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EFFECT OF THERMAL TREATMENT OF THE MELT ON CRYSTALLIZATION KINETICS OF $Al_{91}La_5Ni_4$ AMORPHOUS RIBBONS PREPARED BY RAPID QUENCHING

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Abstract

Differential scanning calorimetry (DSC) and X-ray diffraction techniques were used to study the crystallization kinetics of $Al_{91}La_5Ni_4$ amorphous alloys prepared by a rapid quenching method. The experimental results showed that the thermal treatment of the melt – temperature regime and exposure time – had a significant effect on the crystallinity of the ribbons prepared by rapid quenching, and hence on the crystallization kinetics of the ribbon alloys in the annealing process.

Keywords: Al alloys, crystallization of amorphous ribbons, DSC analysis, rapid quenching

Introduction

A large number of studies have recently reported the manufacture, structure, and properties of new high-strength light metallic alloys of Al [1–3]. It was found that the crystallinity of the alloy has a significant effect on its properties; for example, optimal strength was obtained for about 80% (volume fraction) amorphous Al in the alloy [3].

To obtain the required degree of crystallinity one of two methods may be used:

1) rapid quenching of the melt to produce a totally amorphous state, followed by an annealing step to obtain the desired partial crystallization of the alloy [3]; or

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2) rapid quenching of the melt in properly planning cooling regime so as to produce the desired crystallinity in a single step.

Successful design of these processes must be based on data on the crystallization kinetics of each specific product. Most of the published work relating to kinetic studies focuses on the effects of the composition of the alloys and the annealing process (heating temperature *vs.* time) on the crystallinity [1, 2, 4–5]. However, data on other parameters are essential for better design of the manufacturing process. Manov *et al.* [6] found that the structure and the properties of viscosity, surface tension, and electrical resistivity of the Al alloy $Al_{91}La_5Ni_4$ depends on the initial temperature of the melt before the rapid quenching step. An explanation for this phenomena had previously been given by Popel *et al.* [7], who postulated that the size and density (number of units per unit volume of melt) of the nanocrystals present in the melt depends on the overheating conditions (temperature above the melting temperature and length of time). In the light of this explanation, a new method for producing the desired crystallinity by regulation of the overheating of the melt (temperature *vs.* time) before the rapid quenching step was proposed by Manov *et al.* [6]. However, this method cannot be successfully implemented without a detailed analysis of the peculiarities of the crystallization of such alloys.

In the present work, the crystallization kinetics of $Al_{91}La_5Ni_4$ amorphous alloys prepared by the rapid quenching method was studied by differential scanning calorimetry (DSC) and X-ray diffraction techniques. The study focused on i) the effect of the overheating conditions of the melt – exposure time (designated 'soaking') and temperature – before the rapid quenching step, and ii) on the crystallization kinetics of the amorphous ribbons.

Experimental

The amorphous $Al_{91}La_5Ni_4$ ribbons were prepared as described previously by Manov *et al.* [6]. The procedure consists of the following three stages: i) high-purity aluminum, lanthanum and nickel are melted in an Al_2O_3 crucible under an Ar atmosphere; ii) the cooled alloy is remelted at a rate of 40 K min^{-1} in an arc furnace under a He atmosphere to facilitate homogeneous mixing; and iii) amorphous ribbons are produced by rapid quenching, which is achieved by forcing the melt (at various temperatures) on to a copper drum.

Three 20 μm thick amorphous ribbons were studied, each one prepared at different overheating conditions of the molten alloy before rapid quenching, as follows: sample 1) soaked for 10 min at 1473 K followed by 5 min at 1373 K; sample 2) soaked for 10 min at 1473 K followed by 5 min at 1273 K; and sample 3) soaked for 15 min at 1373 K.

DSC analyses were carried out on a Mettler Toledo DSC 820 instrument in an Al crucible under a nitrogen atmosphere (99.9% pure), at heating rate of

15 K min^{-1} in a temperature range of 300–673 K. The instrument was calibrated with pure indium (melting temperature 429.9 K, heat of fusion 28.4 J g^{-1}). The weight of the samples was in the range of 4–5 mg.

Specimens from the ribbons taken before and after the DSC analysis were also subjected to X-ray diffractometry on a PW 1050/70 Philips diffractometer at a constant temperature of 296±1 K.

Results and discussion

X-ray diffractograms of the three ribbons showed that no crystalline phases could be identified in ribbon 1, whereas a small peak corresponding to Al (111) was exhibited by ribbon 2, and a distinct peak of Al and small peak of Al_4La could be identified in ribbon 3 (Fig. 1). The X-ray diffractograms obtained after the DSC analysis were identical for all three ribbons, irrespective of the initial thermal treatment to the melt, and indicated the presence of three crystalline phases Al, Al_4La and Al_3Ni.

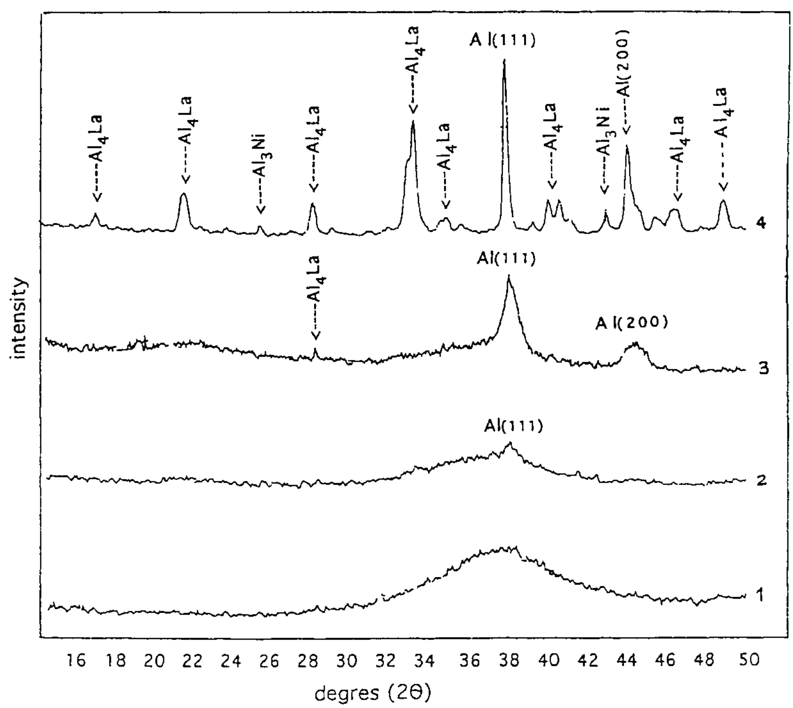

Fig. 1 X-Ray diffractograms for $Al_{91}La_5Ni_4$ alloys. Curves 1, 2 and 3 represent specimens of ribbons 1, 2 and 3 before DSC analysis, respectively; curve 4 represents all three cases after DSC-analysis. Curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

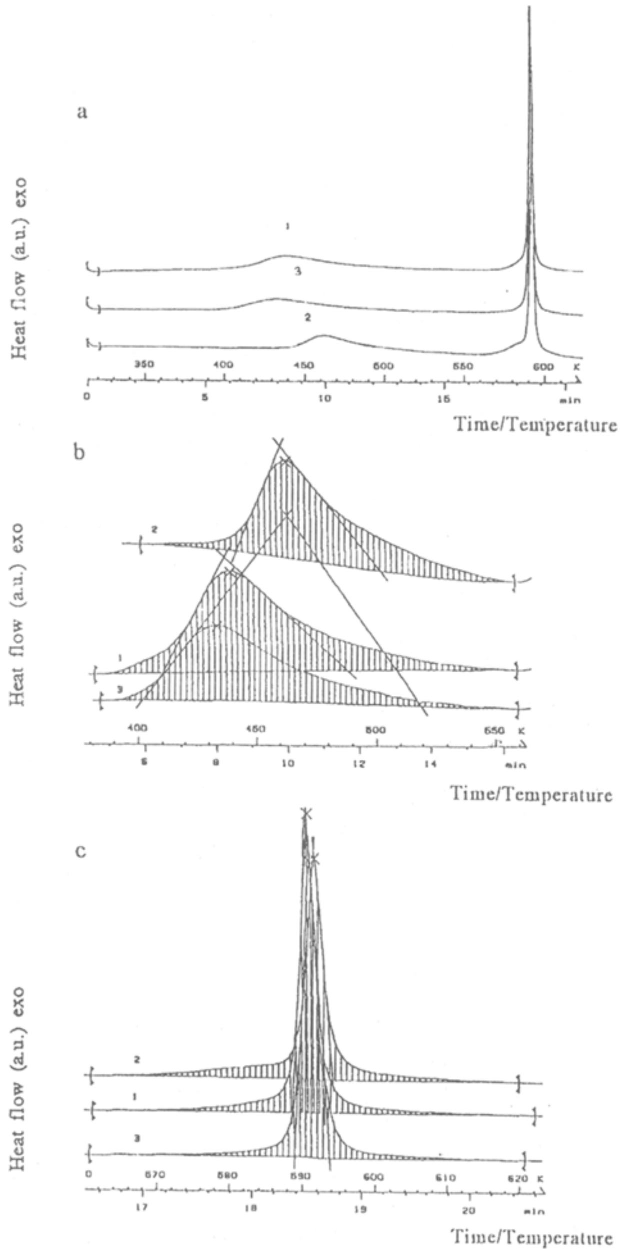

Fig. 2 DSC curves of $Al_{91}La_5Ni_4$ amorphous ribbons prepared by rapid quenching under different conditions of overheating of the molten alloy (a); enlargement of peak 1 of the DSC curve (b); and enlargement of peak 2 of the DSC curve (c). Curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

Table 1 Characteristic temperatures and ΔH for crystallization of $Al_{91}La_5Ni_4$ amorphous alloys

Sample	Enthalpy/ kJ mol^{-1} alloy	Characteristic temperatures/K		
		$T_{x(s)}$	$T_{x(e)}$	T_p
Peak 1				
1	2.39	388	438.9	528.8
2	1.98	408	463.0	542.6
3	1.78	392	433.2	526.7
Peak 2				
1	2.67	568	592.8	616.8
2	2.54	564	593.3	620.5
3	2.67	568	593.0	615.0

$T_{x(s)}$– initial temperature; $T_{x(e)}$– final temperaure; T_p–- peak temperature.

Figure 2 shows the DSC traces for the three cases, which are consistent with the X-ray diffraction analyses. In all three cases, two exothermic peaks were clearly visible, the first one relating to the crystallization of Al, which took place at 388–527 K, and the second to the formation of the crystalline compounds Al_4La and Al_3Ni at 564–621 K.

The characteristic temperatures of the DSC curves and the heats of crystallization are summarized in Table 1. The heats of crystallization for the Al compounds were almost the same – 2.54 to 2.62 kJ mol^{-1} alloy – for all three ribbons, while those for the crystallization of Al were significantly different, being 2.4, 2.0 and 1.8 kJ mol^{-1} alloy for samples l, 2, and 3, respectively.

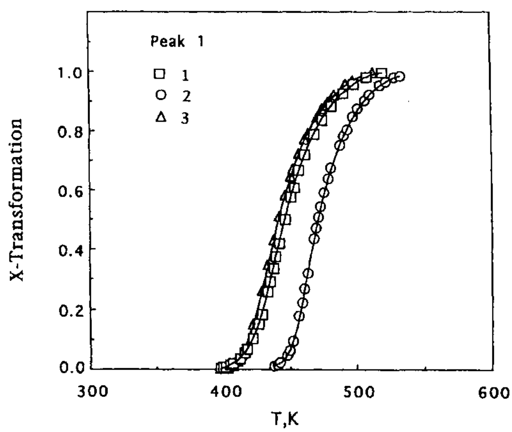

Fig. 3 Fraction of Al crystallized as a function of temperature/time for the three $Al_{91}La_5Ni_4$ amorphous ribbons; curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

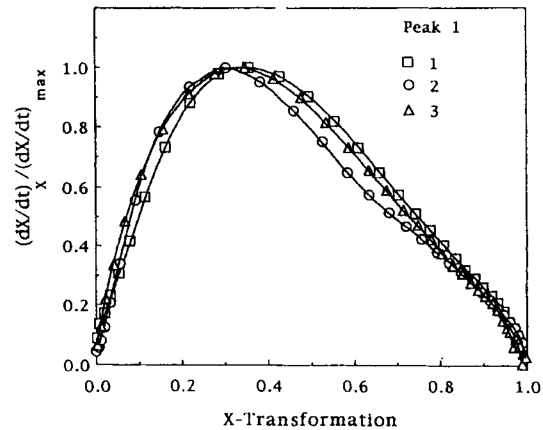

Fig. 4 Normalized crystallization rate of the Al phase *vs.* fraction of Al crystallized for the three $Al_{91}La_5Ni_4$ amorphous ribbons; curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

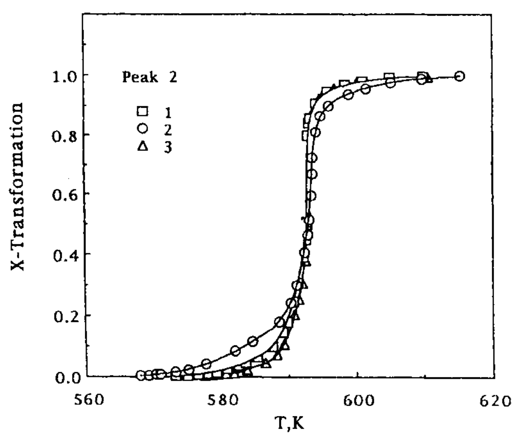

Fig. 5 Fraction of Al_4La and Al_3Ni crystallized as a function of temperature/time for the three $Al_{91}La_5Ni_4$ amorphous ribbons; curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

Assuming in case 1 that the ribbon is completely amorphous and in cases 2 and 3 that the heat of crystallization is independent of the mass fraction of the crystalline state, the conversion X as a function of temperature (or as a function of heating time) could be calculated. The rate of crystallization as a function of conversion could then be obtained.

Figure 3 shows that the crystallization of Al (first peak) in case 2 started at about 35 K higher than in cases 1 and 3. The maximum rate in case 2 was ob-

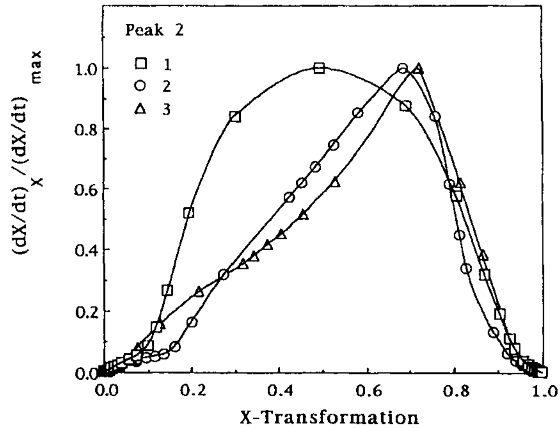

Fig. 6 Normalized crystallization rate for Al_4La and Al_3Ni crystallization *vs.* fraction of both Al_4La and Al_3Ni crystallized for the three $Al_{91}La_5Ni_4$ amorphous ribbons; curve 1 – soaked for 10 min at 1473 K followed by 5 min at 1373 K, curve 2 – soaked for 10 min at 1473 K followed by 5 min at 1273 K, curve 3 – soaked for 15 min at 1373 K

tained at about X=0.25, while in cases 1 and 3 it was found at about X=0.27 (Fig. 4). This finding could be explained by the fact that the initial melt temperature before quenching in case 2 (1273 K) was 100 K lower than that in cases 1 and 3 (1373 K).

The results for the formation of the compounds Al_4La and Al_3Ni are given in Figs 5 and 6. These figures show that the crystallization kinetics were very sensitive to the thermal treatment of the melts. Curve 1 in Fig. 6, which pertains to soaking at the highest average temperature (10 min at 1473 K and 5 min at 1375), has symmetric shape with the maximum crystallization rate being obtained at X=0.5, whereas curves 2 and 3 are asymmetric in shape with the maximum rate shifted to X=0.7 and 0.72, respectively. This finding may be explained on the basis of the difference in the initial conditions of the ribbons in the annealing step. In ribbon 1, which was initially totally amorphous, the crystallization started with primary homogeneous nucleation, while in ribbon 2 that contained Al crystals and ribbon 3 that contained crystals of Al and Al compounds, the crystallization began with secondary heterogeneous nucleation.

Conclusions

On the basis of the DSC and X-ray analyses performed in this study, the following conclusions were drawn:

1. The overheating conditions of the melt (melt temperature and soaking time) had a significant influence on the crystallinity of $Al_{91}La_5Ni_4$ ribbons obtained by rapid quenching. A completely amorphous phase was obtained for the

case in which the melt was soaked for 10 min at 1473 K followed by 5 min at 1375, whereas for the case of soaking for 10 min at 1473 K followed by 5 min at 1273 about 25% of Al had already crystallized in the quenching step.

2. In process of heating the amorphous $Al_{91}La_5Ni_4$ ribbons, the overheating conditions had an insignificant influence on the crystallization kinetics of Al phase but a significant effect on the crystallization of Al_4La and Al_3Ni.

3. The experimental results presented in this paper are in agreement with the concept that the desired crystallinity of the $Al_{91}La_5Ni_4$ ribbons can be obtained by manipulating the overheating conditions of the melts before the rapid quenching step.

In summary, the results demonstrate the importance of the overheating conditions on the degree crystallinity of materials prepared by rapid quenching and on the crystallization kinetics.

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