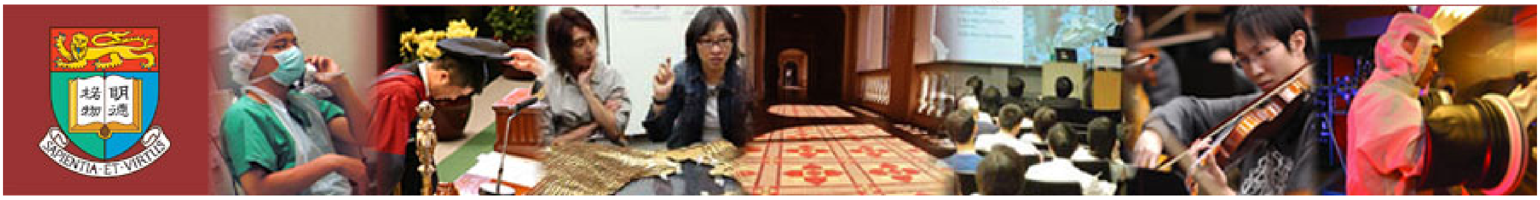

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Hard multilayered thin films of metal–intermetallic Ni/Ni_3Al

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Metal–intermetallic Ni/Ni_3Al multilayered thin films were synthesized by the magnetron sputtering technique. The synthesized films possessed high hardness that could be compared with intermetallic Ni_3Al films. The constituent layers of Ni and Ni_3Al were fully adherent to one another at the multilayered boundaries. The fracture surface of the multilayered films on bending showed the characteristics of local ductile fracture. This novel type of multilayered thin films is expected to be used as hard coatings and miniaturized parts of apparatus in micro-electromechanical systems.

Multilayered films usually exhibit a large enhancement of mechanical properties compared to single layers.[1,2] Multilayers fabricated from constituents with similar structures and modest lattice mismatch often exhibit grain-to-grain epitaxy between the layers, even if the gross structure is polycrystalline.[3] In such a case, distinctive properties such as good strength and toughness of the constituents are expected to be maintained in the multilayers.

It is well known that Ni_3Al and Ni have not only similar structure but also close unit cell dimensions. Ni is an elemental metal with lattice constant of 0.3524 nm in a disordered face-centered-cubic (fcc) unit cell. It is ductile and tough enough in both bulk and thin-film states. Ni_3Al, on the other hand, is an ordered fcc ($L1_2$) intermetallic compound with lattice constant of 0.3570 nm. Polycrystalline Ni_3Al in bulk form is brittle at room temperature. It has existing and potential applications at high-temperatures because of its high melting temperature, high thermal conductivity, oxidation resistance, and the so-called flow stress anomaly at elevated temperatures.[4] Thin-film Ni_3Al possesses more attractive properties than the bulk, especially in surface strength, corrosion, and oxidation resistance.[5,6] One can expect that the combination of Ni_3Al and Ni layers may produce a balanced multilayered thin film with the excellent flexural strength and toughness required by applications such as hard coatings and miniaturized sensors in micro-electromechanical systems.

Multilayered Ni/Ni_3Al films were deposited on (100) silicon wafers at 400 °C by the magnetron sputtering technique. Deposition rates were maintained at 1.2 nm s^{-1} for Ni films using a pure Ni target and 1.3 nm s^{-1} for Ni_3Al films using a Ni/Al multi-target. A detailed description for the preparation of the multi-target can be found elsewhere.[5] The multilayered films consisted of four (Film 1), eight (Film 2), and twelve (Film 3) alternating layers of Ni and Ni_3Al. The thickness of Ni and Ni_3Al layers in the multilayered films were set to be approximately equal, both with the size of approximately 900 nm. All the multilayered films were annealed in a vacuum furnace at 700 °C for 1 h before further characterization of microstructure and mechanical properties.

The Ni–Al atom ratio of the layer sputtered by multi-target was revealed to be 74.85:25:15 by energy dispersive x-ray (EDX) analysis. It was very close to the stoichiometric ratio of 3:1 in Ni_3Al. The strong line profiles of the (111), (200), (220), (110), and (100) diffracting planes of this layer, which were recorded by x-ray diffraction (XRD) with 2θ steps of 0.02°, shown in Fig. 1, indicated that the whole layer was Ni_3Al. Figure 2 shows an atomic force microscopy (AFM) surface morphology of the layer. It can be seen that the Ni_3Al layer was polycrystalline, with an average particle size of approximately 340 nm in diameter.

It should be pointed out that the process of forming a pure Ni_3Al layer by sputtering Ni and Al targets is complicated because some products such as $NiAl_3$, Ni_2Al_3, and NiAl are much easier to form than Ni_3Al, according to a recent dynamics study on the Ni–Al binary system.[7]

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The general trend is that the content of Ni atoms in Ni–Al system increases with the increasing transformation temperature:

$$\begin{aligned} \mathrm{Ni/Al} &\rightarrow \mathrm{Ni/NiAl_3/Al} \rightarrow \mathrm{Ni/NiAl_3}\ (300\text{–}330\ ^\circ\mathrm{C}) \\ &\rightarrow \mathrm{NiAl_3/Ni_2Al_3/Ni} \rightarrow \mathrm{Ni_2Al_3/Ni} \\ &\rightarrow \mathrm{Ni_2Al_3/NiAl/Ni}\ (350\text{–}375\ ^\circ\mathrm{C}) \quad . \end{aligned}$$

When the temperature is high enough, e.g., 700 °C, the pure phase of Ni_3Al can be formed.[5,6]

The mechanical properties of the multilayered thin films were measured using a nanoindentation–atomic force microscope. The force resolution of the instrument is in the range of 100 nN with a maximum force of nearly 10 mN. A three-sided pyramidal diamond tip with an apex angle of 90° was used for indenting and imaging.[8]

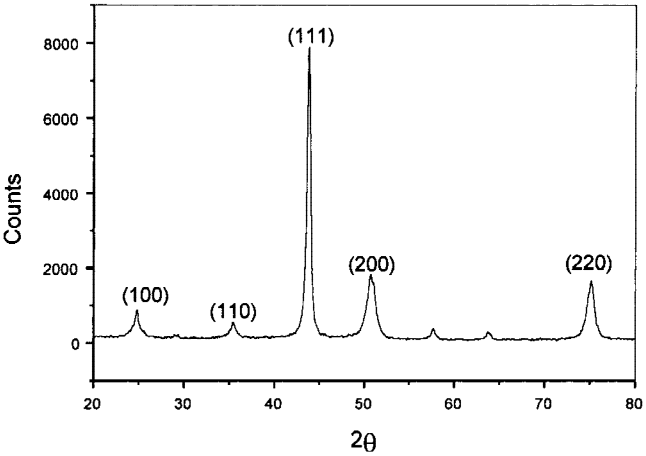

FIG. 1. The XRD pattern of the Ni_3Al layer sputtered by multi-target at 400 °C and then annealed at 700 °C for 1 h. The strong line profiles of (111), (200), (220), (110), and (100) diffracting planes of this layer were recorded by 2θ steps of 0.02°.

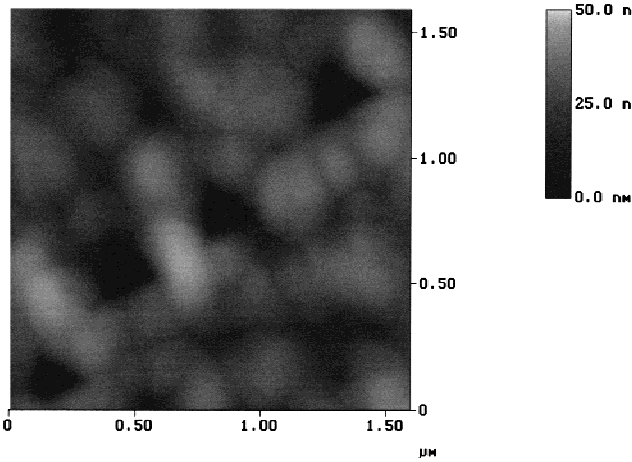

FIG. 2. The AFM surface morphology of the Ni_3Al layer after nanoindentation test. The layer was sputtered by multi-target magnetron sputtering at 400 °C and followed by annealing at 700 °C for 1 h. Four trianglelike shapes correspond to the indentation marks. The surface of the layer was etched by diluted HNO_3 + H_2SO_4 acids to show the grain boundaries clearly. The average grain size of Ni_3Al is approximately 340 nm in diameter.

Figure 3 shows the bare silicon substrate and Ni/Ni_3Al multilayer hardness as a function of indentation contact depth. The hardness of the substrate (100) Si was approximately 11.2 GPa, regardless of indentation depth. The multilayer hardness depends on the film thickness and increases with increasing indention size. The hardness values vary from 4.26 to 8.75 GPa over the range of the indentation depths. It should be pointed out that only indentations with contact depths of less than 10–20% of the film thickness correspond to intrinsic film properties because of the so-called substrate effect.[9] Thus, data for indentation depths below approximately 400, 800, and 1200 nm should be taken for estimating the hardness values of Film 1, Film 2, and Film 3, respectively. It is interesting to note that for lesser depths the multilayer hardness stayed almost constant at approximately 4.3, 4.5, and 4.8 GPa, which can be regarded as the hardnesses of Film 1, Film 2 and Film 3, respectively.

The hardnesses of thin-film Ni and Ni_3Al were reported as approximately 3.5 GPa[3,10] and approximately 5 GPa[5], respectively. It seems surprising that the Ni/Ni_3Al composite films with a Ni and Ni_3Al volume fraction ratio of 1:1 had a high hardness, comparable to that of hard constituent Ni_3Al, especially when the number of the layers was large (e.g. Film 3). The constrained deformation of the constituent layers, caused by their

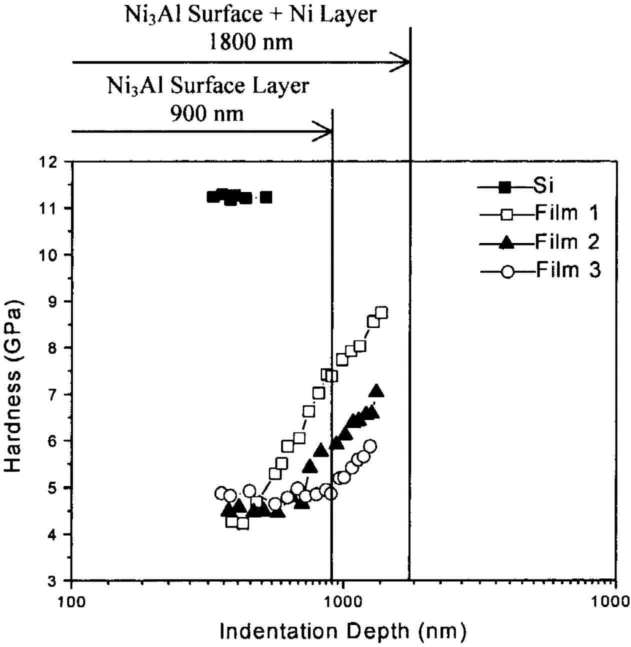

FIG. 3. Plot of the hardness of Film 1, Film 2, and Film 3 as a function of indentation depths. Note that the hardness of the three Ni/Ni_3Al multilayer films stays almost constant at approximately 4.3, 4.5, and 4.8 GPa, corresponding to the respective approximately 10% depths of the multilayer thickness.

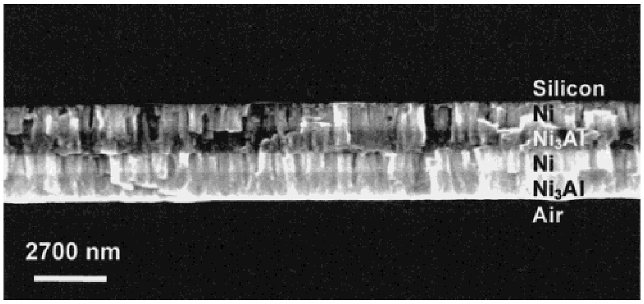

FIG. 4. The fracture cross-section profile of Film 1 by SEM. It can be clearly seen that the fractured striations are continuous, layer through layer, and no delamination appears within the multilayered film.

good adhesion to one another, should be the primary reason for the high hardness of the films. Multilayers fabricated from Ni and Ni_3Al are expected to exhibit grain-to-grain eptaxy between the layers because both the constituents have a fcc structure with a low lattice mismatch (1.3%). Dislocation movement across the coherent interfaces is therefore estimated to be difficult because, for instance, two unit dislocations in the fcc Ni phase will have to be paired up to form a superdislocation upon penetrating into the neighboring fcc ($L1_2$) Ni_3Al or else an antiphase domain boundary will result in the wake of a single dislocation. This is the so-called order/disorder strengthening effect, and so the order/disorder multilayered films become surprisingly hard and strong. One of the reasons why Film 3 was harder than Film 1 and 2 should be that Film 3 contained more order/disorder layers.

Figure 4 shows the fracture cross-section morphology of Film 1 by scanning electron microscopy (SEM). The continuous fracture striations of layer through layer show that the Ni and Ni_3Al constituents fully adhered to one another; i.e., no delamination appeared within the multilayered film. Considering that the fracture life plotted as a function of lattice parameter difference is clearly maximized with minimum difference of lattice parameters of the constituents,[11] the toughness of the multilayered films is also believed to be excellent. The cross-section profile in Fig. 4 shows indeed the characteristic of toughness in fracture of the multilayers.

In summary, a ductile metal Ni and a hard intermetallic compound Ni_3Al were chosen as constituents of a novel type of multilayered thin film in the present study. Because their unit cell dimensions are very close to one another, good atomic coherence and hence good mechanical hardness can be easily maintained at the surface when one of them is grown on top of the other using magnetron sputtering techniques. The hardness varies from 4.3 to 4.8 GPa over the three synthesized Ni/Ni_3Al multilayered films, which is high enough to be comparable with that of Ni_3Al hard films. The hard and tough multilayered films are expected to be used as hard coatings and miniaturized sensors in microelectromechanical systems.

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