Coupled annealing temperature and layer thickness effect on strengthening mechanism of Ti/Ni multilayer thin films

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Abstract

A systematic study was performed on mechanical and microstructural properties of Ti/Ni multilayers with layer thickness from 200 nm to 6 nm and annealing temperature from room temperature to 500 °C. Based on the observed hardness evolution, a coupled layer-thickness and annealing-temperature dependent strengthening mechanism map is proposed. For as-deposited films, the deformation behavior follows the traditional trend of dislocation mediated strengthening to grain boundary mediated softening with decreasing layer thickness. For annealed films, grain boundary relaxation is considered to be the initial strengthening mechanism with higher activation temperature required for thicker layers. Under further annealing, solid solution hardening, intermetallic precipitation hardening, and fully intermixed alloy structure continue to strengthen the thin layered films, while recrystallization and grain-growth lead to the eventual softening of thick layered films. For the films with intermediate layer thickness, a strong orientation dependent hardness behavior is exhibited under high temperature annealing due to mechanism switch from grain growth softening to intermetallic precipitation hardening when changing the loading orientation from perpendicular to parallel to the layer interfaces.

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1 Introduction

Nanoscale metallic multilayers have attracted great scientific interest due to their superior functional properties (e.g. electric, magnetic and optical) as well as mechanical strength when compared to monolithic films of the constituent materials [1-7]. An obvious individual layer thickness/size-dependent hardness behavior is reported in extensive studies [8-12]. A Hall-Petch model based on dislocation pile-up along the interfaces is applicable at the sub-micrometer scales [13-15] and the corresponding Hall-Petch slope indicating the resistance of interface can be utilized to estimate the peak strength of the multilayers. At smaller layer thickness with a few to a few tens of nanometer length scales, dislocation pile-up becomes difficult and a confined layer slip (CLS) model based on Orowan bowing can be used to explain the operative mechanism [16-18]. The multilayer strength reaches a peak value with layer thickness of several nanometers, and the peak strength is set by the interface resistance to single dislocation transmission [19-21]. Several factors can be important to determine the barrier strength in different material systems such as coherent stress [20-22], misfit dislocation [20, 23], Koehler stress [24] and intermixing at the interface [25, 26]. With further reduced layer thickness, softening is usually observed due to the interface crossing by dislocations [27, 28]. In addition, grain boundary/interface sliding or Coble creep can also lead to material softening [29, 30] in polycrystalline metallic multilayers.

Thermal annealing can have an important influence on the deformation behavior and strengthening mechanism in metallic multilayers. Depending on the annealing temperature, various thermal processes could take place such as atomic diffusion, intermixing, recrystallization, grain growth, phase transformation and even intermetallic phase formation. The thermal stability of the microstructure and multilayer strength at elevated temperatures could be significantly influenced if the materials were exposed to

thermal environment. Decreased strength has been observed in different multilayer systems after a relatively high temperature annealing [31-33], and this softening phenomena have been attributed to the microstructure modification such as spheroidization of electrodeposited Cu/Ag multilayers annealed at 150 °C [31] and in-plane grain coarsening of Ni/Ru multilayers annealed at 450 °C [32]. In addition, significant morphological instabilities including complete disintegration of layered structure [34-36] were observed in different multilayer systems, and such breakdown of periodicity can cause a dramatic strength drop [33]. However, our recent work [37] shows a moderately increased rather than decreased strength for Ti/Ni multilayers after low-temperature (up to 200 °C) annealing due to grain boundary relaxation, which was previously considered as a primary strengthening mechanism in bulk nanocrystalline materials. For nanocrystalline materials, grain boundary-mediated processes start to evolve into plastic deformation and grain boundaries are no longer only barriers to dislocation motion but also the primary facilitators for plasticity. A low-temperature annealing process can increase the atomic registry at grain boundaries and thus lead to a more equilibrated and ordered state which suppresses grain boundary shear processes and therefore enhances the material strength [38-40]. For metallic multilayer system, however, the coupled effect of length scale and temperature on grain boundary relaxation strengthening is still not very well-understood.

In this work, a systematic study was carried out on the mechanical strength of Ti/Ni multilayers of varying layer thickness and annealing temperatures. Comparing with our recent work [37], the layer thickness in the current study was expanded to the range of 200 nm down to 6 nm, and the temperature range up to 500 °C. The current work reveals the detailed dependency on annealing temperature and layer thickness of various deformation behaviors and strengthening mechanisms, such as dislocation-mediated motions, grain boundary relaxation, solid solution hardening, precipitation hardening and

alloying. The results not only shed light on the understanding of the deformation behavior and strengthening mechanisms in metallic multilayers, but also provide guidance to control and optimize this engineered material.

2. Experimental details

Ti/Ni multilayer system with individual layer thickness, λ , ranging from 200 nm to 6 nm is utilized to investigate the coupled annealing-temperature and layer thickness effect on the mechanical strength. A dual DC magnetron sputtering system is used to deposit these multilayers on 500 μm thick single crystal (100) Si substrates, with the background pressure around 1×10^{-7} mbar and deposition Argon gas pressure around 1×10^{-3} mbar. During deposition, the DC powers of Ti (99.995%) and Ni (99.999%) targets were both set as 100 W and Ar gas flow rate was maintained at 10 sccm. The sputtering time was programmed to obtain the desired film thickness. Based on the range of λ , the deposited multilayers are divided into three groups: thick-layer cases with λ of 200 and 100 nm, intermediate-layer cases with λ of 50 and 25 nm, and thin-layer cases with λ of 16, 12, 8, and 6 nm. The nominal total film thickness is 4 μm in the thick- and intermediate-layer cases and 2 μm in the thin-layer cases.

A subset of the as-deposited Ti/Ni multilayers were annealed in a furnace under an Ar atmosphere for 2 hours with varying temperatures from 100 °C to 500 °C. Both as-deposited and annealed samples in the thick and intermediate-layer cases were then prepared for cross-section indentation, in which two multilayer samples were mounted face to face on the film side using an epoxy compound. The mounted samples were then mechanically polished on a Buhler polisher with diamond discs of 75 μm and 20 μm

grades, followed by diamond paste in successive grades of 9 μm , 3 μm , 1 μm , 0.5 μm and 0.25 μm , and finally alumina slurry of 0.05 μm . Comparison between cross-section and surface indentations help to demonstrate the mechanical anisotropy of the multilayers.

For mechanical strength, an Ubi1 nanomechanical test instrument (Hysitron, Inc., MN) with a cube corner indenter tip was utilized to obtain the surface and cross-section indentation hardness. The indentation used a trapezoidal loading function including a 10 s loading, 5 s hold and 10 s unloading. A standard Oliver and Pharr method [41] was used to obtain the average hardness from a minimum of 20 indents.

In order to correlate the hardness evolution with microstructural information, x-ray diffraction (XRD) with Cu $K\alpha$ line was used to detect the phase information, and scanning electron microscopy (SEM) was used to examine the microstructural evolution on the surface and cross-section before and after annealing. For the thin layer cases, transmission electron microscopy (TEM) was used to obtain the cross-section morphology for selected samples as SEM is resolution-limited at this length scale.

3. Results and discussions

3.1. Nanoindentation hardness

Fig.1 shows the hardness as a function of annealing temperature (T) for Ti/Ni multilayers with λ ranging from 200 down to 6 nm for both surface (S) and cross-section (CS) indentations. A coupled effect between annealing-temperature and layer-thickness was clearly observed. For the brevity of presentation, the results are divided into four temperature regions: room temperature (RT) for as-deposited films, low-temperature

(low-T) annealing for $T < 300\text{ }^{\circ}\text{C}$, transitional temperature annealing for $T = 300\text{ }^{\circ}\text{C}$ and high-temperature (high-T) annealing for $T > 300^{\circ}\text{C}$. This division of temperature will be used throughout the manuscript. For the thin-layer cases, a monotonically increased hardness is observed with increasing annealing temperature. For the intermediate-layer cases, an increased hardness is observed with increasing temperature up to $300\text{ }^{\circ}\text{C}$, and then a decreased hardness under further high-T annealing. For the thick-layer cases, there is no obvious hardness change under low-T annealing, but an increased hardness is observed for $300\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$, and then a dramatic hardness decrease after $500\text{ }^{\circ}\text{C}$ annealing.

In addition, an obvious orientation-dependent hardness behavior is observed in the thick- and intermediate-layer cases after high-T annealing. In the thick-layer cases, although the same increasing-then-decreasing trend was observed in both cross-section and surface indentations, the hardness drop at $500\text{ }^{\circ}\text{C}$ is much less in the cross-section indentations. A large discrepancy of hardness behavior can be observed in the intermediate-layer cases. Instead of the decreasing trend as in the surface indentation, the hardness from the cross-section indentation continued the previous increasing trend from the low-T annealing.

In order to understand the various hardness behaviors associated with different layer thickness, annealing temperature and loading orientation, it is important to investigate the microstructure evolution of the multilayers after thermal annealing.

Figure 1. Surface (S) and cross-section (CS) indentation hardness of Ti/Ni multilayers as a function of anneal temperature for different layer thickness.

3.2. Microstructure characterization

Figure 2. XRD spectra of as-deposited and annealed Ti/Ni multilayers: (a) $\lambda = 100$ nm and (b) $\lambda = 8$ nm.

Thermal annealing induced microstructure modification of Ti/Ni multilayers can be revealed by XRD patterns. Fig.2 shows the representative XRD spectrum for the thick-layer and thin-layer cases. For samples with $\lambda = 100$ nm, similar XRD spectra were obtained after low-T annealing, while the intensity of Ti peak dramatically decreased or disappeared after 300 °C annealing. In addition, a couple new peaks corresponding to Ti-Ni intermetallic phase were detected at 500 °C. In spite of the disappearance of the Ti peak and formation of the Ti-Ni intermetallic peaks, Ni (111) stays as the strongest peak at all temperatures.

However, a different phenomenon is displayed in the samples with $\lambda = 8$ nm as shown in Fig.2(b). Ni (111) is the only significant peak shown by the as-deposited sample and an obvious left shifting of this peak is observed after low-T annealing which may be caused by the diffusion of Ti atoms into the Ni layer enlarging the Ni (111) lattice. After high-T annealing, only Ti-Ni intermetallic peaks were detected. The disappearance of the Ni

peak indicates possible disintegration of the layers and the formation of fully intermixed and completely alloyed structure. The broad peak located between Ni (111) and Ti-Ni intermetallic peaks at 300 °C annealing is likely a combination of the intermetallic peak and shifted Ni (111) peak.

The different XRD spectra between the thick and thin layer cases indicate a strong layer thickness-dependent microstructure evolution after thermal annealing. In the thin-layer case, atomic diffusion may be activated upon low-T annealing which led to a large extent intermixing between the Ti and Ni layers, and the films evolve into complete Ti-Ni intermetallic phase with high-T annealing. In the thick-layer case, however, Ti-Ni alloys may only have been formed along the interfaces while the layered structure still being maintained.

Cross-sectional SEM and TEM images provide direct evidence and confirmation of the aforementioned postulation of the layer thickness-dependent microstructural evolution after thermal annealing. As shown in Fig.3 (a, e) and Fig.4 (a), the layered structure can be clearly observed for as-deposited Ti/Ni multilayers with different layer thicknesses.

The as-deposited film shows the columnar structure in the Ni layers with a single grain along the thickness direction and the equiaxed structure in the Ti layers. In the $\lambda = 200$ nm case, there is little change in the cross-section morphology even after 400 °C annealing. After 500 °C annealing, however, there is a clearly increased amount of diffusion along the layer interface and grain boundaries, as well as recrystallized Ni grains and voids, while the layered structure still maintained. In contrast, in the $\lambda = 25$ nm case, the layered structure was already disintegrated after 400 °C annealing (Fig.3 (f)), indicating an inferior thermal stability in the thin layer case.

Figure 3. Cross-section SEM images of Ti/Ni multilayers with $\lambda = 200$ nm case: (a) as-deposited, (b) 300 °C annealed, (c) 400 °C annealed, (d) 500 °C annealed; and $\lambda = 25$ nm case: (e) as-deposited, and (f) 400 °C annealed.

Figure 4. Cross-section TEM images of Ti/Ni multilayers with: (a) $\lambda = 12$ nm, as-deposited, (b) $\lambda = 16$ nm, 200 °C annealed, (c) high-resolution TEM for (b). The inset figures are corresponding electron diffraction patterns confirming the various phases shown by the XRD.

In literature, quite a few studies dealt with the thermal stability of Ti/Ni multilayers with thin individual layer, and reported: (1) after high-T annealing, a fully intermixed and completely alloyed structure to replace the layered structure [42-44], and (2) at 300 °C annealing, solid-state reaction leading to amorphization due to a large extent of diffusion [45-47]. The XRD results in Fig. 2(b) only confirmed the complete alloying process after high-T annealing. However, after 300 °C annealing, instead of an amorphous structure, our study showed that a mixed structure including Ti, Ni, Ti-Ni amorphous and Ti-Ni intermetallic is more possible.

Now one aspect still not clear is that whether there is also a large extent of atomic diffusion for the low-T annealed thin layer cases. To answer this question, TEM was performed to obtain important microstructure information. Fig.4 shows the cross-section morphology and diffraction patterns for an as-deposited $\lambda = 12$ nm sample and a 200 °C annealed $\lambda = 16$ nm sample. Distinct interface can be observed in the bright-field high resolution TEM images. In addition, the diffraction patterns confirm the polycrystalline nature and the phases of the Ti and Ni layers shown by the XRD, but do not show any amorphous-structure-induced broadening of the diffraction rings. The fact that the crystal lattices in each layer are clearly observed to extend all the way to the interface in the high-resolution TEM image shown in Fig. 4(c) indicates only moderate diffusion occurred during the low-temperature annealing.

In addition, surface morphology can provide complementary information about layer-thickness and annealing-temperature dependent microstructure evolution. The representative surface SEM images are shown in Fig.5 with one example from each of the thin, intermediate and thick layer cases. Information from the complete set of SEM images showed that for the as-deposited films, surface grain size decreases with

decreasing layer thickness till $\lambda = 25$ nm, below which the surface grain size remains relatively constant around 25 nm. After thermal annealing, the surface morphology (e.g., grain size and shape) changes differently with different layer thickness. In the $\lambda = 200$ nm case, no significant change is observed for annealing up to 300 °C, only slight grain growth after 400 °C and recrystallized grains after 500 °C, and all of these changes are consistent with those indicated from the cross-section SEM. In the $\lambda = 50$ nm case, the surface shows no measurable microstructure change up to 300 °C, but recrystallization upon 400 °C and fully recrystallized grain structures after 500 °C. In the $\lambda = 8$ nm case, the morphology was almost identical after 200 °C to that of the as-deposited, consistent with the TEM observation, confirming insignificant atomic diffusion during low-T annealing. At 300 °C, much sharper grain structure covers the whole surface (indicated by the bright dots), probably due to diffusion-induced grain sharpening and Ti-Ni intermetallic phase. After high-T annealing, a very different surface morphology corresponding to the Ti-Ni alloys is formed.

The information from the above XRD, SEM and TEM characterization and analysis will be utilized to explain the layer-thickness and annealing-temperature dependent hardness and strengthening mechanisms in next section.

Figure 5. Surface SEM images of Ti/Ni multilayers with different layer-thickness and annealing temperature.

3.3 Strengthening mechanisms

3.3.1 Strengthening mechanisms in as-deposited multilayers

In order to understand and confirm the layer thickness effect, the hardness data for the as-deposited samples is re-plotted as a function of layer thickness in Fig.6. In our recent work, a Hall-Petch model based on dislocation pile-up was applied to fit the experimental data with $\lambda > 50$ nm, and a maximum obtainable hardness of 5.9 GPa was predicted [37]. In the current work, when the layer thickness is reduced to 12 nm, a peak strength of 6 GPa was obtained. This further confirms that dislocation pile-up along the interfaces is the dominating strengthening mechanism when $\lambda > 50$ nm.

Furthermore, since the layer thickness in this study is extended down to 6 nm, it is now possible to investigate the complete layer-thickness dependent deformation behaviors and strengthening mechanisms for Ti/Ni multilayers, an fcc/hcp system, which has not been fully studied so far. When λ is on the order of a few tens of nanometers, it is well accepted that the confined layer slip (CLS) model based on single dislocation bowing between interfaces can be used to fit the hardness of multilayers and the modified CLS stress $\sigma_{CLS} = H / 2.7$ is given as [28]:

$$\sigma_{CLS} = \frac{M\mu b \sin \theta}{8\pi\lambda} \left(\frac{4-\nu}{1-\nu} \right) \ln \left(\frac{\alpha\lambda}{b \sin \theta} \right) - \frac{f}{\lambda} + \frac{\mu b}{(1-\nu)L} \quad (1)$$

where M is the Taylor factor of 3.1, μ the shear modulus, b burger's vector, θ the angle between the slip plane and the interface, ν the Poisson ratio, α the core cut-off parameter varying from 0 to 1, f the interface stress with a typical value 2-3 J/m², and L the spacing of the interface dislocation array. Substituting $\mu = 76$ GPa, $b = 0.25$

nm, $\nu=0.31$ for Ni, and taking $\alpha=0.12$, $f=3$, $\theta=60^\circ$ and $L=25$, the CLS model can fit the experimental data well with λ from 75 to 12 nm (blue solid line in Fig. 6(c)). In the modified CLS model, $L = b/\varepsilon$, where ε is in-plane plastic strain with a typical value 1-2% for nanoscale metallic multilayers [13, 28, 48]. Here $L = 25$ nm corresponds to a plastic strain around 1%. The good fitting of the modified CLS model with current experimental data indicates that the single dislocation bowing between interfaces is the dominating mechanism in this λ range. Note that CLS is also the operative mechanism for the thick and intermediate λ range when the loading is along the interfaces as reported earlier [37].

While the peak strength of 6 GPa was reached at $\lambda=12$ nm, a decreased hardness was observed with further decreasing λ . Previous studies reported the maximum strength with λ of a few nanometers and attributed interface crossing by dislocations as the operative softening mechanism with decreasing λ since the interface resistance of single dislocation transmission decreases as the dislocation core approaches λ [27, 28]. However, the λ range of softening in the current study is beyond that for interface crossing mechanism. Both cross-section (Fig.4(a)) and surface morphology (Fig.5) display polycrystalline structure in the thin-layer cases, and thus grain boundary shear is considered as the probable dominating softening mechanism in this λ range.

Figure 6. Hardness results and dislocation-based modeling for as-deposited Ti/Ni multilayers: a Hall-Petch model for λ from 200 ~ 50 nm and a modified CLS model for λ from 75 ~ 12 nm for surface indentation; a CLS model for λ from 200 ~ 25 nm for cross-section indentation. The detailed results and discussions about orientation dependency in the thick- and immediate-layer cases can be found in our recently published work [37].

3.3.2 Strengthening mechanisms in low-T annealed multilayers

Low-T annealing is observed to enhance the multilayer strength without obvious microstructure change. In our previous work [37], a Williamson-Hall fitting of the XRD peak profiles revealed the reduction of the microstrain in low-T annealed Ti/Ni multilayer films, indicating that the grain boundary relaxation is the strengthening mechanism in this temperature range. The same mechanism seems to be operating here with a much enhanced effect on the thin layer cases. To better reveal the coupling between T and λ , the hardness is re-plotted as a function of λ for annealing temperature from RT to 250 °C

in Fig.7. In the small λ cases, the grain size is small and the grain boundary occupies a large volume portion of the material, which promote the grain boundary relaxation strengthening. In addition, grain boundary relaxation strengthening exhibits a strong dependence on annealing temperature. This can be understood that higher temperature can provide more energy to activate more grain boundary relaxation processes and thus more strengthening.

When $\lambda < 16$ nm, as shown in Fig.7, a softening trend with decreasing λ is observed for as-deposited samples due to possible grain boundary mediated motions. After low-T annealing, however, the grain boundary mediated motions may be suppressed due to the more ordered grain boundary structure and the materials deform by dislocation glide, and as a result, a strengthening trend with decreasing λ is observed for low-T annealed samples. In addition, slight diffusion was indicated from the microstructure characterization and the hardness enhancement in thin-layer cases could be partially due to solid solution strengthening from diffused atoms.

Figure 7. Hardness evolution as a function of layer thickness for as-deposited and low-temperature annealed Ti/Ni multilayers.

3.3.3 Strengthening mechanisms in 300°C annealed multilayers

Fig.8 shows the hardness evolution with different λ for 200 °C and 300 °C annealed samples. All layers showed an increased hardness from 200 °C and 300 °C, but a much larger amount of strengthening in the thicker layers. Grain boundary relaxation may continue to be the operative mechanism in the thick- and intermediate-layer cases since almost no microstructure modification is detected for these cases after 300 °C annealing. The slightly higher temperature appears to have provided sufficient energy to activate the grain boundary relaxation process in the thick-layer cases, leading to an initial strengthening. However, the grain boundary relaxation strengthening in the intermediate-layer cases may have approached the saturation limit after low-T annealing, thus only moderate strengthening is observed after 300 °C. In the thin layer cases, however, since a large extent of diffusion and Ti-Ni intermetallic formation were detected, solid solution strengthening and precipitation strengthening of intermetallic should be the dominating mechanisms together with continued grain boundary relaxation.

Figure 8. Hardness evolution with varying layer thickness for 200 °C and 300 °C

annealed Ti/Ni multilayers.

3.3.4 Strengthening/softening mechanisms in high-T annealed multilayers

Based on the microstructure analysis in section 3.2, the strong layer-thickness dependent hardness behavior observed after high-T annealing may be attributed to combined results from grain boundary relaxation, solid solution strengthening, precipitation strengthening, intermetallic strengthening, and grain growth softening. In the thick-layer cases, grain boundary relaxation **could** be the dominating mechanism for the continued strengthening after 400 °C while grain growth is responsible for the dramatic softening after 500 °C. In the intermediate-layer cases, continuously decreased hardness with increasing temperature is also due to the grain growth, while the opposite trend in the thin-layer cases is a result of the fully intermixed and completely alloyed structure.

In addition, the strong orientation dependent hardness behavior observed in the thick and intermediate-layer cases can be attributed to high-T induced crystallographic texture and precipitations. After high-T annealing, the recrystallized and grown surface grains have a size up to hundreds of nanometers (Fig.5), while the grain width is only a few tens of nanometers from the cross-section (Fig.4). In addition, the Ti-Ni intermetallics formed along the interfaces and the fact that cross-section indentation covers two times more interfaces compared to the surface indentation also contributes to the observed mechanical anisotropy after high-T annealing.

3.3.5 Integrated temperature-length-orientation effect

The systematic study on coupled layer-thickness and annealing-temperature effect on the hardness of Ti/Ni multilayers provides new insights on the strengthening/softening mechanisms of nanometric metallic multilayers. **A qualitative strengthening mechanism**

map is proposed in Fig.9 based on the discussions in sections 3.3.1-3.3.4, integrating the effect from layer-thickness, annealing temperature, and the loading orientation. Detailed discussions are presented as following.

Figure 9. Schematic of proposed strengthening/softening mechanism map of integrated layer thickness, annealing temperature and loading orientation effect for Ti/Ni multilayers.

For as-deposited multilayers, dislocation-mediated motions are the dominating strengthening mechanisms with decreasing λ , i.e. dislocation pile-up along interfaces with λ down to tens of nanometers and single dislocation transmission across interfaces with λ ranging from a few nanometers to a few tens of nanometers. However, the latter motion could be the dominating strengthening mechanism with λ up to hundreds of nanometers when the loading orientation switches from perpendicular to parallel to the

interfaces [37]. With λ of a few nanometers, the softening with further reduced λ can be attributed to grain boundary-mediated motions such as grain boundary sliding and rotation.

However, the abovementioned grain boundary mediated processes can be suppressed by annealing-activated grain boundary relaxation. Low-T annealing can trigger this grain boundary relaxation mechanism more easily in thin-layer cases due to the small grain size and large volume of grain boundary atoms. More strengthening is achieved in cross-section loading due to smaller grain width compared to the much larger particle size on the surface.

Continued annealing (e.g. 300 °C) could provide sufficient energy to activate grain boundary relaxation in the thick-layer cases, leading to an initial strengthening. In the intermediate-layer cases, further strengthening is achieved, but moderate since the low-T annealing-induced strengthening may have approached the saturation limit. In the thin-layer cases, however, in addition to grain boundary relaxation, strengthening is also resulted from solid solution of diffused atoms and precipitation of intermetallics.

Under high-T annealing, grain boundary relaxation induced strengthening in the thick-layer cases will eventually be overtaken by recrystallization and grain growth induced softening. In the intermediate-layer cases, high-T induced grain growth softening appears at a lower temperature (e.g. 400 °C vs. 500 °C) compared to the thick-layer cases. However, slight strengthening may continue in the cross-section loading due to high-T induced anisotropic texture and intermetallic precipitates. In the thin-layer cases, a fully intermixed and completely alloyed structure results in a continuously increased hardness with increasing annealing temperature.

Therefore, from as-deposited to annealed multilayers, grain boundary relaxation is the initial strengthening mechanism with higher activation temperature required for thicker layers. The strengthening mechanism transitions from grain boundary relaxation to solid solution and precipitation strengthening with the increase of annealing temperature, due to high thermal energy induced atomic diffusion and intermetallic formation. After high temperature annealing, the hardness evolution is determined by two competing mechanisms – strengthening due to alloy formation and softening due to recrystallization grain growth. For thin layers, the fully intermixed and completely alloyed structure lead to continuously increased hardness. For thick layers, recrystallization and full grain growth within the well-maintained layers lead to eventual softening, despite of the increased diffusion along the layer interfaces. Therefore, the layer thickness controls the mechanism switch between alloy strengthening and grain growth softening in the high temperature regime.

4. Conclusions

In this work, the annealing-temperature and layer-thickness effect on the strengthening mechanisms of Ti/Ni multilayers was studied with a wide range of layer thickness from 200 nm to 6 nm, and annealing temperature from RT to 500 °C. A monotonically increased hardness is observed with the whole range of annealing temperatures for the thin-layer cases. For the intermediate-layer cases, an increasing trend was observed from low-T to 300 °C, and then a decreased hardness was observed with high-T annealing. For the thick-layer cases, the hardness started to show an increase after 300 °C annealing which continued into the high-T (400 °C) annealing, and then a dramatic drop after further increased temperature (500 °C). XRD, SEM and TEM characterization provided useful information on the microstructure evolution. With increasing annealing temperature, increasing amount of atomic diffusion, solid solution formation and

intermetallic precipitation happened along the layer interfaces which led to a fully-intermixed alloy structure in the thin layered films. On the contrary, the thick layered films showed a much higher thermal stability with almost no morphological changes until 400 °C, but further annealing under 500 °C led to significant recrystallization and grain growth.

Based on the detailed mechanical and microstructural analysis, a qualitative strengthening mechanism map integrating the effects from layer-thickness and annealing-temperature is proposed. Under room temperature, with decreasing layer thickness from hundreds to a few nanometer, the deformation behavior of the multilayers transitions from dislocation mediated activities, including both dislocation pile-up along layer interfaces and single dislocation bowing between interfaces, to grain boundary mediated activities. After low-T annealing, grain boundary relaxation is considered to be the dominating strengthening mechanism with increasing activation temperature required for thicker layers. With further increased annealing temperature, the strengthening mechanism transitions from grain boundary relaxation to two competing mechanisms - solid solution and intermetallic precipitation hardening, versus recrystallization and grain growth induced softening. The exact trend for hardness evolution is determined by the layer thickness – large number of interfaces in the thin layers facilitate more solid solution and intermetallic precipitation hardening as well as complete alloying strengthening, while softening dominates the thick layer behavior due to the large extent of recrystallization and grain growth within the layers. For intermediate-layer thickness, the trend of the hardness evolution switches from grain growth softening to intermetallic precipitation strengthening by changing the loading orientation from perpendicular to parallel to the interfaces.

The results in this study highlight the coupled effects of layer-thickness and annealing

temperature on the mechanical strength and thermal stability of metallic multilayer systems. The improved understanding of the deformation and strengthening mechanisms may provide meaningful guidelines on the control and optimization of this important class of future engineered materials.

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