Abstract

NiTi shape memory alloy (SMA) thin films are highly valued for microelectromechanical systems (MEMS) due to their high work energy densities, low power consumption, shape memory effect (SME), and compatibility with silicon micromachining. While bulk SMAs offer significant stroke and force capabilities, they suffer from long response times. Thin coatings, with their high surface-to-volume ratio, cool faster and reduce cycle times, making them more efficient. NiTi thin films also outperform other actuation materials in terms of strain and stress recovery, making them ideal for a wide range of micro-sensors and actuators. Improving NiTi thin film SMA performance requires consistent composition and good mechanical properties.

In the present work, thin films composed of a single layer of nickel and titanium were fabricated using magnetron sputtering at room temperature on a Si substrate and the as-deposited films were subsequently annealed to achieve nickel-titanium (NiTi) shape memory alloys. This is accomplished by annealing the initially deposited films in an inert atmosphere at 500 °C for varying durations to promote crystallization and interface diffusion. A comprehensive analysis of the microstructure, surface and interface morphology, surface properties, and phase formation of both as-deposited and annealed Ni/Ti bi-layer thin films fabricated using magnetron sputtering is presented. Special emphasis is placed on investigating the influence of annealing time on the Ni/Ti bi-layer interface. The study addresses the challenge of achieving desired stoichiometric ratios in NiTi films, detailing the control over film composition and thickness through post-deposition annealing. Utilizing techniques such as atom probe tomography, AFM nanoindentation, and nanoscratch testing, the research provides insights into interdiffusion, structural alterations, and adhesive properties of the films.

A comprehensive study has been done using first-principles simulations, including Density Functional Theory (DFT) and Molecular Dynamics (MD), to understand the structural and thermodynamic properties of Ni/Ti bilayers and the atomic diffusion within them. DFT calculations were employed to determine the interface energies and electronic structure of the bilayer, while MD simulations were used to explore atomic diffusion at 773K over various holding times. The results indicate a predominant diffusion of Ni atoms into the Ti side. Radial Distribution Functions (RDFs) were plotted to analyze the bonding nature between Ni and Ti atoms. Additionally, classical MD simulations were utilized to investigate the deformation

behavior of the bilayer under tension and the impact of annealing time on its mechanical properties. This study provides valuable insights into the intermetallic reaction mechanisms, diffusion processes, and mechanical behavior of Ni/Ti bilayers, which are crucial for optimizing their fabrication and application in various fields.

This research also includes influence of Cu or Co additions on the Ni-Ti-Zr SMAs. NiTi SMAs undergo a phase transformation from a cubic (B2) austenite phase to a monoclinic (B19') martensite phase, but their low transformation temperature (~100°C) limits their use in high-temperature applications. Alloying elements like Zr, Cu, and Co have been introduced to enhance phase transformation temperatures and mechanical properties. NiTiZr alloys, for instance, increase transformation temperatures but suffer from brittleness and reduced ductility. Adding Cu to NiTi improves thermal stability, hysteresis, and shape memory response, while Co enhances ductility and suppresses brittle phases. The impact of Cu/Co and Zr on the lattice parameters, phase stability, martensitic transformation temperature, and electronic properties of NiTi binary alloys is explored using first-principle density functional theory (DFT) calculations. As the Zr content increases, the formation energies of the parent B2 phase and monoclinic B19' phase decrease. Additionally, the mechanical stability of these alloys is assessed through their elastic properties. We thoroughly discuss the electronic structure mechanisms that underline martensitic transformations in relation to the density of states. AIMD (Ab Initio Molecular Dynamics) simulations in the NVT ensemble have examined the stability of both phases using the total energy. The Boltzmann transport equation has been used for the electrical and thermal conductivity of the alloy compositions. Phonon analysis had been used for studying the stability of both austenite and martensite phases in NiTiZrCu and NiTiZrCo alloys, providing insight into their vibrational properties and phase transformations. The study also investigated Ni/Ti/Zr/Cu multilayer films which were deposited on Si substrates by magnetron sputtering and annealed at 350 °C to achieve amorphous phases, followed by high-temperature annealing at 600 °C to form $Ni_{44}Ti_{35}Zr_{15}Cu_6$ shape memory alloys. X-ray diffraction revealed the presence of the martensite phase after annealing at 600 °C. Surface and interface studies highlighted increased surface roughness due to grain growth, and elemental mapping showed a near-uniform distribution of elements.

Keywords: NiTi Shape Memory Alloys (SMAs); Bi-layer films; Magnetron sputtering; ab initio calculations; Electronic structure, Molecular Dynamics; Diffusivity; HTSMAs; Martensitic phase transformation; Ni/Ti/Zr/Cu multilayer films