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PROTECTIVE AND NON-PROTECTIVE OXIDE FORMATION
ON 304 STAINLESS STEEL

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Protective and Non-Protective Oxide Formation on 304 Stainless Steel

D.R. BAER

ABSTRACT

Parameters controlling the formation of protective and non-protective oxides on 304 stainless steel were examined by using Auger electron spectroscopy to monitor oxides formed in the vacuum chamber. Variables found to influence the oxide formation include: oxygen partial pressure, the location of the oxide over a grain or grain boundary, sample grain size, and anneal treatments. Low pressure oxidation ($<10^{-5}$ Torr oxygen pressure) at 800°C produced a thin chromium oxide on annealed samples with 40 μ m grain size; this thin ($\sim 200\text{\AA}$) protective oxide did not grow with 15 minutes additional oxidation in air at 800°C. In contrast, initial oxidation of the same annealed material at oxygen partial pressures greater than 10^{-3} torr caused the formation of thicker iron-rich oxides. The oxides formed at these higher pressures were often non-uniform having thin chromium-rich oxides near grain boundaries and thicker iron-rich oxides over the grains. Annealing treatments influenced oxidation by varying the amount of chromium available at the surface for oxide formation. At temperatures above 800°C chromium evaporates from the sample decreasing the amount of chromium on the surface and altering the chromium profile into the metal. If carbon is present on the sample surface near 500°C a chemically induced chromium segregation occurs (similar to grain boundary sensitization) which also severely alters the chromium distribution in the near surface region of the material.

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INTRODUCTION

The relative abilities of oxygen partial pressure, annealing treatments, and sample morphology to control oxide formation on 304 stainless steel are examined in this paper. Oxygen potential is well established as a means of controlling oxide formation on an alloy.^[1] Often a low-oxygen potential atmosphere is used to form a compact protective Cr_2O_3 layer on a chromium containing alloy.^[2] Recent work by Hultquist and Leygraf^[3,4] has shown that films formed by this low pressure selective oxidation can significantly enhance the resistance of 316 stainless steel to crevice corrosion in a sodium chloride solution. The influence of sample morphology and annealing treatments on oxidation are less well known. Enhanced diffusion of chromium in cold worked or small grained material is believed to aid formation of a protective oxide.^[5,6] For Ni-Cr alloys Cr-oxide is observed to nucleate and grow from grain boundaries.^[7] Annealing can influence later oxidation of a material by changing the sample structure (either grain size or defect concentration) or by altering the elemental composition of a material at the surface.^[8,9,10]

The strong influence of grain size on the ability of 304 stainless steel to form a protective oxide in air at 800°C has been recently reported by Merz.^[11] For material with a large (40 μm) grain size a duplex oxide was formed; a thick Fe-oxide formed over grains while a thinner Cr-rich oxide nucleated at grain boundaries. These results were in contrast to the measurements on small (4 μm) grained samples where a Cr rich oxide was formed^[11] and to measurements by others indicating that only Cr oxide formed on 304 stainless steel at 800°C in air.^[12,13] Additional work by Baer and Merz [to be published in Met. Trans] showed that annealing and polishing treatments could enhance or inhibit the ability of the 40 μm grain size to

form a protective oxide. In particular, annealed large-grained samples formed the duplex oxide, while samples polished after the anneal formed a single more protective oxide.

This study was conducted to answer three specific questions concerning the influence of grain size, annealing treatments, and oxygen potential on oxide formation on stainless steel. First, does the selective nucleation of Cr-oxide at grain boundaries occur at oxygen partial pressures sufficiently low that the growth process could be directly monitored by Auger electron spectroscopy? The role of grain boundaries in the oxidation of stainless steel is subject to debate^[14] and direct observation of oxide formation at grain boundaries could help clarify the issue. Samples that readily show selective oxidation at grain boundaries would be most useful for such a study. Second, under what oxidation conditions will a protective uniform Cr-oxide form on the annealed large-grained 304 stainless steel? Because these samples quickly form a non-protective oxide in air, it is of interest to determine annealing and oxidation conditions for which a protective oxide will form. Third, how does annealing influence the sample surface composition and affect oxidation?

EXPERIMENTAL

A commercial wrought 304 stainless steel with composition 18.1 wt% Cr, 7.6 wt% Ni, 1.6 wt% Mn, 0.9 wt% Si, and 0.02 wt% C was used in this study. All samples were annealed for 2 hours at 1000°C in situ before oxidation using a dc resistance heating method. Heater current leads were carefully arranged to minimize magnetic field effects and much of the Auger data was taken at temperature. The average grain size after annealing was approximately 40µm. In order to study the effects of annealing on oxidation, samples were annealed in three different ways: 1) Some samples were heated slowly to 1000°C; 2) Others were step heated to 500°C or 800°C, then to 1000°C; 3) A few samples were heated directly to 1000°C. With one exception (air oxidation) all samples were oxidized in the vacuum chamber at oxygen partial pressures ranging from 10^{-5} to 0.1 torr. The oxygen pressure was measured using a Varian millitor vacuum gauge.

During and/or after oxidation the samples were examined by Auger electron spectroscopy (AES) using a Physical Electronics 545 scanning Auger system. Sputter depth profiling was used to determine the composition profiles of the samples with oxides. The sputter rate was calibrated for Ta₂O₅ and any depths indicated refer to that standard. The atomic composition of the samples was calculated using elemental sensitivity factors^[15] for the peak to peak height of the $\frac{dN}{dE}$ signal amplitude.

RESULTS AND DISCUSSION

It was possible to vary the oxide formed on 40 μ m grain sized 304 stainless steel at 800°C from a uniform protective Cr-oxide to a uniform non-protective Fe rich oxide by altering the oxygen partial pressure and the in situ sample annealing conditions. The duplex oxide structure first observed on air oxidized sample could be reproduced in the vacuum chamber at oxygen pressures above 10^{-2} torr. Although the annealing and oxidation results are not entirely independent, oxidation and annealing effects will be discussed separately.

Oxidation At 10^{-5} Torr

A primary objective in this study was to determine if selective formation of a Cr rich oxide at grain boundaries could be observed during oxidation at low pressures (less than 10^{-5} torr) where AES could be used to continuously monitor the process. However at these pressures a uniform protective Cr-oxide formed. The desire to observe the nucleation of chromium oxide at the grain boundary during low pressure oxidation was in conflict with the tendency to form protective oxides at the lower pressures^[2]. For a Cr-Ni-Fe alloy Cr_2O_3 is the thermodynamically stable binary oxide, although growth kinetics and local elemental activities usually allow the formation of other oxides^[16]. At low pressures the oxide growth is slower and the most stable oxides are more likely to form. The pressure at which the duplex oxide would give way to a uniform Cr-oxide was not known. Thus, the first effort to form the duplex oxide in the vacuum chamber was done at 10^{-5} torr p_{O_2} .

A large grained 304 stainless steel sample that had been annealed by slowly heating the sample to 1000°C in vacuum was oxidized at 800°C in 10^{-5} torr p_{O_2} for approximately 2 hours (Fig. 1). Initially the sample was heated to temperature and the vacuum system back-filled with oxygen. Because oxygen

quickly combined with carbon to form CO in the presence of a hot sample and various hot filaments, a flow of O_2 was established while keeping the pressure at 10^{-5} torr. The sample was initially covered by S that segregated during heating; the S reacted with the O_2 to form SO_2 as observed in a residual gas analyzer. Only after the S was depleted from the surface did oxidation begin (also see Wild^[17]). The oxide formed was uniform containing mostly Cr-oxide with some manganese oxide. Additional oxidation for 22 min. at 10^{-3} torr produced only minor changes in the oxide by causing the disappearance of the Mn, probably due to evaporation.

A sputter depth profile of the oxide that had formed showed the oxide to be a relatively thin ($\sim 200\text{\AA}$) Cr-oxide [Fig. 2A]. To further test the oxide stability the sample was removed from the vacuum system and oxidized for 15 min. in air at 800°C . This air oxidation treatment was identical to that given other large-grained samples and usually produced several microns^[11] of iron-rich oxide over the grains of the material. However, a sputter profile of the sample initially oxidized at lower pressure showed no additional oxide growth during the air oxidation [Fig. 2B]. A several micron thick oxide did grow in the area of the sample where the protective oxide had been removed during the sputter profile of Fig. 2A.

In this experiment it was not possible to observe the selective nucleation and growth of Cr-oxide at grain boundaries for oxygen pressures below 10^{-5} torr using AES. At no time during oxidation at 10^{-5} torr was there any indication of preferential oxide formation at grain boundaries. At low oxygen pressures, the nucleation and growth of Cr-oxide may occur at many sites and the importance of grain boundary

nucleation may be diminished. Although the formation of the protective Cr oxide was not unexpected, the stability of the film formed to air oxidation at 800°C had not been anticipated. This result suggests that the dramatic improvements in the corrosion resistance of stainless steel to sea water produced by a low pressure oxidation pretreatment^[3,4] also occur for high temperature oxidation conditions.

OXIDATION AT 0.001 - 0.1 TORR

Several samples were oxidized at oxygen pressures ranging from 0.001 to 0.1 torr in the effort to discover the range of oxides that would be formed and to attempt to produce in the vacuum chamber the duplex oxide structure formed during air oxidation. Because the samples were given different annealing treatments, different oxides were sometimes formed for identical oxidation conditions. A summary of the oxides formed and the sample surface composition after the vacuum anneal is given in Table 1. The oxides varied from the nearly pure Cr-oxide formed at low pressure to nearly pure Fe-oxide at higher pressures. For other conditions a mixed Fe-Cr oxide (possibly a spinel) was formed.

Oxides somewhat similar to the duplex oxide which formed in air occurred on several samples. The presence of greater chromium concentration at grain boundaries is shown by the Auger chromium map in Fig. 3. This sample had been annealed by heating directly to 1000°C; the pressure during oxidation at 800°C was 0.05 torr. Although initial scans showed little difference between the oxides over the grains and at grain boundaries, sputter profiles of the two areas [Fig. 4] showed significant differences. An iron oxide covered each area, but the oxide at the grain boundary was considerably thinner and had a very different depth profile. The preferential formation of Fe oxide on stainless steel has been observed frequently^[8,16,18], but the oxide growth pattern that produced these two

different profiles is not yet clear. It is hoped that additional studies of the oxide formation at grain boundaries as a function of oxidation time will help clarify the role of grain boundaries in the oxidation of these materials. The ability to form a duplex oxide in the vacuum system also provides a unique method of creating a surface of varying chemical composition that may be useful in studies of reactivity or chemical adsorption.

The sputter profile of the iron oxide over the grain (Fig. 4) was typical of the uniform iron oxides formed on other samples. The outer oxide was an iron oxide containing very little Cr or Ni. Near the metal oxide interface the Cr increases and Fe drops. This region is often an Fe-Cr spinel. An increased concentration of Ni beneath the oxide metal interface has been observed before^[13] and is attributable to the fact the Ni has the smallest energy of oxide formation^[19]. This result and interpretation contrasts somewhat with the results of Hultquist and Leygraf^[4] who observe Ni in their oxide films formed at low oxygen pressures at a somewhat lower temperature. They find Ni to be a beneficial addition to the film for aqueous corrosion resistance. Based on their observations they assume that the free energy of oxide formation increases in the order $\text{Fe} < \text{Ni} < \text{Cr}$. This assumption is contrary to the generally accepted order of $\text{Ni} < \text{Fe} < \text{Cr}$ ^[16,19] which is consistent with the current results. It should be noted the Betz et al^[13] observe Fe oxide formation on 304 stainless steel around 200°C in spite of the fact that CrO_2 and Cr_2O_3 would be more stable compounds. Frequently the kinetics of oxide growth on an alloy do not allow thermodynamic equilibrium, particularly at lower temperatures^[16].

Vacuum Annealing

Annealing can alter the sample in two different ways. Grain growth, recrystallization, and changes in defect concentrations alter the sample structure and can influence the diffusion kinetics and nucleation sites that are important in oxide formation.^[6,20] Vacuum annealing also alters the elemental composition of the sample because of selective evaporation and surface segregation.^[8,9,10,17] This study considered primarily the changes in sample composition due to vacuum annealing. All samples were annealed in the vacuum chamber with a base pressure of 10^{-10} torr. During anneals, particularly at high temperatures, the pressure momentarily rose to pressures as high as 10^{-8} torr.

Sample composition after annealing

Each of the three different annealing procedures produced samples with characteristically different surface compositions as shown in Table II. Samples slowly heated to 1000°C over a several hour period had a greater Cr concentration on the surface than samples processed in either of the other ways. Samples step heated contained the least Cr for an interesting reason. The Cr to Fe Auger signal ratio for several slow and one step heated samples are shown as a function of temperature in Fig. 5: If a sample is slowly heated, any Carbon on the surface begins to disappear around 350°C and relatively little Carbon remained at 500°C. For these samples, Fe, Oxygen, and Cr were the dominant elements on the surface around 500°C. However, if the samples were heated quickly to above 500°C and the Carbon was not removed, Carbon, Chromium and Oxygen were the primary elements present on the surface and a large change in the Cr/Fe ratio was observed. Chromium carbides are known to form at grain boundaries in 304 stainless in this temperature range and the process is called sensitization.^[21] If carbon is present on the surface between

500 and 700°C the surface equivalent of sensitization occurs. Grain boundary sensitization weakens the corrosion resistance of stainless steel by forming a Cr depleted region of the sample. The surface "sensitization" has a similar effect and these samples were depleted in Cr to a considerable depth after the 1000°C anneal. Samples heated directly to 1000°C have Cr concentrations between those of the slow and step heating treatments.

Material evaporated during the anneal

A cold gold foil was used to collect material evaporated from the stainless steel samples during the anneal and oxidation treatments (also see Wild^[8]). Up to temperatures of 800°C, Mn is the only metal to evaporate from the sample (Table III). By 1000°C significant amounts of Cr, Fe, and Ni are found on the collector. Because the percentage of Cr on the collector is larger than the percentage in the base material, prolonged anneals at 1000°C can deplete the surface region of Cr and decrease the possibility of protective oxide formation,^[8,9,10,22] Although Mn is the only metal collected during an 800°C anneal, Fe and Cr are collected during oxidation at 800°C. CrO_3 is known to have a relatively high vapor pressure^[20] and if formed could account for the chromium on the collector. The source of the Fe is not clear.

The evaporation of Cr and the subsequent alteration of the Cr profile in the metal during the annealing can produce some interesting results during oxidation. Chromium first tends to segregate to the surface before evaporation. Therefore the Cr surface concentration can be greater than the Cr concentration in the near surface region. After a long 1000°C vacuum anneal the Cr concentration at the surface will drop, but the Cr concentration below the surface will also be altered in a major way.

Because the oxidation properties of an alloy depend upon the availability of the various elements, two alloys with nearly identical surface concentrations of Cr, but different Cr depth profiles can form different oxides. The oxides formed on sample III, Table I, show some of this behavior. Initially an iron oxide formed on the sample. This oxide was removed by sputtering in one area of the sample and the alloy was sputtered through the Cr depleted region until the amount of Cr at the surface was nearly the same as on the initial annealed sample. After a second oxidation the oxide observed in the sputtered area was considerably richer in Cr. Although both samples had nearly the same concentration of Cr at the surface, the sample with a Cr depleted region formed an Fe oxide while the region without Cr depletion formed an oxide with more Cr.

Annealing and Surface Damage

The current results can be used to clarify some of the observations reported by Baer and Merz. In that study it was not possible to determine if the duplex oxide formed on large grained samples in air was characteristic of the annealed material or influenced by the oxide that had formed on the sample during the vacuum anneal. For some samples the oxide formed during the anneal had been removed by repolishing the samples and upon oxidation in air, a uniform oxide formed. Because the difference in oxidation behavior occurred between annealed samples, with an oxide, and repolished samples, without the oxide but with surface damage due to polishing, it was not possible to determine the oxidation behavior of annealed but non-oxidized or repolished samples. The observed tendency in the present study of annealed samples, without an oxide coating, to form a duplex oxide structure upon oxidation at 800°C, suggests that surface damage due to polishing caused the formation of the uniform oxide on the repolished samples in the previous study, and that duplex oxide formation is a characteristic of large-grained annealed material during

oxidation in air. The influence of the repolishing supports observations by others^[5,6,20] that surface damage can appreciably influence initial oxide formation.

CONCLUSIONS

The results of this and previous studies show that grain size, surface damage, oxygen partial pressure, and annealing treatments can all influence the oxide formed on stainless steel. The oxide formed at low oxygen partial pressure is very stable and significantly improved the corrosion resistance of the material. A duplex oxide structure tends to form on annealed large grained ($40\mu\text{m}$) samples at pressures as low as 10^{-2} torr. This structure can, therefore, be formed in a vacuum chamber. Annealing treatments can enhance or diminish the Cr concentration in the surface region of a sample and thereby vary the probability of forming a protective Cr-oxide. If a significant amount of C is on the surface of non-passivated stainless steel near 500°C a Cr-carbide is formed which ultimately leads to Cr depletion in the surface region of the sample.

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OXIDATION OF 304 STAINLESS STEEL

TABLE I

Sample	Anneal Treatment	Surface Composition After Anneal (Atomic %)					Comments	Oxidation Pressure		Oxidation Time	Surface Composition After Oxidation (Atomic %)					Oxide Thickness	Grain Effects
		Fe	Cr	Ni	S	P					Fe	Cr	Ni	Mn	O		
IA	1-Slow Heating	60	25	9	7	-		10^{-5}	torr	2 Hrs.	LT 1%	17	-	7	72		No
							Additional Oxidation	10^{-3}	torr	22 Min.		29	-	-	70	$\sim 200\text{\AA}$	No
							Additional Oxidation	Air-		15 Min.		30			70	$\sim 200\text{\AA}$	No
		75	17	8	-	-	Section of Sample Sputter Profiled Before Additional Oxidation in Air	Air		15 Min.		34	-	2	-	63 $\sim 1\mu\text{m}$	No
1B	2-Step Heating	65	9	10	16		Initial Sample Repolished	10^{-2}	torr	8 Min.					60	$6000\text{\AA}$	No
		67	7	10	16		Oxide Removed By Sputtering Before Additional Oxidation	$\sim 10^{-5}$	torr	31 Min.		35	6	3	-	56	No
II	1-Slow Heating	43	25	5	27			0.1	torr	2 Min.		15	-	-	-	60*	$400\text{\AA}$ Yes
III	3-Direct	55	13	8	18	6		.05	torr	5 Min.		45				55	$10,000\text{\AA}$ Yes
IV	2-Step	67	6	14	7	6		.005	torr	7 Min.		41				59	$10,000\text{\AA}$ No
							Additional Oxidation	.005	torr	7 Min.		43				57	
		85	6	9	-	-	Section of sample sputter profiled before additional oxidation	.005	torr	7 Min.		18	21	3		58	

*W from heating wires is also present on this surface.

TABLE II

SAMPLE SURFACE COMPOSITIONS AFTER ANNEALING

Annealing Treatment	Surface Composition At End Of 2 Hour 1000°C Anneal					Surface Composition at ~550°C							
	P	S	Cr	Fe	Ni	S	N	C	O	Cr	Fe	Ni	
1 - Slow Heating	-	7	25	60	9	11	2	5	18	19	39	6	
	4	26	25	40	5	1	-	2	37	28	26	6	
2 - Step Heating	-	16	9	65	10	3	-	30	36	18	12	3	
	13	11	6	55	14	5	-	18	44	24	8	1.5	
	6	7	6	67	14	-	-	-	-	-	-	-	
3 - Direct to 1000°C	6	18	13	55	8	-	-	-	-	-	-	-	

TABLE III

MATERIAL COLLECTED ON GOLD FOIL

% Atomic Composition of Elements on Foil

S	Ce	C	O	Mn	Cr	Fe	Ni	
Material collected upon heating a cold uncleaned sample to 800°C for 15 min.	7	2	33	22	36	-	-	-
Second heating of the same sample for 12 min.	-	-	-	-	100	-	-	-
Heating sample to 1000°C for 2 hours	24	-	-	-	-	25	46	5
Material collected during oxidation at 800°C	-	-	-	68	12	10	11	-

Figure 1 - Surface composition of 304 stainless steel during oxidation at 800°C in 10^{-5} torr oxygen pressure.

Figure 2 - Sputter depth profile of oxide formed at 10^{-5} torr oxygen pressure as formed (A) and after additional oxidation in air.

Figure 3 - Secondary electron image and scanning Auger Cr map of sample oxidized in 0.05 torr oxygen pressure. The Cr observed at grain boundaries is similar to oxidation observed in air.

Figure 4 - Sputter depth profiles of grain and grain boundary areas of sample oxidized at 0.05 torr oxygen pressure.

Figure 5 - Chromium to iron Auger signal ratio observed during vacuum annealing. If considerable carbon is on the surface near 500°C excess chromium segregates to the surface.

SS OXIDATION AT 10⁻⁵ TORR

Fig 1

AFTER OXIDIZATION AT 10^{-5} TORR

700

AFTER ADDITIONAL OXIDATION IN AIR

SPUTTER RATE 200 A min

Fig 2

SEM PICTURE OF 304 STAINLESS
STEEL SAMPLE OXIDIZED IN
 10^{-2} TORR O_2 AT $800^\circ C$ [x200]

AUGER MAP OF Cr IN OXIDE ON
STAINLESS STEEL SAMPLE [x200]

Fig 3

SPUTTER DEPTH PROFILE SS 304—OXIDIZED 10⁻² TORR

AT GRAIN BOUNDARY

OVER GRAIN

SPUTTER RATE 200 Å/min

Fig 4