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# The structure and hardness of magnetron sputtered Ti–Al–N thin films with low N contents (<42 at.%)

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**Abstract**

Thin films of Ti–Al–N were deposited by d.c. magnetron sputtering on M2 (AISI) steel substrates. Two targets configurations were used: pure targets of Ti and Al placed at 90° and two facing targets of titanium encrusted with aluminium rods (composite targets). The nitrogen flow was varied from 0 to 12 sccm. The N/(N+Ti+Al) and Al/(Al+Ti) atomic ratios in the films ranged from 0% to 41.9% and 24% to 28.6%, respectively. The deposition rate was almost two times higher for the films deposited from composite targets. Both the deposition rate and the aluminium content started to decrease at 6 sccm for the films deposited from pure targets and only at 12 sccm for the films deposited from composite targets. For both target configurations, polycrystalline α-Ti was deposited at low N contents and, as more nitrogen was added, a progressive loss of crystallinity was observed until amorphous films are deposited. Ti(Al)N was deposited from pure targets at the highest nitrogen content. The hardness of the films deposited from composite targets smoothly increases from 12.5 to 27 GPa with increasing nitrogen. Within the α-Ti nitrogen deposition range, the hardness of the films deposited from pure targets slowly increases from 15 to 17.5 GPa while much higher hardness values were measured for the amorphous and the Ti(Al)N film (36 and 34.5 GPa, respectively).


*Keywords:* Titanium; Aluminium; Sputtering; Magnetron; X-ray diffraction; Vickers hardness test

## 1. Introduction

Low-strength materials, such as aluminium alloys, are used in the mould industry mainly for prototyping purposes as they allow fast and easy manufacturing of the moulds. However, the low-strength materials severely limit the lifetime of the moulds which cannot be used for final production. The use of hard coatings to improve the lifetime of prototyping moulds could allow for the production of a higher number of prototype parts and, in the best case, to use the low-strength materials moulds for the production of low and mid-series. For this purpose, coatings of the Ti–Al system are one of the most promising solutions. These coatings should allow achieving much higher thermal expansion coefficients than the traditional nitride systems [1], such as WN, TiN and TiAlN, reducing the residual stresses in the films. Furthermore, the addition of low N contents should allow improving the mechanical properties of the Ti–Al films, as it is the case for W doped with 5 at.% N [2] and reaching a good compromise between high hardness and low friction coefficient.

In a previous work [3], the structural and mechanical properties of thin films of the Ti–Al system deposited by magnetron sputtering were studied within a large range of chemical compositions. The best compromise between hardness and friction coefficient of the Ti–Al films was found at an Al/(Ti+Al) atomic ratio between 19.9% and 32.5%, which yielded the deposition of dual-phase films (quasi-amorphous+hcp Ti poorly crystallized phases). Following this previous study, the main objective of the present work is to analyze the influence of N addition on the structural evolution and hardness of Ti–Al–N coatings with an Al/(Al+Ti) atomic ratio close to 25%. At industrial level, two main target configurations can be used to deposit Ti–Al–N films: pure targets of Ti and Al or composite Ti–Al targets usually made of titanium targets encrusted with Al rods as the sputtering yield of Al is higher. Comparison of both configurations will also be carried out in this work.

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## 2. Experimental

The Ti–Al–N thin films were deposited by dc magnetron sputtering in a closed-field magnetron system (Teer Coatings UDP 650) using two different target configurations: two individual pure targets of Ti and Al (30 × 17 × 0.6 cm) placed at 90° in the deposition chamber (pure targets configuration) and two titanium targets (30 × 17 × 0.6 mm) with 30 encrusted aluminium rods (8 mm of diameter) facing each other (composite targets configuration). Both composite targets were operated with a 7.5-A current in all experiments while currents of 1.5 and 9 A were applied to the Al and Ti targets, respectively. All films were deposited on polished AISI M2 steel substrates (round substrates with 5 mm diameter and a thickness of 1.5 mm) placed on a rotating cylinder (5 rotations/min). The substrate bias voltage was kept constant at −50 V and a 20-sccm Ar flow was always used, resulting in deposition pressures in the order of 0.16 Pa. Two series of five experimental runs were carried out by varying the nitrogen flow from 0 to 12 sccm. A Ti interlayer was grown during 2 min before film deposition (Ti target current = 7.5 A and bias voltage = −100 V). For this purpose, in the composite target configuration, a third target of pure Ti was used, placed at 90° relatively to the composite targets.

The structure of the coatings was studied by X-ray diffraction (XRD) using a Phillips diffractometer operated in Bragg–Brentano configuration with Co(Kα) radiation. The chemical composition of the coatings was determined by Electron Probe Microanalysis (EPMA) using a Cameca SX-50 equipment. Each presented value is the result of five measurements resulting in a standard deviation less than 0.21 at.% for Al, 0.33 at.% for O, 0.38 at.% for Ti and 0.34 at.% for N. The hardness tests were performed by depth-sensing indentation technique using a Fisherscope H100 with a Vickers indenter and a maximum indentation load of 20 mN. Each hardness value is a result of at least five indentation tests. Due to geometrical imperfections of the indenter and indentations, the $h_p$ values were corrected by the method proposed by Antunes et al. [4].

## 3. Results and discussion

The coating thickness was determined by the ball crater method and yielded values between 1.5 and 2 μm for the films deposited using the pure targets configuration and between 2.6 and 2.9 μm for the films deposited using the composite targets configuration.

The deposition rate of the films obtained using both target configurations is shown in Fig. 1 as a function of the nitrogen flow. The results are presented using two *Y* scales in order to clearly show the influence of the nitrogen flow. For both target configurations, the deposition rate is almost constant up to 3 sccm, assuming values of ≈17 and ≈31 nm/min when pure targets and composite targets are used, respectively. The deposition rate starts to decrease at 6 sccm for the films deposited from pure targets and continuously drops until it reaches ≈13 nm/min at 12 sccm. When composite targets are used, the deposition rate remains fairly constant up to 9 sccm and finally drops to ≈29 nm/min at 12 sccm. As will be discussed later, for both deposition configurations, the observed behaviour of the deposition rate is closely related to the poisoning of the targets by nitrogen gas.

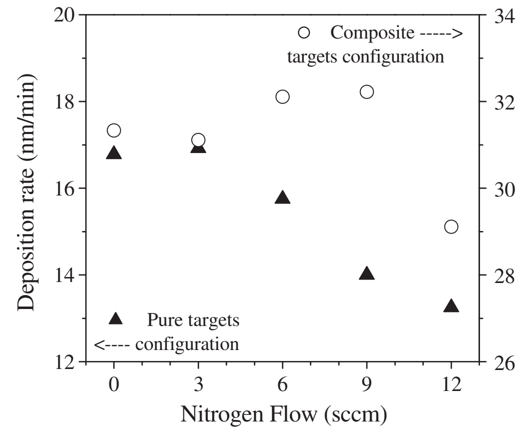


Fig. 1. Deposition rate as a function of nitrogen flow.

The deposition rate of the films prepared from composite targets is almost two times higher than for the films deposited using pure targets. This result is a consequence of the experimental conditions; as in the pure target configuration, the total current applied to the targets (7.5 A to each target) is almost 1.5 times higher than for the pure target configuration conditions (1.5 A for the Al target and 9 A for the Ti target). In industrial conditions, maximizing the deposition rate is an important way of lowering process costs and, within this perspective, the use of composite targets may be a significant advantage since higher deposition rates can be achieved using the same number of targets.

The oxygen and carbon contents in the films were evaluated by EPMA. Oxygen contamination levels between 3 and 5 at.% were measured for both the films deposited using pure and composite targets. The C content of the films was always under the EPMA detection limit (under ≈0.5 at%). The N/(N + Ti + Al) atomic ratio in the films, as measured by EPMA, is shown in Fig. 2 as a function of the nitrogen flow. When pure targets were used, the N content in the films increases almost linearly with increasing nitrogen flow. The same behaviour is observed, up to 9 sccm, for the films deposited using the composite target configuration. However, in the later case, a steep increase is observed as the nitrogen flow rises from 9 to 12 sccm, which is related to the poisoning of the composite targets, as will be explained later. The incorporation of nitrogen in the films is more efficient when the pure target configuration is used, and as a consequence, the maximum nitrogen content reached for the pure target configuration series is significantly higher than for the composite target configuration (N/(N + Ti + Al) = 41.9% and 27%, respectively). This result is mainly due to the higher deposition rate of the films deposited from the composite targets which allow less nitrogen to be incorporated in the films for the same nitrogen partial pressure in the chamber.

Even if the nitrogen flow was the only deposition parameter that varied within each series of films, it is well known that this