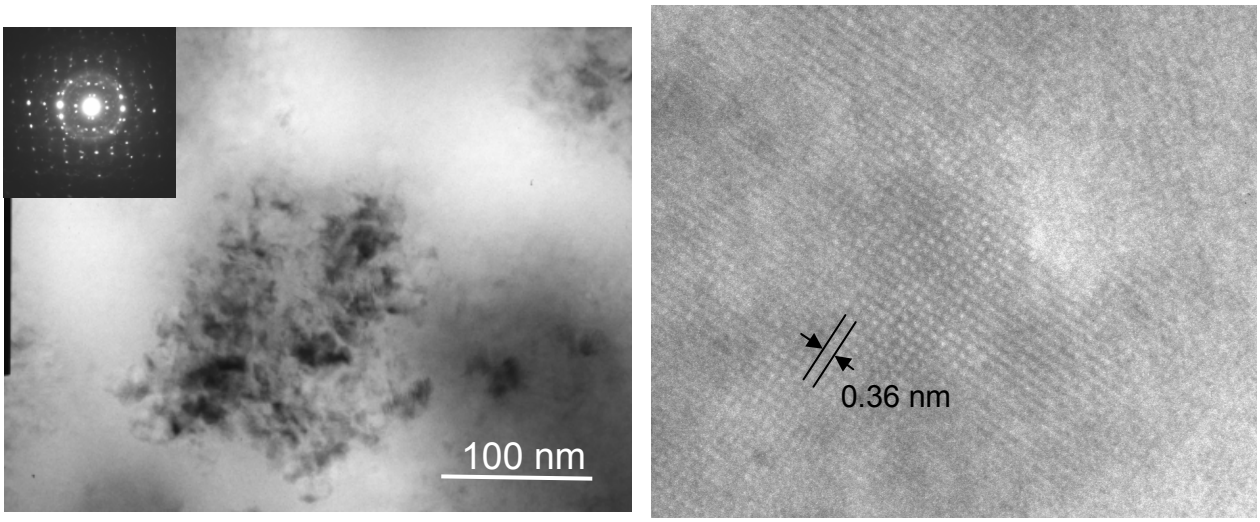


Fig. 4 Three dimensional position of Zr-, Ni- and La-rich clusters in a 8x8x16 nm^3 large volume of $Al_{87}Ni_5La_7Zr_1$ as-quenched ribbon.

The size of such clusters ranges from 1.5 to 3 nm. TEM investigations of similar samples show no indications of crystalline phases in the nanometer region. The matrix remains amorphous even after heat treatment up to 210°C for 2 h (not shown here). After annealing at 245°C for 2 h small crystals grouped in clusters embedded in the amorphous matrix form (figure 5). One of these crystals with an interplanar spacings of 0.36 nm can be seen in the HRTEM image in figure 5b. The corresponding SAED pattern of such a cluster given in the inset exhibits diffraction pattern arising from many differently oriented crystals.

The element fluctuations measured by TAP in the amorphous matrix could probably act as nuclei for the formation of crystals [7] observed after annealing at 245 °C. As the fluctuations are enriched in Zr, Ni or La the nucleation barrier for the formation of intermetallic compounds with these elements could be lowered. Thus preferential crystallization of such phases rather than that of α-Al may take place. In all other cases in which the crystallization behaviour of Zr-Ni-La glasses [3] even with Zr addition [4] was investigated the crystallization starts with formation of α-Al phases. Thus it is not yet clear how the rather small variations of the amount of the elements Ni, La and Zr

influence the crystallization behaviour. Possible further influences such as the conditions during solidification which could lead to the formation of nuclei play an important role.



a) b)

Fig. 5 a) BF TEM image of microstructure of $Al_{87}Ni_5La_7Zr_1$ alloy aged at 245°C for 2 h. The corresponding SAD pattern is given in the inset. b) HRTEM image of one of the fine crystal.

Summary

The $Al_{87}Ni_6La_7$ and $Al_{87}Ni_5La_7Zr$ alloys were produced by melt spinning. The resulting ribbons of $Al_{87}Ni_6La_7$ were fully amorphous whereas the ribbons of $Al_{87}Ni_5La_7Zr$ contained a low number of primary crystals. The amorphous matrix between the primary crystals in the Zr-containing glass shows fluctuations of all minor elements on the nanometer scale. It is suggested, that these fluctuations act as nucleation zones for the crystallization of the glass during annealing.

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