

# Microstructure, composition and oxidation resistance of nanostructured NiAl and Ni–Al–N coatings produced by magnetron sputtering

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## Abstract

Nanostructured NiAl and Ni–Al–N thin films were RF magnetron sputtered from a NiAl compound target in different argon–nitrogen atmospheres. The structure and stoichiometry of as-deposited coatings were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Differential thermal analysis (DTA) was also conducted to study the oxidation kinetics of the films at high temperatures. Microstructural and compositional changes of the coatings after isothermal oxidation were investigated using XRD, SEM, and Rutherford backscattering spectrometry (RBS). The results show that: (1) denser and more completely crystallized Ni–Al–N thin films can be tailored through controlled ion bombardment during deposition, (2) nano-composite NiAl–AlN thin films were synthesized with nitrogen atomic concentrations up to 30%, and (3) the NiAl and Ni–Al–N coatings exhibited good oxidation resistance even at temperatures above 1273 K. The addition of AlN to NiAl resulted in decreased activation energies for oxidation. The oxidation study also revealed different rate controlling mechanisms for NiAl and Ni–Al–N (21.4 at.% N) films isothermally oxidized in air at 1273 K.

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**Keywords:** Microstructure; Composition; Oxidation resistance; NiAl; Ni–Al–N; Magnetron; Sputtering; Nanostructured

## 1. Introduction

The B2 intermetallic compound  $\beta$ -NiAl exhibits many attractive properties such as low density (approx. 5.9 g/cm<sup>3</sup>), high melting point (approx. 1995 K), good oxidation resistance, and metal-like electrical and thermal conductivity [1–3]. Consequently, thin film materials based on  $\beta$ -NiAl have been used for a wide variety of engineering applications, including: underlayers in magnetic recording media, high temperature protective coatings, surface catalysts, and thin film thermistors in micro-electronic device applications [1–5]. In this work, coatings in the Ni–Al–N ternary system have been developed as non-sticking (by molten glass) [6], oxidation resistant, and wear resistant [7] coatings for glass molding dies and forming tools. One of our previous papers [8] reported the preliminary study of this coating system. The purpose of this paper is to

systematically report the microstructure, composition and oxidation resistance of nanostructured NiAl and Ni–Al–N thin films produced by magnetron sputtering.

## 2. Experimental procedure

NiAl and Ni–Al–N coatings have been deposited using RF magnetron sputtering in different argon–nitrogen atmospheres from a NiAl compound target synthesized by a one step self-propagating high temperature synthesis (SHS) - consolidation technique [9]. If sputter cleaning of the substrate was performed prior to the deposition, the substrate bias was set to –500 V, producing a glow discharge sputter etching of the substrate. When a titanium adhesion layer was deposited, a 50-nm thick titanium thin film was sputtered from a titanium target using 3 W/cm<sup>2</sup> power from a 40 kHz AC plasma source. The sputter deposition was carried out using a RF power density of 11.2 W/cm<sup>2</sup>, a substrate bias of –50 V or floating potential, and partial pressure control of the

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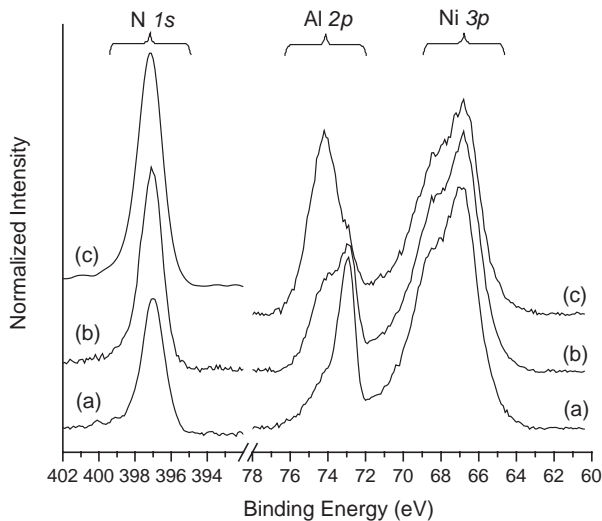


Fig. 1. XPS high resolution spectra of Ni–Al–N thin films deposited on AISI 304 stainless steel in a varied (Ar–N<sub>2</sub>) sputtering atmosphere: (a) 5% N<sub>2</sub>, (b) 10% N<sub>2</sub>, and (c) 20% N<sub>2</sub>.

reactive gas with a total gas pressure of 0.4 Pa. Detailed deposition conditions and characterization procedures are well documented elsewhere [7,8].

A Siemens (KRISTALLOFLEX-810) X-ray diffraction (XRD) unit with Cu K $\alpha$  radiation was used to characterize the film's crystal structure. Both scanning electron microscopy (SEM) (JEOL JXA-840) and scanning transmission electron microscopy (STEM) (PHILIPS CM200) were used to capture photomicrographs and study the film's microstructure. X-ray photoelectron spectroscopy, XPS (KRATOS Model: OEMO5R), was used to investigate the film's composition.

The coatings used for oxidation studies were all deposited with  $-50$  V substrate bias, since the unbiased coatings exhibited poor mechanical properties [7]. To investigate the oxidation resistance of the coatings, two types of experiments were conducted: (1) reaction kinetics from differential thermal analysis (DTA) using a Netzsch model STA-409C simultaneous thermal analyzer; and (2) structure (by XRD), composition (by Rutherford backscattering spectrometry), and surface morphology (by SEM) analyses of thin film samples conventionally oxidized in air using a tube furnace. Rutherford backscattering spectrometry (RBS) (General Ionex, Model 4175) with a 2 MeV  $4\text{He}^+$  ion beam and a backscattering angle of  $171^\circ$  was used in the RBS analyses. Detailed procedures for investigating oxidation behavior of the NiAl and Ni–Al–N coatings were exactly the same as those for Ti–B–C–N coatings which are well documented elsewhere [10].

### 3. Results and discussion

#### 3.1. Stoichiometry/composition

The NiAl and Ni–Al–N thin films deposited in different argon–nitrogen atmospheres exhibited the near equatomic

NiAl phase [8]. For nitrogen partial pressure levels in the working gas environment of 5%, 10% and 20%, the resultant Ni–Al–N films exhibited an increasing atomic nitrogen content of 9.1%, 21.4%, and 29.6%, respectively [8].

As shown in the XPS high-resolution spectra (Fig. 1), varying the sputtering atmosphere, the Ni 3p peaks remained essentially the same as metallic nickel (binding energy of approx. 67 eV) [11]. The Al 2p peak for the Ni–Al–N film formed using 5% nitrogen in the sputtering atmosphere mostly remained at the position for aluminum metal (binding energy of 72.9 eV) [12]. Increasing the nitrogen amount to 10% in the sputtering atmosphere resulted in a shoulder being evident at around the binding energy of 74 eV, which indicates a chemical state shift to a higher binding energy. This shift of Al 2p corresponds to the transition of aluminum to AlN, in excellent agreement with literature [12]. As the nitrogen reached 20% in the sputtering atmosphere, the Al 2p at a binding energy of 74 eV becomes the dominant peak, compared with the peak at the aluminum metal position. This result indicates that a large amount of aluminum was present in nitride form in the film, replacing the intermetallic Ni–Al bonding. All Ni–Al–N films showed a signal in the N 1s region at a binding energy of approx. 397.2 eV, in excellent agreement with the literature [13].

#### 3.2. Microstructure

The microstructure of NiAl and Ni–Al–N thin films was tailored through biasing the substrate. As seen in Fig. 2, applying a substrate bias of  $-50$  V during deposition resulted in larger  $\beta$ -NiAl grains and crystallization of cubic AlN particles. The broadened diffraction lines were used to perform relatively crude measurements of the particle sizes of the crystallographic phases by the well-known Scherrer formula [14]. Comparing the coatings produced with the substrate floating and with a negative substrate bias, the NiAl particle sizes increased from approximately 12–15 nm

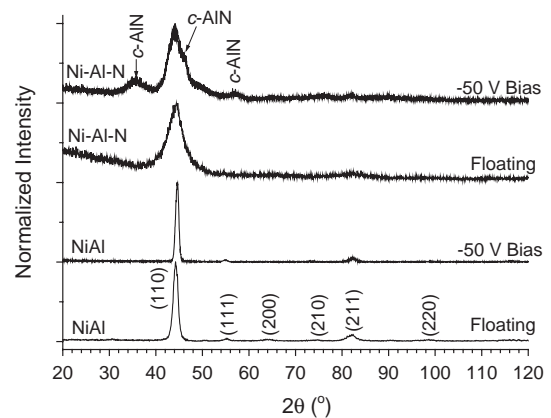


Fig. 2. XRD pattern comparison of NiAl and Ni–Al–N (21.4 at.% N) films deposited on AISI 304 stainless steel substrates without substrate bias or with  $-50$  V DC substrate bias, respectively.

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