Surface & Coatings Technology xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effects of Cu on the microstructural and mechanical properties of sputter deposited Ni-Ti thin films

M. Callisti [a,*], F.D. Tichelaar [b], B.G. Mellor [c], T. Polcar [a,d]

[a] National Centre for Advanced Tribology at Southampton, Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK
[b] Delft University of Technology, Kavli Institute of Nanoscience, National Center for HREM, Lorentzweg 1, 2628CJ, Delft, The Netherlands
[c] Materials Research Group, Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK
[d] Department of Control Engineering, Faculty of Electrical Engineering, Czech Technical University in Prague, Technická 2, Prague 6, Czech Republic

ARTICLE INFO

Available online xxxx

Keywords:
Shape memory alloys
Thin films
Magnetron
Sputtering
Nanoindentation
Grain boundary segregation
Precipitation

ABSTRACT

The microstructure of sputter deposited Ti-rich Ni-Ti thin films doped with Cu in the range 0–20.4 at.% and annealed for 1 h at 500 and 600 °C has been investigated and correlated with the mechanical properties of the films measured by depth-sensing nanoindentation. X-ray diffraction analysis showed the microstructural evolution of Ni-Ti thin films when doped with Cu and annealed at different temperatures. Heat treatments promoted the nucleation and growth of Ti_2Ni precipitates in Ti-rich Ni-Ti thin films, which affected the stability of austenitic and martensitic phases at ambient temperature. Doping with Cu caused the formation of $Ti(Ni, Cu)_2$ plate precipitates, which became more finely and densely dispersed in the grains with increasing Cu content. TEM analysis showed a columnar grain morphology extended through the whole films thickness, while with increasing Cu content a noticeable lateral grain refinement was induced by segregation of a (Ni, Cu)-rich phase to grain boundaries. The nano-hardness increased almost linearly with increasing Cu content owing to this grain refinement, though differences between samples annealed at different temperatures were found which could be related to the evolution of $Ti(Ni, Cu)_2$ plate precipitates with annealing temperature and Cu content. The Young's modulus exhibited a similar dependence on Cu content as nano-hardness, though no significant differences were observed with increasing annealing temperatures.

1. Introduction

Ni-Ti shape memory alloys are known to exhibit unusual mechanical and functional properties even at the micro- and nano-scale when they are produced in the form of thin films by PVD techniques [1]. Many studies have thus investigated the behaviour of sputter deposited Ni-Ti thin films for their prospective use in micro-electro-mechanical systems (MEMS) owing to their ability to recover a large transformation stress and strain during thermal cycling, as well as possessing a high actuation rate and work output-to-volume ratio compared to other types of actuators [2]. However, considerably fewer studies have investigated the potential use of such smart thin films as protective or functional layers for tribological applications [3–5].

Although considerable breakthroughs have been achieved by means of extensive research, there are still some concerns regarding the use of these films in industrial applications on account of the inability to control precisely their response to external stimuli. Moreover, in addition to this limitation, low hardness and wear resistance further limit their field of application. To counter these deficiencies much effort has been directed to making Ni-Ti thin films more attractive and the use of a third element as dopant has emerged as an effective approach for changing or modulating their properties [6,7].

Among the possible candidate dopants elements, Cu is one of the most promising as it reduces the compositional sensitivity of the transformation temperatures, reduces the temperature hysteresis, stabilizes the shape memory effect and increases the actuation rate and the recoverable strain, even under a stresses as high as 1 GPa [8–12]. The properties reported above are strictly dependent on the films microstructure and in particular on the grain size, the formation of different types of precipitates as a function of Cu content and the post-deposition heat treatment [13]. The microstructural evolution of relatively thick (7–9 μm) Ti-rich [14,15] and (Ni, Cu)-rich [16] Ni-Ti-Cu thin films for a wide range of Cu content and annealing temperatures has been studied. Essentially, annealing temperatures close to that of crystallisation cause the formation of fine plate precipitates coherent with the matrix. In Ti-rich compositions, they are considered to be Guinier-Preston (GP) zones with a body centred crystal structure and a coherent interface with the austenitic (B2) matrix. In (Ni, Cu)-rich compositions, precipitates are still coherent with the matrix and with a plate-like shape but with a C_{11b}-type crystal

* Corresponding author at: National Centre for Advanced Tribology at Southampton – Highfield Campus, Building 5 (Eustice)/ Room 3025, Mailpoint M7, Southampton, Hampshire SO171BJ, United Kingdom. Tel.: +44 23 8059 2351.
E-mail address: mc3a09@soton.ac.uk (M. Callisti).

0257-8972/$ – see front matter. Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.06.040

structure [17,18]. As this is metastable phase, with increasing annealing temperature these precipitates evolve losing their coherency with the matrix promoting the formation of semi-coherent spherical precipitates for Ti-rich compositions, or still plate-like but semi-coherent precipitates for (Ni, Cu)-rich compositions, as well as grain boundary precipitates. It has been reported that coherent plate precipitates can disturb the movement of twin boundaries, though the growing martensite can pass through such precipitates deforming them elastically. On the other hand, semi-coherent precipitates in the grain disturb or impede the growth of martensite variants, thus decreasing the amount of strain accommodated in a reversible manner [8,19].

The effects of different annealing temperatures on the mechanical properties have been investigated by analysing the nanoindentation response of both Ni-rich and Ti-rich Ni-Ti-based film compositions. It has been observed that with increasing annealing temperature both hardness and Young's modulus increase [20,21]. The observed trends have been attributed to the increased resistance to plastic deformation induced by precipitation hardening, as well as to a change of the phase transformation sequence and thus of the transformation strain [22]. Zarnetta et al. [23] investigated the mechanical properties of austenitic and martensitic Ni-Ti-Cu thin films through nanoindentation. Even in this case, off-stoichiometric compositions with a constant Cu content exhibited, both at ambient and high temperatures (~80 °C), higher hardness and Young's modulus resulting from precipitation hardening.

The effects of Cu and of the annealing temperature on the functional behaviour of Ni-Ti-(Cu) films have been extensively studied, as well as the mechanical response of these films when changing the Ni/Ti ratio for a constant Cu content. However, no investigations have been performed in order to evaluate the effects of Cu on the mechanical properties of sputter deposited Ni-Ti thin films.

Therefore, as Cu additions can change effectively the microstructure of Ni-Ti thin films, it is of interest, especially for the purpose of using such films as protective layers, to assess their mechanical properties as a function of the microstructure produced with respect to the Cu content and annealing temperature. Therefore in this study a Ti-rich Ni-Ti thin film was doped with different amounts of Cu, and its microstructural and mechanical properties were investigated.

2. Experimental details

Ni-Ti thin films with increasing Cu content were deposited on (100) Si wafers (450 μm thick) by a Plasma-Assisted Magnetron Sputtering (PAMS) system (Helios, Leybold Optics GmbH, Alzenau, Germany). The dense argon plasma generated by an inductively coupled RF plasma source (fitted in the process chamber door) was used to pre-treat the substrate at the beginning of each process, as well as to remove fast growing structures during the deposition, so as to increase the density as well as to reduce the level of defects in the films structure. The chamber was pumped down to a base pressure of 1×10^{-7} mbar and each deposition was carried out at a pressure of 5×10^{-4} mbar (35 sccm Ar flow) for approximately 35 min. The Ni/Ti power ratio was kept constant while the power for the Cu target was raised linearly to increase the Cu content in the films. The substrate holder was rotated at 180 rpm in order to avoid the formation of multilayer-type structures. So as to produce films with an amorphous structure, depositions were performed without any deliberate heating of the substrate; moreover the balanced configuration of the sputtering system did not promote excessive heating of the substrate.

The chemical composition of the thin films was measured by energy dispersive X-ray spectroscopy (EDX, semi-quantitative analysis) attached to a JEOL JSM 6500 F field emission gun scanning electron microscope (FEG-SEM), through which the surface and cross-sectional morphology of the films was also observed.

After sputtering, the as-deposited thin films were isothermally annealed in a high vacuum (8×10^{-5} mbar) for 1 h at 500 and 600 °C, in order to induce a crystalline structure as well as to promote different microstructures. In order to avoid delamination induced by thermal stresses a heating/cooling rate of 5 °C/min was adopted above 400 °C while below this temperature samples were allowed to cool down naturally to ambient temperature.

The phases produced by annealing were investigated by grazing incidence X-ray diffraction (GIXRD). The grazing angle was set at 5° with a scan step size of 0.02°over an angle range of $2\theta = 30–80°$. The diffraction data were collected by using an X'Pert-Pro Philips diffractometer (PANalytical, ALMELO, The Netherland) with a Cu-target ($\lambda = 1.540598$ Å). The tube was set at an accelerating voltage of 40 kV and a current of 30 mA. The XRD spectra were analysed by the X'Pert HighScore Plus software together with a ICDD PDF-2 database.

The structure of the annealed samples was characterised by transmission electron microscopy (TEM) using a FEI Tecnai F20ST/STEM scanning transmission electron microscope (STEM) at an accelerating voltage of 200 kV. Cross-sectional thin foils for TEM and STEM (scanning transmission electron microscopy) observations were prepared by mechanical grinding and polishing followed by further thinning to an electron transparent thickness by a dual ion miller (Gatan PIPS, model 691).

Mechanical properties were measured using depth-sensing nanoindentation (Nano-Test Platform 2, Micro-Materials Ltd., Wrexham, UK). A diamond Berkovich indenter (tip radius < 100 nm) was used to perform multiple-load nanoindentation experiments at ambient temperature (~20 °C). Each indent consisted of 12 cycles, starting with a penetration depth (first cycle) of approximately 25 nm and with a depth step of ~25 nm per cycle. A final penetration depth greater than 1/10 of the film thickness was deliberately chosen in order to facilitate the interpretation of such measurements, although the mechanical properties for the thin films were evaluated only for penetration depths within 1/10 of the film thickness. The experiments were carried out using a loading rate of 0.1 mN/s whereas an unloading rate of 0.05 mN/s was set in order to have a larger number of points which could be fitted accordingly to the procedure outlined by Oliver and Pharr [24,25]. A partial unloading of 30% relative to the maximum load per cycle was assessed to be sufficient for the application of the procedure referred to above. A holding time of 20 s at every maximum load was selected to saturate creep effects before unloading. Thermal drift correction on the load-displacement curves was performed using the mean value of the pre- and post-indentation drift calibration data collected during a holding time of 60 s. For each film nano-hardness was determined as the average of the hardness values measured after the size effect was saturated and before the appearance of substrate effects, while Young's moduli were calculated from the averaged reduced Young's moduli determined for indentation depths within 1/10 of the film thickness.

3. Results and discussion

3.1. Chemical composition and surface morphology

Eight Ti-rich Ni-Ti thin films with increasing Cu in the range 0 – 20.4 at.% and a thickness of 1.4 μm were produced. Table 1 reports the chemical compositions measured by EDX on the as-deposited films. It was noted that when the power to the Cu target was increased Ni and Ti content decreased at approximately the same rate, indicating no preferential re-sputtering effect of Ni and Ti atoms on the growing structure. For Cu content higher than 4 at.% the chemical composition of the thin films changed from being Ti-rich to (Ni, Cu)-rich. In view of the chemical affinity of Ti and O, the chemical composition of some of the Ti-rich thin films was also measured by EDX after heat treatments at 500 and 600 °C and no oxygen was detected on the surface. However, annealing at different temperatures promoted the formation of precipitates with different structure and chemical composition, thus altering the chemical composition of

Please cite this article as: M. Callisti, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.06.040