ABSTRACT

In this Ph.D. work, aluminum based in-situ bulk amorphous nanocomposites were synthesized by spark plasma sintering of milled amorphous ribbon particles and mechanically alloyed amorphous powders. Comparative study has been carried out to understand the difference in sintering behavior between the amorphous powders obtained from the two different methods. Activation energies for crystallization at various transition temperatures were determined to understand the effect of evolved crystalline phases on thermal behavior of the as-cast ribbons, milled ribbon particles and corresponding sintered samples. Subsequently, indentation and tribological properties were evaluated to study the effects of crystalline phase evolution on nanomechanical properties of the as-cast ribbons and consolidated amorphous nanocomposites.

Two aluminum based multicomponent systems (Al86Ni8Y6 and Al86Ni6Y4.5Co2La1.5) were selected based on efficient cluster packing model to fabricate in-situ bulk amorphous nanocomposites. Amorphous ribbons of both the compositions were synthesized by melt spinning, which were then ball milled to powder form for subsequent consolidation. Ball milling led to partial crystallization of the milled ribbon particles, ascribed to mechanical crystallization. Amorphous powders of Al86Ni6Y4.5Co2La1.5 composition were synthesized by mechanical alloying for 200 h. It is important to study crystallization behavior of metallic glasses for further processing at high temperatures (viz. consolidation) and for practical applications, as crystalline phases affect mechanical properties. Thus, in-depth thermal analysis of the as-cast ribbons, milled ribbon particles and sintered samples were carried out by differential scanning calorimetry at various heating rates. The ribbons of both the compositions and the mechanically alloyed amorphous powders exhibited three-stage crystallization behavior, related to formation of nanocrystalline FCC Al, growth of Al and formation of various intermetallic phases, respectively. In case of the as-cast ribbons, glass transition temperature could not be detected due to minute difference between the onset temperature of first stage crystallization and the glass transition temperature. On the other hand, the mechanically alloyed amorphous powders exhibited glass transition temperature at 210 °C and the onset temperature of first stage crystallization at 258 °C, leading to a supercooled liquid region of 48 °C. Interestingly, the first stage crystallization disappeared after milling of the ribbons and the milled ribbon particles showed only two stage crystallization behavior. The onset temperature of the second stage crystallization with related activation energy shifted to lower values, whereas the transition temperatures and related activation energies of the third stage crystallization shifted to higher values in the milled ribbon particles compared to that of the corresponding as-cast ribbons. The disappearance of first stage crystallization and shift in transition temperatures along with activation energies in the milled ribbon particles are due to formation of various crystalline phases in the amorphous matrix and various microstructural changes occurred during milling of the ribbons. Al-based bulk amorphous nanocomposites of both the compositions were fabricated by consolidating the milled ribbon particles and mechanically alloyed amorphous powders via spark plasma sintering. The sintering parameters for the milled ribbon particles were optimized at 700 MPa and 300 °C for 10 min hold. Various crystalline phases such as FCC Al, Al4NiY, AlNi, Al5Co2 and Al13Co4 evolved in the amorphous matrix of the sample sintered from milled ribbon particles. Evolution of higher amount of crystalline phases in the bulk samples decreased all the transition temperatures and related activation energies compared to the corresponding milled ribbon particles. The mechanically alloyed amorphous powders were consolidated at sintering temperatures varying from 250 °C to 500 °C and uniaxial pressure of 500 MPa. Crystalline phases such as FCC Al, Al4Ni3, Al3Ni5, La2Ni3, Y3Co2, NiY3 and Al13Co4 evolved in the samples sintered at temperatures ≥ 400 °C. Estimation of Viscosity of the mechanically alloyed amorphous powders by Frenkel's equation revealed decrease in viscosity with increase in sintering temperature, which led to improvement in densification. Comparison of sintering behavior revealed better inter-particle bonding in the samples sintered from the milled ribbon particles than the ones consolidated from the mechanically alloyed powders. This is ascribed to incorporation of the lower amount of contaminations in the milled ribbon particles, as revealed by EDS spectra.

Nanoindentation technique has been proved as an effective method in studying the effects of individual nanometric phases on mechanical properties of a composite microstructure. Thus, Nanoindentation, microhardness and nanoscratch tests were performed on the as-cast ribbons and the sintered samples to understand the effects of partial crystallization on nanomechanical properties. The consolidated samples from the milled ribbon particles exhibited higher nanohardness and lower wear volume loss compared to the corresponding ribbons due to evolution of hard intermetallic phases in the amorphous matrix. The average hardness and elastic modulus of the higher temperature sintered samples from the mechanically alloyed amorphous powders increased due to improvement in densification and evolution of various crystalline phases. Pronounced indentation size effect was observed as the hardness values decreased with increase in indentation load in all the bulk samples. Summarily, aluminum based in-situ amorphous nanocomposites were synthesized by spark plasma sintering of milled ribbon particles and mechanically alloyed amorphous powders. Activation energies of crystallization at all transition temperatures of the sintered samples decreased compared to that of the corresponding as-cast ribbons and milled ribbon particles, assigned to evolution of various crystalline phases. The sample sintered from the milled ribbon particles possessed superior particle bonding due to incorporation of lower amount of contaminations compared to the sample sintered from the mechanically alloyed amorphous powders, which led to consequent development of better nanomechanical properties.

Keywords: Al based metallic glass systems; Melt spun glassy ribbon; Mechanical alloying; Spark plasma sintering; Crystallization; Thermal behavior; Indentation and tribology study