The Oxidation Resistance of Fine-Grained Sputter-Deposited 304 Stainless Steel

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The air oxidation of free standing 0.1 cm thick sputter-deposited and wrought 304 stainless steel specimens was studied and the long term oxidation weight gains of the sputter-deposited material were much less than weight gains for the wrought material at 800, 900, and 1000°C. The amount of scaling was also much less on the sputtered material and a thin, adherent oxide formed. The oxide on the sputtered material was more uniform in composition and was higher in chromium and manganese compared to oxide on wrought stainless and eventually formed $MnCr_2O_4$ after long periods of exposure. No stratified oxide layers, as typically observed in wrought stainless steel, formed on the fine-grained sputtered material. The improved scaling resistance of the sputter-deposited steel was attributed to a combination of grain boundary enhancement of chromium diffusion, reduced stresses in the oxide and mechanical keying of the oxide to closely spaced grain boundaries. The stability of grain size for the sputtered material (grain size ≤ 6 μm) also contributed to the better oxide adherence.

IN surveying fine-grained sputter-deposited 304 stainless steel for unusual properties, little scaling was observed during high temperature oxidation in air, Fig. 1. To determine the mechanism for the improved oxidation resistance, specimens of both sputter-deposited and wrought 304 stainless were oxidized at 800, 900 and 1000°C for periods as long as 1000 h and weight gains were continuously monitored. The compositions near and in the various oxides were examined and the morphology of oxides were compared to assess chemical and stress effects responsible for the improvement in oxidation resistance.

The oxidation of Fe-Cr-Ni alloys involves the appearance of several oxides including spinels, rhombohedral phases and solutions of these phases and often the surprising appearance of large amounts of oxide high in concentration of minor alloy constituents such as manganese. The formation of these various oxides is very dependent on alloy composition, oxidation temperature, surface preparation and water content of the gaseous phase. Therefore, even though a number of previous studies were done on alloys with the Fe-18Cr-8Ni composition of the present study, it was considered necessary to do a control study on wrought material of the same composition as the sputtered alloy under the same test conditions. The earlier study of Giggins and Pettit[1,2] on a Ni-Cr alloy indicated that reduced grain size improved oxidation resistance and the possibility that a similar mechanism involving formation of Cr-rich oxide might exist in a fine-grained sputter-deposited Fe base alloy was worthy of further investigation. This paper describes the general characteristics of oxidation in sputter-deposited stainless steel and the details of oxide composition and morphology that appear dependent on alloy microstructure.

EXPERIMENTAL

The starting material was a commercial wrought 304 stainless steel with composition of 18.1 wt pct Cr, 7.6 wt pct Ni, 1.6 wt pct Mn, 0.9 wt pct Si, and 0.02 wt pct C. The wrought material was 50 mm diam (2 in.) bar and the sputtering target was fabricated from the same stock. The sputtered material was deposited on a water-cooled copper substrate (metallographically polished) at a rate of 50 μm/h (0.002 in./h) to a thickness of 0.1 cm (0.04 in.). The sputtering gas was krypton and the copper substrate was removed prior to evaluation. Several deposits were made during the course of the study and the structure and properties were reproducible. In the as-deposited condition the material was fine-grained (~0.5 μm) and had the bcc structure, as observed by Dahlgren.[3] Both the sputter-deposited material and the wrought material were given a 2 h anneal at 1000°C in vacuum prior to the oxidation tests. The oxidation specimens were 6 × 6 × 1 mm for both the wrought and sputter-deposited materials. Thus, possible geometrical factors that might affect oxide adherence were the same in both cases; for example, thin sputter-deposited coating or coatings on substrates might behave dif-

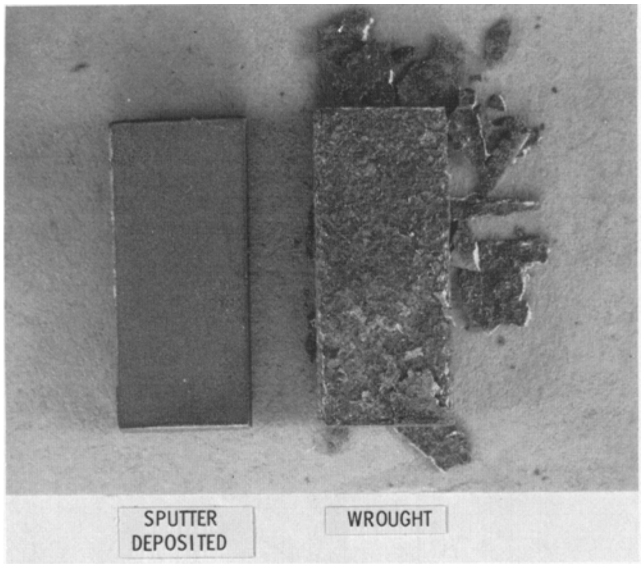

Fig. 1—Improved scaling resistance of sputter-deposited 304 stainless steel compared to wrought 304 stainless steel, 62 h at 1000°C in air.

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ferently than free standing specimens because of stress effects. All specimens were abraded to a 600 grit SiC paper finish before the 2 h 1000°C anneal in vacuum. Auger and SEM examination revealed only a very thin oxide layer prior to the air oxidation tests. The post anneal grain size of the wrought stainless was 40 μm and that of the sputter-deposited material was 3 to 4 μm. The final structure was fcc in both materials.

The oxidation was monitored by continuous weight change recording with a Cahn microbalance. The specimens were held upright in a platinum dish to capture any spalling oxide. Continuously recorded weight gains agreed with before and after weights measured with an analytical balance. The furnace tube was fused silica surrounded by a resistive heating element. Temperature was controlled to ±2°C. No attempt was made to control the water content of the oxidizing atmosphere (air). Thus the moisture content of the air was approximately 5000 ppm based on the typical humidity in the laboratory.

RESULTS

The oxidation rate of sputter-deposited 304 stainless (S304) at 800 and 900°C decreased with time at temperature and showed no sign of film breakdown to times of 1000 h, Fig. 2. The wrought 304 stainless steel (W304), in contrast, initially oxidized at a lower rate than the S304, but after 80 to 120 h the oxidation rate increased drastically and the total weight gain rose well above the S304, Fig. 2. The oxidation rate of S304 at 1000°C likewise decreased with time but after about 50 h accelerated slightly, Fig. 3. Thus, in all cases, after long times the amount of oxidation was less in the S304 than in the W304 specimens.

The visual appearance of the specimens after long periods of oxidation indicated that the oxide film on the S304 was more adherent and the amount of oxidation much less. The amount of spalled oxide was always greater for the W304 than for the S304. Only a cursory examination of thermal cycling effects has been completed, but the results indicate that the oxide on S304 is also more adherent during cycling.

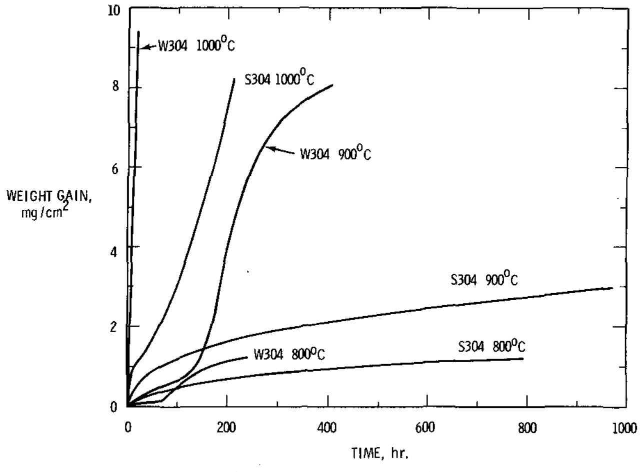


Fig. 2—Weight gains of sputter-deposited 304 stainless steel (S304) and wrought 304 stainless steel (W304) *vs* time at various temperatures.

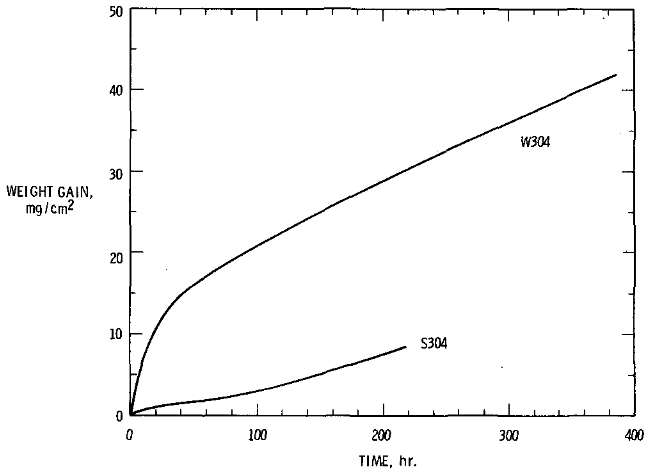


Fig. 3—Weight gains of sputter-deposited 304 stainless steel (S304) and wrought 304 stainless steel (W304) *vs* time at 1000°C in air.

The characteristics of the oxide film and the composition changes in the metal near the film were examined by optical microscopy, scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS) compositional analyses. The superior oxide adherence to the sputter-deposited material was evident in polished sections, Fig. 4. The layered nature of the oxide on the wrought material after long exposures has been referenced by many investigators and apparently is related to the breakdown of the initial Cr-rich film that forms on Fe-Cr-Ni alloys.[4-6] In contrast, the oxide on the sputtered material was thin and showed no sign of repeating layers. Instead, the oxide provided nearly continuous coverage of the base metal even after long periods of oxidation.

The examination of composition by EDS in the SEM revealed that for the sputtered material the metal beneath the oxide was more highly depleted in Cr and Mn compared to the oxidized wrought material and also that the amounts of Cr and Mn in the oxide on the S304 were higher. A composition profile of Fe, Ni, Cr and Mn was obtained by EDS at 10 μm intervals for both the sputtered and wrought materials, Fig. 5. The primary difference between S304 and W304 was the greater depletion of Cr and Mn for the sputtered material. The composition of the layered oxide on the wrought material varied from Cr-rich and Fe-Ni rich in a periodic manner, Fig. 6. This layered structure is consistent with reported observations and the notion that oxide breakdown involves an accelerated attack of Cr-depleted regions and/or that iron diffuses through a Cr-rich spinel to form a disrupted Fe-rich oxide. In contrast the oxide layer on the S304 was uniform in composition and had a much higher Cr and Mn content than any of the oxide in the layered scale on the W304 specimens. The Cr/Fe ratio was very high for the S304 oxide compared to the W304 with Fe as low as 0.1 wt pct and Cr and Mn as high as 30 wt pct each. There were occasional isolated areas on the wrought material where the oxide composition, appearance and the related composition profile beneath the oxide were nearly identical to those of the sputtered counterpart, but these areas were a small fraction of the surface area and were located primarily near grain boundaries.

The bulk composition of the S304 material was compared to the W304 material by EDS, Table I. No significant differences were found. The amount of carbon in the deposit was not determined. However, previous studies in Fe-C with iron 2 to 5 wt pct carbon indicated that carbon contents of deposits were very nearly the same as the target material.[7] The unusual stability of the small grains in the sputter-

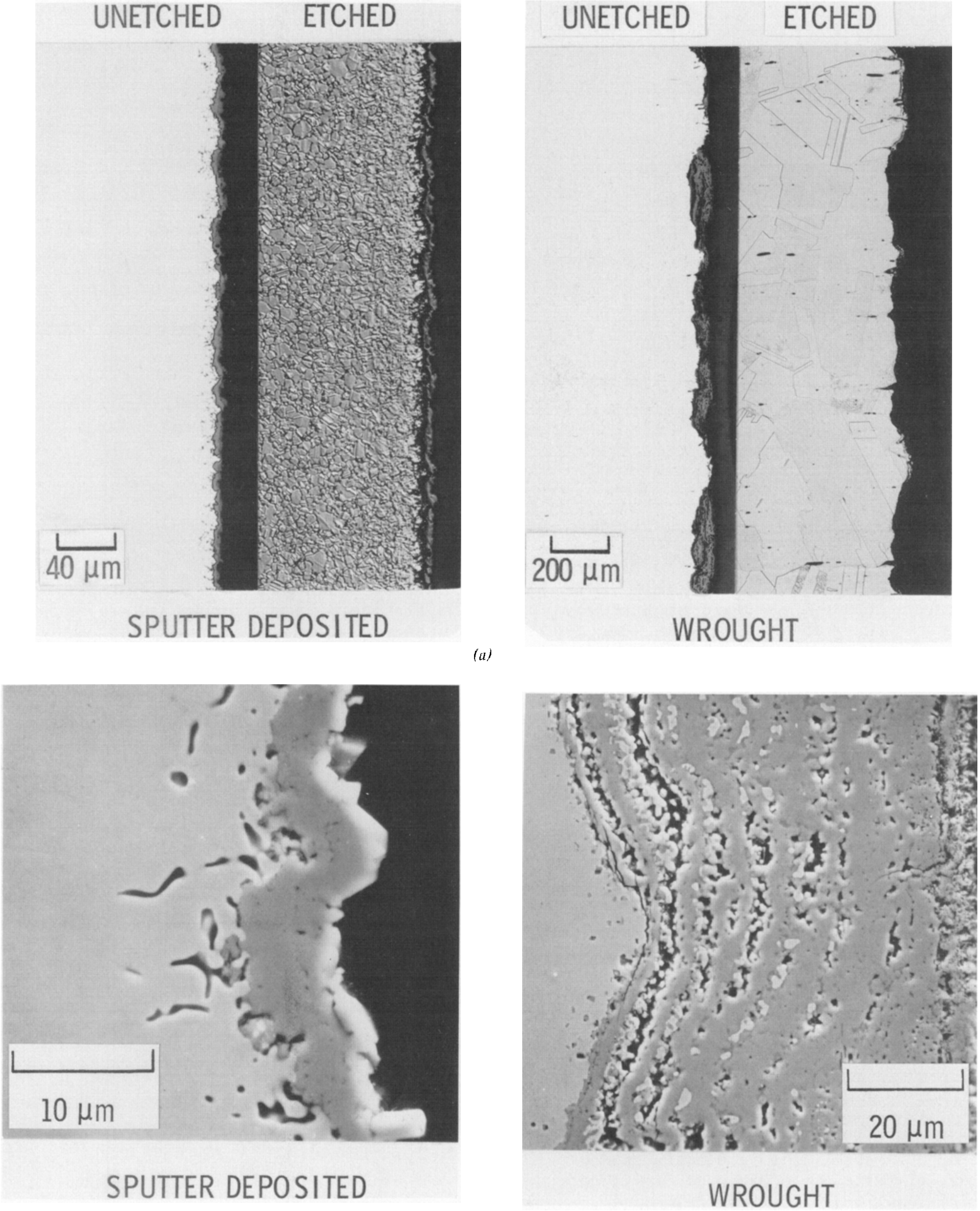
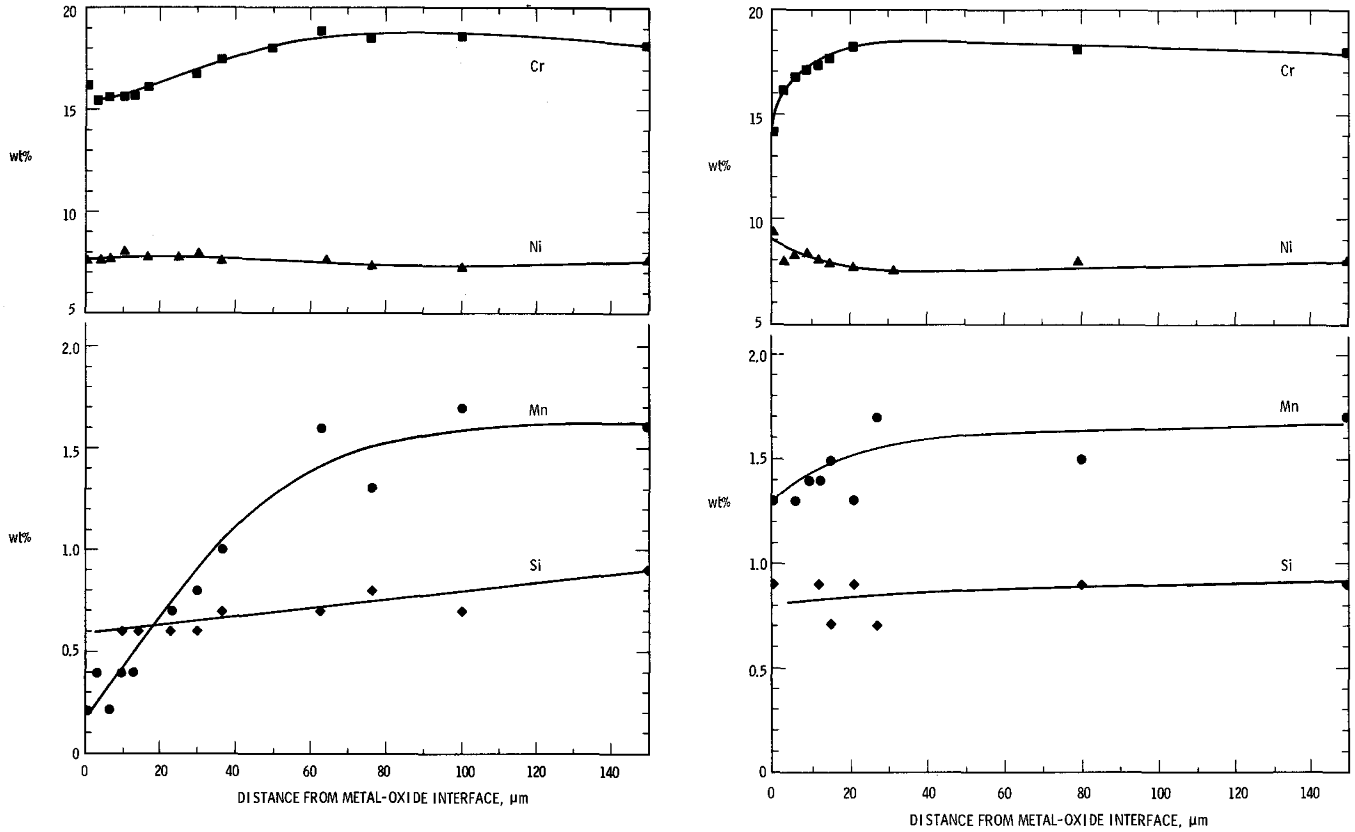


Fig. 4—Oxides on S304 and W304 specimens after 62 h at 1000°C. Note magnification difference.



(*a*) (*b*)

Fig. 5—(*a*) Composition of metal beneath oxide after 62 h at 1000°C sputter-deposited 304 SS. (*b*) Composition of metal beneath oxide after 62 h at 1000°C wrought 304 SS.

deposited material prompted us to examine the materials by TEM for krypton bubbles caused by sputtering gas entrapment. Indeed, about 35 ppm krypton was estimated from the size and density of bubbles.[8] Thus, entrapped krypton was at least partially responsible for the stable fine grain size through the pinning effects of krypton bubbles.

DISCUSSION OF RESULTS

From the observed weight gain results, Figs. 2 and 3, and the observations on oxide adherence, the difference in oxidation resistance of the sputter-deposited and wrought materials is due to the breakdown of the oxide on the wrought material. The important question then is why the oxide on sputtered material remains intact and protective. Giggins and Pettit[2] noted in binary Ni-Cr alloys that decreases in grain size reduced the oxidation rate which they attributed to selective oxidation of chromium at grain boundaries. They concluded that lateral diffusion of chromium from grain boundary regions to the center of grain surfaces contributed to the formation of a protective Cr_2O_3 layer, an effect that was enhanced by shorter diffusion distances in materials with grain sizes under 10 µm. Their results are therefore consistent with the results observed here on 304 stainless steel, though, of course, the various oxides are of more varied compositions for the Fe-Cr-Ni steel.

The reasons for the superior oxide adherence on the S304 specimens can not be unequivocally determined from the observations made so far. As other investigators[5,9] have mentioned, it is difficult to isolate chemical effects in ternary and more complicated alloys, and further work is required to fully understand the phenomena. Nevertheless, the observation on the materials studied here tentatively indicate that the fine grain size of sputter-deposited material is the source of the improved oxidation resistance. The mechanism was narrowed to three possibilities:

1) An increase of chromium in the oxide by grain

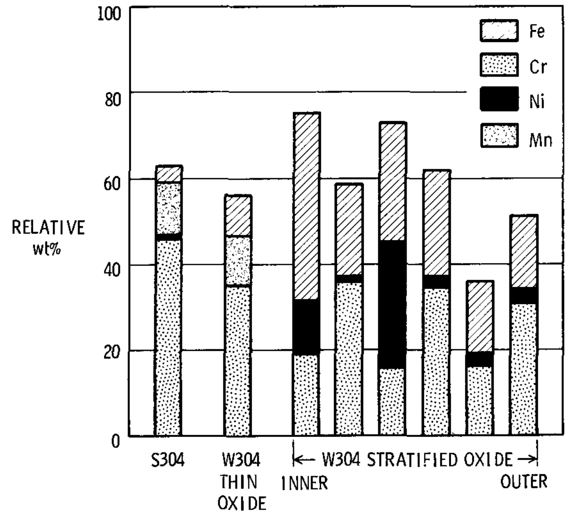


Fig. 6—Periodic composition variation of stratified oxide on W304 compared to oxide on S304 and thin oxide seen occasionally on W304. Voids made total counts low in some cases. 62 h at 1000°C.

Table I. Chemical Composition of Sputter-Deposited (S304) and Wrought (W304) Specimens, Wt Pct

	Fe	Ni	Cr	Mn	Si
S304	72	7.6	18.1	1.6	0.9
W304	72	7.5	18.7	1.6	0.7

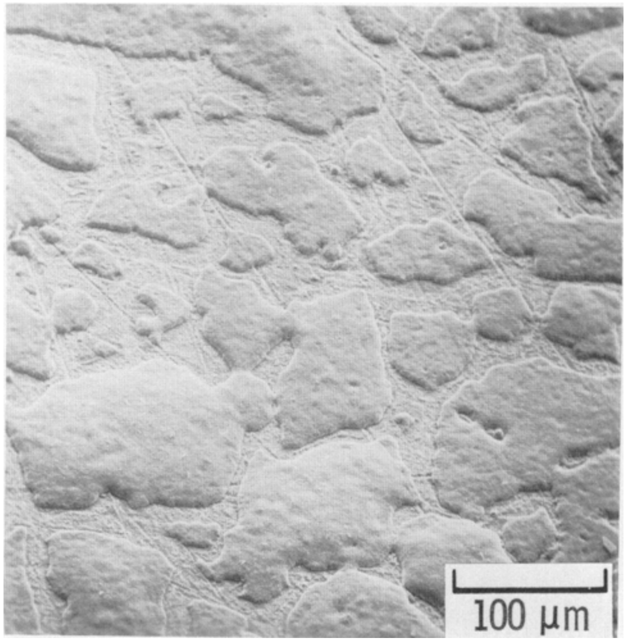


Fig. 7—Oxide on W304 after 30 h at 800°C. Islands are relatively iron-rich and surrounding areas are Cr-rich and above grain boundaries.

boundary diffusion of chromium which contributes to a more adherent chromium-rich oxide,

2) A more favorable distribution of stresses in the oxide and,

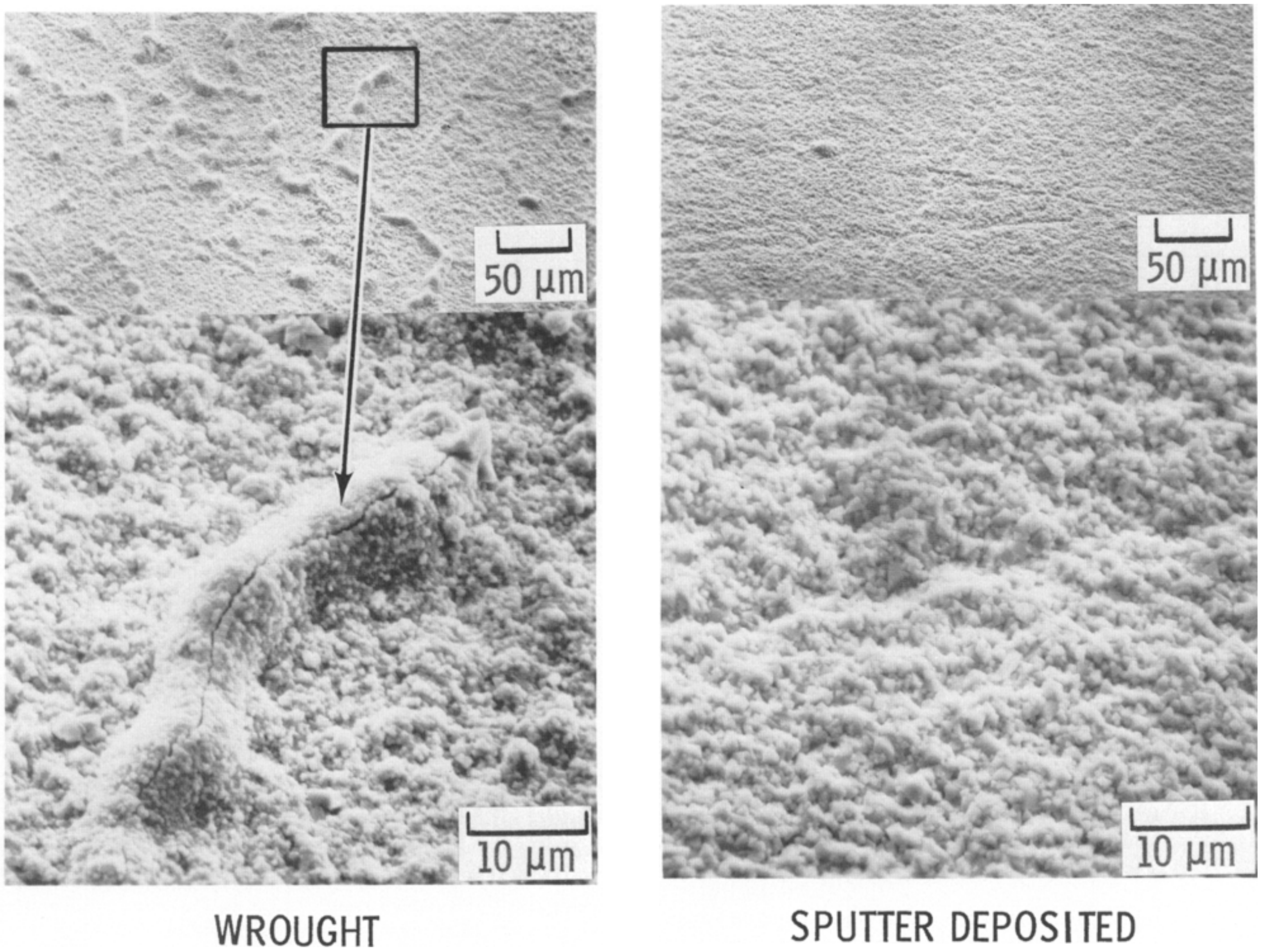
3) Mechanical keying of the oxide to closely spaced microstructural features.

The purpose of the remainder of this section is to discuss observations made on both W304 and S304 specimens that indicate these mechanisms of improved oxide adherence.

An important observation confirming the rapid transport of chromium by grain boundaries was the existence of chromium-rich regions above grain boundaries in the W304 material, *e.g.* at 800°C after 30 h, Fig. 7. The surface Cr/Fe ratio was ~0.96 in these regions compared to ~0.04 in the regions over the grain centers. This difference was observed even after very short oxidation times at 800°C and indicated that chromium mobility was enhanced by grain boundaries as reported by Smith.[10] Considering the values of grain boundary diffusivity of chromium derived by Smith on 316 stainless steel, the expected enhancement in diffusion flux of chromium for a 4 μm grain size compared to 100 μm grain size is approximately a factor of 7 at 1000°C and a factor of 120 at 800°C. Thus, the fine stable grain size of S304 enhances chromium diffusion over the entire temperature range of these studies. Because chromium mobility is rapid in grain boundaries, it might be expected that larger amounts of Cr_2O_3 will form near grain boundaries in 304 specimens much as Giggins and Pettit observed in Ni-Cr alloys. The enhancement of chromium diffusion by grain boundary short circuiting in the fine-grained sputter-deposited material may be the cause of the initially higher weight gains in the sputtered material at 800 and 900°C. Once a protective chromium oxide is formed, the rate begins to decrease. At 1000°C, in contrast, the W304 material appears to oxidize more rapidly than S304 from the start. However, scale breakdown in the W304 material occurred at about 1 mg/cm^2 (~6 μm thickness) at 1000°C and because the oxidation rates are very high, it was actually difficult to make a valid comparison of the relative initial rates. In any case, at 1000°C grain boundary enhancement of chromium is much less than at 800 and 900°C.

The uniformity and composition of oxides on the S304 specimens were different than on the W304 specimens. It was clear from the observations that the oxides formed in a heterogeneous manner on the W304 specimens compared to more compositionally and geometrically uniform oxide on the S304 specimens. This was attributed to the finer grain size of the S304 specimens which enhanced chromium oxide formation over the entire surface during the early stages of oxidation. In contrast, an iron-rich oxide formed over grain interiors on the W304 specimens. Beneath this iron oxide a porous region with a chromium-rich oxide was found. At regions over and near grain boundaries a chromium-rich oxide formed. The compositions of the various oxides were examined and the S304 specimens had a low amount of Fe (~1 to 2 wt pct) in the protective oxide. The oxide on the S304 after long periods was a Mn-Cr oxide approaching 1 : 2 Mn/Cr ($MnCr_2O_4$) at 800 and 1000°C, the ratio being consistent with observations of $MnCr_2O_4$ by Yearian *et al.*[11] X-ray diffraction confirmed the $MnCr_2O_4$ spinel with 8.50Å lattice parameter. Minor amounts of rhombohedral Cr_2O_3-Fe_2O_3 were also detected; the amount being greater at 1000°C. The depletion of chromium and manganese in the underlying material was consistent with the existence of the high Cr-Mn oxides and indicated the dependence of oxide formation on the flux of Cr and Mn through the base metal. The appearance of $MnCr_2O_4$ has in fact been related by previous investigators to high Cr concentrations, *e.g.*, steels with Cr > 21 wt pct, and to conditions where the rate of attack is low. Thus, the appearance of $MnCr_2O_4$ in S304 is the consequence of a stable, protective oxide with an enhanced flux of chromium and manganese to the surface via closely spaced grain boundaries. The protective nature of the oxide on S304 is likely due to the formation of a continuous Cr_2O_3 film during the initial stages of oxidation in contrast to the Fe-rich oxide that forms over grain interiors in W304.

In addition to the chemical effects, some consideration has been given to stress effects that may contribute to the superior oxide adherence on S304. In one case after 150 h oxidation of W304 at 900°C (just past the breakaway oxidation, Fig. 8), there was evidence of cracking of the high chromium oxide that remained after spalling of the outer Fe-rich oxide. In contrast, the oxide on S304 showed no evidence of



WROUGHT

SPUTTER DEPOSITED

Fig. 8—Oxides on sputter-deposited and wrought 304 stainless steel specimens. 150 h at 900°C. Note crack in oxide on wrought 304.

cracking, Fig. 8. A more uniform distribution of stresses probably existed in the fine-grained S304 material because of the more homogeneous nature of the oxide, though further experiments are necessary to confirm this assertion. Mechanical keying of the oxide at closely spaced grain boundary grooves may contribute to this mechanism, similar to a mechanism suggested by Giggins *et al*[12] for Al_2O_3 adherence on NiCrAl and CoCrAl alloys where irregularities on a micro scale improved oxide adherence. Grain growth of the base metal during oxidation has been cited as the cause of oxide breakdown in an Fe-17 wt pct Cr alloy,[13] especially when the initial grain size was small and considerable grain growth occurred *i.e.*, an initial grain size of 35 μm grew to 150 μm in approximately 1 h at 1000°C. In the W304 specimens there was grain growth *e.g.*, at 1000°C in 62 h the grain size increased from 40 to 100 μm, whereas in the S304 specimens, the grain size increased only slightly from 3-4 to 5-6 μm. Thus, the relative stability of the S304 grain size may additionally contribute to the oxide adherence especially at 1000°C where considerable grain growth occurs in the W304 specimens.

SUMMARY

Fine-grained sputter-deposited 304 stainless steel oxidized less than coarse-grained wrought stainless steel at all temperatures studied, 800, 900 and 1000°C, for times as great as 900 h.

The improvement in oxidation resistance of the sputter-deposited material was attributed to the effects of a fine, stable grain size. Chromium diffusion was enhanced and the oxide on the sputter-deposited stainless steel was rich in chromium and manganese. The chromium oxide on the sputter-deposited stainless steel was similar, though of higher chromium concentration, to the oxide formed near grain boundaries in wrought stainless steel. Thus, the presence of closely spaced grain boundaries was concluded to be the cause for formation of a uniform, low Fe, $MnCr_2O_4$ in the sputter-deposited material. The oxide on sputter-deposited 304 stainless steel was relatively thin and adherent and exhibited none of the layered structure characteristic of spalling oxide found on wrought stainless steel. Mechanical keying of the oxide to closely spaced grain boundary grooves may contribute to better oxide adherence for the sputter-deposited stainless steel.

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