Nanocrystallization in Al$_{85}$Ce$_8$Ni$_5$Co$_2$ amorphous alloy induced by heat treatment and severe plastic deformation

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Abstract. Al$_{85}$Ce$_8$Ni$_5$Co$_2$ metallic glass ribbon was devitrified by heat treatments just below its glass transition temperature and by severe plastic deformation applying ball milling and high pressure torsion. Evolution of the microstructure, thermal stability and further thermal history were compared for the different devitrification processes. Based on this mapping of phase selection processes, microstructural changes can be predicted for high temperature and/or high stress compaction which are often required for application of this light weight alloy.

1. Introduction
Severe plastic deformation (SPD) techniques like high pressure torsion (HPT) are frequently used for producing highly dense, ultrafine-grained bulk materials [1]. This method can also be applied successfully to produce massive samples from melt-quenched amorphous ribbons by room temperature consolidation [2,3].

Compaction has a crucial role in the application of light-weight, high-strength Al-based amorphous materials, because there is no other method to obtain bulk samples [4-6]. Since metallic glasses are inherently metastable, they tend to transform into crystalline phases when subjected to heat treatment or large plastic deformation. Therefore, the different crystallization routes influencing the various mechanical properties are in the focus of recent investigations.

In this work Al$_{85}$Ce$_8$Ni$_5$Co$_2$ amorphous alloy was chosen as a model system. We have already shown that in this thermally eutectic-like crystallizing alloy HPT yields the formation of α-Al nanocrystals [3,7,8]. In order to explore the crystallization routes of Al$_{85}$Ce$_8$Ni$_5$Co$_2$ special heat treatments and a different SPD technique was applied. Characterizing the as-produced new metastable states, a crystallization map can be constructed, in accordance with the crystallization sequences and the thermal behavior.

2. Experimental
As-quenched Al$_{85}$Ce$_8$Ni$_5$Co$_2$ribbon was obtained using a single roller melt spinning technique in inert atmosphere. Selected area electron diffraction image confirmed the fully amorphous nature of the
alloy. A part of the ribbon was cut into small pieces (flakes), and then placed between anvils of the HPT device. The deformation was performed by subjecting the flake to five rotations under hydrostatic pressure of 6 GPa, which results in several porosity free disks with a diameter of 10 mm and thickness of about 120 µm.

Another part of the ribbon was milled in a SPEX-8000 mixer-mill, using stainless steel container and balls. The milling was carried out under pure argon atmosphere and the ball to powder ratio was chosen as 300:1 in order to achieve high impact energy. Microstructure was examined by a Philips diffractometer (PW1130) in a Guinier-chamber. The chamber has a diameter of 100 mm and the patterns were recorded on Image Plates (IP). Isothermal annealings and linear heating scans at 40 K/min were performed in a Perkin-Elmer power compensated differential scanning calorimeter (DSC) under an argon atmosphere.

3. Results

3.1. Heat treatment 1. (HT1)

Al₈₅Ce₈Ni₅Co₂ amorphous alloy exhibits a well defined glass transition, with the glass transition temperature of Tg=555K and a two-stage crystallization process (the corresponding exothermic DSC peaks in Fig. 1a are labeled with T₁ and T₂). During the first transformation event (T₁) α-Al, Al₃Ce and a metastable crystalline (Φ) phases nucleate simultaneously. The final microstructure, attained above T₂ contains of α-Al, Al₃Ce₅, Al₅Co₂ and Al₅Ni phases (see Fig. 1b). In order to compare the crystallization products under isothermal condition with the microstructure formed after continuous heating the as-quenched alloy was subjected to isothermal heat treatments at Tₐₙₐₙ=547.5K (denoted hereafter as HT1) for different annealing times tₐₙₐₙ=15, 45 and 180 minutes. The DSC curves of the subsequent linear heating scans carried out on the isothermally annealed samples illustrate that tₐₙₐₙ=15 min heat treatment has only a slight effect on the thermal behavior, however, HT1 for tₐₙₐₙ=45 min results in drastic change in the peak shapes (Fig. 1c). Firstly just T₁ peak is affected, until it totally diminishes at tₐₙₐₙ=180 min and new high temperature exothermic peak (T₂) develops after HT1 larger than 180 min. The corresponding XRD patterns in Fig. 1d show important changes in the microstructure of the alloy occurring during annealing. After HT1 for tₐₙₐₙ=15 min the Bragg peaks of fcc-Al and Φ phase appear, meanwhile after HT1 for tₐₙₐₙ=25 min some new crystalline peaks of Al₃Ce emerge. During heat treatment for tₐₙₐₙ=30min devitrification of the glass proceeds by the continuous transformation of Φ and Al₃Ce phases to the more stable Al₃Ce₅, Al₅Co₂ and Al₅Ni ones.

3.2. Heat treatment 2. (HT2)

Additionally isothermal heat treatments were carried out at different annealing temperatures Tₐₙₐₙ=535 K, 542.5 K and 550 K for tₐₙₐₙ=30 min (denoted hereafter as HT2). The DSC curve of the sample annealed at Tₐₙₐₙ=535 K is just slightly affected as seen in Fig. 1e. Heat treatment at Tₐₙₐₙ=542.5 K results in intensity decrease of T₁ and the appearance of a new high temperature exothermic peak (T₂), meanwhile at Tₐₙₐₙ=550 K both T₁ and T₂ totally disappear. The XRD pattern of the heat treated sample at Tₐₙₐₙ=535 K shows an amorphous halo with superimposed Bragg peaks of α-Al and Φ. After annealing at higher temperatures the amorphous halo decomposes (Tₐₙₐₙ=542.5 K) and crystalline Al₃Ce appears (Fig. 1f).

3.3. High pressure torsion (HPT)

Linear DSC scans performed on the HPT disk is illustrated in Fig. 1g. As seen, in the case of deformed sample T₁ disappears and a new high temperature exothermic peak T₃ appears. Fig. 1h depicts the XRD patterns of HPT disk, which exhibits a featureless halo and the Bragg peaks of α-Al.

3.4. Ball milling (BM)

High energy ball milling of Al₈₅Ce₈Ni₅Co₂ ribbon was performed for durations tₐ₈₅=340 s, 800 s and 1200 s. The continuous heating DSC curve of the sample milled for tₐ₈₅=340 s is almost unaffected.
Further milling for t_{BM}=800 s results in the simultaneous decrease of T_1 and T_2, while in the case of t_{BM}=1200 s just a low temperature exothermic peak (T_1*) is present (Fig. 1i).

The XRD pattern obtained after t_{BM}=340 s depicts some Bragg peaks of Al_11Ce_3 and a featureless amorphous halo. After milling for t_{BM}=800 s the equilibrium phases can be identified and as seen in Fig. 1j further milling up to t_{BM}=1200 s doesn’t cause any visible change in the patterns.
4. Discussion and conclusions
In order to compare the thermally and deformation activated devitrification process in an amorphous \( \text{Al}_{85}\text{Ce}_8\text{Ni}_5\text{Co}_2 \) alloy, a schematic free energy landscape has been constructed depicting the different crystallization products (Fig. 1). The relative position of each state on the map is proportional to the residual enthalpy obtained from the linear heating DSC scans. As was demonstrated, the formation of equilibrium compounds through two steps (AQ → M → E). Applying special conditions of heat treatments (HT1, HT2, see Figs. 1), the system reaches its equilibrium state (E) through an additional high temperature metastable stage (MH) (AQ → M → MH → E). The crystallization path of HPT alloy differs from that of heat treated samples. According to the large deformation the system traps in a different metastable state (MD), having high excess free energy. Prolonged ball milling results in the formation of all the equilibrium phases by passing all the metastable states (AQ → E).

Figure 2. Schematic free-energy landscape of the different states (AQ: as-quenched state, M: metastable state, E: equilibrium, MD: deformation induced metastable state, MH: high temperature metastable state) of the \( \text{Al}_{85}\text{Ce}_8\text{Ni}_5\text{Co}_2 \) amorphous alloy. Arrows denote the different crystallization routes.

According to the experimental results, the appearance of \( T_1 \) high temperature transformation strongly depends on the parameters of thermal annealing and the deformation mode. As a consequence, the presence of the metastable \( \Phi \) phase is extended up to higher temperature.

As a conclusion, we showed firstly that after isothermal heat treatments and HPT, a new high temperature exothermic DSC peak appears in amorphous \( \text{Al}_{85}\text{Ce}_8\text{Ni}_5\text{Co}_2 \), which has not been observed so far in this system.

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