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HIGH-TEMPERATURE OXIDATION RESISTANCE OF THIN IRON-CHROMIUM-ALUMINUM ALLOY SHEET

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RESTRICTED DATA

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The oxidation resistance of thin sheets of iron-28 w/o chromium-2.67 to 10.0 w/o aluminum alloys, nominally 0.004, 0.006, 0.008, 0.012, and 0.016 in. thick, was determined by exposure in static air for 100 hr at 2100 and 2300 F. A minimum of 3.67 and 9.37 w/o aluminum was necessary to prevent excessive oxidation of 0.004-in.-thick sheet material at 2100 and 2300 F, respectively. Correspondingly, specimens of lower aluminum content and greater thickness withstood the oxidation attack. Oxidation of iron-chromium-aluminum alloys appeared to be related to the diffusion of aluminum to surfaces of the sheet to form an adherent protective layer of Al_2O_3.

INTRODUCTION

Iron-chromium-aluminum alloys possess good high-temperature oxidation resistance and utilization of these alloys for high-temperature service in air is based on this property, since their strength decreases rapidly above 1100 F because of their ferritic nature. A desirable property of iron-chromium-aluminum alloys for reactor application is their relatively low thermal-neutron-absorption cross section. Hence, thin sheet of iron-chromium-aluminum alloy is attractive as a cladding material for high-temperature reactor service in air or other oxidizing gases.

The fundamentals of the theory of oxidation of iron-chromium-aluminum alloys have been set forth by Kornilov.[1,2]* The process of oxidation of such alloys has been assumed to take the form of two successive and interconnected reactions, i.e., a primary process, the oxidation of all three metals, aluminum, chromium, and iron, and a secondary process, the diffusion of aluminum caused by the latter's preferred oxidation at the surface of the alloy. The oxidation resistance of the alloy is a function of the rate of oxidation of aluminum, the nature of the oxide film, and the rate of diffusion of aluminum from the inner zones to the surface zone.

The heat resistance of the ternary alloys depends chiefly on the formation of an adherent aluminum oxide scale. For example, the scale formed on oxidizing an iron-25 w/o chromium-5 w/o aluminum alloy for 240 hr in air at 2190 F is substantially pure alumina, which is replenished during such exposure by the preferential oxidation of the aluminum.[3] While both aluminum and chromium increase the oxidation resistance of the iron-chromium-aluminum alloys, it has been shown that aluminum is the more effective.[3,4,5]

The present investigation was undertaken to determine the effect of sheet thickness on the oxidation resistance of iron-28 w/o chromium-2.67 to 10.0 w/o aluminum alloys. Oxidation tests were conducted in still air at 2100 and 2300 F. All surfaces of

*References at end.

duplicate sheet specimens of each alloy were exposed and the data reported and ana-
lyzed on the basis of weight gain per unit surface area per 100 hr at temperature. The
average and maximum depths of oxide penetration were also evaluated.

ALLOY PREPARATION AND TESTING

The iron-chromium-aluminum alloys were prepared from electrolytic iron,
electrolytic chromium, and 2S aluminum. The alloys were induction melted in the fol-
lowing manner: the iron was melted first, then chromium was added and melted. SiMn
and CaSi were added as bath deoxidizers. Chromium was recovered from the slag by
the addition of NiMn. Sheet or rod aluminum was added, and the melt was poured as
soon as the aluminum became molten. Pouring temperatures were in the 2750 F range
and the molds were preheated to approximately 1000 F.

The alloy ingots were hammer forged at 2300 F. Some edge cracking occurred in
the ingots containing 8 w/o or more aluminum. This condition was remedied during
forging by hot grinding to remove the edge cracks soon after formation. The thickness
of the as-forged billets varied from 1.13 to 0.70 in.

The billet material was hot rolled at 2100 F to 0.350-in. sheet with approximately
7 per cent reduction per pass. The sheet was reheated after every pass. Hot rolling
continued at 2000, 1800, 1600, and 1500 F with corresponding sheet reduction to 0.250,
0.175, 0.110, and 0.020 in., respectively. An average of 10 per cent reduction per
pass was taken. The sheet was then annealed at 1500 F for 15 min and water quenched.

The thinner sheets were fabricated by cold reduction in steps to 0.016, 0.012,
0.008, 0.006, and 0.004 in. Samples of the sheet to be tested were taken at each step.
The sheets were annealed at 1500 F and water quenched between each step and vapor
blasted after each anneal. Prior to oxidation testing, the thin sheet was annealed at
1400 F for 15 min, water quenched, and vapor blasted.

Test specimens, 0.75 by 0.40 in., were cut from the nominal 0.016-, 0.012-,
0.008-, 0.006-, and 0.004-in.-thick iron-chromium-aluminum sheet. The length,
width, and thickness of each specimen were accurately measured and the dimensions
subsequently used to calculate the surface area and volume. The specimens were
cleaned in acetone, dried, and weighed. They were placed in glazed porcelain crucibles
and the crucible and specimen were weighed together.

Oxidation tests were conducted in horizontal open-tube Globar furnaces at 2100
and 2300 F. Two specimens of each alloy and thickness were exposed for 100 hr in air
at temperature. At the conclusion of the 100-hr run, each oxidized specimen was air
cooled and weighed together with all the oxide that had spalled into the crucible, and a
weight-gain value was determined. Each tested specimen was mounted in Bakelite such
that one edge was exposed and polished. The maximum and average thicknesses of the
unaffected metal, measured with a filar eyepiece at suitable magnification, were sub-
tracted from the before-test thickness of the specimen. The differences, divided by
two, were the maximum and average oxide penetrations into one side of the sheet
specimen. A photomicrograph was taken of the as-polished edge of each partially

oxidized specimen after exposure at elevated temperatures. Only weight-gain data were available from specimens which had completely oxidized.

RESULTS AND DISCUSSION

Results of the oxidation tests have been evaluated on the basis of weight gain per unit area per 100 hr at test temperature. In all cases, failure in test is termed to mean the complete loss of the metallic properties of the sheet specimens. Likewise, specimens termed "oxidation resistant" maintained their metallic properties under a protective oxide coating.

Tests at 2100 F

With the exception of the nominal 0.004-in.-thick specimens of the iron-28.90 w/o chromium-2.67 w/o aluminum alloy, sheet specimens of all thicknesses tested at 2100 F were oxidation resistant. The failure of the thin-sheet specimen indicated a lack of sufficient aluminum to form and maintain a protective oxide coating during high-temperature exposure. The rate at which aluminum content diminishes in the process of oxidation is highest in the alloy having the lowest aluminum content in the initial state.[3] The probable failure of the next thickest sheet specimen (nominally 0.006 in.) of the iron-28.90 w/o chromium-2.67 w/o aluminum alloy is indicated by the relatively high weight-gain values of 0.0028 g/(cm^2)(100 hr). Weight-gain values of the remaining alloys were in the range 0.0009 to 0.0021 g/(cm^2)(100 hr), which resulted from the formation of an oxide coating of practically pure alumina. Higher weight-gain values were associated with higher aluminum contents in the alloys. No apparent correlation existed between specimen thickness and weight-gain values of the oxidation-resistant iron-chromium-aluminum alloys tested at 2100 F. Penetration data indicated that some growth had occurred in the alloys during oxidation.[6] The growth factor was prevalent in the alloys containing less than 5 w/o aluminum and very possibly obscured a correlation between oxide penetration and weight-gain values and/or oxidation resistance of the alloys. Oxide penetration into these specimens did not exceed 0.0020 in. and averaged about 0.0012 in.

Tests at 2300 F

Failure after 100 hr at 2300 F was predominant in iron-chromium-aluminum sheet containing less than 9.37 w/o aluminum. An aluminum content of 8.07 w/o insured oxidation resistance of the nominally 0.006 in. or thicker alloy sheet while 9.37 w/o aluminum was needed to maintain oxidation resistance of the nominally 0.004 in. or thicker sheet. Increased rates of aluminum diffusion and oxidation were associated with the higher exposure temperature of 2300 F in comparison with exposure at 2100 F. This was indicated by higher weight-gain values of the oxidation-resistant sheet tested at 2300 F, which were in the range 0.0019 to 0.0105 g/(cm^2)(100 hr). Generally, oxide penetration was of the same order for specimens tested at both 2100 and 2300 F. Only

the iron-28.60 w/o chromium-5.86 w/o aluminum alloy exhibited growth during 100-hr exposure at 2300 F. The same alloys which exhibited growth in tests at 2100 F had completely oxidized in tests at 2300 F and, hence, penetration (or growth) measurements could not be taken. Excessive oxidation, though not to failure, was evident for the alloys containing 9.37 and 10.05 w/o aluminum. Apparently, 100-hr exposure at 2300 F substantially depleted the aluminum content of the alloy sheet; hence, constant replenishment of the protective alumina coating could not be maintained and failure was imminent. No correlation existed between specimen thickness and weight-gain values of the oxidation resistant iron-chromium-aluminum alloys tested at 2300 F.

A summary of the constant-temperature oxidation tests at 2100 and 2300 F is given in Tables 1 and 2, respectively.

Metallography

Photomicrographs were taken of the as-polished surface edge of each specimen which had survived high-temperature exposure.

As seen in Figures 1 and 2, the oxidation of the test specimens proceeded from the surface to the interior in a rather uniform manner. In ferritic alloys, the grain boundaries play a very minor role for the attack by oxygen.

CONCLUSIONS

The ferritic iron-chromium-aluminum alloys show excellent oxidation resistance at 2100 F. An iron-28 w/o chromium-3.67 w/o aluminum alloy, nominally 0.004-in. thick, will sustain 100 hr at 2100 F without failure. As little as 2.67 w/o aluminum is needed to insure oxidation resistance of nominally 0.006 in. or thicker alloy sheet at 2100 F.

At 2300 F, however, specimens thinner than a nominal 0.008 in. and containing less than 5.31 w/o aluminum were susceptible to complete oxidation. A 9.37 w/o aluminum content insured the oxidation resistance of the nominally 0.004-in.-thick specimen for 100 hr at 2300 F.

The excellent oxidation resistance of the iron-chromium-aluminum alloys at high temperature would appear to warrant a study of the rate of oxidation and time to failure of alloys undergoing oxidation.

TABLE 1. OXIDATION TESTS OF VARIOUS SHEET THICKNESSES OF IRON-CHROMIUM-ALUMINUM ALLOYS AT 2100 F IN AIR

Chemical Analysis (Balance Iron), w/o		Sheet Thickness, in.	Weight Gain[a], g/(cm²) 100 hr	Penetration[b], in.	
Chromium	Aluminum			Maximum	Average
28.90	2.67	0.0037	0.0149	(b)	(b)
		0.0054	0.0028	(c)	(b)
		0.0081	0.0009	0.0007	(b)
		0.0118	0.0011	0.0002	(b)
		0.0166	0.0011	(c)	(b)
27.45	3.67	0.0040	0.0011	0.0003	(b)
		0.0060	0.0009	0.0002	(b)
		0.0078	0.0011	(c)	(b)
		0.0118	0.0010	(c)	(b)
		0.0168	0.0011	(c)	(b)
25.00	5.00	0.0040	0.0013	0.0004	0
		0.0061	0.0013	0.0002	0
		0.0080	0.0015	0	(c)
		0.0120	0.0014	0.0003	0.0002
		0.0160	0.0014	0.0004	0.0001
28.90	5.31	0.0040	0.0009	0.0011	0.0006
		0.0063	0.0009	0.0008	0.0007
		0.0082	0.0011	0.0010	0.0005
		0.0132	0.0010	0.0012	0.0010
		0.173	0.0011	0.0011	0.0007
28.60	5.86	0.0039	0.0012	0.0011	0.0005
		0.0065	0.0012	0.0012	0.0007
		0.0080	0.0013	0.0016	0.0007
		0.0125	0.0013	0.0018	0.0012
		0.0172	0.0014	0.0016	0.0010
27.90	7.00	0.0040	0.0013	(b)	(b)
		0.0060	0.0016	(b)	(b)
		0.0080	0.0014	(b)	(b)
		0.0120	0.0017	(b)	(b)
		0.0163	0.0015	(b)	(b)
26.80	8.07	0.0044	0.0018	0.0004	0.0001
		0.0057	0.0018	0.0010	0.0007
		0.0083	0.0019	0.0007	0.0005
		0.0120	0.0016	0.0011	0.0009
		0.0161	0.0014	0.0014	0
26.95	9.37	0.0042	0.0021	0.0007	0.0002
		0.0059	0.0020	0.0011	0.0006
		0.0078	0.0020	0.0015	0.0008
		0.0128	0.0021	0.0010	0.0006
		0.0171	0.0013	0.0010	0.0005
26.55	10.05	0.0049	0.0017	0.0009	0.0006
		0.0060	0.0016	0.0009	0.0005
		0.0085	0.0015	0.0008	0.0005
		0.0124	0.0016	0.0008	0.0004
		0.0165	0.0013	0.0005	0.0002

Footnotes for Table 1.
(a) Average of two tested specimens.
(b) No penetration measurements were made on the iron-27.90 w/o chromium-7.00 w/o aluminum alloy. No penetration measurements could be obtained on the specimens which had been oxidized severely and were subsequently too brittle to mount in Bakelite.
(c) The specimen had grown during oxidation.

TABLE 2. OXIDATION TESTS OF VARIOUS SHEET THICKNESSES OF IRON-CHROMIUM-ALUMINUM ALLOYS AT 2300 F IN AIR

Chemical Analysis (Balance iron), w/o		Sheet Thickness, in.	Weight Gain[a], g/(cm²)(100 hr)	Penetration[a], in.	
Chromium	Aluminum			Maximum	Average
28.90	2.67	0.0039	0.0152	(b)	(b)
		0.0059	0.0228	(b)	(b)
		6.0081	0.0087	(b)	(b)
		0.0118	C.0019	0.0008	0.0004
		0.0166	0.0021	0.0013	0.0009
27.45	3.67	0.0040	0.0166	(b)	(b)
		0.0060	0.0234	(b)	(b)
		0.0073	0.0195	(b)	(b)
		0.0122	0.0030	0.0015	0.0009
		0.0165	0.0034	0.0007	0.0004
25.00	5.00	0.0039	0.0150	(b)	(b)
		0.0058	0.0229	(b)	(b)
		0.0078	0.0036	0.0017	0.0014
		0.0121	0.0036	0.0026	0.0010
		0.0159	0.0040	0.0010	0.0005
28.90	5.31	0.0039	0.0140	(b)	(b)
		0.0061	0.0017	0.0010	0.0007
		0.0078	0.0018	0.0007	0.0003
		0.0120	0.0023	0.0014	0.0008
		0.0160	0.0021	0.0017	0.0009
26.60	5.86	0.0040	0.0143	(b)	(b)
		0.0060	0.0127	(b)	(b)
		0.0078	0.0023	0.0003	(b)
		0.0121	0.0022	0.0001	(b)
		0.0161	0.0029	0	(b)
27.90	7.00	0.0037	0.0137	(b)	(b)
		0.0060	0.0223	(b)	(b)
		0.0080	0.0169	0.0007	0.0002
		0.0123	0.0039	0.0005	0.0003
		0.0166	0.0045	0.0017	0.0010
26.80	8.07	0.0046	0.0118	(b)	(b)
		0.0058	0.0044	0.1010	0.0007
		0.0082	0.0034	0.0007	0.0004
		0.0121	0.0032	0.0011	0.0009
		0.0161	0.0029	0.0013	0.0006
26.95	9.37	0.0039	0.0072	0.0007	0.0002
		0.0057	0.0031	0.0011	0.0006
		0.0082	0.0031	0.0010	0.0008
		0.0122	0.0030	0.0010	0.0006
		0.0167	0.0026	0.0010	0.0005
26.55	10.05	0.0045	0.0105	0.0009	0.0005
		0.0055	0.0035	0.0012	0.0009
		0.0076	0.0043	0.0012	0.0005
		0.0125	0.0033	0.0006	0.0003
		0.0168	0.0047	0.0012	0.0005

(a) Average of two tested specimens.
(b) No penetration measurements could be obtained on the specimens which had been oxidized severely and were subsequently too brittle to mount in Bakelite.
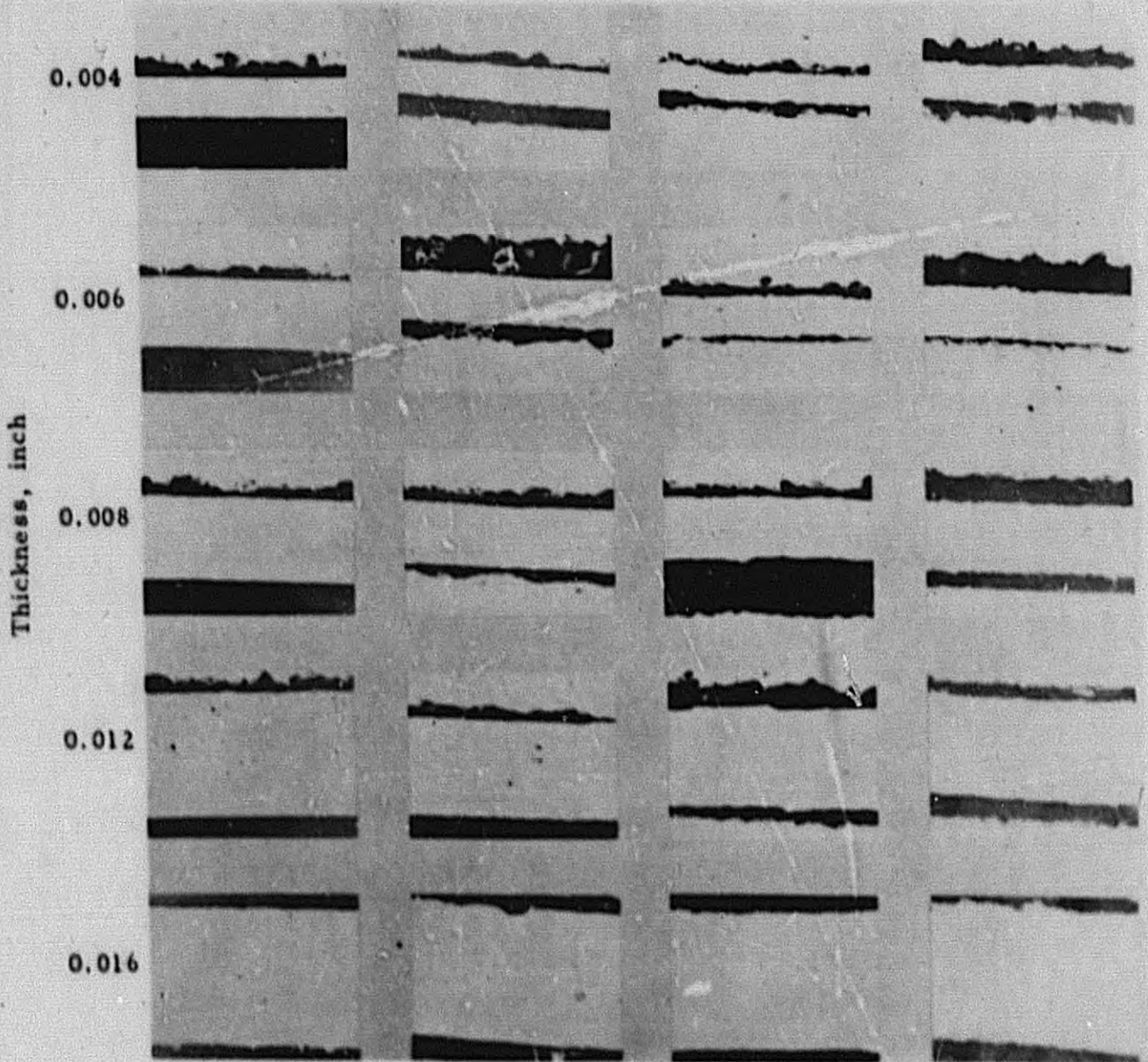
FIGURE 1. OXIDATION OF IRON-CHROMIUM-ALUMINUM ALLOYS
IN AIR AT 2100 F

Exposure time, 100 hr; original magnification 250X, re-
duced for presentation.
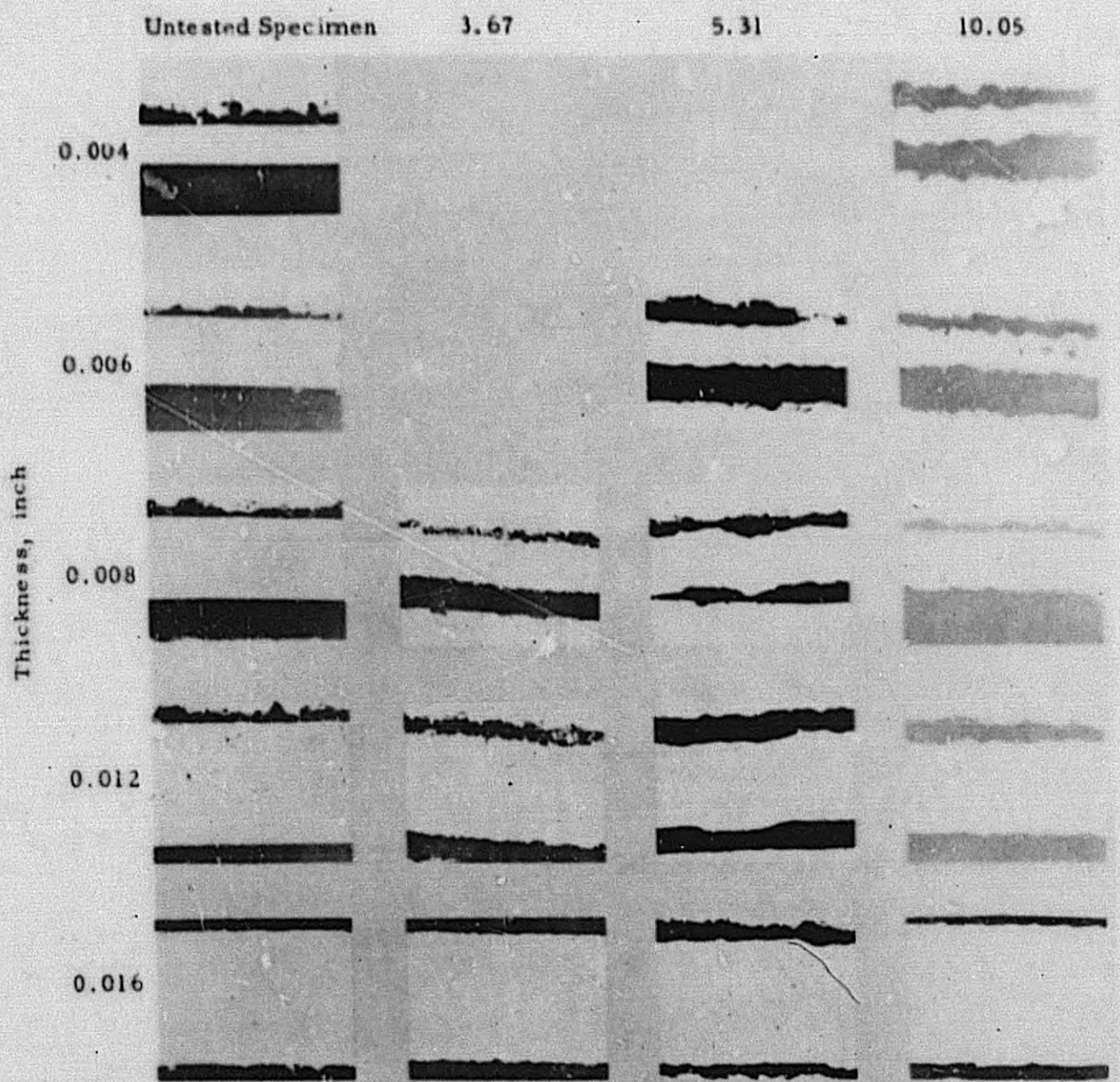
FIGURE 2. OXIDATION OF IRON-CHROMIUM-ALUMINUM ALLOYS IN AIR AT 2300 F

Exposure time, 100 hr; original magnification 250X, reduced for presentation.

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