Metallography of Sputter-Deposited SS304+Al Coatings

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Received: 31 May 2013 / Revised: 24 July 2013 / Accepted: 7 August 2013 / Published online: 10 September 2013
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Abstract Plasma-enhanced magnetron sputtered coatings of 304 stainless steel (SS304)+Al containing nominally 0, 4, 7, and 10 wt% Al were deposited on SS304 substrates. The sputter-deposited coatings were characterized for their phase formation and grain size using x-ray diffraction, scanning electron microscopy, and transmission electron microscopy techniques. The sputter-deposited SS304 coatings with no Al contained the metastable phases α and σ , while all other coatings that contained different levels of Al showed the presence of equilibrium phases, namely α -ferrite and B2. The grain size in the coatings varied from nanocrystalline to micron size and showed an increasing trend with an increase in the Al content. Reasons for the formation of the metastable phases and variation of grain size with the Al content in the coatings are discussed.

Keywords Electron microscopy · Stainless steel · Sputter deposition · Metastable phases · Phase transformation

Introduction

Sputter-deposited coatings containing nanocrystalline or ultrafine grains have been shown to exhibit superior cyclic oxidation resistance [1, 2] and corrosion resistance [3, 4]

compared to their counterparts with coarse grain sizes. This was explained on the basis of the formation of a continuous oxide scale on the surface by the selective oxidation of reactive elements such as chromium (Cr), aluminum (Al), or silicon (Si) and their higher diffusivity in the fine-grained iron (Fe)-, cobalt (Co)-, and Cr-based materials [5]. The oxide scales in nanocrystalline coatings have been shown to form at much lower concentrations of the reactive elements, which also exhibit better adherence and resistance to spallation [6–8]. In recent years, there has been interest among different research groups on sputter-deposited Fe–Cr–Ni (steel) coatings containing Al as a reactive element [8–13]. In an earlier work, Cheruvu et al. [9] sputter-deposited 304 austenitic stainless steel (SS304)+Al coatings on SS304 substrates with different Al concentrations and studied their cyclic oxidation resistance. In their work, the sputter-deposited SS304+ x Al (where $x = 0, 4, 7$, and 10 wt%) coatings with and without Al showed better cyclic oxidation resistance compared to uncoated SS304. We have carried out a detailed microstructural analysis of these coatings. The microstructural features of the SS304+10 wt% Al coatings were reported earlier [14]. The objective of this article is to report on the crystallographic and microstructural observations of SS304+ x Al ($x = 0, 4, 7$, and 10 wt%) coatings prepared by sputter deposition. Since the grain size plays an important role in the cyclic oxidation resistance, we also present the grain size measurements and their variation with Al content, in addition to the phase analysis of the four coatings.

Experimental Procedure

Figure 1 shows a schematic representation of the experimental procedure adopted in this investigation. The four coatings of nominal composition Fe–18Cr–8Ni– x Al

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($x = 0, 4, 7$, and 10 wt%) were deposited on the SS304 substrate using plasma-enhanced magnetron sputter deposition (PEMS) method. (Henceforth, the Al content in the coatings will be referred to only by the Al content, without mentioning the wt%). Two targets, one of SS304 and the other of Al, were used. The compositions of the SS304 target and SS304 substrate are listed in Table 1.

In this dual-target PEMS coating process, the power on the SS304 target was 4 kW while the power on the Al target was varied with the Al content; 0.4 , 0.7 , and 1.1 kW, respectively, were used for $x = 4, 7$, and 10 Al. SS304 and Al were co-sputtered simultaneously onto the SS304 substrate while the substrate was rotated to achieve a uniform coating. The resultant coating thicknesses after 4 – 5 h of deposition were 27 , 28 , 28 , and 32 μm for the $0, 4, 7$, and 10 Al, respectively. The minimum distance between the target and the substrate was 85 mm.

The four as-deposited coatings were characterized by x-ray diffraction (XRD), scanning electron microscopy, and transmission electron microscopy methods. XRD was also carried out on the SS304 target and SS304 substrate for comparison purposes. XRD was performed using Cu K α ($\lambda = 0.1541$ nm) radiation, and the patterns were recorded in the 2θ range from 20° to 100° . The constituent phases were identified and their lattice parameters were calculated using the Nelson–Riley extrapolation function [15].

The surface morphology and composition of the coatings were evaluated using scanning electron microscopy while the microstructural features were evaluated using a transmission electron microscope, operated at 300 kV. Bright field (BF), dark field (DF), selected area diffraction (SAD), and energy dispersive spectroscopy (EDS)

techniques were utilized for this study. Specimens for transmission electron microscopy examination were prepared mainly using focused ion beam (FIB) ex-situ lift out technique. Other preparation methods also were used, e.g., FIB in-situ lift out and also mechanical thinning combined with ion milling in the final stage was also used. The thinned transmission electron microscopy specimens were placed on carbon-coated Cu grids and were plasma cleaned before each transmission electron microscopy observation. The microstructural features were similar irrespective of the sample preparation method used.

Results

X-ray Diffraction

Figure 2(a) shows the XRD patterns of the SS304 target and the SS304+0Al coating. The XRD pattern of the SS304 target showed mostly the presence of the austenite (γ) phase, as expected; a very small amount of the ferrite (α) phase was also present. The austenite phase had the face-centered cubic (FCC) structure with a lattice parameter of $a = 0.3590$ nm. In contrast, the SS304 coating exhibited a complex diffraction pattern showing predominantly the ferrite (α) phase, along with an intermetallic phase sigma (σ). The detailed peak indexing of the XRD pattern of the SS304 coating is presented in Fig. 2(b). The lattice parameter(s) of the observed α phase with the body-centered cubic (BCC) crystal structure was $a = 0.2875$ nm and those of the σ phase with the tetragonal structure were $a = 0.884$ nm and $c = 0.458$ nm.

Figure 3 shows the XRD patterns of all the four coatings. The vertical lines represent the angular positions of the (110), (200), (211), and (220) peaks of the ferrite (α) phase. Even though the 2θ positions of the peaks were matching with those of the powder diffraction data of ferrite, the relative intensities of the peaks did not match, suggesting that texture exists in the coatings. The relative intensity of the (110) peak was much higher than the standard value (and also of the other peaks), from which we concluded that (110) texture is present in the SS304+4Al and SS304+7Al coatings. On the other hand, the intensity of the (200) peak is much higher in the SS304+10Al coating suggesting a (200)-type texture. Another difference was that in the SS304+10Al coating, there was an additional peak present at 2θ of approximately 31° , which could perhaps belong to the ordered cubic B2 phase.

The precise lattice parameters of the four coatings were calculated from the positions of the diffraction peaks and are listed in Table 2. It is noted that the lattice parameter of the α -Fe phase increased slightly with the Al content up to 7 wt% and then remained virtually constant.

Fig. 1 Schematic representation of the experimental procedure followed to prepare and characterize the coatings

Table 1 Composition (in wt%) of the target and substrate used for sputter deposition

Element	Cr	Ni	Si	Mn	Mo	C	S	P	N	Fe
Target	18.52	8.13	0.41	1.36	0.33	0.01	0.16	0.03	...	Balance
Substrate	18.25	8.09	0.36	1.25	0.35	0.02	0.00	0.03	0.32	Balance

Fig. 2 (a) XRD patterns of the SS304 target and the SS304 coating. While the target shows predominantly the FCC- γ phase, the coating shows the presence of the BCC α -ferrite and BCT- σ phases. (b) Detailed indexing of the XRD pattern of the coating giving the indices of the different diffraction peaks from the α (marked inside rectangles) and σ phases (all other indices)

Scanning Electron Microscopy

Figure 4 shows the scanning electron micrographs of the as-deposited SS304+Al coatings in plan view; all exhibit different surface morphologies. The coating without any Al content (SS304+0Al) exhibits convex shape grain topography as shown in Fig. 4(a). The SS304+4Al coating (Fig. 4b) shows platelet-type morphology of aligned grains with preferred orientation among the grains. On the other hand, the SS304+7Al coating (Fig. 4c) exhibits finely

Fig. 3 XRD patterns of the SS304+Al coatings with different Al contents. Except for the four α peaks (vertical lines) in the SS304 coating, all other peaks belong to the σ phase. Note that the SS304+4Al and SS304+7Al coatings have the (110) texture, while the SS304+10Al coating has the (200) texture

Table 2 Precise lattice parameters (a) calculated from the peak positions in the XRD patterns of the target and the SS304+Al coatings

Sample	wt% Al	Phase	Crystal structure	a (nm)	c (nm)
Target	0	Austenite	FCC	0.3590	...
SS304+0Al	0	Ferrite	BCC	0.2875	...
		σ	Tetragonal	0.8840	0.4580
SS304+4Al	4	Ferrite	BCC	0.2881	...
SS304+7Al	7	Ferrite	BCC	0.2885	...
SS304+10Al	10	Ferrite	BCC	0.2885	...

divided pyramid-type surfaces. Finally, the SS304+10Al coating shows a bimodal grain structure with floral-type grains as shown in Fig. 4(d).

Transmission Electron Microscopy

SS304 Coating

Figure 5(a) shows a BF image of the as-deposited SS304 coating (SS304 without any Al). The microstructure contains predominantly nanocrystalline columnar grains oriented perpendicular to the substrate. Throughout the

Fig. 4 Scanning electron micrographs from SS304+Al coatings. (a) SS304+0Al: smooth morphology with separation between the grains, (b) SS304+4Al: preferred orientation, (c) SS304+7Al: pyramid grain morphology, and (d) SS304+10Al: floral-type morphology

Fig. 5 (a) Typical bright-field electron micrograph showing the presence of nanometer-sized columnar grains in the SS304 coating. These columnar grains are oriented in a direction parallel to the direction of deposition. (b) Semi-ring SAD pattern with indexing that demonstrates the presence of the two phases— α and σ in the SS304 coating

microstructure, the columnar grains exhibit a network of dark regions, and electron diffraction was used to identify the phase(s) responsible for the dark network.

Figure 5(b) shows a selected area electron diffraction (SAD) pattern. In conformity with the result of the XRD pattern, this SAD pattern clearly confirmed the presence of the two phases (σ and α) in these samples. Most of the continuous rings in all the SAD patterns from this sample originate from the ferrite phase, while the spotty, and occasionally faint, rings arise from the σ phase. DF micrographs were recorded to evaluate the distribution of the phases. Figure 6(b) shows the DF image recorded from the faint rings in the SAD pattern obtained from Fig. 6(a). Since the dark network in Fig. 6(a) lighted up in the DF

image, it was concluded that the dark network belongs to the σ phase [16].

SS304+4Al Coating

Figure 7(a) shows a typical BF electron micrograph from the SS304+4Al coating. The grain size distribution varied quite significantly. (For the purpose of the present investigation, we have defined the grain size as the width of the columnar grains). While there were several grains with a columnar width of less than 100 nm, there were also grains with sub-micron size and some that were more than a micron in size. Figure 7(b) shows an SAD pattern of this coating. The inset SAD pattern in Figure 7(b) clearly

Fig. 6 (a) Bright-field and (b) Dark-field transmission electron micrographs from one of the σ containing areas. Based on diffraction and dark-field evidence, it was inferred that the dark network belonged to the σ phase

Fig. 7 (a) Densely packed columnar grain structure in the bright-field transmission electron micrograph of the SS304+4Al coating. (b) SAD pattern from a single grain. *Inset* indexing reveals the presence of α with [001] zone axis. Presence of B2 phase can also be deduced from the superlattice spots in the SAD pattern, even though these spots are very weak

shows the presence of superlattice spots in the [001] zone axis, suggesting that the B2 phase is also present in this coating. But, the intensity of the superlattice spots in the SAD patterns in the same zone axis is much weaker than in SS304+7Al and SS304+10Al coatings. Hence, it was concluded that the B2 phase is the minor phase and α -ferrite the major phase. XRD patterns from this coating, however, did not reveal the presence of the B2 phase and this shows that the B2 phase was localized, and its quantity was lower than the detection limit by XRD.

SS304+7Al Coating

Figure 8 shows two BF electron micrographs of the SS304+7Al coating. Similar to the SS304+4Al coating, the columnar grain size in this coating ranges from a few nanometers to more than one micrometer. It was observed from Fig. 8(b) that both large and small grains co-existed as nearest neighbors.

Figure 9 shows single crystal SAD patterns from the larger grains in two different orientations. The SAD

patterns indicated that the phase was either α -ferrite, B2, or both. As the superlattice spots could not be observed in the [111]-type zone axis, the presence of the ordered B2 phase was determined from the weak superlattice spots, which were obtained by tilting the sample toward the [001] zone axis.

SS304+10Al Coating

Figure 10(a) shows a BF electron micrograph from the SS304+10Al coating. The microstructure exhibited uniformly distributed columnar grains, which grew in a direction perpendicular to the substrate. The average grain size in this sample was relatively large reaching a maximum of approximately 3 μm .

SAD patterns (Fig. 10b) confirmed the existence of the ordered B2 phase and/or α -phase. Detailed transmission electron microscopy and three-dimensional atom probe microstructural analysis of this coating were reported in an earlier publication [14].

Fig. 8 (a), (b) Bright-field electron micrographs of the SS304+7Al coating. Dense columnar grains (without any porosity) were observed in this coating. A few grains are very large compared to the others as seen in (b)

Fig. 9 SAD patterns from the SS304+7Al coating. Electron beam parallel to (a) $[1\bar{1}1]$ zone axis and (b) $[001]$ zone axis (indexed)

Fig. 10 (a) Microstructure of the SS304+10Al coating in the as-deposited condition. (b) An indexed SAD pattern from the SS304+10Al coating shows the presence of both the fundamental and superlattice spots

Variation of Grain Size with Al Content

As mentioned earlier, the grain size was measured in terms of the columnar grain width (CGW). Figure 11 schematically shows the method by which the grain size was quantified. The width of each grain was measured and recorded as the size of that particular grain. If a grain was tapered, the maximum CGW of the grain was recorded as

the grain size. The size of each observed grain was measured and recorded as a data point. All data points were grouped for each coating and the grain size was plotted as a function of measured grain number from the lowest to the highest size.

Figure 12(a) shows the variation of grain size of the coatings with different Al contents. The grain size of a minimum of 50 grains was measured in each case and

Fig. 11 Method of measuring the grain size in the as-sputtered coatings

plotted from the smallest size to the largest size. In the SS304 (without any Al) coating, the grain size varied from about 20 to 270 nm with an average of 100 nm. In the SS304+4Al coating, the grain size varied from about 30 nm to 1.2 μm with an average grain size of 290 nm. Similarly, the grain size of the SS304+7Al coating was observed to vary from 20 nm to 1.6 μm with an average of 320 nm. Finally, the grain size of the SS304+10Al coating was found to vary from as low as 130 nm to as high as 2.8 μm with the average grain size of 980 nm.

The average grain size of the coatings increased with increasing Al content in the coatings as shown in Fig. 12(b). There is a significant increase in the average grain size from 0 to 4Al and from 7 to 10Al. However, there is no significant difference in the average grain size in the 4 and 7Al coatings. The error bars on the chart show standard deviation and the minimum and maximum values of the grain size are also indicated for each Al content. The standard deviations in the measurement of the grain sizes in the four coatings were 50, 280, 330, and 620 nm, respectively, in the order of increasing Al content. The standard deviation values also increased with the Al content, indicating that the addition of Al increased the spread in grain size variation.

Discussion

Phase Formation in the SS304+Al Coatings

SS304 Coating: Formation of the α -Ferrite Phase

From both XRD and SAD patterns, it was noted that α -ferrite and σ phases formed in the SS304 (i.e., Al-free) coating. The columnar grains predominantly consisted of the α -ferrite phase and the DF micrographs confirmed that the network of dark areas comprised the σ phase. Formation of the α -ferrite phase in sputter-deposited SS304 was

Fig. 12 (a) The variation of grain size in the SS304+Al coatings with different Al contents. (b) Effect of Al content on grain size in the SS304+Al coatings. The *extreme bottom* and *top* of the *lines* indicate the minimum and maximum grain sizes in each of the coatings. The *thick vertical lines* represent the standard deviation range of the grain size variation

in agreement with other studies in the existing literature [17–27]. In addition to vapor deposition, other non-equilibrium processes such as rapid solidification processing [28, 29], laser processing [30], and mechanical alloying [31] have also been shown to result in the formation of the ferrite phase from austenitic SS304.

Several explanations have been postulated by researchers to explain the formation of the ferrite phase in the as-sputtered condition, even though the austenitic stainless steel has an FCC structure under equilibrium conditions. Since Ni is a strong austenite stabilizer, the quantity of Ni becomes important in determining the relative stabilities of the ferrite and austenite phases.

Zhang et al. [24] related the formation of BCC ferrite to marginal Ni depletion from 8 wt% in the SS304 target to 7.3 wt% in the sputter-deposited films. Cusenza et al. [25] suggested that the phase selection in this system is related to

three factors: (i) the nanocrystalline grain size of the sputter deposit (30–80 nm), (ii) Ni content, and (iii) substrate temperature during deposition. The driving force for this phase transformation was assumed to be the variation of surface Gibbs free energy as a function of the smaller grain size, due to Gibbs–Thomson effect. They further suggested that a minimum of 9–10 wt% Ni was required to obtain the austenite phase in sputter-deposited SS304 samples at temperatures lower than about 300 °C, while about 6–7 wt% Ni was enough at deposition temperatures of above 650 °C. If these conditions are not satisfied, then a metastable phase, e.g., α -ferrite with the BCC structure was reported to form.

Our results are in agreement with these reports. While our SS304 target contained about 8.1 wt% Ni, the SS304 coating had only about 7.0 wt% Ni. Further, the grain size of our coatings is comparable to that of Cusenza et al. [25]. Additionally, our deposition temperature (estimated to be ~ 300 °C) is much lower than 650 °C required to produce the austenite phase at this Ni content. All these factors, which are in agreement with the three conditions mentioned by Cusenza et al. [25], favored the formation of the ferrite phase in our sputter-deposited SS304 coating.

SS304 Coating: Formation of the σ Phase

σ phase is a complex intermetallic phase known to be present in at least 43 binary systems [32]. In steels, it is generally observed at relatively high temperatures and usually forms after prolonged heat treatments together with a higher content of σ -forming elements like Cr, V, Nb, and Mo [33]. Precipitation of the σ phase typically requires hundreds of hours and high temperatures between 500 and 800 °C [34–36]; its formation was observed to occur faster during friction stir welding [37] and also during mechanical alloying [38].

Formation of the σ phase during vapor deposition of 304-type austenitic stainless steels was briefly reported by the current authors [14, 16]. Other reports on σ phase formation in Fe–Cr–Ni steels were limited to Cr-enriched compositions [39–41] or Cr-based Cr–Ni–Fe ternary alloys [42]. The influence of several factors, namely nanocrystalline grain size, strain in the coatings, and enrichment of alloying elements Cr and Ni was discussed; but none of these factors could satisfactorily explain formation of the σ phase in sputter-deposited SS304 coating [16]. It is noteworthy, however, that vapor deposition of SS304 did not lead to σ phase in majority of the earlier work [17–27]. This clearly indicates that the conditions in sputter deposition processing used in our current study are different from those employed by others.

SS304+xAl Coatings: Ferrite and B2 Phases

Ferrite was the main phase in the as-deposited SS304+4Al, SS304+7Al, and SS304+10Al coatings. Since Al is a BCC

stabilizer, it is not surprising to observe the formation of α -ferrite in these coatings. None of the three coatings contained the σ phase. With the addition of 4 wt% Al, formation of the σ phase was completely suppressed. It is also interesting that, along with the suppression of the σ phase, Al addition resulted in the formation of the (ordered) B2 phase. This is clear from the faint superlattice spots that appeared in the SAD patterns even at low Al content; however, ordering is more pronounced at higher Al contents. The SS304+7Al coating demonstrates the importance of the transmission electron microscopy technique in phase identification compared with XRD. While the superlattice spots could be clearly observed in the SAD patterns in the transmission electron microscope, no such peaks corresponding to the superlattice structure were seen in the XRD patterns. It is speculated that the ordered regions were too localized and too few in quantity to be detected via XRD. Utilizing high resolution transmission electron microscopy and the fast Fourier transformation technique, the presence of B2 domains in localized regions was demonstrated in our earlier work [14].

The ternary Fe–Cr–Ni and Fe–Ni–Al phase diagrams were used to compare the phases identified in the sputter-deposited samples with the phases predicted under equilibrium conditions. The main elements of SS304+Al alloys make a quaternary system (Fe–Cr–Ni–Al). In order to determine the equilibrium phases of these alloys, an assumption was made to simplify the quaternary system to a ternary one by assuming that Cr behaves similarly to Fe, thus reducing it to the ternary Fe–Ni–Al system. This assumption seems reasonable, since both Fe and Cr have the same crystal structure (BCC) and similar lattice parameters ($a_{\alpha\text{-Fe}} = 0.288$ nm and $a_{\text{Cr}} = 0.287$ nm). Figure 13 shows the truncated Fe–Ni–Al ternary phase diagram [42] in which 4, 7, and 10Al compositions are indicated with the three filled circles. At these compositions, two phases are present in the phase diagram at 20 °C; α -ferrite (indicated as α_1) and B2 (indicated as α_2). Even at a temperature of 600 °C, the phases are the same [42]. This assessment of phases from the ternary equilibrium diagram is in excellent agreement with our XRD and transmission electron microscopy results. Hence, it is possible to conclude that sputter-deposited coatings contained the equilibrium phases in the SS304 alloys to which Al was added.

From the ternary Fe–Ni–Al phase diagram (Fig. 13) and also from the Fe–Cr–Ni phase diagram, it is clear that at the composition of the SS304, the equilibrium phase is γ (austenite); however, on sputter deposition, the phases formed are α (predominant) and σ . Since sputter deposition is a far from equilibrium processing method [43], it is possible that metastable phases could form during this process. Even though a clear explanation is not readily available, it is reasonable to conclude that formation of the

Fig. 13 Truncated ternary Fe–Ni–Al phase diagram at room temperature (20 °C) [42]. Two phases—ferrite (marked as α_1) and B2 (marked as α_2)—are present in alloys containing 4, 7, and 10Al. Increase in the Al content increases the relative amount of the B2 phase

metastable phases is related to the chemical interaction behavior of Al with the elements of the SS304 alloy. Al has a very high negative heat of mixing with both Fe and Ni [44]; therefore, Al interacts readily with Fe and Ni and forms equilibrium phases. On the other hand, in Al-free alloys, even though Fe, Ni, and Cr still have a negative heat of mixing, the values are lower and therefore may produce metastable phases.

Grain Size

Figure 14 shows the overall bar chart of the average grain size distribution in the coatings. The grain sizes are classified into four ranges, the first one is the grain size range containing CGW less than 100 nm (Zone A), the second range is from 100 nm to 1 μ m (Zone B), the third is from 1 to 2 μ m (Zone C), and the last is from 2 to 3 μ m (Zone D). The percentage of small grains (with <100 nm in grain size) decreased significantly with an increase in the Al content. In contrast, Zone B and Zone C exhibited an increase in the percentage of small grains with increasing Al content (except in 10Al in Zone B). Large grains were not observed in Zone D, except in the SS304+10Al coating. The above data indicate that, with an increase in the Al content, the fraction of nanocrystalline grains decreased and the fraction of the sub-micron and micrometer-sized grains has increased with increasing Al content. From this observation, it can be inferred that the fraction of the larger grains increased with increasing Al content in the coatings (Fig. 15a).

Reasons for Grain Growth

In the present discussion, increase in average grain size with increasing Al content is attributed to two reasons. First is the power applied on the Al sputtering target and

Fig. 14 Histogram of SS304+xAl ($x = 0, 4, 7$, and 10) coatings and their grain size distributions. Zone A grains with <100 nm size; Zone B grains with size from 100 nm to 1 μ m; Zone C grains with size from 1 to 2 μ m; Zone D grains with size from 2 to 3 μ m

Fig. 15 Effect of Al content on the (a) average grain size and (b) texture as measured from the relative intensities of the (110) and (200) peaks of the SS304+xAl ($x = 4, 7$, and 10Al) coatings

consequent rise in deposition temperature of the coatings. Usually, higher sputtering target powers increase thermal energy of ions and raise the temperature of the resultant coatings [45]. Further, the sputtering powers used for depositing the coatings in this study are hundreds of watts, which are much higher than those typically used for making thin films (few tens of watts). Moreover, higher target powers were used for higher Al contents, which result in higher temperatures of the deposits with increased Al content. Based on the nature of the columnar grains (fibrous, V-shaped, linear-type grains with and without porosity) in the overall microstructure, approximate deposition temperatures of the coatings were estimated [16]. These were 259 °C (but up to 436 °C) for 4Al, 251 °C (up to 426 °C) for 7Al, and 416 °C (up to 588 °C) for 10Al coatings. These higher deposition temperatures were one of the reasons for the observed large grain sizes.

The second possible reason for grain growth is the presence of (200) crystallographic texture. It has been reported that surface or interfacial energy minimization during grain growth leads to the development of restricted crystallographic orientations; in other words, texture in thin films [46, 47]. While the (110) texture was present in the SS304+4Al and SS304+7Al coatings, the texture changed to (200) in the SS304+10Al coating, suggesting that the texture was changing with an increase in the Al content in the coating. Figure 15(b) shows the plot between $I_{(200)}/I_{(110)}$, which is the ratio of integrated intensity of the (200) peak to that of the (110) peak, and the Al content. The value of $I_{(200)}/I_{(110)}$ increases with increasing Al content moderately from 4 to 7Al and strongly from 7 to 10Al coatings. This trend is very similar to the trend of grain size variation with the Al content (Fig. 15a), suggesting that Al addition probably has an influence on texture, which in turn has an influence on the grain size.

The presence of (200) texture in the higher Al content coatings can also be due to the higher substrate temperature and a few other parameters that may be varied during the sputter deposition process. Feng et al. [48] systematically studied the texture evolution in sputter-deposited Cr and reported that (i) higher substrate temperatures (250 °C), (ii) lower sputtering powers (25 W), and (iii) moderate Ar pressures (10 mTorr) with no applied bias voltage favored (200) texture. The effect of substrate temperature appears to be the most important of all. It was noted that if the substrate was at room temperature during sputter deposition, the films exhibited the (110) texture, whereas if the temperature was about 250 °C, the films exhibited the (200) texture. Since the deposition temperature in the current study was estimated to be between 370 and 400 °C, it is reasonable to conclude that this high temperature helped the (200) texture in the SS304+10Al coatings.

Texture development in polycrystalline thin films could also result from grain coalescence [47]. Grain coalescence was reported experimentally in metallic Cr, Au, and Ag thin films [48–51]. In ion-bombarded Ag thin films, it was reported that the texture changed from (111) to (200), which was accompanied by grain growth [51]. In the SS304+10Al coating, it is possible that the (200) oriented grains coalesced, became larger ones in preference to (110) orientation and consequently led to this (200) texture. This chemically and thermally induced (200) texture is another reason for the observed grain growth in these coatings. The fact that the grain size and texture show similar trend with respect to the Al content (Fig. 15) strengthens this hypothesis.

Conclusions

The phase formation and grain size of sputter-deposited SS304+Al (with 0, 4, 7, and 10Al) coatings have been characterized by XRD and transmission electron microscopy techniques. The metastable phases ferrite and σ were found to be present in the as-deposited SS304 coating, whereas the equilibrium phases, ferrite and B2, were found in the coatings containing Al. Though the formation of ferrite is not unusual in sputter-deposited SS304 alloys, formation of the σ phase was not reported previously. Even though some general correlations have been established with grain size, Ni content, and deposition temperature, further work is needed to clearly establish the reasons for its formation. The average grain sizes of these coatings were 100, 290, 320, and 980 nm, respectively, for the films containing 0, 4, 7, and 10Al. The increase in grain size with an increase in the Al content could be attributed to the temperature rise during deposition due to the higher sputtering powers on the Al target and higher (200) texture with an increase in the Al content.

Acknowledgments The authors are thankful to Dr. N.S. Cheruvu and Dr. R. Wei of the Southwest Research Institute, San Antonio, TX for providing the sputter-deposited samples and also for many useful discussions.

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