ABSTRACT

A study has been carried out on the processing-structure-property inter-relationship of the Ni-Zr alloy thin films fabricated by DC magnetron co-sputtering of high purity elemental targets (≈ 99.99 %) in argon atmosphere on Si-(100) substrate with variation of either Zr-target power from 75 W to 175 W at a constant Ni DC power of 200 W or negative substrate bias voltage (0 V to -80 V). Although the deposition rates of the as-deposited films obtained from the thickness measurement using the contact-type surface profilometer have been found to increase with the increase in Zr target power, but decrease with the application of negative bias voltage. Using the energy-dispersive X-ray spectroscopy analysis, it has been observed that the Zr concentration increases at the expense of Ni concentration with increasing target power or negative substrate bias voltage. The microstructural observation using the grazing incidence X-ray diffraction (GIXRD), as well as conventional and high-resolution transmission electron microscopy (HRTEM) suggests that the increase in Zr target power, as well as negative substrate bias voltage, leads to increase in the volume fraction of amorphous phase, alongwith limited increase in amount but decrease in size of Ni3Zr phase. Whereas the nanoindentation hardness increases, the Young's modulus decreases with increasing amount of amorphous phase. The electrical resistivity measured by Van-der Pauw four-probe method increases with increasing volume fractions of both Ni3Zr and amorphous phase. Surface roughness and coefficient of friction obtained respectively, by atomic force microscopy and nano-scratch experiments decrease, whereas corrosion resistance in 3.5 wt% NaCl solution increases with the increase in Zr concentration. Resistance to pitting corrosion in case of the film with higher Zr content is facilitated by the formation of ZrO2-rich passive film, as confirmed by X-ray photoelectron spectroscopy.

The stages of crystallization of amorphous Ni63Zr37 film have been investigated by differential scanning calorimetry (DSC) at different heating rates and in-situ annealing at 300 oC by use of a heating stage with the HRTEM. These results have been further confirmed by GIXRD analyses of thin-film specimens annealed ex-situ at 300 oC for various durations. The temperature for crystallization found by DSC has been found to increase from 371 oC to 434 oC with increase in heating rate from 3 oC/min to 10 oC/min, and the activation energy has been found as □260.2 kJ/mol from the Kissinger plot. In-situ studies on HRTEM using the heating stage have shown crystallization after annealing for 10 min at ~300 oC, a temperature lower than that found by DSC, due to structural relaxation facilitated by large surface area. In-situ HRTEM studies have shown that Ni3Zr forms first due to its large negative enthalpy of formation, followed by the formation of Ni-rich solid solution (Niss) grains. Moreover, grain rotation with the formation of partial dislocations at Ni3Zr-Niss interfaces as well as twinning followed by detwinning in the Niss matrix to reduce interfacial energy have been observed.

Three selected compositions with increasing Zr content and degree of amorphous phase have been considered for the strain rate and time-dependent nanoindentation study to understand the deformation mechanism in the micro-scale. The nanoindentation experiments have been carried out to a maximum load of 1 mN at three different loading strain rates of 1, 0.1 and 0.01 s-1, followed by a holding time of 20 s at the maximum load. The results reveal negative strain rate sensitivities (SRSs) over the investigated range of compositions, although the effect becomes more pronounced with an increase in the Zr-content having a higher value of amorphous phase content. Further, with the aid of molecular dynamics (MD) simulation, it has shown that simultaneous occurrence of time-dependent relaxation and rate-dependent deformation leads to the negative value of SRS in amorphous film. Moreover, the size and activation volume of the shear transformation zones, estimated by MD simulations for various loading strain rates are found to be consistent with the proposed mechanism of negative SRS. Further, the effect of loading strain rates and composition on the nanoindentation creep behavior have been studied for the holding time of 20 s. In particular, creep displacement, strain rate, hardness, compliance and retardation spectra during the creep have been evaluated to provide valuable insight into the timescales associated with the time-dependent relaxation mechanisms. While the decrease in crystallinity improves the creep resistance, an increase in the loading strain rate is found to give rise to fast relaxation mechanisms corresponding to relatively smaller timescales. This study has also highlighted the prospects of analyzing the instantaneous strain rate sensitivity measured during the nanoindentation creep.

Keywords: *Ni-Zr alloy thin films, microstructure, nanoindentation hardness, Young's modulus, nano-scratch, corrosion-resistance, electrical resistivity, crystallization behavior, in-situ annealing, differential scanning calorimetry, strain rate sensitivity, molecular dynamics simulation, nanoindentation creep.*