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Laser annealing of amorphous NiTi shape memory alloy thin films to locally induce shape memory properties

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Abstract

We present the results of a crystallization study on NiTi shape memory thin films in which amorphous films are annealed by a scanning laser. This technique has the advantage that shape memory properties can be spatially distributed as required by the application. A kinetics study shows that nucleation of the crystalline phase occurs homogenously in the films. Consequently, the laser annealing process produces polycrystalline films with a random crystallographic texture. The crystallized films have a uniform microstructure across the annealed areas. The material in the crystalline regions transforms reversibly to martensite on cooling from elevated temperature and stress measurements show that a significant recovery stress is achieved in the films upon transformation.

Keywords: Shape memory alloy thin films; Laser annealing; Crystallization kinetics; Martensitic phase transformation

1. Introduction

Shape memory alloys (SMAs) are active materials that derive their unique properties from a thermoelastic martensitic transformation. They have been studied extensively over the last 50 years with most attention focused on bulk materials. Recently, the shape memory effect has been demonstrated in thin films of these alloys [1–7], making them attractive candidates for use as actuators in microelectromechanical systems (MEMS). It is, however, difficult to induce an intrinsic two-way shape memory effect in thin films and a biasing spring is generally needed to restore the initial state after actuation. As a result, use of SMA actuators in MEMS has been limited to bimorph-like mechanisms. The technique of laser annealing of shape memory alloys (LASMA) recently emerged as a promising approach for the fabrication of planar mechanisms [8]. Using this technique, shape memory properties can be spatially distributed across a material: crystallized material has shape memory properties and can be used as an actuator, untransformed material is passive and provides the restoring force. Various aspects of the LASMA process, especially for thin films, have yet to be explored. In this paper, we present the results of a crystallization study in which a laser was used to crystallize selected areas of amorphous NiTi films.

2. Experimental

NiTi thin films with a thickness of approximately 1.5 μm were deposited on 1 mm thick fused quartz substrates by direct current magnetron sputtering. The

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background pressure of the sputter chamber was less than 5×10^{-8} Torr; the pressure of the Ar working gas was 1.5 mTorr. All depositions were performed at room temperature. The films were grown by co-sputtering an equiatomic NiTi alloy and an elemental Ti target. The composition of the films was controlled by varying the power to individual guns [7]. The nominal target–substrate distance was 100 mm and the deposition rate was approximately 0.3 nm/s. During deposition, the substrates were rotated at a speed of 20 RPM to maintain film thickness and composition uniformity. The composition of the films was measured to be 50.5 ± 0.2at.%Ti using electron microprobe analysis (EMPA). X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) confirmed that the structure of the as-deposited films was entirely amorphous.

In order to crystallize the NiTi films, samples were annealed by scanning a laser beam over the surface of the films. A fiber-injected CW high power near-IR laser diode (coherent/925 nm) was used in this study. The laser beam had a Gaussian power distribution and a diameter of approximately 0.9 mm (i.e., the diameter at $1/e$ intensity) as determined using the knife-edge approach. The specimen was mounted on a platform with three degrees of freedom, capable of planar translational and rotational motions with micron resolution. The platform (Yaskawa, Robotworld) is fully programmable and its acceleration, speed, and position can be accurately controlled. A program was developed to define repeatable and reconfigurable annealing patterns. In the experiments, the laser power was varied from 5 to 9.4 W; the scan speed was varied from 1 to 8 mm/s. All scans were performed in air in a thermally stabilized environment. During laser annealing a thin oxide coating was formed on the NiTi films. The oxide thickness was determined from the reflectivity spectrum measured using a spectrophotometer (Jasco V-570 NUV/VIS/NIR) and was typically in the range of 50–100 nm for the laser annealing parameters used in this study [9]. As expected the oxide thickness increased with increasing laser power and decreasing scan speed. Oxide formation could of course be reduced by performing the experiments in an inert atmosphere. The microstructure of the films after laser annealing was investigated using Philips EM420 and JEOL 2010 transmission electron microscopes (TEM). TEM specimens were prepared by cutting 3 mm diameter discs from the samples. The discs were dimpled and the area of interest was thinned to electron transparency by ion beam milling with a 4 kV argon beam. Multiple line scans were performed to create large crystalline areas. Samples for texture analysis were cut from these areas. XRD was used to investigate the texture of the films after laser annealing. During the texture measurements, the samples were heated to ensure that only the austenite phase was present. Pole figures were obtained for the {200}, {110} and {211} reflections. In order to investigate the evolution of the residual stress in the crystallized region as a function of temperature, multiple line scans were performed to create arrays of parallel lines where the film was crystalline. A short dwell time was introduced at the end of each line scan to allow the sample to cool down between adjacent scans. Films with various volume fractions of crystalline material were produced by varying the laser annealing parameters and the line spacing. The annealing parameters and corresponding volume fractions of crystalline material are listed in Table 1. For each volume fraction, two sets of rectangular specimens ($6\text{ mm} \times 25\text{ mm}$) were cut from these large arrays, i.e., one set with the long edge of the specimen parallel to the laser scan direction (labeled as RD in the figures) and one set perpendicular to the scan direction (labeled as TD). The stress in the long direction of the specimens was measured using the substrate curvature technique [10]. Using this approach, the residual stresses both parallel and perpendicular to scan direction could be measured. Stresses were calculated using the well-known Stoney equation [11], assuming a Young's modulus of 72 GPa and a Poisson's ratio of 0.16 for the fused quartz substrate.

3. Results and discussion

Fig. 1 compiles the optical and TEM observations of the structure of the annealed NiTi films as a function of laser power density and scan speed. At a given scan speed, the film transitions from amorphous to partially crystalline and eventually fully crystalline with increasing laser power. The TEM micrographs in Fig. 1 show the microstructure close to the center of the laser trace where the annealing temperature is the highest. At low laser power, only a few isolated grains are formed in an amorphous matrix. Once the laser power is large enough to fully crystallize the film, the microstructure at the center is approximately independent of laser power. A similar transition occurs when the scan speed is varied at constant laser power. If the laser power density is too large, film and substrate crack due to thermal shock. As a result of the Gaussian intensity profile of the laser, a temperature gradient is introduced in the film in the direction perpendicular to the laser trace. After the laser scan, a crystalline band a few hundred micron wide forms along the laser track. The width of the band increases with increasing power density and decreasing scan speed. Fig. 2 shows the microstructure in the direction normal to the scan. Again, grain size and distribution are the same across the entire crystalline region. Most grains are 1–1.5 μm in diameter although there are a few grains as small as 0.3 μm. Combined with Fig. 1, Fig. 2 confirms that a uniform microstructure