Effect of Rare Earth and Transition Metal Elements on the Glass Forming Ability of Mechanical Alloyed Al–TM–RE Based Amorphous Alloys

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The present work aims to compare the amorphous phase forming ability of ternary and quaternary Al based alloys ($Al_{86}Ni_8Y_6$, $Al_{86}Ni_6Y_6Co_2$, $Al_{86}Ni_8La_6$ and $Al_{86}Ni_8Y_{4.5}La_{1.5}$) synthesized via mechanical alloying by varying the composition, i.e. fully or partially replacing rare earth (RE) and transition metal (TM) elements based on similar atomic radii and coordination number. X-ray diffraction and high resolution transmission electron microscopy study revealed that the amorphization process occurred through formation of various intermetallic phases and nanocrystalline FCC Al. Fully amorphous phase was obtained for the alloys not containing lanthanum, whereas the other alloys containing La showed partial amorphization with reappearance of intermetallic phases attributed to mechanical crystallization. Differential scanning calorimetry study confirmed better thermal stability with wider transformation temperature for the alloys without La.

1. Introduction

Bulk metallic glasses (BMGs) exhibit excellent mechanical properties (e.g., high mechanical strength and elasticity), good corrosion resistance, and exceptional soft magnetic properties, owing to the absence of long-range atomic periodicity and defects (dislocations and grain boundaries)[1]. With such exceptional properties, BMGs find widespread potential applications in medical and electronic devices, sporting goods, advanced defence and aerospace technologies[2]. Al-based BMGs with high Al content (>80 at.%) are of major significance for advanced structural applications due to their high specific strength, low density, good bending ductility and excellent corrosion resistance[1,3–6]. Most Al-based amorphous alloys possess high tensile strength, as much as 1000–1300 MPa, which is about 2–3 times higher than that of conventional aluminium alloys[3,4]. However, the primary challenge for synthesizing Al based metallic glasses via rapid solidification technique is the requirement of extremely high cooling rates to avoid recrystallization attributed to the very low glass forming ability of these alloys[1]. Modifications in designing alloy composition and adaptation of advanced processing techniques in the last few years have made

it possible to synthesize Al-based BMGs via rapid solidification. However, the maximum thickness of monolithic Al-based BMGs synthesized by rapid solidification is still limited to millimeter range, which limits the engineering application of these alloys[7–10].

Solid state synthesis route, especially mechanical alloying with certain advantages, is considered to be a viable alternate technique for synthesizing amorphous powder. Major advantages of mechanical alloying over rapid quenching process are (i) wide glass forming composition range, (ii) virtually no restriction of phase diagram, (iii) potential of synthesizing novel alloys with unique composition and (iv) ability to synthesize large amount of amorphous powder. Al (>80%)–TM (transition metals)–RE (rare earth elements) system is considered to be the best glass forming Al-based alloy system[11]. Suryanarayana et al.[12], Eckert et al.[13] and Kim et al.[14] attempted to synthesize this class of amorphous alloys via mechanical alloying and to enhance the amorphization ability by modifying the composition and concentration of solute atoms, and processing parameters[12–14]. Recently, Zheng et al.[15] successfully produced a bulk sample by consolidating partially amorphized pentanary system $Al_{87}Ni_{8.5}Ce_3Fe_3Cu_{0.5}$ via mechanical alloying.

Amorphization of Al–TM–RE alloys via mechanical alloying requires particular compositional ratio of transition metals (Ni and Co) and rare earth elements (Y and La). Column and row substitution method, based on similar element substitution, has been applied by various researchers to produce various (e.g. Cu, Mg and La based)

high glass forming ability alloys[16–18]. Sheng et al.[19] determined Al-solute bond distance and the coordination number in the solute-centered cluster (each solute atom is surrounded by Al atoms only) by carrying out *ab initio* calculations[19]. The determined optimum glass forming composition by this method was $Al_{85.8}Ni_{9.1}Y_{5.1}$ in the Al–Ni–Y system, which was close to their experimental $Al_{86}Ni_8Y_6$ composition[19]. However, the effects of the various solute atoms on the glass forming ability of Al–TM–RE alloys are yet to be fully understood.

In the present work, ternary and quaternary Al–TM–RE based amorphous alloys were synthesized via mechanical alloying. The microstructural evolution and solid state phase transformation (i.e. formation of various intermetallics, nanocrystalline FCC Al and amorphous phase) and effects of the solute atoms on glass forming ability of these alloys were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC).

2. Materials and Methods

Four alloy compositions of Al–TM–RE alloy ($Al_{86}Ni_8Y_6$, $Al_{86}Ni_6Y_6Co_2$, $Al_{86}Ni_8La_6$ and $Al_{86}Ni_8Y_{4.5}La_{1.5}$, in at.%) were selected by fully or partially replacing the transition metals or rare earth elements. Y was completely replaced by La in $Al_{86}Ni_8La_6$ in comparison with $Al_{86}Ni_8Y_6$, and the ratio of Ni/Co (3:1) and Y/La (3:1) in $Al_{86}Ni_6Y_6Co_2$ and $Al_{86}Ni_8Y_{4.5}La_{1.5}$ were kept constant based on efficient cluster packing[19]. Al (99.5%, –44 μm, Ni (99.996%, –125 μm), Co (99.5%, –44 μm), Y (99.9%, –420 μm) and La (99.9%, –44 μm) powders were procured from Alfa Aesar (MA, USA) and Strem Chemicals (MA, USA) and were blended in respective proportions to make the elemental powder blends of composition $Al_{86}Ni_8Y_6$, $Al_{86}Ni_6Y_6Co_2$, $Al_{86}Ni_8La_6$, and $Al_{86}Ni_8Y_{4.5}La_{1.5}$. In order to perform mechanical alloying of these powder mixtures, the mixtures were milled in a planetary ball mill (Retsch GmbH, Germany, Model: PM200) in a hardened steel vial using hardened steel balls (diameter: 10 mm) with disc revolution per minute and ball to powder weight ratio of 300 and 15:1, respectively. Toluene was used as process controlling agent (PCA) to restrict agglomeration and contamination during mechanical alloying, and stearic acid (0.08 wt%) was added with the powder mixture to restrict welding of the powders.

XRD (D8 Advance Diffractometer, Germany) was performed using Cu$K\alpha$ ($\lambda = 0.154$ nm) radiation to find out the extent of microstructural phase transformation in mechanically milled powder. XRD patterns were used also to estimate the average crystallite size and lattice microstrain for each multi-component system applying double Voigt method, which considers both Cauchy and Gaussian contributions. Philip's X'pert Plus software was used for stripping $K\alpha_2$ from the broadening of Al_{111} and Al_{200} peaks, measuring area, intensity, full width half maxima (FWHM), 2θ and integral width[20]. Field emission gun-scanning electron microscopy (FEG-SEM, SUPRA 40, Carl Zeiss AG, Germany) was carried out to find out reduction in powder size with the increasing milling time. High resolution transmission electron microscopy (HRTEM, JEM-2100, 200 kV, JEOL Inc., USA) was carried out to understand microstructural evolution in the milled powder in terms of nanocrystallinity, amorphous phase and other intermetallic phase formation. Differential scanning calorimetry was conducted (DSC Q20, TA Instruments) at 20 °C/min heating rate in the range of 100–500 °C to find out thermal stability of each component milled at respective amorphization time.

3. Results and Discussion

3.1. Variation in particle size, crystallite size and lattice microstrain

The effect of impact energy on the powder morphology during the mechanical alloying of one of the powder mixtures ($Al_{86}Ni_8Y_{4.5}La_{1.5}$) at the intervals of 1 h, 20 h, 40 h and 80 h is shown in Fig. 1. The average particle size decreased continuously from 10 μm (1-h milling) to 1–2 μm (80-h milling) attributed to the repeated process of powder flattening, cold welding and fragmentation under continuous plastic deformation, which largely depends on the total impact energy experienced by the powders. The morphological change of powders during mechanical alloying depends on the total impact energy being experienced by the powder particles, and the impact energy varies with various milling parameters such as milling intensity, ball to powder weight ratio and number of balls. Total impact energy (E_t) transferred per unit weight of powder for a given milling time can be calculated using the following equation:

$$E_t = E_b n_b f_b t / W_p \qquad (1)$$

where E_b is impact energy imparted by one ball, N_b is the number of balls used in the experiment, f_b is the impact frequency of the ball, W_p is the weight of the powder used and t is the time of milling[21]. The energy imparted on powder mixture calculated based on the current planetary ball mill specification (mentioned in Section 2) after 1 h, 20 h, 40 h and 80 h are 19.44 kJ/g, 388.80 kJ/g, 777.60 kJ/g and 1555.20 kJ/g, respectively. It can be observed from Fig. 1 that the major reduction in powder size took place until 40 h of milling (Fig. 1(c)), after which the extent of powder size reduction was comparably less. In high energy ball milling, a large number of dislocations gets generated inside the grains due to heavy plastic deformation, and thus, formation of several sub-grain boundaries occurred in the individual grains due to the rearrangement of dislocations[12]. However, this process was more prevalent until the 40 h of milling in the present case, as it can be envisaged from the powder size at different time intervals. Saturation in dislocation density and thus in strain hardening occurred after a particular stage of deformation, after which reduction in particle size was minimum.

Variations in crystallite size and lattice microstrain with milling time of the various powder mixtures are shown in Fig. 2. It can be observed for all the four powder compositions that the crystallite size decreased and the lattice microstrain increased with increasing milling time attributed to the increase in dislocation density leading to grain refinement and strain hardening. As it was observed in the decrease of particle size (Fig. 1), the change in crystallite size and lattice microstrain was also observed in higher extent up to 40 h of milling. The crystallite size was reduced below 25 nm and lattice strain was found to be around 0.8%–1% in all alloy compositions after 40 h of milling. Dislocation generation via Frank–Read source was not any more possible attributed to requirement of very high Peierls–Nabarro stress in such small grains[22]. Thus, dislocation density reached a very high value at this stage and further tangible grain size reduction was not possible after this. The crystallite size has only been reported until 100 h for the four powder compositions, as the very high impact energy at 140 h of milling destabilized the atomic periodicity, which has been discussed later in this paper during analyzing the XRD and TEM results (Sections 3.2 and 3.3, respectively). Certain variation in crystallite size (20–30 nm) and lattice strain (0.20%–0.30%) can be observed in Fig. 2 for the various alloy composition milled for 1–80 h. This variation in crystallite size and strain may be attributed to the compositional inhomogeneity and difference in solid solubility of solute elements (Ni, Co, Y, and La) in solvent (Al) in the various powders.

3.2. Effect of alloying elements on the degree of amorphization

The XRD spectra of the four alloys ($Al_{86}Ni_8Y_6$, $Al_{86}Ni_6Y_6Co_2$, $Al_{86}Ni_8La_6$, and $Al_{86}Ni_8Y_{4.5}La_{1.5}$) at different milling time are shown in Fig. 3, which depicts the sequential dissolution of solute atoms (i.e. Ni, Y and La). Transition metals i.e. Ni and Co dissolved initially