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Reactive magnetron sputtering of Inconel 690 by Ar–N_2 plasma

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Abstract

M and M–N coatings, where M is nearly the metal composition of Inconel 690 (57 at.% Ni, 32 at.% Cr, 9.5 at.% Fe…) were sputter-deposited on glass and steel substrates in pure argon and in Ar–N_2 mixtures using a round planar magnetron. The influence of nitrogen gas flow rate inlet in argon on chemical composition and microstructure was studied. The as-deposited ($T<100$ °C) M–N films containing up to 30 at.% nitrogen are a nanocrystalline supersaturated face cubic centered (fcc) solid solution (γ_N). The pure metallic films have a pronounced<111>fcc crystallographic texture, while the M–N films exhibit a strong<100>fcc crystallographic texture. The effect of temperature on the microstructure of M–N films was studied by increasing the substrate temperature during preparation and by tempering of an as-deposited M–N films. For M–N films prepared at 400 °C, the X-ray diffraction analysis reveals a magnetic γ phase with a very low nitrogen content, while electron probe microanalysis gives an overall high nitrogen content in the layer (up to 25 at.%). It is concluded that the layers consist of two phases when prepared or tempered at high temperature ($T>400$ °C): an fcc CrN nitride and a γ (Ni,Fe,Cr) depleted in nitrogen.

Keywords: Deposition process; Nickel; Nitrides; Coatings

1. Introduction

Inconel 690 is a nickel based alloy characterized by a high chromium content (around 30 at.%) that has a broad range of potential applications, for example in the aerospace, navy and marine industries as well as nuclear reactor technology. It is also used in steam generators of pressurized water reactors [1]. We have shown that low temperature plasma assisted nitriding (PAN) treatments of Inconel 690 produce a peculiar phase usually called expanded austenite, *S* phase, *m* phase or γ_N phase [2–4], as observed by Williamson et al. [5]. This phase was originally discovered in low temperature PAN of austenitic stainless steels [6]. Although the identification of this phase is still the subject of many studies [7], it is generally recognized as a metastable supersaturated face cubic centered (fcc) nitrogen solid solution and is referred to as the γ_N phase in this paper. The nitrided layer of Inconel 690 was found to be rather complex. It is constituted by two or even three distinct layers depending on the plasma reactivity [2–4]. These layers are respectively associated to two different metastable fcc nitrogen solid solutions, denoted γ_{N1}, γ_{N2} [2].

Reactive sputtering of Fe–Cr–Ni austenitic stainless-steel targets in different Ar–N_2 gas mixtures offers the possibility to synthesize homogeneous films constituted by the γ_N phase [8–16]. This phase was also obtained by a filtered arc process using an AISI 316 cathode in nitrogen [17]. A study intended to compare the 310 stainless-steel–nitrogen coatings prepared by reactive magnetron sputtering and the diffusion layers obtained by direct current (dc) PAN treatment was conducted in our laboratory [9]. Strong structural analogies were found between the phases prepared by these two techniques. There are not many studies in regards to nickel based alloy deposition. NiCr–N coatings were prepared by dc reactive magnetron [18–20] or radio frequency [21] sputtering for the purpose of nanocomposite material achievement or for electrical properties improvement. It has recently been shown that CrNi–N coatings with low Ni content (<10 at.%) can form superhard materials associated with relatively low Young's modulus compared to other superhard films [18,19].

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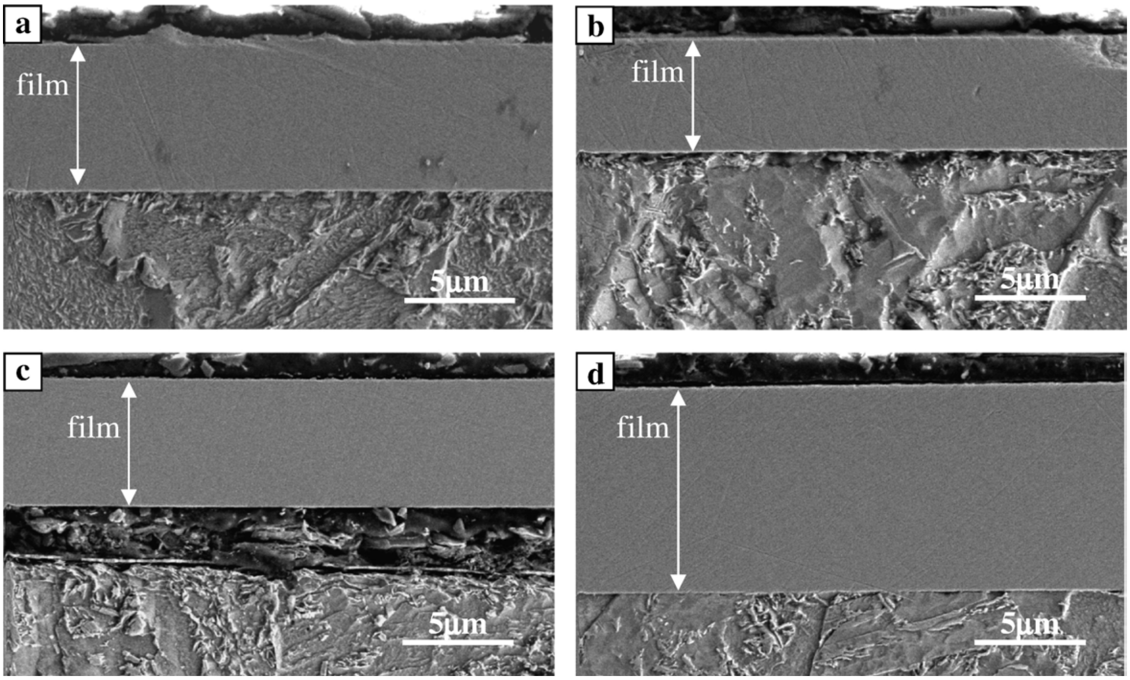

Fig. 1. SEM cross-sectional micrographs of M–N films deposited in different gas mixtures at 400 °C: 30 sccm Ar (a), 30 sccm Ar + 10 sccm N_2 (b), 30 sccm Ar + 25 sccm N_2 (c) as deposited, and 30 sccm Ar + 15 sccm N_2 (d).

Some results obtained by reactive sputtering of Inconel 690 were published for the purpose of comparing layers resulting from low temperature PAN processing [4]. The aim of this paper is to present additional results on reactive sputtering of Inconel 690, especially those concerning the decomposition of the γ_N phase as a function of temperature, by in-situ X-ray diffraction measurements. In addition, a cross-sectional analysis of *an* M–N coating by transmission electron microscopy (TEM) is presented.

2. Experimental

The 62 mm diameter targets were made of Inconel 690 supplied by Tecphy. The bulk composition (wt.%) obtained from electron probe microanalysis (EPMA) analysis is 59.2% Ni, 29.7% Cr, 9.5% Fe, 0.3% Mn, 0.3% Si, 0.2% Al, 0.1% Ti, plus balance. Metal and Metal–Nitrogen coatings (where M is nearly the composition of Inconel 690) were deposited by reactive sputtering in different Ar–N_2 gas mixtures. The reactor, described elsewhere [22], is a 30 l cylinder, pumped down by an oil diffusion pump to a base pressure of about 10^{-4} Pa. The target was powered using a 3 kW and 20 kHz pulsed dc supply at a constant target current of 0.8 A. The pressure was measured using an MKS Baratron absolute gauge, and the inlet gas was controlled by MKS flow meters. In all experiments, the drawn distance was fixed at 80 mm and the argon gas flow rate was 30 sccm. Glass and stainless steel were used as substrates. The stainless-steel substrates were mechanically polished, ultrasonically degreased, rinsed in alcohol, dried in hot air and submitted to in-situ ion etching 30 min immediately before deposition. The samples were placed on a heating holder (substrate temperature up to 500 °C) and, for the steel substrates, biased to −30 V. Without using the heating holder, the as-deposited sample temperature was maintained at less than 100 °C for a 1 h deposition time. The total pressure was between 0.31 and 0.46 Pa as nitrogen was introduced into argon.

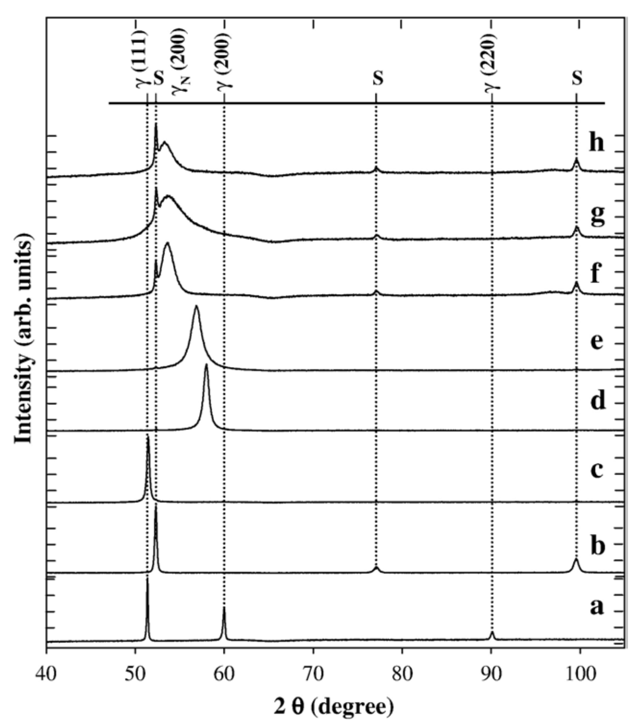

Fig. 2. X-ray diffraction patterns from: (a) Inconel 690 target, (b) bcc structural steel substrate, (c) M film and M–N films for different nitrogen flow rate introduced into the reactor (d) 3 sccm, (e) 5 sccm, (f) 10 sccm, (g) 15 sccm and (h) 20 sccm (curved detector configuration, incident angle 25°).