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Annealing Study of Stainless Steel To Conserve Critical Metals

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UNITED STATES DEPARTMENT OF THE INTERIOR

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BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	kPa	kilopascal
Å/min	angstrom per minute	L/min	liter per minute
°C	degree Celsius	min	minute
cm	centimeter	mm	millimeter
cm^3	cubic centimeter	μm	micrometer
g	gram	mt	metric ton
ga	gauge	nm	nanometer
g/cm^3	gram per cubic centimeter	Pa	pascal
h	hour	pct	percent
keV	kilo electron volt	wt pct	weight percent

ANNEALING STUDY OF STAINLESS STEEL TO CONSERVE CRITICAL METALS

By A. Visnapuu,[1] J. S. Volosin,[2] and R. B. Schluter[3]

ABSTRACT

The U.S. Bureau of Mines investigated the oxidation of American Iron and Steel Institute (AISI) Type 304 stainless steel (SS) during annealing in simulated combustion products from several air-CH_4 fuel ratios. Atmospheres representing air-CH_4 ratios of 14:1 and 18:1 contained free O_2, while atmospheres representing 10:1 air-CH_4 ratio did not. A Cr_2O_3 layer formed on SS samples annealed in atmospheres containing free O_2, while a Cr-Fe spinel layer formed in atmospheres with no free O_2. The Cr_2O_3 layer was adherent and presented a protective barrier to metal diffusion, effectively limiting oxidation of the metal substrate. The Cr-Fe spinel was not protective and allowed the diffusion of Fe through the spinel to the gas-oxide interface where it was oxidized to magnetite, which spalled from the surface. This resulted in thick scale layers on samples annealed in atmospheres containing no free O_2, as compared to layers formed on samples annealed in atmospheres containing free O_2. These results confirmed and explained industrial operators' observations that thick, smoky (fine spalled magnetite) scales form on SS annealed in low free-O_2 atmospheres, while thin protective oxide layers form on sheets in atmospheres containing free O_2.

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INTRODUCTION

The United States annually imports 50 to nearly 100 pct of its Cr and Ni needs. These metals are considered critical to the Nation's industrial base and are essential in maintaining a normal domestic economy. Chromium is used to prepare SS, alloy, high-strength low-alloy, and electrical steels. Nickel is used as an alloying addition in SS, high-temperature steel, superalloys, and other nonferrous alloys. Nickel is also used extensively in electroplating and as a catalyst in chemical processing. There was no domestic primary mine production of Cr in 1991, and mine production of Ni was only 7,600 mt of contained Ni (*1-2*).[4] The domestic sources of these metals were primarily from recycling or byproducts from other mining or refining operations. The nearly complete dependence on imports for these critical metals makes the United States vulnerable to uncertain foreign sources. To reduce this potentially serious loss, the U.S. Bureau of Mines has conducted research to conserve these metals by more efficient utilization, substitution, and processing, in addition to research on their recovery from available or potential domestic sources. This report summarizes the results of a laboratory study to reduce the loss of Cr and Ni during annealing and pickling of SS by investigating the parameters that govern the scale-forming gas-metal reactions that occur on the alloy surface during the annealing phase.

The corrosion resistance of SS is due to a highly passive surface resulting from the presence of Cr and Ni in the steel. During mechanical processing, the alloy becomes work hardened and must be annealed to restore the preferred mechanical properties for either end use or further processing. Sheet SS production requires that these mechanical-forming and annealing processes be repeated a number of times. Annealing is performed in continuous or batch furnaces normally fired by natural gas, and the resulting annealing atmosphere can be made reducing, neutral, or oxidizing. Although low-O_2 atmospheres are used for certain special applications, most of the continuous annealing furnaces are operated under oxidizing conditions because these conditions are more fuel efficient and less costly. The continuous annealing process is of short duration, with the metal leaving the furnace within a minute or less after it attains the desired annealing temperature. For Type 304 SS alloys, the annealing temperatures employed are between 1,100 and 1,150° C. Scale is formed during each of the anneals and is subsequently removed by pickling in a mixture of nitric and hydrofluoric acids. Since Cr is oxidized preferentially, the annealing process results in the formation of a Cr-depleted layer in the metal adjacent to the metal-oxide interface. The Cr content of the steel, which gives the alloy its corrosion resistance, also causes the scales to be resistant to attack by mineral acids. A conditioning step is normally used prior to pickling to oxidize the Cr content of the scale to the Cr^{6+} state to enhance the removal of both the oxide and the Cr-depleted layer. Acid pickling then undercuts the oxide, resulting in removal of the surface down to the bulk alloy composition. Removal of scale and the Cr-depleted metal layer results in loss of material, along with generation of spent pickling liquors and sludge wastes that are not readily amenable to metal value recovery and must be disposed.

The annealing atmosphere can have a significant impact on the chemical composition of the surface scale and underlying metal substrate and effect the subsequent response of the SS to further processing and/or service conditions. Current information on the oxidation of SS's in atmospheres similar to continuous annealing furnaces is insufficient to predict the outcome of the annealing process. Since either gas or oil can be used to fire the continuous annealing furnaces, the relative quantities of H_2O, CO_2, and other combustion products can vary as to fuel type and the air-fuel ratio. The resulting scale can vary in composition, structure, and thickness. Excess or tenacious scale is wasteful since the metal content of the scale is not recovered, which increases the cost of SS products because of material loss and added processing expense.

A large volume of information has been published on the oxidation of metals, and several investigators have researched oxidation in the temperature ranges used for annealing. However, the amount of information available dealing with scale formation under the conditions existing during the annealing process are limited. Rapp (*3*) has discussed the high-temperature oxidation of metals forming cation-diffusing scales. His observations are that pure Cr forms a convoluted Cr_2O_3 layer where physical contact between the oxide and metal is lost. The formation of convoluted scale could be avoided if the metal was vacuum annealed at 1,100° C for 15 min prior to oxidation. Whittle and Wood (*4*) investigated the long-term oxidation of an 18-pct-Cr alloy at 800°, 1,000°, and 1,200° C. They observed uniform adherent layers of Cr_2O_3 at 800° and 1,000° C, while at 1,200° C the Cr_2O_3 layer

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[4] Italic numbers in parentheses refer to items in the list of references at the end of this report.

contained bubbles and was highly irregular. They performed concentration profile analyses through the oxide layer and into the adjacent metal. The scale layers on their samples were up to 100 μm thick. Failure of the adherent oxide layer resulted in rapid oxidation, followed by the formation of a new "healing" layer of Cr_2O_3 and a slowed oxidation rate until the oxide layer again failed. If the Cr content of the metal at the oxide-metal interface was insufficient to form a Cr_2O_3 layer, a Cr-Fe spinel layer was formed that did not have the protective qualities of Cr_2O_3. Fabis and Covino (*5*) studied the Cr-depleted layer formed during the annealing of Type 304 SS using analytical electron microscopy and observed Cr depletion in the top 100 nm of the metal. Saito, Furuya, Sugisaki, Koga, Wakasugi, and Ogi (*6*) measured the Cr depletion profile of Type 316 SS under low pressures of O_2 (7.2×10^{-18} Pa). They determined that the Cr depletion layer extended as deep as 6 to 8 μm after 240 h at 700° C. Stott and Wei (*7*) concluded that a healing Cr_2O_3 layer forms on Types 310 and 321 SS's in O_2 at 800° and 1,000° C, which eventually forms blisters that fail, exposing the underlying Cr-depleted alloy to the O_2 atmosphere. The protective Cr_2O_3 layer reformed more rapidly on the Type 310 SS, which has a higher Cr content at 1,000° C, but at 800° C a Cr-Fe spinel was formed on both steels. Allen, Dyke, Harris, and Morris (*8*) observed a Cr-Fe oxide inner layer with a Fe oxide outer layer on Type 304L SS oxidized in air for times as short as 2 min at 600° C. They concluded the duplex nature of the oxide scale was due to the greater mobility of Fe as compared to Cr through the existing Fe-Cr oxide layer, resulting in the formation of nearly pure Fe oxide as the outermost scale. The relative mobility of the metals in the spinel is $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Cr^{3+}$. Lobb and Evans (*9*) determined the Cr concentration necessary for healing layer formation during the oxidation of 20 pct Cr, 25 pct Ni, and 6 pct Nb SS's. Healing was not obtained at 700° C unless the Cr content of the surface metal was ≥18.5 pct, while healing occurred at 1,000° C if the Cr content was 15.2 pct. This inverse effect was attributed to the coarse grain size of the test material. Lobb and Evans also investigated the oxidation of 20-pct-Cr austenitic steels containing from 0.0 to 2.25 pct Si at 900° C. They found a minimum scale thickness for alloys containing between 0.5 and 1.0 pct Si, with an SiO_2 layer forming between the metal and the Cr_2O_3 layer. The Cr_2O_3 layer formed on the Si-containing alloys was more uniform and less buckled (convoluted) than those on Si-free alloys. When a spinel layer was present on the outside of the Cr_2O_3 layer, the presence of an SiO_2 layer reduced the Fe content of the spinel to near zero. Farrow and Nagelberg (*10*) used Raman spectroscopy to study the oxide layer formed on Type 310 SS. They found that scale oxide formed above 600° C was predominantly Cr_2O_3; however, when several percent Mn was present in the alloy, it formed an outer spinel layer with Cr.

From the above discussion of oxidation of metals, the high-temperature oxidation of SS appears to be significantly affected by temperature, atmosphere, and the presence of minor elements such as Si and Mn. The major effects manifest themselves in the structure of the oxide formed, its chemical composition, and its adherence, or lack of, to the metal substrate. When an adherent Cr_2O_3 layer is formed, it is protective and significantly reduces the oxidation rate until the scale fails and the base metal is exposed to the oxidizing atmosphere. Manganese, if present, appears on the outer surface of the Cr_2O_3 layer as a Cr-Mn spinel. As long as the Cr_2O_3 layer is intact, further oxidation proceeds at a relatively slow rate. When breakthrough occurs, oxidation proceeds rapidly until a healing Cr_2O_3 layer reforms if the Cr content of the metal substrate is sufficient. Failure to reform a protective Cr_2O_3 layer results in continuing catastrophic oxidation. Silicon has been reported to form an SiO_2 layer between the Cr_2O_3 layer and the metal for some alloys and can have an effect on the adherence properties of the Cr_2O_3 layer. If a Cr-Fe spinel layer is initially formed, Fe ions diffuse rapidly through the layer and are oxidized to magnetite, or even hematite, at the gas-oxide interface. Under these conditions, oxidation continues unabated by a protective layer.

When Mn and Si are considered from a thermodynamic standpoint, they form the most stable oxides, followed in turn by Cr, Fe, and Ni. Of the major metals present in the SS alloy, the formation of a Cr oxide would be favored in preference to Fe or Ni oxides. However, under certain conditions a layer of Cr-Fe spinel is initially formed on the metal surface, after which Fe oxides continue to rapidly form at the gas-oxide interface, with only a slow growth of the spinel layer. Since this is not favored by the thermodynamics, the explanation must lie with the mobility of the metal ions through the spinel layer. The literature indicates that low temperatures (<600° C) favor the formation of an initial spinel layer. At higher temperatures, such as those used for annealing, the picture is less clear and the conditions that control the character of the initial oxide formed are not obvious.

It was the goal of this work to examine the annealing process to delineate the effects of annealing conditions and, in particular, the composition of annealing atmospheres on quantity and type of scale formed. Since SS is mechanically worked prior to annealing, the effect of cold working on scale formation was also examined.

EXPERIMENTAL PROCEDURE

The annealing tests were performed in a 7.6-cm-inside diameter tube furnace lined with an alumina tube, connected at one end to a metered gas supply manifold used to generate simulated annealing atmospheres. The furnace was computer controlled, programmable, and capable of sustained operation at 1,600° C. Furnace temperature was controlled to ±1° C of the set value and specimens temperatures were monitored to the same tolerance. The annealing atmosphere, except water vapor, was metered through six calibrated mass-flow controllers. The gases were injected into the manifold under computer control to a tolerance of ±2 pct. Water vapor was generated in a pressure vessel operating at 69 kPa, metered through a heated line (140° C), and injected into the furnace through a calibrated flowmeter along with the other gases. SS samples were inserted through the opposite end of the furnace past a baffle used to prevent backflow of air into the furnace. The furnace-gas metering system was capable of completely automated operation and data logging, with the exception of insertion and removal of the specimens and metering of water vapor.

The compositions of the annealing atmospheres were selected on the basis of air-CH_4 ratios. Ratios of air-CH_4 from 10:1 to 18:1 were used. The 10:1 ratio was selected to represent a gas mixture resulting from stoichiometric combustion of CH_4 in air (no O_2). The 14:1 ratio represents the gas mixture from excess air combustion that contains 5.3 pct O_2 and represents target O_2 levels in commercial continuous annealing operations. The 18:1 ratio was selected to represent combustion that produces a high level of O_2 (8.4 pct) in the gas mixture. Metered quantities of CO_2, H_2O, N_2, and O_2 were used to produce the desired mixtures of gases. On the basis of equilibrium calculations, traces of CO and H_2 would have been present in the atmospheres; however, the amounts were too small to meter and these gases were not employed in the annealing tests. Table 1 gives the composition of the annealing atmospheres used at several air-CH_4 ratios.

Table 1.—Composition (volume percent) of annealing atmospheres at several air-CH_4 ratios[1]

Air-CH_4 ratio	N_2	H_2O	CO_2	O_2
10:1	72.7	18.2	9.1	0.0
14:1	74.7	13.3	6.7	5.3
18:1	75.8	10.5	5.3	8.4

[1] Data arranged by decreasing order of atmospheric constituent gases.

Coupons of Type 304 SS, nominally 2.5 by 3.2 cm, were prepared from hot-rolled and annealed plate supplied by Allegheny Ludlum Corp. (ALC), by cold rolling to 40-, 50-, and 75-pct reduction on a standard four-roller laboratory rolling mill. Chemical analysis of the alloys rolled to 50-pct reduction is given in table 2 (sample 1). A second sample of cold-rolled Type 304 SS sheet was also obtained from ALC, and similar coupons were cut from it (sample 2). A third sample of cold-rolled Type 304 SS was obtained from J&L Specialty Products Corp. (J&L) (sample 3). Samples 2 and 3 had received approximately 50-pct cold reduction in a commercial rolling mill. A summary of the SS samples used in the annealing study is presented in table 3. From the table, it can be seen that the primary variation before annealing is the degree of cold work and sample thickness.

Table 2.—Partial chemical analyses (weight percent) of Type 304 SS used in annealing study[1]

Sample	Fe	Cr	Ni	Mn	C	Si	P	S
1	Bal	18.9	8.2	1.7	0.08	0.53	0.03	0.01
2	Bal	19.4	9.1	1.6	.11	.58	.02	.01
3	Bal	20.4	8.3	.9	.08	.49	.02	.01

Bal Balance.

[1] Data arranged by decreasing order of alloying elements.

Table 3.—Thickness of Type 304 SS sheet cold rolled to several reduction levels

Sample	Thickness, mm	Reduction, pct
1	1.52	40
	1.22	50
	.64	75
2	.99	50

Acetone was used to clean and degrease the coupons prior to annealing. Between degreasing and annealing, the samples were stored in a desiccator. Each 2.5- by 3.2-cm coupon was supported on a sled that was fabricated from Kanthal[5] wire and was inserted individually into the furnace. The coupon was held edgeways to the gas stream by a wire clip positioned at the front of the Kanthal sled (fig. 1). Coupon temperature was measured with a fine (22 ga) Chromel-Alumel thermocouple wrapped around the specimen. The thermocouple fit over the coupon, and the bead was bent backward so that it fit into a notch filed in the leading edge of the sample, approximately 3 mm down from the top. The sample, the attached thermocouple, and the sled were pushed into the furnace hot zone by a wire extension rod. A real-time video display was used to obtain a complete sample temperature profile. Each component gas (N_2, O_2, CO_2, and H_2O) flow volume was monitored throughout the annealing test. Total gas flow was approximately 2.5 L/min. Annealing duration was measured from the time the specimen temperature reached 90 pct of the target temperature. Temperature profiles of thermocouples without samples consistently showed a more rapid temperature increase, indicating that with this arrangement the actual specimen temperature profile was being measured. A typical heating curve for a 1-mm-thick sample is shown in figure 2.

At the conclusion of the timed annealing test, the sample was rapidly withdrawn from the furnace into atmospheric air to cool. The sample sleds were placed on large metal sheets to prevent contamination of any spalled scale. Cooling occurred within a few seconds, as shown in figure 2, and for this reason, reactions between the sample and room air were assumed to be minimal. In some tests, scale formation was so severe that the oxide coating would separate during cooling, necessitating provisions to catch the separated scale. Therefore, a 25-cm SS bowl was placed over the hot sample to capture any scale violently ejected from the sample surface.

Techniques used to characterize the adherent scale coatings and substrates on the annealed specimens included scanning electron microscopy (SEM) and/or energy dispersive X-ray (EDX) analysis and Auger electron spectroscopy (AES) surface analysis. All specimens were weighed before and after annealing to determine the weight gain. The weight of any spalled scale was also determined whenever possible. The separated scale and any loose scale were analyzed for structure and chemical composition by X-ray diffraction and inductively coupled plasma emission spectroscopy, respectively.

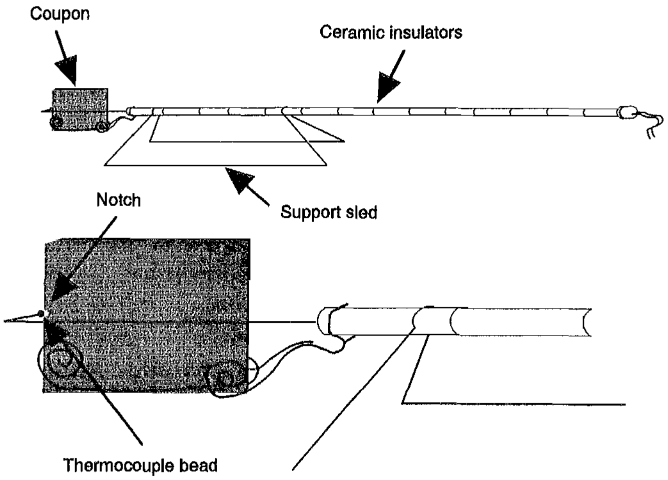

Figure 1.—Sample holder for coupons showing position of temperature-measuring thermocouple.

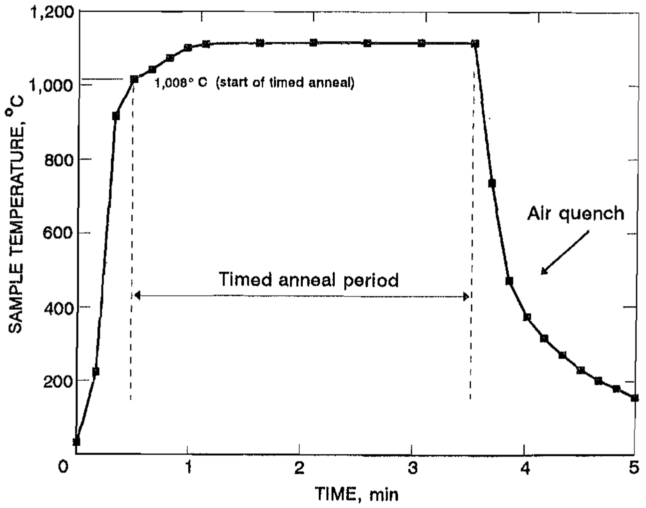

Figure 2.—Annealing temperature profile for Type 304 SS coupon.

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[5] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

RESULTS AND DISCUSSION

DEGREE OF COLD WORK

Either hot or cold working precedes the SS annealing process. During the working process, metal grains are deformed and mechanical energy in the form of residual stress is stored in the deformed metal grains. The residual energy and grain deformation was thought to possibly have an impact on the oxidation reactions. Therefore, the thickness of scale formation was compared to the degree of cold work a test coupon had received. Cold work was selected over hot work as the independent variable because the amount of residual energy and grain deformation would be larger for cold working and no oxide scale would be formed during the cold process.

Coupons of Type 304 SS that had been cold rolled to 40-, 50-, and 75-pct reduction were annealed at 1,150° C for 3 min under atmospheres having air-CH_4 ratios of 10:1, 12:1, and 14:1 to determine if the degree of cold working had an effect on the thickness of scale formed as determined by sample weight gain. The results are shown in figure 3. As can be observed, the composition of the annealing atmosphere had a significant effect on the thickness of scale formation, while the degree of cold work had little or no discernable effect. The scale thicknesses formed under air-CH_4 atmospheres of 10:1 on the 40- and 75-pct-reduced samples are nearly the same, while the scale thickness on the 50-pct-reduced sample is somewhat thinner. At air-CH_4 ratios of 14:1, the scale formed for all three degrees of reduction is essentially the same. Therefore, the variation appears to be attributable to other effects, such as loose scale that was lost and not accounted.

Additional coupons from the same cold-rolled lots were also annealed for 9 and 27 min. The longer annealing times resulted in the disappearance of the atmosphere effect on scale formation. SEM and microscopic examination of these coupons revealed that "breakthrough" oxidation had occurred on these samples at the extended annealing times. This had effectively destroyed the protective Cr_2O_3 layer, allowing rapid oxidation to proceed as evidenced by the mounds and bubbles in the scale. Figure 4 shows a sample that was annealed at 1,120° C for 9 min under an air-CH_4 atmosphere of 18:1. The major mound has fractured, and the oxide was about to undergo catastrophic failure at this spot. The other mounds had not failed, but probably would have if the annealing had been continued for a longer duration. The missing piece of scale just above the fractured mound was most likely spalled from the sample upon cooling. Based on these results, all future samples were annealed under conditions where breakthrough oxidation was not observed; i.e., 1,120° C for 9 min or less. Since continuous industrial annealing of sheet products is normally for 1 min or less at temperature, this did not present a significant limitation to the test work.

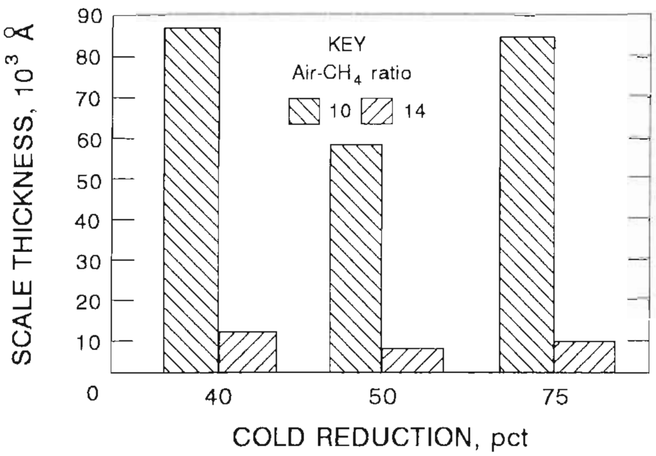

Figure 3.—Scale formation as function of cold reduction on Type 304 SS coupons.

Figure 4.—Annealed coupon showing impending failure of protective Cr_2O_3 layer.

EFFECT OF ATMOSPHERE ON SCALE FORMATION

Coupons cut from the cold-rolled Type 304 SS strip supplied by ALC and J&L (samples 2 and 3, table 2) were annealed at 1,120° C for 0.33, 0.66, 1, 3, and 9 min in atmospheres with air-CH_4 ratios of 10:1, 14:1, and 18:1. The thickness of the scale formed during annealing was approximated by using weight gain data to calculate the thickness of the scale formed. The calculation was carried out using the following assumptions:

1. The scale was of uniform thickness over the entire coupon, including the sides and the edges.
2. The ratio of the coupon's length to width was 1.25:1.
3. The density of the coupons was 7.85 g/cm^3.
4. The density of the scale formed was 5.18 g/cm^3.
5. The O_2 content of the scale was 28 wt pct.

On this basis, the scale thickness in angstroms is a function of the ratio of the scale volume to the total surface area of the sample multiplied by 100 million. The relationships for coupon surface area and oxide volume are, respectively,

$$A = 2w/(7.85t) + 3.6\ \{(1.25w \times t)/7.85\}^{1/2}, \quad (1)$$

where A = surface area, cm^2,

w = sample weight, g,

and t = sample thickness, cm.

The term 2w/(7.85t) in equation 1 represents the two flat sample surfaces and the term $3.6\ \{(1.25w \times t)/7.85\}^{1/2}$ represents the sample edges.

$$V = (100\ \Delta M/28) \times (1/5.18) = \Delta M/1.45 \quad (2)$$

where V = scale volume, cm^3

and ΔM = sample weight gain, g,

then

$$T = (V/A) \times 10^8, \quad (3)$$

where T = scale thickness, Å.

The annealing results at 1,120° C for three air-CH_4 ratios are shown in figure 5. The calculated scale thicknesses for the 10:1 air-CH_4 samples are significantly larger than for the samples annealed under air-CH_4 ratios of 14:1 and 18:1. This is consistent with commercial practice where it is known that annealing in low-O_2 atmospheres results in heavy scale formation. Oxidation in the low-O_2 atmosphere (air-CH_4 ratio of 10:1) is continuing at a fast rate even after 3 min; whereas, the oxidation rate in the atmospheres containing free O_2 (air-CH_4 ratios of 14:1 and 18:1) slows significantly after 1 to 3 min. The latter is indicative of the formation of a protective oxide layer in the atmospheres containing free O_2; however, the scale formed in the low-O_2 atmosphere did not form an oxide layer that presented a significant barrier to continued oxidation.

AUGER ELECTRON SPECTROSCOPY ANALYSIS OF ANNEALED TYPE 304 STAINLESS STEEL SURFACES

A series of Type 304 SS coupons were annealed at 1,120° C under three atmospheres, representing CH_4-air ratios of 10:1, 14:1, and 18:1. Annealing was conducted as described in the experimental procedure with holding times of 0.33, 1, 3, and 9 min after the coupon had attained 90 pct of 1,120° C (1,008° C). Each of the 12 samples was then subjected to AES analysis of the oxide scale coating formed during the annealing process. A constant sputtering rate of 180 Å/min was employed, with a total penetration of about 12,000 Å attained on each sample. The AES results obtained from the 0.33-min annealing are given in figure 6. These and the 1 min results probably most closely represent the annealing duration encountered in continuous annealing of sheet products. The scale-gas interface is at zero sputter

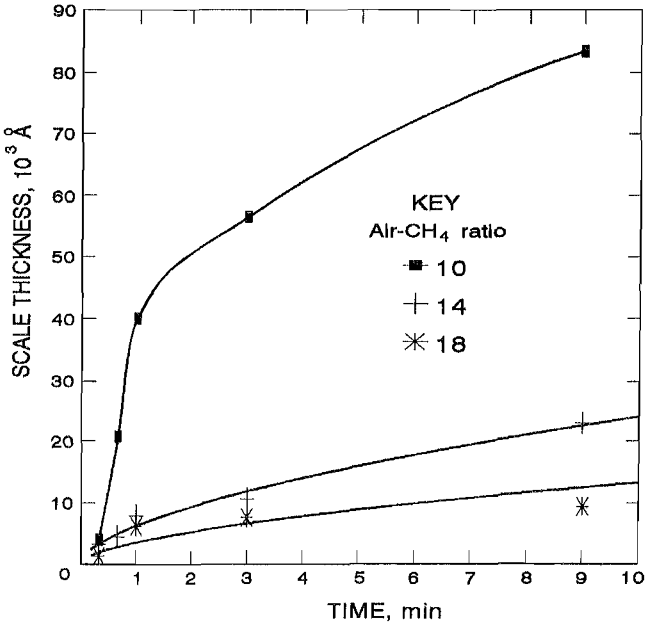

Figure 5.—Calculated scale thickness for annealed Type 304 SS coupons.

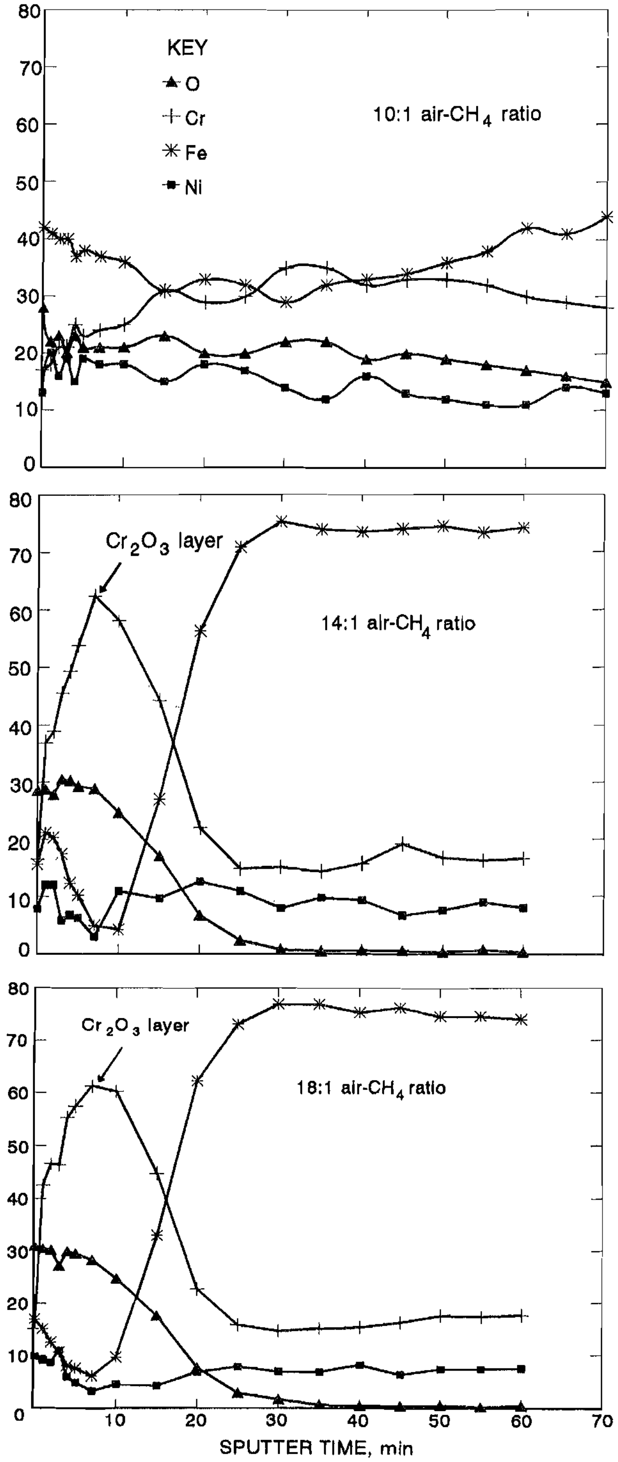

Figure 6.—AES analyses of annealed Type 304 SS coupons under several atmospheres.

time, and as the beam sputters away the oxide scale, the analyses begin to approach those of the base alloy. For the coupons annealed in simulated combustion atmospheres with air-CH_4 ratios of 14:1 and 18:1 (figure 6, middle and bottom) the Cr and Fe analysis of the scale near the metal-oxide interface shows the classic chromite layer where the Fe content is almost zero and Cr becomes the predominant metal in the oxide. This confirms that, under these atmospheres, a protective chromite layer is established and oxidation of the metal surface is effectively halted within 1 to 3 min at 1,120° C. Under these conditions, oxidation will proceed slowly until breakthrough; i.e., a break in the continuity of the Cr_2O_3 layer allows the atmosphere to penetrate the protective layer and oxidation again proceeds until a new protective layer is established.

However, the coupon annealed at an air-CH_4 ratio of 10:1 (figure 6, top) did not display this predominance of Cr content in the oxide scale, indicating that a protective chromite layer was not formed. The sputtering rate of 180 Å/min, shown in figure 6 (top) did not result in penetration to the base metal because of the thick scale formed on this sample. To confirm that an inner chromite layer did not exist below what was apparently spinel-type oxides on this sample, an additional sample annealed under an air-CH_4 atmosphere of 10:1 was subjected to AES analysis using a 500 Å/min sputtering rate for an extended time. These results appear in figure 7. As can be observed, no evidence of a Cr_2O_3 layer was detected, confirming that the inner portions of the oxide layer also had an apparent spinel structure. The AES analyses of both coupons would imply that a layer of Fe-Cr oxide spinel had formed

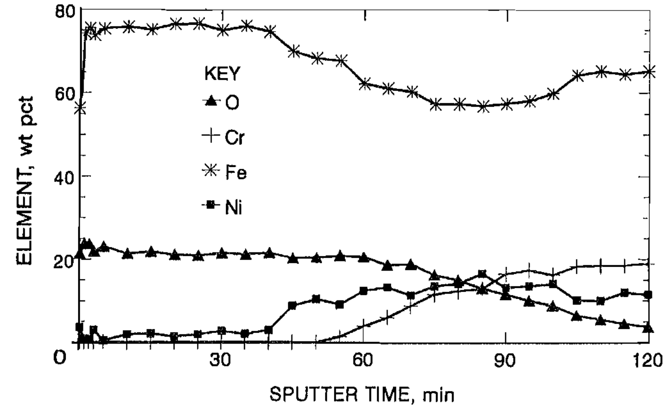

Figure 7.—AES analysis of annealed Type 304 SS coupon under atmosphere with 10:1 air-CH_4 ratio.

in place of the Cr_2O_3 layer formed under air-CH_4 atmospheres of 14:1 and 18:1. The continued rapid increase in thickness of the oxide layer with time would also indicate that this spinel layer was not an effective diffusion barrier and that Fe was rapidly diffusing through this layer to be oxidized at the gas-oxide interface, as was further evidenced by the scale spalled from the sample surface. X-ray diffraction and chemical analysis consistently confirmed that the separated and loose scale was predominantly magnetite. It has been reported in the literature that Fe diffuses rapidly through spinel scales because of the concentration gradient between the bulk metal and the spinel at the oxide-atmosphere interface, while Cr diffuses more slowly than Fe through this same layer (*8*). The formation of spinel-type oxide scales has been reported by Stott and Wei (*7*) for oxidation of SS's at temperatures below 1,000° C, while the same authors also reported that, at temperatures of 1,100° C and above, a chromite layer was formed at the metal-oxide interface. The evidence presented here indicates that the O_2 potential of the annealing atmosphere also has an effect on the oxide structure formed at 1,120° C. This offers an explanation why the oxidation of Type 304 SS proceeds more rapidly in atmospheres having a low-O_2 pressure (no free O_2) but a large supply of oxidizing gases in the form of CO_2 or H_2O, the oxidation rates being dependent on the scale structure formed as determined by annealing atmosphere composition.

This annealing system is in contrast to atmospheres where a low-O_2 pressure is due to a vacuum or an inert gas atmosphere with trace amounts of O_2. In these systems, the oxidation reaction is limited by the supply of O_2; whereas in the system used in this study, a large supply of oxidizing gases were available as CO_2 and H_2O and could support a rapid oxidation rate. The failure to form a protective chromite layer at annealing temperatures results in rapid oxidation of the metal, and in particular the Fe content of the SS steel, because of the greater mobility of Fe through the spinel layer.

Nickel is also a major alloying element in austenitic SS. Observation of the AES analysis (figs. 6-7) indicates that Ni is present in the Cr-Fe ferrite at levels about the same or slightly higher than that present in the bulk alloy. However, it is nearly absent from the Cr_2O_3 layer (figure 6, middle and bottom) and is absent from the outer magnetite layer formed under air-CH_4 ratios of 10:1 (fig. 7). This would indicate that Ni is substituting for Fe in the Cr-Fe ferrite but is not being transferred through the ferrite as fast as Fe. This is in agreement with previous investigations that Fe is more mobile than Ni in the ferrite phase. The lack of Ni in the Cr_2O_3 phase is explained by the lack of plus 2 sites oxidation in the lattice, which excludes both Fe and Ni from this phase. Under the conditions present in this system, Fe does not oxidize to the ferric state, except at the gas-oxide interface after long-term exposure to strongly oxidizing atmospheres. A phenomenon was observed with several samples that were annealed under atmospheres containing free O_2 (air-CH_4 ratio of ≥14:1). The concentration of Ni on the outer surface of the oxide, or in one instance a small amount of spalled oxide, contained large amounts of Ni (up to 70 pct in the spalled material). Although this study did not provide an explanation for this phenomenon, high Ni oxide was probably formed before the test coupon had attained annealing temperature.

SCANNING ELECTRON MICROSCOPY ANALYSIS OF ANNEALED TYPE 304 STAINLESS STEEL COUPONS

To support the analytical results obtained from AES analysis of the surface oxides (scale) present on Type 304 SS after annealing in simulated combustion atmospheres, several annealed coupons were subjected to SEM analysis, including semiquantitative determination of Cr, Mn, Fe, and Ni. Figures 8 and 9 show SEM photomicrographs (secondary electron images) of SS samples annealed for 3 min at 1,120° C under air-CH_4 atmospheres of 10:1 and 14:1, respectively. The convoluted uniform oxide in figure 9 is typical of the oxide layers formed during annealing in atmospheres containing free O_2. This layer is essentially Cr_2O_3 and virtually identical in appearance to the photomicrograph of the oxides formed during the oxidation of pure Cr (*3*). In contrast, the photomicrograph of the sample annealed in the air-CH_4 atmosphere of 10:1 (fig. 8) shows magnetite octahedrals atop a layer of smaller-grained oxide, which is most likely Cr-Fe spinel. These photomicrographs clearly support the AES findings and indicate the presence of spinel oxide and Cr_2O_3 layers on Type 304 SS annealed under air-CH_4 atmospheres of 10:1 and 14:1, respectively.

The semiquantitative EDX analyses were conducted at acceleration voltages of 10 keV to limit depth of penetration into the surface oxides. The estimated beam penetration for a solid with a density of 5 g/cm^3 (oxide) is 7,000 Å at 10 keV. For material with a density of 8 g/cm^3 (metal), the estimated penetration is 4,500 Å at 10 keV. The thicknesses of the oxide scales for 1-min anneals, as determined by sample weight gain (fig. 5), are approximately 38,500, 6,300, and 3,000 Å for annealing atmospheres with air-CH_4 ratios of 10:1, 14:1, and 18:1, respectively. The analytical results obtained are given in table 4. It is apparent that sample A, annealed in an air-CH_4 atmosphere of 10:1, has a distinctly different composition from samples B and C, while the scale compositions of B and C are quite similar and rich in Cr content. The Fe-Cr ratio in the oxide scale (sample A) for the air-CH_4 ratio of 10:1 indicates that Fe is present at about a 1.2:1 ratio to Cr, which confirms the AES results in that the oxide appears to be a Fe-Cr spinel. Iron diffuses rapidly through the spinel layer and reacts with CO_2 and H_2O to form magnetite at the oxide-gas interface. This magnetite is nonadherent and tends to spall both during annealing and subsequent cooling. Chromium is less mobile through the spinel, and the formation of magnetite predominates at extended annealing times. As mentioned previously, X-ray diffraction and chemical analysis of spalled oxide indicated that magnetite was the major constituent, with only minor amounts of Cr being present. This type of oxidation is also observed on commercial annealing lines when the free-O_2 content of the annealing atmospheres is low (<2 pct). The thick layer of black oxide scale, most likely spinel, and the fine, loosely-adhered magnetite give the sheet a black, sooty surface. The annealing line operators refer to this phenomenon as a smoky anneal.

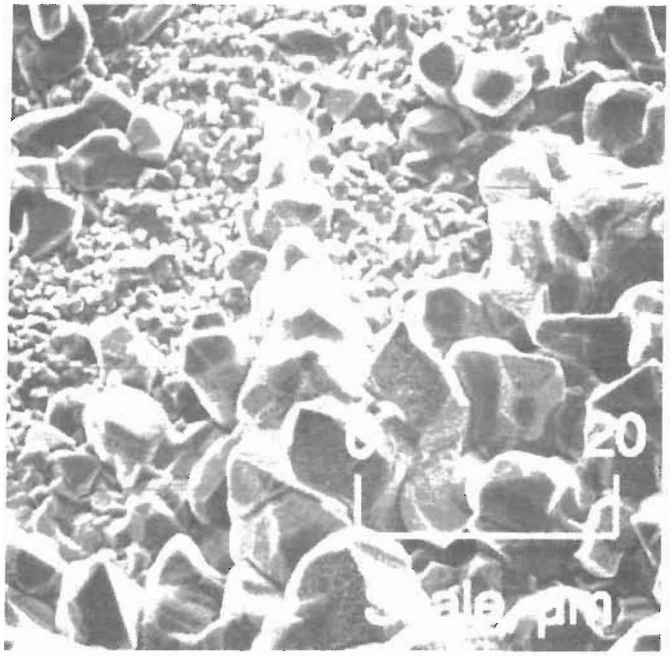

Figure 8.—View of magnetite octahedrals formed on annealed Type 304 SS coupon.

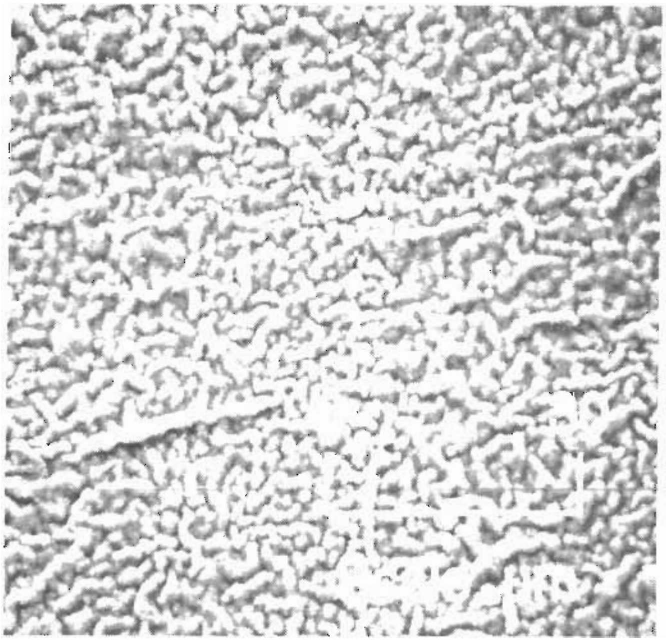

Figure 9.—View of convoluted oxide formed on annealed Type 304 SS coupon.

Table 4.—EDX microanalysis (weight percent) of Type 304 SS annealed 1 min at 1,120° C and acceleration voltage of 10 keV

Sample	Air-CH_4 ratio	Fe	Cr	Ni	Mn
A	10:1	51	41	3	6
B	14:1	17	60	1	20
C	18:1	16	62	2	17

Under more oxidizing atmospheres (samples B and C), Cr predominates in the scale, indicating the presence of a Cr_2O_3-type oxide scale. The presence of 16 to 17 pct Fe is most likely because of penetration of the beam through the thin oxide layer formed under air-CH_4 atmospheres of 14:1 and 18:1. This oxide presents an almost impenetrable diffusion barrier to both Cr and Fe, which results in a marked slowdown in oxidation until catastrophic failure of the oxide occurs. This type of failure did not occur during the short annealing times (<9 min) used in this study and is not normally observed on commercial annealing lines.

The Mn content of the oxide for samples B and C is as much as 20 pct. This tends to confirm previous findings (*8*) that Mn is highly mobile and concentrates in the oxide. However, the relatively large amounts detected were not anticipated. The finding that Mn is concentrated in the oxide layer is substantiated by the drop of Mn concentration to 7 pct with increased (30 keV) acceleration voltage. This, in effect, results in averaging the Mn concentration of the oxides with that of the base metal.

DISCUSSION AND CONCLUSIONS

Sample coupons of cold-rolled Type 304 SS were annealed for times varying from 0.33 to 9 min at 1,120° C in simulated combustion atmospheres with air-CH_4 ratios from 10:1 to 18:1. The annealed coupons were evaluated by weight gain, chemical analysis, SEM (including EDX) analysis, and AES surface analysis.

Annealing oxide scale thickness was not found to be dependent on the degree of cold rolling. The initial premise that the cold-working energy stored in the metal could have an effect on the subsequent annealing reactions turned out not to be a factor in the extent of surface oxidation during annealing.

The weight gain results showed that oxidation of the metal was several times faster at low-O_2 levels. This is consistent with observations on commercial annealing lines. Oxidation at low-O_2 levels continued throughout the annealing period, resulting in thick oxide scales compared with those observed at higher O_2 levels (air-CH_4 ratios of 14:1 and 18:1). The coupons annealed in the high-O_2 atmospheres (air-CH_4 ratio of 18:1) oxidized for a short time, and then the oxidation reaction slowed essentially to a stop. This resulted in scale thicknesses that were comparatively thin (<7,000 Å at 1 min).

AES analysis of the oxide layers explained why oxidation was more rapid in low-O_2 atmospheres than in atmospheres containing free O_2. The analysis of the surface oxides indicated that the structure of the oxide shifted from a Cr_2O_3 layer in the high-O_2 atmospheres to a Fe-Cr spinel layer in the low-O_2 atmospheres. Thermodynamically, Cr should oxidize before Fe or Ni, and the oxidation rate should increase with increased O_2 content of the atmosphere. However, in the case of Type 304 SS, the oxidation rate becomes dependent on the structure of the oxide scale formed. If sufficient free O_2 is present, an adherent Cr_2O_3 oxide layer is formed that blocks diffusion of metal atoms to the gas-metal interface and gas atoms to the oxide-metal interface. This is the same principal that gives SS its corrosion protection. When a spinel oxide layer is formed in low-O_2 atmospheres, the spinel has a variable composition through which Fe ions are much more mobile than Cr or Ni ions. This results in Fe diffusion through the spinel to the oxide-gas interface where Fe is oxidized to magnetite. Oxygen is supplied by the CO_2 and H_2O contents of the atmosphere, both of which oxidize Fe and Cr at annealing temperatures. The magnetite formed at the gas-oxide interface is nonadherent and subsequently spalls from the surface, exposing the spinel layer to the annealing atmosphere. This results in Fe being oxidized in preference to Cr because Fe is more mobile in the spinel structure and is available at the oxide-gas interface, where it is rapidly oxidized and subsequently spalls from the surface. Cr diffuses slowly through the spinel and is also oxidized, but at a rate much slower than Fe.

SEM analysis of the oxide scale tends to agree with the AES analysis, except it indicated high levels of Mn in the surface oxides formed in the high-O_2 atmospheres. Manganese is difficult to determine by AES analysis because of low-intensity peaks and consequently was not determined. The spinel oxides formed at air-CH_4 ratios of 10:1 did not contain significant Mn concentration above that of the bulk metal. The mobility of Mn and its tendency to concentrate in the Cr_2O_3 layer formed in high-O_2 atmospheres has been reported by other investigators (*10*). Since Mn is present at the 2-pct level in the bulk alloy, the high levels found in the oxide, up to 20 pct of the metal content, were not anticipated. Whether or not the Mn content of the oxide is critical to the formation of the diffusion barrier could not be determined in this study.

The information developed in this annealing study explains the variation in oxide scales formed on Type 304 SS under atmospheres with varying free-O_2 content. The agreement between the results presented here and those observed by other investigators and industrial operators on somewhat similar systems confirms the validity of the results. The observation that annealing atmospheres can also affect the structure and composition of the oxide scale clarifies the occurrence of thick scales and smoky anneals due to the nonprotective nature of the spinel scales at annealing temperatures. The results, however, do not answer the effect of Mn on the annealing process or explain why spinel oxides form in the absence of free-O_2 atmospheres and Cr_2O_3-rich oxides in the presence of free O_2. Similarly, the behavior of Ni early during sample heatup has not been clarified. Clearly, there is a need for additional research in this area.

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