Influence of nitrogen in TiAlNO coatings fabricated by co-sputtering

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Abstract. TiAlNO coatings were obtained on corning glass by means of the co-sputtering technique. Two series were fabricated. In the first one the argon flux was maintained at 12 sccm, while the nitrogen flux was varied in 3, 6 and 9 sccm; in the second one the argon flux was 15 sccm and the nitrogen flux was varied in 2, 3, 4, 5 and 6 sccm, which produced a working pressure variation. For co-sputtering in the first series, three targets were occupied: titanium, alumina and aluminium; meanwhile in the second series, two targets were used: titanium monoxide and aluminium plus an amount of titanium, specifically, 3.5 gr in the aluminium target, occupying 40% of the total effective area of the target. Structural, mechanical and electrical properties were obtained through X-ray diffraction, the Vickers microhardness test and resistivity probes, respectively. For first series, X-ray diffraction detected titanium nitride (TiN) in the crystalline phase; for the second series, aluminium nitride and titanium oxide (TiO)3.38. The difference in the crystalline structure obtained for the series explains the microhardness values; in the first series a maximum value of 20.4 GPa at 2 sccm of nitrogen was obtained, whereas in the second series the maximum value obtained was 8 GPa. As one can observe, the increase in nitrogen flux is not an advantage to hardness, but in electrical resistivity it has a positive effect. The results suggest that TiAlNO is versatile material that could be used for both mechanical and electronic applications; however, it is important to control fabrication conditions.

1. Introduction
Nowadays there is a need for materials with excellent and diverse properties to be applied in different scientific areas like metal mechanics and the electronic industry. Metal transition coatings fabricated by physical methods are used for mechanical, optical and electrical applications due to their excellent thermal and chemical stability1, good wear resistance, attractive colors and excellent diffusion barrier
properties. The most used synthesized coatings are TiN and CrN; however, these coatings have been developed by adding another element like Al, Si, C, Zr, or even by being fabricated in an oxidant environment to obtain oxides (ceramics materials); said addition improves the properties of the material base but depends on property requirements.

H.C. Kim and T.L. Alford studied the behaviour of TiAlxNyOz coatings as barriers against diffusion, using the sputtering technique. For this they used a TiAl target and incorporated gases of Ar, N2 and O2. They found the maximum value to be 4.2 µΩ-cm, and that this value diminishes as the temperature from the thermic treatment increases.

J. Sjölén and co-authors analyzed the structure and the mechanical properties of TiAlNO coatings fabricated with an electric arc. They found hardness values up to 35 GPa, which diminished as the oxygen flow was increased. Such high values of hardness, measured by means of nano-indentation techniques, are attributed to a nano-crystalline phase of TiN immersed in amorphous phases of Al2O3, Ti(O,N), and AlN. Similarly, Fanghua Mei and co-authors obtained 35 GPa of hardness by using a mosaic type of Ti/Al target for sputtering, varying the gases of oxygen and nitrogen. Other authors have focused on studying the chemical stability diagram of this quaternary system.

In this work, TiAlNO coatings were fabricated by co-sputtering under different working conditions; this resulted in two different series of samples showing a difference between each other. The structure, hardness and resistivity of both series were analyzed. In the first series, high hardness and low resistivity values were found, whereas high resistivity and low hardness values were found in the second series.

2. Experimental Details

The two series of coatings were fabricated in a Sputtering V3 INTERCOVAMEX system. In the first series, we used three targets: Titanium-Ti (99.99%) in DC source, alumina-Al2O3 (99.99%) in RF source and silicon-Si (99.99%) in RF source, maintaining Argon gas at 12 sccm and nitrogen flux variation at 3, 6 and 9 sccm. In the second series, we used two targets: titanium monoxide-TiO (99.99%) in DC source and aluminium-Al (99.99%) plus 3.5 gr of Ti in RF source, using Argon flux at 15 sccm and 2, 3, 4, 5 and 6 sccm of nitrogen flux variation. Table 1 describes specific details of coatings series fabrication.

| SERIES | SAMPLES | N2 Flux (sccm) | Ar Flux (sccm) | TARGETS | DC POWER (W) | RF POWER (W) | RF POWER (W) | Thickness (µm) |
|--------|--------|-------------|-------------|---------|-------------|-------------|-------------|--------------|
| 1      | S1     | 3           | 12          | Ti, Al & Al2O3 | 200         | 150         | 200         | 0.5          |
|        | S2     | 6           |             |         |             |             |             |              |
|        | S3     | 9           |             |         |             |             |             |              |
| 2      | SA     | 2           | 15          | TiO & Al+ 3.5 gr Ti | 100         | 250         | N/U*        | 0.5          |
|        | SB     | 3           |             |         |             |             |             |              |
|        | SC     | 4           |             |         |             |             |             |              |
|        | SD     | 5           |             |         |             |             |             |              |
|        | SE     | 6           |             |         |             |             |             |              |

Table 1. Fabrication Details
3. Characterization

3.1. X-ray diffraction

For X-ray analysis, an X-ray diffractometer BRUKER D8 Advance with Göbbel mirror primary optics and scintillation detector was used, along with generator parameters of 40 kV and 40 mA for both sets and with $\theta = 2^\circ$ and $2\theta = 30-90^\circ$. The X-ray diffraction data of the first series in Figure 1 show only the TiN crystalline phase (PDF: 01-087-0632). In the case of the second series, the aluminium nitride (AlN) (PDF: 00-025-1495) and titanium oxide (TiO)$_{3.38}$ crystalline phases (PDF: 01-075-0310) were observed, Figure 2.

3.2. Vickers’ Microhardness

A Vickers’ Microhardness Test Machine (HM-124, MITUTOYO) was used to obtain the mechanical properties of the coatings. The applied loads were 0.001 kgf up to 0.5 kgf during 10 seconds, each one being applied three times. The hardness values of the coatings were obtained by applying Koursunky’s model Eq.1. For the first series the maximum value was 20.4 GPa for S1 and the minimum value was 6.52 GPa for S2. For the second series, sample A (SA at 2 sccm N2) was the hardest with 7.25 GPa, whereas sample C (SC at 4 sccm) was the least hard with 4.85 GPa. A comparison between the series of coatings is shown in Figure 3, where the difference is distinguishable, the value of the least hard sample in Series 1 being almost the same as the maximum value in Series 2.

$$H_{TOT} = H_S + \frac{H_L - H_S}{1 + k\beta^2}$$  \hspace{1cm} \text{Eq. 1}
3.3. Electrical Resistivity

The electrical measurements of the series were obtained with a Resistivity Test Fixture, KEITHLEY 6517-B, 8009. In series 1, all the samples have a semiconductor/insulator behavioural trend with values between $3.88 \times 10^3 \, \Omega \cdot \text{cm}$ and $4.081 \times 10^5 \, \Omega \cdot \text{cm}$; on the other hand, series 2 presented insulator behaviour, the values being between $5.77 \times 10^6 \, \Omega \cdot \text{cm}$ and $9.904 \times 10^2 \, \Omega \cdot \text{cm}$.

4. Results and Discussion

In figure 1, it is observed for the first series that all the diffraction peaks correspond to the TiN crystalline phase. Because there is no evidence of any other crystalline phase in Figure 1, energy dispersive spectroscopy measurements were realized, but only two elements, titanium and nitrogen, were detected. In this case, it was assumed that aluminium and oxygen could not be deposited in the coatings under the initial growth conditions proposed. The nitrogen flow variation causes a change in the preferential crystallographic direction of the coating $S_1$ to $S_2$, which is maintained up to the $S_3$ coating and can be noted as an intensified diffraction peak. Moreover, upon increasing the nitrogen flow it can be observed that the diffraction peak located at $2\theta = 42.8^\circ$ shows a shift to the right with respect to the reference line, which indicates that there are compressive stresses in the coatings. On the other hand, the increase in the nitrogen flow considerably affects the hardness values, decreasing them from 20 GPa to 6.5 GPa. The growth parameters of the first series of coatings were changed without obtaining the values of resistivity, because it was not possible to obtain the quaternary system of TiAlNO.

In the second series, TiAlNO coatings with a thickness of 500 nm were achieved. With XRD, two crystalline phases were identified, AlN and TiO. Upon increasing the nitrogen flow, the diffraction peaks showed a shift toward the left with respect to the reference line, indicative of the presence of tensile stress. At high values of nitrogen flow, the shift and the intensity of the diffraction peak are...
greater. Energy dispersive spectroscopy measurements confirmed the presence of the 4 elements of the quaternary system, Al, N, O and Ti, Figure 4. The harder coating was obtained at 2 sccm and corresponds to the SA coating with a value of 8 GPa; when the value of the nitrogen flow increases, the hardness decreases down to a minimum value of 4.8 GPa for the SC coating. To continue increasing the nitrogen flow, the hardness values are increased again until reaching a value of 6 GPa for the SE coating. Electrical resistivity values decrease with the increase in the hardness values, reaching a maximum value of $5.77 \times 10^6 \text{\Omega-cm}$ for the SC coating; therefore the flow of nitrogen is an important variable to consider in deposition processes, depending on the application required. Growing conditions for the SC coating would favor its application in the diffusion barriers in integrated circuits\textsuperscript{5}, while the SA coating conditions have greater application in the metalworking industry, where high-speed steel parts are used for cutting\textsuperscript{9,11}.

![Fig. 4. Results of EDS confirming the presence of the 4 elements desired.](image)

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