Analysis of hardness of nanocrystalline coatings of aluminum-rich $\text{Ti}_{1-x}\text{Al}_x\text{N}$

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Abstract. Titanium aluminum nitride coatings were fabricated by a d.c. magnetron sputtering system from a Ti–Al (60/40wt%) target. Coatings were deposited on steel substrates, at a substrate temperature of 250 °C and a bias voltage of –80 V. The nitrogen flow was varied from 1.5–6 sccm and the Ar flow was kept constant at 20 sccm. The morphology and microstructure of the coatings were analysed by X-ray diffraction and scanning electron microscopy. The results of X-ray diffraction showed the presence of two cubic crystalline phases, TiN and AlN, which were confirmed by X-ray photoelectron spectroscopy. The Vicker hardness was obtained by the effective model of indentation. It was observed that the hardness of the coatings decreases from 22.8–9.5 GPa with an increased nitrogen content from 1.5–4.5 sccm. Subsequently, the hardness increased to 22.1 GPa by increasing nitrogen to 6 sccm. The behavior of hardness with grain size variation is consistent with the Hall-Petch relationship. The high value in the hardness of the coatings is mainly attributed to small grain sizes and the compressive stress present.

Keywords. Hard coatings; hardness; fracture toughness; Ti–Al–N.

1. Introduction

The development of hard coatings based on the nitrides of transition metals such as titanium has found increasing application in materials resistant to corrosion and wear (Wolf *et al* 1989; Hirvonen 1991; Ensinger *et al* 1992; Mayrhofer *et al* 2006). The need to determine the mechanical properties of novel coatings and to inspect their production and quality has led to the development of different, faster and more reliable procedures (Bunshah 2001). Nanostructured titanium aluminum nitride ($\text{Ti}_{1-x}\text{Al}_x\text{N}$) was born due to the need to improve the resistance to abrasion and corrosion that titanium nitride (TiN) cannot offer (Münz 1986). Titanium aluminum nitride ($\text{Ti}_{1-x}\text{Al}_x\text{N}$) coatings with high aluminum content ($x \geq 0.7$) deposited by PVD provide high wear resistance, high operating temperatures, oxidation resistance and low thermal conductivity (Endrino *et al* 2006).

It has been shown that the structure of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings depends on the amount of Al added to TiN (Musil and Hrubý 2000). Depending on the x value, it is possible to form nanocrystalline or amorphous nanocomposite coatings with one or two phases, which is a key factor when we are seeking to produce coatings with better wear resistance at high temperatures, where titanium nitride is not effective (Chawla *et al* 2010). In $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings obtained by sputtering, it

has been found that in the interval $0.5 \leq x \leq 0.85$, two kinds of nanocomposites are formed: first, two-phase nanocomposite coatings consisting of a mixture of grains of TiN and AlN with NaCl-type and wurzite-type structure, respectively and second, single-phase nanocomposite coatings composed of a mixture of AlN grains of different crystallographic orientation with a wurzite-type structure. In particular, it has been reported that coatings with atomic ratio Al/(Al + Ti) between 0.54 and 0.69 undergo a phase change from *fcc* to *hcp* phase, causing a decrease in hardness (Kutschej *et al* 2005).

The aim of this study was to fabricate $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings in the interval of $x = 0.70$ – 0.74 in order to obtain high hardness values, in contrast to the low hardness values that can be expected from those already published, due to a transition from a cubic structure to a wurzite structure (Suzuki *et al* 2000). To achieve this, a bias potential of –80 V, a d.c. power of 250 W and a substrate temperature of 250 °C were applied, because these deposition conditions have helped to maintain a high value of hardness (Zywitzki *et al* 1999). These hardness values are analysed by scanning electron microscopy and are explained in terms of their structure and type of linkage present.

2. Experimental

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings were deposited on steel AISI D2 substrates by d.c. magnetron sputtering using a Ti–Al (60/40 wt %)

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target (diameter, 2 in). The substrate was cleaned by rinsing in ultrasonic baths of acetone, ethanol and distilled water. The depositions were carried out under an Ar/N₂ atmosphere and the chamber pressure was kept at 1×10^{-5} mbar. The Ar gas flow was fixed at 20 sccm during sputtering, while the N₂ gas flow was varied in the 1.5–6 sccm range to obtain samples with an Ar/N₂ flow ratio of 3.3 (*M1*), 4.4 (*M2*), 6.7 (*M3*) and 13.3 (*M4*) sccm. The Ti_{1-x}Al_xN coatings were deposited under the following conditions: the d.c. power and the substrate temperature were maintained at 250 W and 250 °C, respectively. In addition, the bias voltage was -80 V, and the deposition time was 2.5 h, with a working pressure of 8.5×10^{-3} mbar.

Vicker's micro-hardness of Ti_{1-x}Al_xN coatings was measured with a microhardness system (MITUYOTO HM-124) applying loads of 10, 25, 50, 100, 200, 300 and 500 gf. The chemical composition of the coatings was determined by energy dispersive spectroscopy (EDS) using a PHILIPS XL30 ESEM scanning electron microscope (SEM). The structure of the Ti_{1-x}Al_xN coatings were analysed by X-ray diffraction (XRD) in a Bruker diffractometer, model D8 ADVANCE, working with Cu K α radiation (1.5406 Å). The morphological images of the Vickers indenter impression and thickness of the coatings were obtained by a PHILIPS XL30 ESEM electron scanning microscope (SEM).

Figure 1. X-ray diffraction patterns for coatings with different Ar/N₂ flow ratios.

The analysis of the surface morphology was carried out by an AFM (dimension, 3100-Nanoscope IV of Digital Instruments). The chemical composition of the *M1* coating was investigated through X-ray photoelectron spectroscopy (XPS) carried out by a JEOL JPS-9200 system with an Mg K α X-ray source. The characteristic of the surface region coating was obtained from an XPS depth profile.

3. Results and discussion

Figure 1 shows X-ray diffraction data from four coatings fabricated to different Ar/N₂ flow ratios: *M1* = 3.3, *M2* = 4.4, *M3* = 6.7 and *M4* = 13.3. The diffraction patterns of the coatings show the presence of two cubic phases, TiN (card # 1-087-0632) and AlN (card No. 25-1495), regardless of the Ar/N₂ flow ratios. No alternate changes in the preferred orientations are observed as the Ar/N₂ flux ratio increases. The coatings showed a preferred TiN (111) and AlN (111) orientation. The presence of TiN and AlN phases is confirmed by XPS, the results of which are shown later.

The chemical compositions and stoichiometry of the coatings obtained by EDS are shown in table 1. The Al content in as-deposited Ti_{1-x}Al_xN coatings, defined as $x = \text{Al}/(\text{Al} + \text{Ti})$, was maintained in the interval of 0.70–0.74 by varying the Ar/N₂ flow ratios. As it has been reported (Morimoto *et al* 1998; Schuler *et al* 2001), due to the vacuum conditions when the samples are prepared, there is always a non-negligible amount of oxygen contamination present in the chamber, which explains the high oxygen content in the samples. It has been reported that at vacuum pressures of $\sim 1 \times 10^{-4}$ Pa the amount of oxygen contamination in the samples is roughly 30–40% (Morimoto *et al* 1998), at conditions that are similar to those reported here.

However, XRD measurements showed that the peak positions of the *M1* coating were located at 2θ values above the standard positions of the TiN and AlN structure, which suggested an increase of compressive stress due to the hindered annihilation of point defects, thus increasing lattice distortion (Donohue *et al* 1999). This behaviour is also observed in the case of *M4* coating. For *M2* and *M3* coatings, diffraction peaks that are very close to the standard peak positions of TiN and AlN were observed, thus revealing the presence of low intrinsic stress.

Figure 2 shows SEM micrographs from the cross-section of the thick deposits for each sample, indicating that the microstructure is predominantly columnar and that the columnar crystals are separated by dense, fine and imperfect

Table 1. Chemical compositions of coatings sputtered to different Ar/N₂ flow ratios.

Sample	% At N	% At O	% At Al	% At Ti	$x = \text{Al}/(\text{Ti} + \text{Al})$	Ti _{1-x} Al _x N
<i>M1</i>	11.7	27.86	44.24	16.20	0.73	Ti _{0.27} Al _{0.73} N
<i>M2</i>	17.79	37.03	33.50	11.68	0.74	Ti _{0.26} Al _{0.74} N
<i>M3</i>	19.47	31.57	35.83	13.13	0.73	Ti _{0.27} Al _{0.73} N
<i>M4</i>	31.8	24.10	31.0	13.10	0.70	Ti _{0.30} Al _{0.70} N

regions. The thickness is obtained via the measurement of the contrast phase by SEM-EDS. The difference in phase contrasts makes it possible to differentiate the interface between the coatings and the substrates. The cross-section corroborates the high homogeneity of the coatings' surface after the deposition process, obtaining thicknesses between 3.5 and 4.5 μm . Finally, our analysis coincides with the views

discussed by various authors (Park and Kim 2001; Rafaja *et al* 2004; Amini *et al* 2011), in which a certain amount of Al added to TiN causes the microstructure to become finer in grain size and more random-oriented in crystallographic direction.

Vicker's hardness of the $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings was obtained by applying a load of 10, 25, 50, 100, 200, 300 and 500

Figure 2. Cross-sectional SEM micrograph showing thickness of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings.

Figure 3. Schematic plot of coated system hardness vs relative indentation depth for all samples.

Figure 4. SEM images obtained during several indentation Vicker's tests showing cracks with radial shape: (a) 100 grf, (b) 200 grf, (c) 100 grf and (d) 100 grf.

grf, with at least five indentations done per load. An indentation working model was employed to eliminate effect of the substrate and to determine hardness of the coating alone (Korsunsky *et al* 1998). The hardness analyses of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings were plotted in accordance with the relative indentation depth, denoted by β . When a logarithmic scale is used for β , a characteristic knee-shaped profile is observed, as shown in figure 3. Under the lowest loads and in the absence of fracture due to the indenter, the curve approaches the value of real coating hardness.

Scanning electron microscopy images of the indentation impressions are shown in figure 4. These SEM images correspond to the first fractures observed with the increase in the load applied. SEM results showed that *M1*, *M3* and *M4* coatings become fractured under an applied load of 100 grf, whereas in the *M2* coating this is observed at 200 grf. In the *M2* coating the lower diagonals are observed. These results suggest that the *M2* coatings show a higher fracture toughness, due to a microstructural dependence of the coatings, as well as the grain size.

The microstructural information obtained from the X-ray line profile analysis (figure 1) as a function of Ar/N_2 ratio is shown in figure 5(a). X-ray line profiles of the coatings were obtained with the Warren–Averbach method (McKeehan and Warren 1953) by using a Pearson VII function. With this method, the X-ray diffraction pattern peaks were corrected for the broadening of the diffraction lines, Lorentz dispersion, and diffraction due to the $\text{Cu-K}\alpha_2$ line and then submitted to Fourier analysis. The Warren–Averbach method assumes that peak widening is due to the size distribution of the crystalline grains and deformations from internal stress in the lattice. As the Ar/N_2 ratio is increased, an interrelationship between hardness and grain size for the TiN and AlN

Figure 5. (a) Dependence of crystalline size of TiN and AlN and hardness of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ coating on Ar/N_2 ratio and (b) dependence of hardness values on average size d of grains.

phases is observed. In figure 5(a), it is observed that the hardness decreases until maximum grain size, which is estimated at ~ 4 and 5 nm for the TiN and AlN phases, respectively

is reached. It increases again if the grain size is under this maximum. According to the latest results, harder coatings

have smaller crystalline grain size and reveal the presence of compressive stress. This behaviour is described by the Hall–Petch relationship and is shown in figure 5(b) (Hall 1951; Petch 1953), in which a decrease in the average size d of grains is observed.

These results are considered very interesting, as they are able to produce hard coatings of TiAlN with a high aluminum content around $x = 0.7$ without formation of the wurtzite phase, which has been considered as the main cause of reduction in hardness, modifying some industrial applications.

Figure 6 shows XPS bands: (a) Al $2p_{3/2}$, (b) Ti $2p_{3/2}$ and (c) N $1s$ for the M1 sample obtained at an Ar/N₂ ratio flux of 3.3. This measurement was obtained at a depth of ~ 300 nm. The results were obtained by subtracting the background with Shirley (1972) method and deconvoluting the spectra through the Gauss–Lorentz method. The deconvolution of the Al $2p_{3/2}$ band (figure 6(a)), gives rise to two peaks. The peak at 74.1 eV can be attributed to the presence of the Al₂O₃ phase, while the neighbouring peak at 73.5 eV corresponds to the AlN phase, which is supported by XRD measurements and by the corresponding N $1s$ peak (figure 6(c)). In figure 6(b), the Ti $2p_{3/2}$ is resolved into three peaks. The peak at 458.3 can be attributed to the Ti₂O₃ phase, which appears normally in this system. The second peak located at 456.1 is attributed to TiN, which is corroborated by the corresponding N $1s$ peaks (figure 6(c)). The last peak is attributed to metallic Ti. The N $1s$ spectra of the coating in figure 6(c) show a typical characteristic of nitride coatings (Shum *et al* 2003). The peak at 396.1 eV can be attributed to the TiN phase and the peak at 396.5 eV corresponds to the AlN phase. These results are consistent with the X-ray diffraction results because both methods provide specific evidence for the presence of *fcc*-TiN and *fcc*-AlN phases.

Figure 6. XPS bands for M1 coatings (a) Al $2p_{3/2}$, (b) Ti $2p_{3/2}$ and (c) N $1s$.

Figure 7. AFM images of TiAlN coatings of surface topography.

The images of the surface topography of the coatings are shown in figure 7, for which a scanning rate of 1.0 Hz was used in an area of $5.0 \times 5.0 \mu\text{m}^2$, each coating showing irregularly shaped agglomerates with a size of about one-half micron. The coatings presented different roughness values, which were in a range between 17 and 51.5 nm. They were obtained through calculations of mean square roughness (RMS). The sample, M3, showed the lowest value of roughness, 17 nm, and a low hardness. The sample, M2, showed an RMS of 37.6 nm, with darker areas than the other three coatings, which may correspond to the nanocrystalline TiN phase.

4. Conclusions

$\text{Ti}_{1-x}\text{Al}_x\text{N}$ coatings were produced by using the sputtering technique, with a high aluminum content and an interval of $x = 0.70$ to 0.74 on AISI D2 steel substrates, and by varying the nitrogen flow from 1.5 to 6 sccm, with increase of 1.5 to 4.5 sccm. SEM analysis permitted an accurate measurement of diagonals of the prints produced by the Vickers indenter and thickness of the coatings, which were in a range between $3.5 \mu\text{m}$ and $4.5 \mu\text{m}$. Through this analysis we determined that the M2 coating showed higher fracture toughness.

By means of XRD, we identified two crystalline phases, TiN and AlN, which were corroborated by XPS. Unlike coatings reported in other studies, both phases have an *fcc* structure, which in this x range leads to the hexagonal phase of AlN, affecting their hardness values. The maximum hardness of 23 GPa was achieved by the flows of nitrogen from 1.5 to 6 sccm.

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