**An Assessment of the Mechanical Strengths of Aluminide-based Thin Coatings**

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## ABSTRACT

Titanium aluminide and nickel aluminide-based thin coatings were synthesized by magnetron sputtering from intermetallic TiAl and $Ni_3Al$ alloy targets on nickel substrates. Both types of aluminide coatings exhibited high surface hardness values that varied with the degree of heat treatment. The hardness of the coatings was investigated using micro- and nano- indentation techniques. In order to estimate the intrinsic strength of the films, the indentation size effects of the apparent hardness were analyzed by the Jönsson-Hogmark model and a model recently proposed by the authors. The analysis indicated that the strengths of the aluminide coatings may considerably exceed their strengths in bulk.

## INTRODUCTION

Thin films are widely used nowadays as functional, protective or decorative coatings. Measurement of the mechanical properties of these coatings, however, is not a straightforward matter. Micro- and nano-indentation are plausible methods, but the influence of the substrate may become significant to the effect that what is actually measured may be a composite hardness of both the film and the substrate. A general rule is to indent within 10% of the film thickness to reduce the influence from the substrate, but this critical depth-to-thickness ratio would depend on the relative hardness of the film and substrate and is therefore not a tangible quantity. Another problem is that hardness values obtained with ultra-low loads are well-known to exhibit strong indentation size effects (ISE), and it is not known precisely how these could be corrected to give, for example, the yield strength of the material.

In order to make thin film strength measurements more convenient and reliable, several "rule-of-mixture" models have been proposed [1-3]. These models assume that the overall hardness is some rule of mixture between the film and substrate hardness. A representative one is the Jönsson-Hogmark model [1], which assumes that the overall hardness obeys a rule of mixture based on the projected areas of the indent interior and the periphery. Recently, the present authors have developed a mechanistic model based on the plastic zones of the film and the substrate [4]. In this paper, we will attempt to compare the applicability of these two models in Ti-Al and Ni-Al thin films deposited on Ni substrates.

## EXPERIMENTAL DETAILS

Ti-Al thin films with approximately 1 Ti : 1 Al ratio and Ni-Al thin films with 3 Ni : 1 Al ratio were deposited on Ni substrates (>99.92% pure) by magnetron sputtering from intermetallic Ti-47 at.% Al-3 at.% Nb-2 at.% Fe-0.6 at.% Cr and Ni-25 at.% Al alloy targets. The substrates were first annealed at 1000°C for 4 hours to relieve residual stresses. They were then polished down to 1 micron prior to deposition. The thickness of the deposited films ranges from 2 to 8 μm and more details are listed in Table I. The thickness was determined by cross-sectional scanning electron microscopy after fracturing the deposited substrate along a pre-notch manufactured on the back-side of the substrate.

Nano-indentation was performed on a Hysitron transducer mounted on a Thermomicroscopes CP scanning probe microscope. Micro-indentation was performed on a Buehler Micromet 2100 micro-hardness tester. The loads used are listed in Table II.

**Table I**. Sputtering conditions of films

| Target material | | | | | |
|---|---|---|---|---|---|
| Ti-46.8at.% Al-3.2at.% Nb-1.7at.% Fe-0.6at.% Cr | | | Ni-25at.% Al | | |
| Power (W) | In-situ heating | Thickness (μm) | Power (W) | In-situ heating (°C) | Thickness (μm) |
| 60 | Nil | 6 | 50-70 | 400 | 9 |
| 60 | Nil | 2 | 50-70 | 400 | 7 |
| | | | 50-70 | 400 | 5 |

**Table II**. Indentation loads used in nano- and micro- indentation

| Nano-indentation (μN) | | | | | | | Micro-indentation (gf) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2000 | 3000 | 4000 | 5000 | 6000 | 7000 | 8000 | 10 | 25 | 50 | 100 | 200 | 300 | 500 |

## RESULTS AND DISCUSSION

Fig. 1 shows the measured micro-hardness of the bare Ni substrate, the various deposited films on Ni, and, for comparison, a bulk TiAl alloy and a bulk $Ni_3Al$ alloy. It can be seen that the hardness values for bulk Ni, TiAl and $Ni_3Al$ are fairly constant except for loads smaller than ~ 50 gf at which the hardness shows a small rise. This indicates that in the load range concerned these three materials do not exhibit a strong ISE. Fig. 1 also indicates that all the coatings possess higher hardness than bare Ni. Moreover, the coatings, especially the Ni-Al ones, exhibit a very prominent increase in the hardness value as the indentation load decreases. At very low loads, i.e. less than 50 gf, the Ni-Al films exhibit hardness values even higher than that of the bulk $Ni_3Al$ alloy and the hardening is greater for thicker films. The 7.04 and 8.82 μm thick Ni-Al films exhibit hardness in excess of 500 Hv at low loads, while the hardness of the bulk $Ni_3Al$ alloy is only about 380-420 Hv. Being deposited at 400 °C, these films were found to crystallize into extremely fine crystallites [5]. The nano-crystalline film structure is expected to result in a significant strengthening effect.

The increase in hardness with decreasing loads for deposited films can be interpreted as a consequence of the reduced influence of the softer Ni substrate as penetration depth decreases. For the Ti-Al films, the composite hardness is lower than that of bulk TiAl for all indentation loads. This may be due to the fact that these Ti-Al films were deposited without any in-situ heating, so that the films were amorphous as confirmed by X-ray diffraction analyses. Fig. 2 shows the nano-hardness of the two Ti-Al films. The indentation depths in these tests were smaller than about 10% of the film thickness, so that the substrate effect should be minimal. This can be seen from the fact that the discrepancy between the hardness results for the 2 μm thick and the 6 μm thick films is reduced compared with the micro-hardness results in Fig. 1. As before, in Fig. 2, the measured nano-hardness is lower than that of bulk TiAl alloy for all indentation loads. This indicates that the amorphous film material is indeed intrinsically softer than the bulk TiAl alloy. Note that the nano-hardness values in Fig. 2 are significantly higher than the micro-hardness values for the same materials in Fig. 1. This is the well-known intrinsic ISE which is more pronounced in the nano-hardness range.

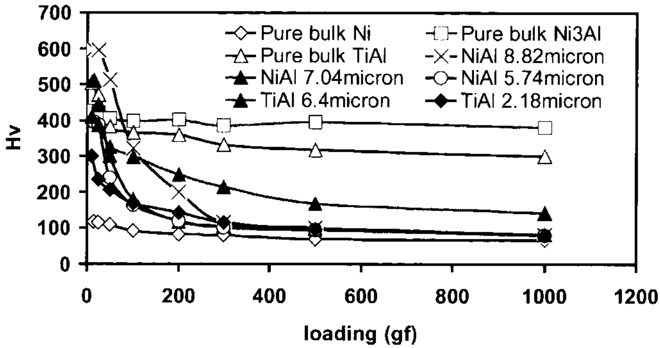


***Figure 1.*** *Micro-hardness measured for pure Ni (substrate), bulk TiAl alloy, bulk $Ni_3Al$ alloy and films.*

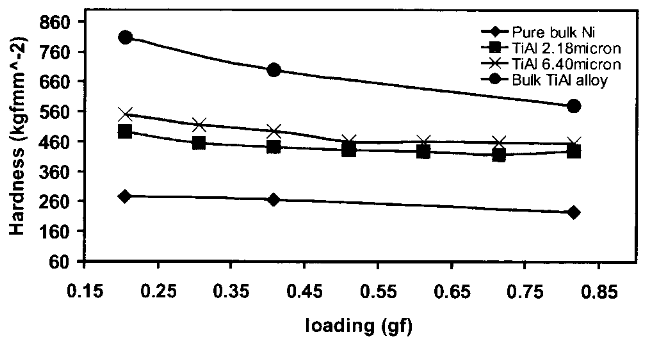


***Figure 2.*** *Nano-hardness for bulk TiAl alloy, bulk Ni alloy and the TiAl film.*

Fig. 3 (a-b) show the composite hardness measured by micro-indentation for the Ti-Al and Ni-Al coatings against indentation depth ($h$) normalized by the film thickness ($t$). It can be seen that the hardness curves for different film thickness coincide when plotted against the normalized depth $h/t$. This suggests that in the microhardness range, the hardness of these films obeys geometric similarity with the film thickness being the characteristic length scale. The hardness values in this range are therefore dominated by strengthening effects due to the film/substrate interface. This geometric similarity with respect to the film thickness, however, breaks down when the indent is very shallow, as the *intrinsic* ISE of the film material itself would then dominate and such an effect does not scale with the film thickness. In Fig. 3(c) are plotted the nano-hardness values of the two Ti-Al coatings. It can be seen that in the nano-hardness range the hardness curves for the two thickness values do not seem to overlap.

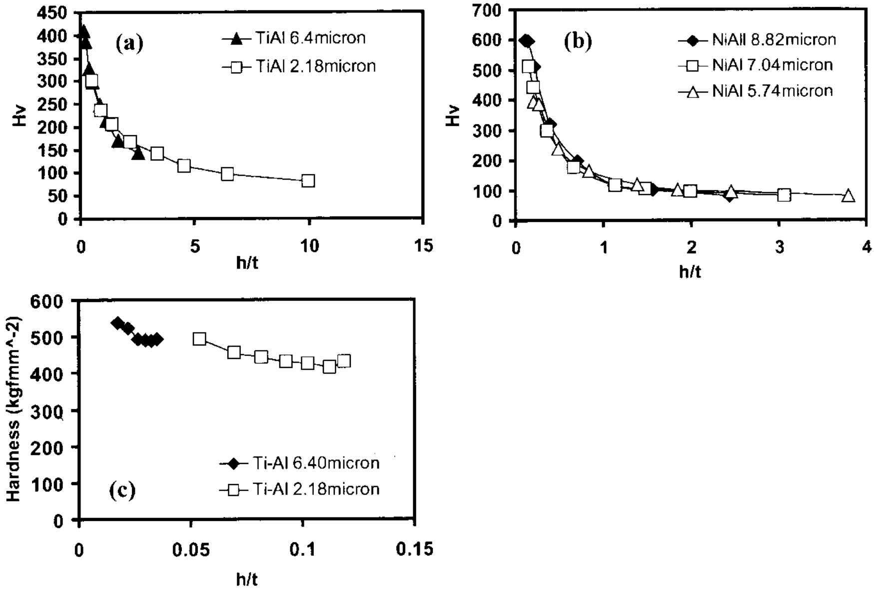


***Figure 3**. (a-b) Micro-hardness against (h/t) for (a) TiAl, (b) Ni-Al films. (c) Nano-hardness against (h/t) for TiAl. h = indentation depth, t = film thickness.*

When the intrinsic ISE is insignificant as in the micro-hardness range, it becomes meaningful to speak of the *true strength* or *true hardness* of the film material itself. In order to determine the true strengths of the films from the apparent hardness, we will now apply two models to analyze the micro-hardness results. The first is the Jönsson-Hogmark (J-H) model [1], in which it is assumed that the film is very hard compared with the substrate, so that once the indenter has pierced through the film, the film merely acts as a rigid interlayer between the indenter and the deforming substrate. The J-H model is more applicable to the post pierce-through situation. In this case, the hardness $H$ is predicted to be

$$H = H_s + (H_f - H_s)\left[2C\left(\frac{t}{h}\right) - C^2\left(\frac{t}{h}\right)^2\right] \quad \text{for } h > t \qquad (1)$$

where $H_s$ and $H_f$ are the intrinsic hardness of the substrate and film respectively, and $C = 2\sin^2 11°$. The second is a model recently proposed by the present authors [4]. In this model, the film and the deforming part of the substrate are pictured as two spherical plastic zones surrounding a hydrostatic cavity. This assumption is more valid when the film and the substrate have no so different strengths and when the indenter has not pierced through the film. The hardness is predicted as

$$H = H_o + 2(Y_f - Y_s)\ln\left(\frac{t}{h}\right) \qquad \text{for } h < t \qquad (2)$$

where $Y_f$ and $Y_s$ are the yield stress of the film and substrate respectively, and $H_o$ is a constant. As both models consider only strengthening due to the film/substrate interface, for reasons stated above, we only analyze the micro-hardness data here, as the nano-hardness values are dominated by intrinsic ISE which does not scale with the film thickness.

In fig. 4(a-d) are shown the measured micro-hardness of the Ti-Al and Ni-Al coatings against $2C(t/h)\text{-}C^2(t/h)^2$ and $2\ln(t/h)$ respectively. The data for both types of coatings fall reasonably well on straight lines. The slopes of the best straight lines in Fig. 4(a) and (b) represent the value $(H_f - H_s)$ according to eqn. (1). The slopes are 863 kgfmm$^{-2}$ for the Ti-Al coatings and 711 kgfmm$^{-2}$ for the Ni-Al coatings. The Ni substrate hardness was determined to be around 64 kgfmm$^{-2}$. Therefore, according to the J-H model, the true hardness of the Ti-Al and Ni-Al film materials is 927 kgfmm$^{-2}$ and 775 kgfmm$^{-2}$ respectively. Using the assumption that yield strength is one-third of hardness, the estimated strength is 3.09 GPa for Ti-Al and 2.58 GPa for Ni-Al.

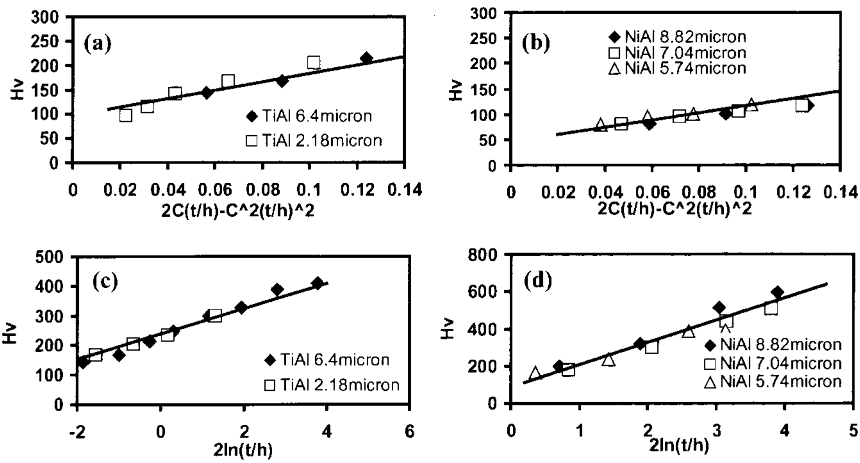


*Figure 4. Micro-hardness against $2C(t/h)\text{-}C^2(t/h)^2$ for (a) Ti-Al, (b) Ni-Al and $2\ln(t/h)$ for (c) Ti-Al, (d) Ni-Al.*

From eqn. (2), the slopes of the best straight lines in Fig. 4(c) and (d) should correspond to $(Y_f - Y_s)$. The slopes for the Ti-Al and Ni-Al coatings are 42.5 kgfmm$^{-2}$ and 120.5 kgfmm$^{-2}$ respectively. A tensile test was performed on the Ni substrate material and its yield strength was determined to be 168 MPa. As a result, the estimated yield strength for the Ti-Al film material is 593 MPa and that for the Ni-Al film material is 1.37 GPa.

The true strengths obtained by the two models are compared in Table III. It can be seen that the values estimated by the J-H model are much higher than those estimated by eqn. (2), namely, about two times for Ni-Al (2.58 GPa vs 1.37 GPa), and five times for Ti-Al (3.09 GPa vs 593 MPa). For the Ti-Al films, the results in Fig. 2 for depths lower than 10% of the film thickness suggest that the expected true hardness of the Ti-Al films should not be greater than 600 Hv. Therefore, it is unlikely that the film should have a yield strength as high as 3.09 GPa as estimated by eqn. (1). Such an over-estimation may be due to the fact that the J-H model assumes the film to be non-deformable, while in practice this can hardly be the case. The estimated strength by eqn. (2) for the Ni-Al films is 1.37 GPa. This may seem high compared to bulk $Ni_3Al$, but as stated before, this is not unexpected because of the extremely fine crystallite structure of the film [5]. Ishida et al [6] have performed tensile tests on sputtered Ti-Ni films which also had a fine nano-structure. They found that their films possessed tensile yield strengths ranging from 650 MPa to 1.5 GPa. It seems therefore that yield strengths in the range of 1±0.5 GPa are common amongst sputtered alloy films.

**Table III**. Film strengths estimated by the two models.

| Jönsson and Hogmark | | Equation (2) | |
|---|---|---|---|
| 3Ni/Al | Ti/Al | 3Ni/Al | Ti/Al |
| 2.58 GPa | 3.09 GPa | 1.37 GPa | 593 MPa |

## CONCLUSIONS

In this study, we have attempted to estimate the yield strength of sputtered alloy films from the apparent hardness values. It is believed that the Jönsson-Hogmark model is not suitable for films other than the extremely hard ones on soft substrates. The model in eqn. (2), on the other hand, gives more realistic results for alloy films on metallic substrates.

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