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Synthesis and thermal stability of ball-milled and melt-quenched amorphous and nanostructured Al-Ni-Nd-Co alloys

M. CALIN*,‡, H. GRAHL, M. ADAM‡, J. ECKERT, L. SCHULTZ
IFW Dresden, Institut für Metallische Werkstoffe, P.O. Box 270016, D-01171 Dresden, Germany
E-mail: m.calin@ifw-dresden.de; mcalin@decknet.ro

In this work the $Al_{85}Ni_9Nd_4Co_2$ alloy was used as a starting point for examining the possibility of forming bulk glassy Al-based materials by combining rapid quenching and ball milling techniques. Fine glassy powders were obtained by ball milling melt-spun amorphous ribbons using a severe cryogenic processing regime. The thermal stability data of the powders as obtained by constant-rate heating and isothermal DSC experiments together with viscosity measurements are discussed with respect to feasible consolidation conditions. The powder compaction was done by two methods (uni-axial hot pressing and extrusion) at 513 K for up to 15 min. Only the uni-axial hot pressing led to bulk $Al_{85}Ni_9Nd_4Co_2$ samples with similar glassy structure and Vickers microhardness values comparable to those of the initial melt-spun ribbons.

1. Introduction

Since the earliest experiences with melt quenching methods [1], Al-based systems have received a strong and continuing attention motivated by the steady discovery of new microstructures and property enhancements [2, 3]. Especially the glass-forming Al-TM-RE alloys (TM: transition metal, RE: rare earth), which contain about 85–90 at.% Al, have attracted considerable interest because of their high strength-to-weight ratio which makes them very useful as structural materials in transportation applications [4, 5].

Since the practical use of melt-quenched ribbons for applications is obviously limited, the possibility to produce Al-based amorphous and/or nanostructured alloys in form of bulk samples was checked [6–9]. Mainly these attempts were done by powder metallurgical methods, where powders were synthesized either by gas atomization or solid state reaction and then they were compacted using hot pressing or hot extrusion [7, 8]. As an alternative to produce bulk amorphous Al-based alloys also the metallic mold casting technique was used but without the expected success [9].

In this work the $Al_{85}Ni_9Nd_4Co_2$ alloy was used as a starting point for examining the possibility of forming bulk glassy Al-based alloys by combining rapid quenching and ball-milling techniques.

2. Experimental

$Al_{85}Ni_9Nd_4Co_2$ ingots were produced by arc melting a mixture of pure Al, Ni, Nd and Co metals with a purity of about 99.99% in argon atmosphere. Glassy alloys were prepared using a single-roller melt spinner with a wheel surface velocity of 21 m/s. The resulting ribbons were typically $\sim$25 μm thick and 6 mm wide.

Milling experiments starting from pure elemental powder mixtures as well as from the as-quenched ribbons were performed using a FRITSCH P5 (for mechanical alloying experiments) and a RETSCH PM 4000 (for pulverizing the melt-spun ribbons) planetary ball mill with hardened steel vials and balls at different intensities and times and a ball-to-material weight ratio of 13:1. All powder handling was done under argon atmosphere (O_2, $H_2O < 1$ ppm).

For mechanical alloying, the milling was performed at a rotational velocity of 180 rpm for different times, as a sequence of 15 min milling intervals interrupted by 15 min breaks to avoid a strong temperature rise and to suppress recovery processes in the low melting metal aluminium. For pulverizing, the ribbons were cut into small pieces and sealed in the vials under argon atmosphere in a glove box. Milling experiments of ribbons were conducted at 200 rpm for 9 h using a severe cryogenic regime (a sequence of 30 min milling intervals interrupted by 30 min breaks while the vials were

*Author to whom all correspondence should be addressed.
‡On Leave from University "Politehnica" of Bucharest, Materials Science and Engineering Faculty, Spl. Independentei 313; Ro-77206 Bucharest, Romania.

cooled with liquid nitrogen to minimize the temperature increase).

The as-milled powders were consolidated under argon atmosphere by uni-axial hot pressing as well as by extrusion using a Weber hot-press facility. During the compaction the powders were constant-rate heated at 40 K/min to the consolidation temperature.

Structural characterization was done by X-ray diffraction (XRD) using a Philips PW 1820 diffractometer with Co-Kα radiation and by transmission electron microscopy (TEM) using a Philips CM20 microscope. The thermal stability of the samples was analysed by differential scanning calorimetry (DSC) (in a Perkin Elmer DSC 7) at a heating rate of 40 K/min under flowing argon. Viscosity measurements were carried out by parallel plate rheometry in argon atmosphere using a Perkin Elmer TMA 7. The hardness was measured using a Vickers hardness tester.

3. Results and discussion

In order to obtain glassy $Al_{85}Ni_9Nd_4Co_2$ powders, the milling experiments were done starting from pure crystalline elemental powder mixtures and from melt-spun amorphous ribbons. In the first case, the severe mechanical deformation was used in order to induce amorphization by mechanical alloying. In the second case, the aim was to change the shape of sample (from ribbons into powders) without any modification of the structure.

Fig. 1 shows the XRD traces illustrating the structural states induced by the severe mechanical deformation compared with those of the as-quenched ribbon. The XRD pattern for the elemental powder mixture after milling is presented in Fig. 1c. During the mechanical alloying process, Al, Ni, Nd and Co are repeatedly flattened and cold-welded by the colliding balls, leading to the formation of rather large agglomerates. No powder was obtained even after prolonged milling. Even milling up to 400 h did not lead to a crystal-to-amorphous solid state transformation because of the severe sticking of aluminium to the milling tools, which causes a shift from the desired stoichiometry to significantly lower Al content (down to about 70 at.% Al) and, in turn, higher Ni, Nd, and Co contents.

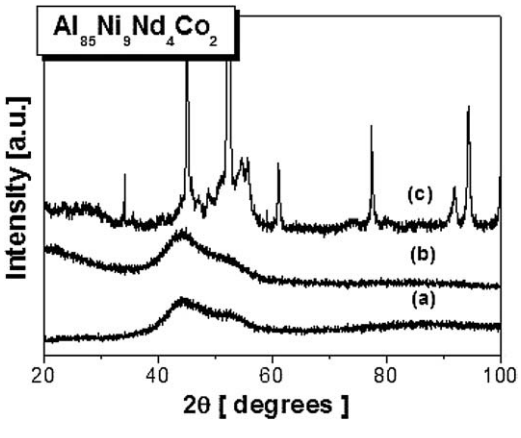

Figure 1 XRD patterns of $Al_{85}Ni_9Nd_4Co_2$ in different states: (a) as-quenched glassy ribbon, (b) as-milled powder from ribbons (200 rpm, 9 h), and (c) mechanically alloyed sample (180 rpm, 140 h).

In contrast, milling the melt-spun amorphous ribbons was successful and fine powders were obtained. A severe cryogenic milling regime was used in order to overcome the very high ductility of the ribbons and to avoid a strong temperature rise, which could facilitate the crystallization. From Fig. 1a and b one can observe that the as-milled powders have similar structural characteristics like the initial melt-spun ribbons. The XRD traces exhibit no distinct crystalline peaks but a broad maximum with a hump at higher angles, which is typical for amorphous Al alloys with low concentration of rare earth elements [10]. The patterns were interpreted as corresponding to an amorphous phase with embedded very fine fcc-Al nanocrystals. TEM images (Fig. 2) revealed the presence of such nanocrystals with a size of about 5 nm within the amorphous phase.

DSC measurements were done in order to evaluate the thermal stability of the samples and to clarify the effect of mechanical deformation on the crystallization behavior. Fig. 3a displays the DSC traces of the as-milled powder and the as-quenched ribbon specimens. For the ribbon sample, one can observe a clear endothermic heat flow event characteristic of a glass transition, followed by exothermic heat release events. Although the supercooled liquid region of the ribbon sample, ΔT_x, between the glass transition (T_g) and crystallization (T_x) temperatures, is rather small (18 K) it was possible to accurately identify the T_g and T_x values. T_g is defined as the onset of the endothermic DSC event and T_x as the onset temperature of the first exothermic event (see the enlarged part of the DSC curve in Fig. 3a). The values are $T_g = 531$ K and $T_x = 549$ K, which indicates a good thermal stability of the glassy structure.

For the as-milled powder, the glass transition is less pronounced. The major crystallization exotherm following the glass transition is slightly shifted to higher temperatures suggesting an enhancement of thermal stability of the remaining amorphous phase due to the increasing the concentrations of the solute elements [2]. Beside this, a very weak and broad low-temperature exothermic signal starting at about 390 K can be clearly seen (dashed arrow in Fig. 3a), which may be related to the formation of a higher volume fraction of Al-nanocrystals. The presence of this signal indicates that the mechanical constraints provided by milling accelerate the nanocrystal formation resulting in a lower thermal stability of the powder.

In order to prepare a bulk product by compaction of glassy powders it is necessary to correctly estimate the consolidation parameters in order to avoid further crystallization. With this aim, isothermal DSC and viscosity measurements were performed.

Fig. 3b shows the isothermal DSC traces of powders held for 1 h at different temperatures around T_g. They were used to estimate the incubation time for crystallization in the supercooled liquid region (viscous state).

Fig. 4 displays the results of viscosity measurements for ribbons and powders. The viscosity behavior upon heating is quite similar. The viscosity first decreases with increasing temperature upon heating from about 4×10^9 Pa s at 440 K to 5×10^8 Pa s at around

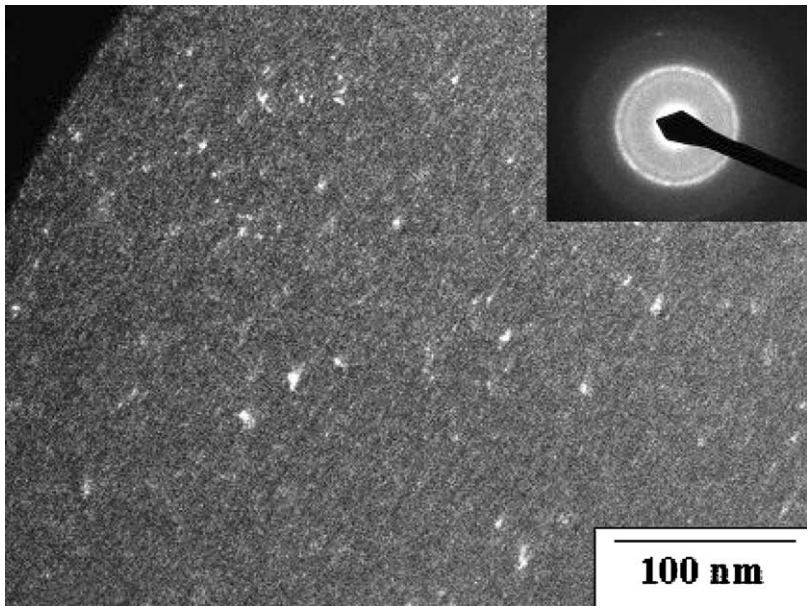

Figure 2 Dark-field TEM micrograph and electron diffraction pattern of melt-spun $Al_{85}Ni_9Nd_4Co_2$ ribbon.

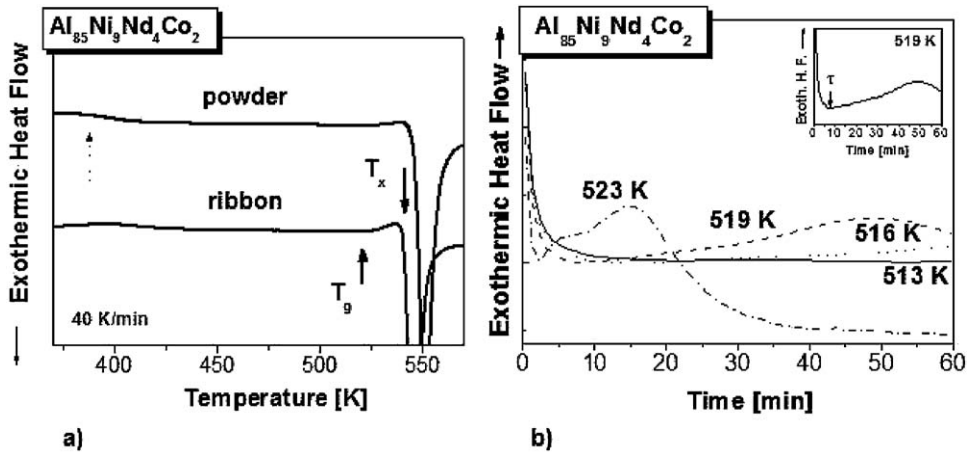

Figure 3 DSC traces for glassy $Al_{85}Ni_9Nd_4Co_2$: (a) non-isothermal curves recorded for the ribbon and powders specimens (heating rate 40 K/min) and (b) isothermal scans recorded for as-milled powders at different temperatures.

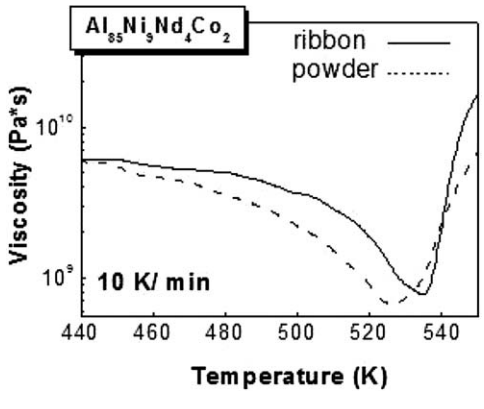

Figure 4 Viscosity of the glassy ribbon and powder as a function of temperature (heating rate 10 K/min).

530 K. Above 530 K the viscosity rapidly increases, suggesting the start of crystallization of the remnant amorphous phase. For the melt-spun ribbon, the minimum value of viscosity is reached at slightly higher temperatures compared with the ball-milled powder. For consolidation, temperatures corresponding to the supercooled liquid region should be chosen where the viscosity is quite low (Fig. 4).

The viscosity data and the results from the isothermal DSC runs were used to consolidate the powders by two methods: uni-axial hot pressing and extrusion. The isothermal DSC measurements reveal that the incubation time decreases considerably with a small increase in temperature. Thus, at temperatures higher than 523 K the incubation time is too short to be feasible for pressing experiments. Since at lower temperatures the deformation necessary for the material flow and, hence, for successful consolidation is essentially hindered, a temperature of 513 K has been chosen as a compromise. The incubation time for crystallization is longer than 1 h at 513 K. The powder consolidation was done at 513 K using pressures of about 700 MPa for $\leq$15 min. Upon increasing the temperature by only 6 K the incubation time τ decreases significantly ($\tau = 9$ min at 519 K, see inset in Fig. 3b) making the pressing quite complicated.

The extrusion experiments were not successful, because the glassy powders crystallized. In contrast, uniaxial hot pressing of glassy powders yielded billets

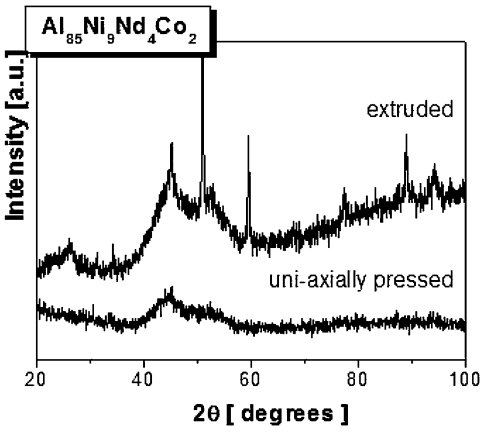

Figure 5 XRD patterns of $Al_{85}Ni_9Nd_4Co_2$ consolidated bulk samples.

(about 10 mm in diameter and up to 6 mm in thickness) containing as little as 6% volume fraction of voids, with no induced crystallization detected.

Fig. 5 compares the XRD patterns of the bulk samples after extrusion and uni-axial hot pressing. The broad maximum without no distinct crystalline peaks for the uni-axially pressed sample proved that the material is amorphous and quite similar as the milled powders and the initial ribbons.

Because of the presence of voids, the samples were not proper for reliable compression tests. Nevertheless, the mechanical properties evaluated by microhardness measurements are promising. Vickers microhardness tests gave values of about 382 H_v for the as-quenched glassy ribbons and about 380 H_v for the consolidated glassy sample, both values being much higher than those ($100 \div 190$ H_v) of conventional high-strength crystalline Al-based alloys [11]. These values are comparable with those (340 H_v) reported for melt-spun amorphous $Al_{85}Ni_5Y_8Co_2$ [12].

The presented results are encouraging for obtaining bulk glassy Al-based alloys with improved mechanical properties through powder metallurgy processing. For full consolidation (without voids), the interplay between consolidation pressure, incubation time, crystallization temperature and viscous flow should be optimized. This seems to be rather difficult in the case of Al-based amorphous alloys, because generally they have a rather narrow supercooled liquid region and an extremely high nucleation rate for crystallization [13, 14].

4. Summary

$Al_{85}Ni_9Nd_4Co_2$ was selected for examining the possibility of forming bulk glassy Al-based alloys. Milling experiments were done starting from pure crystalline elemental powder mixtures (mechanical alloying) and from glassy melt-spun ribbons. The glass formation in $Al_{85}Ni_9Nd_4Co_2$ by mechanical alloying was not successful due to the pronounced sticking of aluminium to the milling tools, which determines composition deviations of the powder.

Pulverization of the glassy ribbons in a planetary ball mill using a severe cryogenic milling regime allowed the preparation of fine glassy powders, which were afterwards consolidated by two methods: uni-axial hot pressing and extrusion.

The viscosity data together with the results from isothermal DSC runs were used for choosing the consolidation parameters (temperature and time). Powder consolidation by uni-axial hot pressing at 513 K using pressures of ~700 MPa for less than 15 min yielded bulk samples with a density of about 94%, without inducing crystallization. The as-pressed bulk $Al_{85}Ni_9Nd_4Co_2$ samples showed a glassy structure similar to that of the initial melt-spun ribbons. Vickers microhardness tests gave values of about 380 H_v for both glassy ribbons and consolidated bulk samples.

Acknowledgements

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