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Structure and morphology of stainless steel coatings sputter-deposited in a nitrogen/argon atmosphere

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ABSTRACT

Reactive magnetron sputtering was used to deposit coatings from a 304 stainless steel target (nominal composition 18%Cr, 8% Ni, balance Fe). Deposition was carried out in a mixed argon/nitrogen atmosphere with Ar:N_2 ratios of 4, 1.5 and 1, and a total gas flow of 25 sccm for all cases. Substrate temperatures ranged from 150 to 600 °C, along with substrate bias levels from −100 V to −140 V. X-ray diffraction analyses showed the structure of the coatings were strongly temperature dependent: above 450 °C, the films were a mixture of CrN, bcc-Fe and Ni; below 450 °C the S-phase (a N-supersaturated fcc structure) was observed. While this structure is nominally cubic, the commonly observed anomaly of (*hkl*)-dependent lattice constants, where $a_{200} > a_{111}$, was also found in the present study. Area-detector based X-ray diffraction studies, which allowed peak position measurements as a function of the inclination of the diffraction vector (angle ψ), showed a_{200} declined with increasing ψ, but always remained greater than a_{111}, which was relatively constant with ψ. SEM cross-sections for samples deposited below 450 °C had discontinuous, angular crystallites, whereas at higher substrate temperatures the structure had the appearance of a loose particle aggregate. At higher nitrogen has concentrations (Ar:N_2 of 1:1) a more typical columnar structure was found. Hardness testing gave values between 450 and 1968 kg/mm^2, with higher bias, temperatures and N_2 gas concentrations promoting higher hardness levels.

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1. Introduction

Austenitic stainless steel alloys, such as AISI 304 and 316, provide moderate to good levels of strength and toughness along with excellent corrosion resistance in many corrosive environments. However, the wear resistance of these alloys is generally poor, which has motivated research to develop surface treatments that improve hardness and reduce wear rates. One method of surface hardening involves implanting or diffusing nitrogen to create a hardened surface layer. The most common methods involve exposure to a nitrogen-containing plasma at elevated temperatures [1–8]. Ion implantation methods have been used by employing a low-energy (~0.7 keV), high flux ion beam [1] or by use of the plasma immersion ion implantation method [2–4], where the sample is immersed in a plasma and negative high-voltage pulses are applied to the substrate. Typical substrate temperatures range from 300 to 500 °C. The resulting surface treated alloys can provide significantly improved wear resistance in comparison to untreated stainless steel [8].

In parallel with these plasma-based surface treatment studies, research has also been conducted on the deposition of nitrogen-containing stainless steel coatings using reactive magnetron sputtering [9–15]. Saker et al. [9] showed high levels of nitrogen supersaturation in an austenite (fcc) lattice along with a compressive residual stress and improved hardness levels. In contrast with the plasma-treated bulk samples, high levels of nitrogen could be obtained at temperatures as low as 25 °C [15]. In fact, stoichiometric films (MN, M = metal) with a zinc blende structure were reported by Kapaganthu and Sun [11,12].

The crystal structure of both plasma-treated and thin-film coatings of nitrogen-containing stainless steels has been examined in most of these studies, typically using X-ray diffraction methods. For processes using substrate temperatures above 500 °C, CrN is typically formed. Below 400 °C, a supersaturated-fcc phase is formed, and has been variously denoted as "expanded austenite (EA)" [16], γ_N [1,9], the S-phase [2,5], or the m-phase [17,18]. The phase is characterized by a colossal interstitial content (CIC), with nitrogen contents typically between 20 and 40 at.%. X-ray diffraction patterns of this phase show a typical fcc-based structure, with one persistent and notable anomaly – the position of the (200) peak is found to be at lower angles than expected based on the lattice parameter calculated from the position of the (111) peak. This could imply a non-cubic structure (such as tetragonal or monoclinic), both of which have been proposed in past studies [17,18]; however, more detailed diffraction studies using synchrotron radiation failed to produce good matches between these non-cubic structures and typical experimental diffraction patterns [16]. Other explanations for the anomalous (200) peak position include the possibility of multiple phases [1,3], the effects of stacking faults [16], or the effects of stress

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under the assumption of a high degree of elastic anisotropy [19]. A recent study [20] employing high-resolution transmission electron microscopy showed a high density of stacking faults present in the structure. However, the authors proposed that the (200) peak position anomaly was due to a slightly non-cubic structure, namely a rhombohedral structure with an included angle of 91.6°. It is interesting to note the structural details of the S-phase are still controversial despite over 30 years of research investigations.

In the present study nitrogen containing stainless steel films were deposited by reactive magnetron sputtering using an AISI 304 stainless steel target. The purpose of the study was to evaluate the effect of deposition parameters on nitrogen incorporation into the films; the resulting film morphology in relation to nitrogen content and deposition parameters; and the mechanical properties of these films. In addition, the structural nature of the S-phase was further examined using area-detector based X-ray diffractometry.

2. Experimental procedures

Films were deposited in a high-vacuum system (base pressure of 10^{-6} Torr (1.3×10^{-4} Pa)) by reactive magnetron sputtering. A commercial-grade 304 stainless steel target (18% Cr, 8% Ni and 74% Fe) was employed. The target-to-substrate distance was 8 cm. Sputtering was carried out in a mixed Ar/N_2 gas, with the proportion of N_2 in the sputter gas varied by changing the Ar and N_2 flow rate. Three cases were used with the following gas flowrates (in sccm): $20Ar/5N_2$; $15Ar/10N_2$; and $12Ar/12N_2$. The total gas flow rate remained approximately constant at 25 sccm, and the chamber pressure during sputtering was 5 mTorr (0.66 Pa). A 50-mm diameter magnetron sputter gun was used and driven by an rf-power supply. For each film a metallic stainless steel bond layer was first deposited using only Ar and applying a bias of −50 V. The thickness of this layer was approximately 60 nm. All depositions with mixed Ar/N_2 were carried out at 150 W. The film thickness during deposition was monitored using a quartz crystal microbalance and later verified using SEM cross-sections. Deposition times of 2 h were used, with a typical rate of 1 μm/h; several samples were deposited for 5 h to improve peak position measurements in XRD studies.

The structural characterization of the films was analyzed using X-ray diffraction (XRD) on a Shimadzu 6100 equipped with Cu Kα radiation ($\lambda = 1.54$ Å). The measurements were done in the range of 2θ angles between 30–65° and 70-120°, in order to avoid the large Si substrate peak at 69.2°, as well as highlight weaker peaks in the higher 2θ range. Further data analysis was conducted using the Materials Data, Inc. (MDI) Jade 9 program, which was used to fit the peaks and determine peak positions. Additional XRD investigations were carried out using a Bruker/AXS general area detector diffraction system (GADDS), which employed CoKα tube ($\lambda = 1.79$ Å).

The composition of the coatings were applied by X-ray photoelectron spectroscopy (XPS) to determine the atomic percentage of each element and calculate the N/Me ratios. The analyses were carried out on a Kratos Analytical instrument using monochromatic MgKα X-ray source operating at 15 kV and running at a current of 10 mA. For each run, acquisition was carried out in the range of 0 to 1200 eV, with a dwell time of 200 ms, a step size of 1 eV with a pass energy of 160 eV. To remove surface contaminants, a 4 keV Ar^+ ion beam was used to etch the surface before analysis. The peaks analyzed were the Fe 2p, Cr 2p, Ni 2p, N 1s, and O 1s. To determine the accuracy of the results, the metal content measured for each film was renormalized to 100% and compared to the concentrations in 304 stainless steel (73.3 at.% Fe, 19.2 at.% Cr and 7.6 at.% Ni). The average deviation was ±1.5 at.% and the standard deviation in the average was ±1.1 at.%; using these values the error range for the N/Me ratio was determined for each sample.

The morphology of films was studied by fracturing the Si substrates and examining the films in cross-section with a Tescan Lyra FIB-SEM system operating at 6 keV. The same instrument was used to prepare cross-section TEM samples using the FIB method. The TEM samples were then examined in a Zeiss Leo-922 TEM.

The hardness of the films was measured using micro-indentation and a Knoop indenter. Films were tested using a 10-gram load. For films with hardness levels near or above 1000 kg/mm^2, which are of primary interest here, the depth of indentation was ~15–20% of film thickness. Films with lower hardness levels are likely to exhibit some substrate effects, but due to the surface roughness of many films the higher indenter load was necessary to obtain satisfactory results. Nonetheless, the results provide insight into how the substrate temperature, bias and film composition influence the relative film hardness.

3. Results

3.1. Film composition analysis

Films were deposited under a wide variety of deposition conditions and substrate temperatures as described in the previous section. The results of the composition analysis by XPS for selected films are shown in Table 1. The relative concentrations of Fe, Cr and Ni should correspond closely with the nominal composition of 304 stainless steel. To test this, the Cr/Fe and Ni/Fe ratios were calculated as shown in the last two columns of Table I. The average Cr/Fe ratio was 0.28, while for Ni/Fe the ratio was 0.11. These values correspond well with the nominal values of 0.26 for Cr/Fe and 0.10 for Ni/Fe. The oxygen content of the films is also shown, and in most cases the oxygen level was below the detection limit for the XPS (about 2%). In samples where oxygen was detected, the average concentration was 5.4%

The nitrogen content of the film was measured as an absolute value as shown in Table 1 and then the ratio of nitrogen to metal (Fe + Cr + Ni) was calculated from these results. Fig. 1 shows the N/Me ratio vs. substrate temperature for films deposited at various substrate bias levels and sputter gas compositions. The general trend observed here is for the nitrogen level to decrease as the substrate temperature increases, although the extent of this varies with deposition conditions. The samples deposited at −140 V ($20Ar/5N_2$) show the least overall impact of substrate temperature on nitrogen content. The corresponding samples deposited at −100 V show a small decrease up to 450 °C, followed by a sharp decline. The effect of process gas composition is also shown, and it can be seen that at higher N_2 concentrations, $15Ar/10N_2$ and $12Ar/12N_2$, the nitrogen levels in the films are general higher, but undergo a significant decline with substrate temperature. However, little difference is seen between these higher two gas concentrations in terms of nitrogen content in the films.

3.2. X-ray diffraction

Fig. 2 shows the X-ray diffraction patterns for films deposited on Si substrates at −100 V bias, $20Ar/5N_2$, with substrate temperatures ranging from 150 to 600 °C. In addition, reference peak position patterns are shown for CrN, γ_N (S-phase), and bcc-Fe. The results show two general forms of X-ray patterns: one for samples ranging from 500 to 600 °C and a second for 150–350 °C, with the pattern at 450 °C representing a transitional state. At higher temperatures, the patterns match well with the CrN and bcc-Fe reference patterns. In addition, the small peak near 52° *2θ* is close to the expected (200) reflection for Ni (note the (111) of Ni (44.6°) would be nearly coincident with the (110) bcc-Fe peak, at 44.7°). Therefore, the films appear to have a multiphase structure containing CrN, bcc-Fe and a small amount of fcc-Ni.

Films within the lower temperature range are nominally consistent with an fcc diffraction pattern, showing (111), (200), (311) and (222) reflections, as expected within the scanned ranges (the (220) cannot be observed due to Si substrate peak overlap). The reference γ_N pattern was calculated using a lattice parameter based on the position of the (111) peak at 150 °C. The corresponding (200) peak is shifted significantly from position that would be expected based on this calculation.

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