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# Neutron diffraction and calorimetric study on Al-based metallic glasses

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## Abstract

The kinetics of transformation of the melt spun  $\text{Al}_{87}\text{Ni}_7\text{Nd}_3\text{Cu}_3$  alloy was analysed by differential scanning calorimetry (DSC) and neutron diffraction (ND) experiments. The study of the emerging nanocrystalline grained structure by in situ heat treatment on quenched ribbons of the aluminium rich alloy composition indicates that no detectable nanocrystallisation occurs till temperatures of about 370 K. Changes of the structure occur in two well defined and not overlapped temperature ranges. The thermodynamic optimisation of the Al-rich part of the Al–Ni–Nd–Cu system, by computing calculation of the equilibrium and metastable phase diagrams, is applied to the kinetics of the crystallisation of the face-centered-cubic (fcc)-(Al) for the  $\text{Al}_{87}\text{Ni}_7\text{Nd}_3\text{Cu}_3$  alloy. The fcc-(Al) precipitation occurs in a temperature interval of  $\sim 200$  K, although the most rapid structural changes occur at temperatures around 380 K. These results are indicative of the diffusion control of the last stages of the first crystallisation event. Eutectic precipitation of fcc-(Al) +  $\text{Al}_3\text{Ni}$  is promoted when temperature is about 520 K. The overall analysis shows that primary fcc-(Al) crystallisation is kinetically hidden. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Al-based alloys are possible candidates for the development of nanostructured materials [1–3]. The achievement of such a microstructure depends on the processing conditions and may be improved by controlled heat treatment of the rapidly quenched, typical cooling rate  $\gtrsim 10^5$  K s<sup>-1</sup>, alloys. A key point for future development is understanding

the microscopic mechanism, that determines thermally activated nanostructural changes on the nanometer scale.

The purpose of the paper is to present differential scanning calorimetry (DSC) and time-of-flight (TOF) neutron diffraction (ND) experiments, (performed on the LAD instrument at the ISIS Facility) to study the emerging nanocrystalline grained structure by in situ heat treatment on quenched ribbons of an aluminium rich alloy, of  $\text{Al}_{87}\text{Ni}_7\text{Nd}_3\text{Cu}_3$  composition. The ND experiment was run in the temperature range between 320 and 650 K under controlled heating at a rate of 0.33 K

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$\text{min}^{-1}$  whereas DSC experiments were performed under isothermal regime and at scan rates in between 5 and 40  $\text{K min}^{-1}$ .

The thermodynamic functions of the several equilibrium phases predicted for compositions in the Al-rich corner of the quaternary system were evaluated using the Calphad method [4–9]. The computed thermodynamical data set was used to calculate the thermodynamic functions needed to model nucleation and crystal growth from the supercooled liquid alloy.

## 2. Results

The most significant DSC results concern the relative rate of transformation during both transformations [10,11]. Fig. 1 shows the data observed due to face-centered-cubic (fcc)-(Al) primary precipitation and growth, whereas Fig. 2 shows the relative rate of transformation at the eutectic precipitation of fcc-(Al) and  $\text{Al}_3\text{Ni}$ . The crystallisation process has a marked asymmetry in between the accelerated and decelerated temperature intervals of the process. With regard to the eutectic transformation, some overlap between two different thermally activated processes is apparent at moderately low scan rates ( $\sim 0.1 \text{ K s}^{-1}$ ).

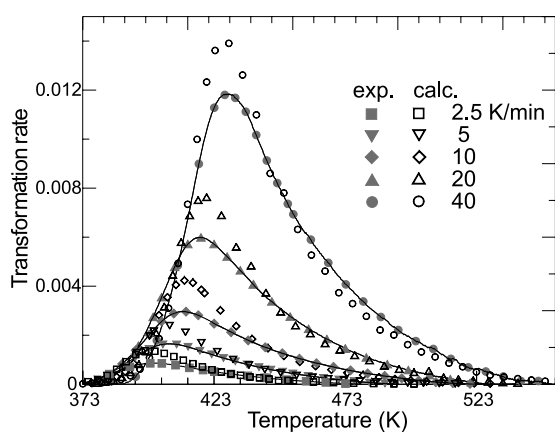


Fig. 1. Comparison of calculated and experimental data (obtained by DSC) of the temperature dependence of the transformation rate during fcc-(Al) nanocrystallisation, at different heating rates.

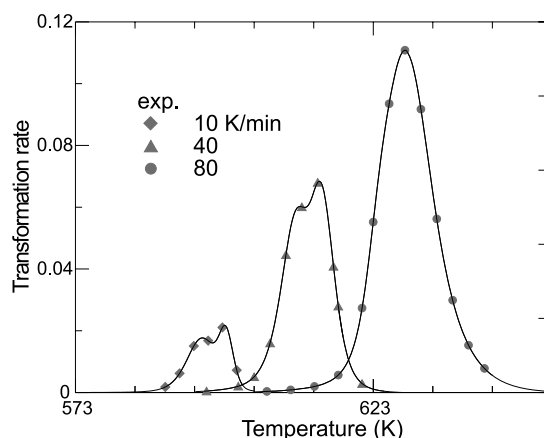


Fig. 2. Temperature dependence of the transformation rate during fcc-(Al) +  $\text{Al}_3\text{Ni}$  eutectic crystallisation, obtained by DSC at different heating rates. Lines are drawn as guides for the eye.

The neutron diffractograms shown in Fig. 3 were obtained when heating the sample at a mean rate of  $0.33 \text{ K min}^{-1}$  (10 min heating at  $0.5 \text{ K min}^{-1}$  + 5 min isotherm) in the temperature interval 360–550 K. Changes of the structure of the sample occur in two steps: primary precipitation in between 370 and 480 K followed by eutectic precipitation in the interval 510–530 K [12].

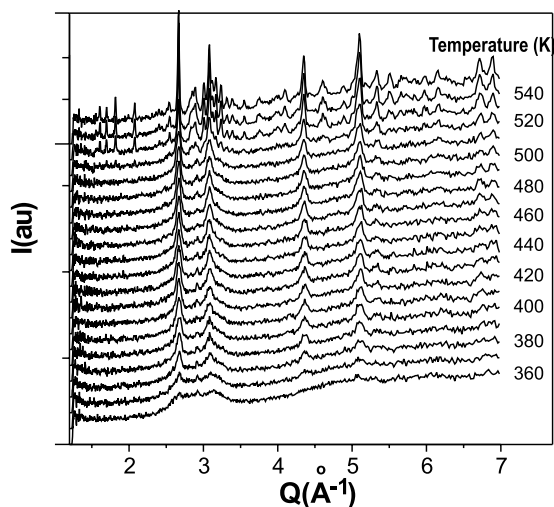


Fig. 3. Neutron diffraction intensities (in arbitrary units) for selected temperatures in the interval 360–550 K as a function of the scattering vector  $Q$  through continuous heating.

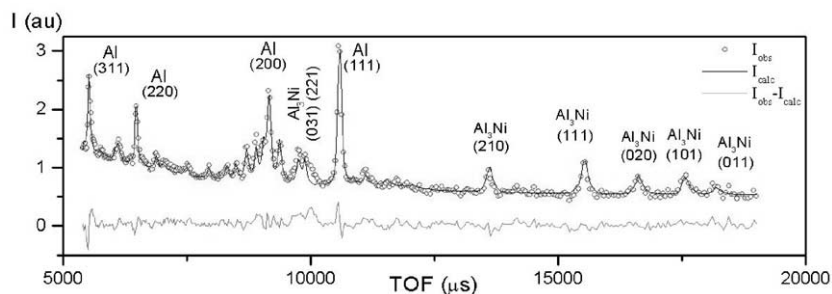


Fig. 4. Neutron diffraction pattern (intensity in arbitrary units) as a function of time-of-flight (TOF) showing the contribution of crystalline fcc-(Al) and  $\text{Al}_3\text{Ni}$  to the calculated pattern obtained from a Rietveld refinement procedure. The spectrum corresponds to a temperature of 550 K. The bottom curve represents the difference between calculated and experimental spectra.

The ND pattern of the  $\text{Al}_{87}\text{Ni}_7\text{Cu}_3\text{Nd}_3$  alloy at 550 K was analysed using FullProf, a program based on Rietveld structure refinement [13]. Fig. 4 shows the fit between the data and the calculated profile for fcc-(Al) and  $\text{Al}_3\text{Ni}$  (orthorhombic). Peaks that are not indexed belong to the  $\text{Al}_3\text{Ni}$  phase, and are the superposition of multiple reflections.

### 3. Discussion

The relative thermal stability of the Al-rich supercooled liquid has been analysed using the Calphad method. These include the evaluation of the Gibbs energy and enthalpy for Al primary precipitation as well as the crystallisation enthalpy as a function of the degree of attainment of metastable equilibrium (saturated supercooled liquid + Al crystals) [14,15].

Comparison of the experimental crystallisation enthalpy, as a function of thermal treatment, with predicted calculated enthalpies indicates that under isothermal regime crystallisation of Al grains proceeds up to a volume fraction of  $(5.0 \pm 0.2) \times 10^{-2}$  at temperatures of 390 K, whereas it attains a volume fraction of  $(15 \pm 0.5) \times 10^{-2}$  under continuous heating at 40  $\text{K min}^{-1}$ . That is, Al crystallisation is kinetically hindered since the final state reached upon heat treatment depends on the thermal path.

The analysis of the ND patterns confirms that the fcc-(Al) phase crystallises in the first tempera-

ture range and fcc-(Al) +  $\text{Al}_3\text{Ni}$  are the main secondary products after the second reaction. The difference in full width at half maximum, FWHM, of the fcc-(Al) peaks with temperature (see Fig. 3) is correlated with the size increase of the crystallites during the crystallisation process.

The results of the Rietveld analysis indicate that at these temperatures (after heating at 0.33  $\text{K min}^{-1}$  the melt spun sample) the total crystallised volume is shared by the fraction  $(73 \pm 7)\%$  of fcc-(Al) and  $(27 \pm 3)\%$  of  $\text{Al}_3\text{Ni}$ . An increase in the lattice parameter of the fcc-(Al) phase by 0.06% at 410–450 K to 0.11% at 550 K is also observed. This change could be related to an increased Ni and/or Cu incorporation into the Al structure to reach the metastable equilibrium composition from an initial defective crystal. An orientation in the [1 1 1] direction was also needed to improve the fitting of the fcc-(Al) phase at 550 K.

Following a procedure already established also for Finemet alloys [16–19], primary nucleation and crystal growth has been modelled for the supercooled liquid. For the particular quaternary  $\text{Al}_{87}\text{Cu}_3\text{Nd}_3\text{Ni}_7$  alloy composition, there are several experimental evidences that precipitation of fcc-(Al) competes with the disordered homogeneous alloy at temperatures  $> 400$  K. From the point of view of growth, there is an initial growth transient, for each individual grain, in which the local equilibrium in between the emerging crystal and the liquid ahead of the crystal–liquid interface is established; afterwards, diffusion becomes the controlling mechanism [20]. According to the

continuous change in composition of the remaining liquid during primary crystallisation, smaller degrees of supersaturation are always reached in the course of the transformation [17]. However, if the initial conditions are those of supersaturation, most of the transformation occurs under this regime [18]. The simplest approach is to assume that the transient is interface controlled up to some grain size and then becomes diffusion controlled. Under this assumption, from the Avrami formalism [19] the evaluation of the rate of the transformation can be made. Due to the simplified expressions for the onset of the process, the coupling of continuous heating and isothermal data is able to provide most of the relevant kinetic parameters that are not accessible by direct measurement [19]. Once these quantities are evaluated, the mechanisms acting when crystallisation proceeds depend on the diffusion coefficient of the slowest diffusing atoms, which again, may be evaluated by the overall time/temperature dependence of the degree of advancement of the process.

The computed transformation rates, under continuous heating, are compared to the experimental ones in Fig. 1. The agreement is within  $\pm 10\%$ , that is, close to the experimental error, but discrepancies in the general trend remain. For the modelling, an initial density of critical nuclei of  $1 \times 10^{17} \text{ cm}^{-3}$  has been assumed, as deduced from transmission electron microscopy (TEM) [10].

From the overall model obtained from the LAD experiment we extend the study of the nucleation and growth mechanism already advanced to explain the crystallisation kinetics from DSC, XRD and TEM experiments and analysis.

#### 4. Conclusions

DSC and ND kinetic data on the primary and eutectic transformation of melt spun  $\text{Al}_{87}\text{Ni}_7\text{Nd}_3\text{Cu}_3$  alloys have been determined by in situ heat treatment. The primary crystallisation of melt spun  $\text{Al}_{87}\text{Ni}_7\text{Nd}_3\text{Cu}_3$  alloys has been studied by considering thermodynamic driving forces to attain metastable equilibrium between primary

crystals and saturated disordered matrix and kinetic inhibition due to the diffusion processes.

The main model of the kinetic process is predicted by suitable use of extrapolated thermodynamic data to model metastable equilibrium coupled with assumptions on the nucleation and growth habit due to the continuous change of the mean concentration of the overall matrix. The analysis assumes that most of the fcc-(Al) nuclei form from embryos already present in the rapidly quenched alloy. Experimental TEM analyses agree with that assumption and ND data are consistent with initial defective Ni/Cu Al nuclei.

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#### References

- [1] H. Kimura, K. Sasamori, A. Inoue, *Mater. Trans. JIM* 37 (1996) 1722.
- [2] A. Inoue, H. Kimura, K. Sasamori, T. Masumoto, *Mater. Sci. Eng. A* 217 (1996) 401.
- [3] T.H. Lee, Y. Kawamura, A. Inoue, S.S. Cho, T. Masumoto, *Scr. Mater.* 36 (1997) 475.
- [4] N. Clavaguera, Y. Du, *J. Phase Equil.* 17 (1996) 107.
- [5] Y. Du, N. Clavaguera, *J. Alloys Compounds* 237 (1996) 20.
- [6] Y. Du, N. Clavaguera, *Scr. Metall. Mater.* 34 (1996) 1609.
- [7] Y. Du, N. Clavaguera, *Calphad* 20 (1996) 289.
- [8] S. An mey, *Calphad* 16 (1992) 255.
- [9] Y. Du, N. Clavaguera, *Phase Equilibrium Relationship in Ni-Aluminides*, CEASI, Ni Aluminide Meeting, Barcelona, September 1995.
- [10] N. Clavaguera, J.A. Diego, M.T. Clavaguera-Mora, A. Inoue, *NanoStruct. Mater.* 6 (1995) 485.
- [11] N. Clavaguera, M.T. Clavaguera-Mora, *Scand. J. Metall.* 30 (2001) in press.
- [12] N. Clavaguera, M.T. Clavaguera-Mora, J.L. Touron, W.S. Howells, in *CD-ISIS99: ISIS Experimental Reports 1999*, RB No 9989 on LAD; <http://www.isis.rl.ac.uk/>.

- [13] H.M. Rietveld, *Acta Crystallogr.* 22 (1967) 151.
- [14] Y. Du, N. Clavaguera, *Calphad XXV Meeting*, Erice, Italy, May 1996.
- [15] J. Groebner, N. Clavaguera, Thermodynamic calculations in the systems Al–Cu–Nd–Ni, Al–Fe–Nd–B and Ga–Te, Final Report Postdoctoral Fellowship (PIEC, SGR, CIRIT), Universitat de Barcelona, 1997.
- [16] M.T. Clavaguera-Mora, N. Clavaguera, *J. Alloys Compounds* 247 (1997) 93.
- [17] M.T. Clavaguera-Mora, N. Clavaguera, *Recent Res. Nanostruct.* 1 (1999) 23.
- [18] N. Clavaguera, M.T. Clavaguera-Mora, in: M. Koiwa, K. Otsuka, T. Miyazaki (Eds.), *Solid–Solid Phase Transformations I*, JIM, 1999, p. 133.
- [19] M.T. Clavaguera-Mora, N. Clavaguera, D. Crespo, T. Pradell, *Progress in Materials Science*, in press.
- [20] N. Clavaguera, M.T. Clavaguera-Mora, in: J.S. Im, B. Park, A.L. Greer, G.B. Stephenson (Eds.), *Thermodynamics and Kinetics of Phase Transformations*; *Mater. Res. Soc. Symp. Proc.* 398 (1996) 319.