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OXIDATION OF COLUMBIUM-CHROMIUM ALLOYS AT ELEVATED TEMPERATURES

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INTRODUCTION

Screening studies of the oxidation characteristics of binary alloys of columbium (Ref. 1) showed that chromium was an additive element worthy of intensive study. The screening studies showed that chromium additions were especially helpful in decreasing the oxidation rate of columbium at 1000° C and were somewhat less beneficial at 1200° C. It is the purpose of this investigation to study the oxidation characteristics of binary columbium-chromium alloys in more detail.

Inouye (Ref. 2) has shown that above 600° C in air columbium scales according to the linear rate law. Brauer (Ref. 3) reported that the only oxide formed at elevated temperatures has the formula Cb_2O_5 and exists in three allotropic forms. The low-temperature, or L-form, is stable between 500° and 900° C; the intermediate temperature, or M-form, is stable between 1000° and 1100° C; and the high temperature, or H-form, exists above 1100° C. Contrary to this, H-Cb_2O_5 has been reported (Ref. 2) to form during the oxidation of pure columbium at temperatures as low as 800° C. L-Cb_2O_5 is isomorphic with Ta_2O_5 (Ref. 3), and, according to Zachariasen (Ref. 4), it has a pseudohexagonal orthorhombic crystal structure. The structures of the M and H forms are not known, but they are similar to each other and quite different from L-Cb_2O_5 (Ref. 3). Kubaschewski (Ref. 5) tentatively lists Cb_2O_5 as a metal-excess semiconductor. The color of columbium oxide is white to yellow-white.

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Numerous investigations have shown that chromium oxidizes in air above 500° C in a parabolic manner (Ref. 6). The green oxide, Cr_2O_3, is the only stable oxide in air at elevated temperatures. Its crystal structure has been reported as hexagonal (Ref. 7) and as orthorhombic (Ref. 8). There is also some question as to whether Cr_2O_3 is metal-excess (Ref. 9) or metal-deficit (Ref. 10).

Columbium and chromium form an intermetallic compound, $CbCr_2$, as indicated in the phase diagram in Fig. 1 (Ref. 11). The solubility of chromium in columbium is limited to about 12 to 13 atomic percent even at the high temperature of 1500° C and is undoubtedly less at lower temperatures.

The free energy of oxidation of columbium is much lower than that of chromium, so that the oxide formed on columbium-chromium alloys with high columbium concentrations would tend to be substantially Cb_2O_5. Chromium would be expected to be present as the plus-3 ion, corresponding to the Cr^{+3} ion in Cr_2O_3. Because the Cr^{+3} ion and the Cb^{+5} ion are very similar in size, a high degree of solubility of chromium in the oxide of columbium can be expected. The replacement of Cb^{+5} ions by ions of similar size but lower valence might stabilize the scale and make it mechanically more sound. This was suggested by the results of the screening studies (Ref. 1).

In the present detailed studies, continuous weight-gain curves were determined at 800°, 1000°, and 1200° C for columbium alloys containing 0.8 to 11.6 atomic percent chromium. From these curves the degree of protection could be determined.

PROCEDURE

Specimens were prepared from high purity (99+percent) -325 mesh columbium from Fansteel Metallurgical and electrolytic chromium powders by the powder metallurgy method described in reference 1. The specimens were in the shape of disks, measuring 1/2-inch in diameter by approximately 1/8-inch in thickness (approx. 2 grams in weight). Processing details are summarized in table I. Sintering was done in both purified argon and vacuum.

The processing of the alloys was complicated by the high volatility of chromium at the sintering temperatures. This made the control of both the composition and porosity difficult. Although the starting compositions contained as much as 17 atomic percent chromium; the final composition after sintering was limited to about 12 atomic chromium.

Three groups of columbium-chromium alloys were prepared as shown in table 1. Group 1 specimens were sintered in vacuum and lost considerable chromium. The use of argon during sintering group 2 specimens was reasonably successful in reducing the loss of chromium except for the 17 a/o chromium alloy. Group 3 specimens were sintered an extra half hour at 3500° F to increase their homogeneity. The nominal compositions of the group 3 alloys were selected on the bases of results from the first two groups and the use of argon during sintering again reduced chromium losses.

The densities listed in table I were determined from the differences in the weights of sintered specimens suspended in air and in water, and compared with a theoretical density calculated by assuming a solid solution. (Neither density measurements nor X-ray diffraction studies were performed on group 1 specimens due to a lack of a sufficient number of samples.)

The specimens with low chromium contents were ductile and easily repressed at room temperature. At high chromium contents (about 7 percent and more) the specimens were more brittle and increasingly difficult to repress without cracking. This brittleness is probably associated with the presence of a second phase in the grain boundaries (Fig. 2(b)). According to the phase diagram, the second phase is $CbCr_2$. The concentration of the second phase was too low to detect by X-ray diffraction.

After sintering the specimens were polished through 3/0 emery paper and cleaned in acetone. Individual specimens were suspended from one arm of a chainmatic balance into a vertical tube furnace that was closed at the bottom and open at the top. Tests were conducted at 800°, 1000°, and 1200° C. Temperature was measured by a thermocouple located adjacent to the specimen. The oxidation runs were for $2\frac{1}{2}$ hours, during which time the specimens were weighed at frequent intervals without removal from the furnace. After the test the oxide was examined visually, the d-values determined by X-ray diffraction, and the composition determined by chemical analyses. Metallographic specimens showing the structure of the metal and oxide were prepared whenever the oxide was sufficiently sound to permit mounting and polishing.

RESULTS

The description of the oxides and their compositions are summarized in table II. By comparing the results for similar compositions in different groups, it can be seen that the fabrication technique had no appreciable effect on the scale characteristics.

Chemical analyses of the scales showed that at all temperatures the chromium in the scale increased as the chromium content in the alloy increased and also that the chromium was present as the +3 ion.

Tables 3 and 4 list d-values and intensities of the various oxides formed on these columbium-chromium alloys at 800° and 1000° C. These are compared with interplanar distances for the oxides on pure columbium obtained in this investigation and those reported by Inouye (Ref. 2).

At 800° C the colors of the scales ranged from a light tan at low chromium contents to a dark brown at high chromium contents as contrasted to white to yellow-white for pure columbium. The type of scale went from a thick, adherent, disk-like scale at low chromium contents to a very thin, hard, adherent, disk-like scale at around 5 atomic percent chromium. With increasing chromium contents, its texture gradually became powdery, and the scale finally became a nonadherent powder at around 10 atomic percent chromium.

X-ray diffraction patterns of the scale (table 3) showed only the L-form of Cb_2O_5 to be present at alloy concentrations up to about 4 atomic percent chromium. Certain "d-values" of these scales appeared consistently smaller than the corresponding d-values of the scale on pure columbium, which is also the L-form of Cb_2O_5 at 800° C. This indicates that the addition of chromium has contracted crystal lattice of the scale in some directions. Above 4 atomic percent chromium, the H-form of Cb_2O_5, also slightly contracted in certain directions compared to the H-form found on pure columbium reported by Inouye (Ref. 2), was found along with the contracted L-form. Metallographic examinations indicated that the scales were all single layered.

Figure 3 shows the scales formed on pure columbium and on group 2 specimens after $2\frac{1}{2}$ hours oxidation at 800° C. It illustrates the change in scale character with changes in the chromium content of the alloy. The scale on the specimen containing 4.86 atomic percent chromium; was the thinnest, hardest, least porous, and most protective of any of the scales found on the columbium-chromium alloys at any of the temperatures. A photomicrograph of this scale is shown in the insert. The porosity in the scale is similar to that in the metal, except that the smaller pores in the metal are not present in the scale. This is probably due to sintering of the scale. This scale was extremely tough and adherent; it could not be separated from the metal by scraping with a knife. Specimens containing 9.9 and 10.2 atomic percent chromium had scaled to fine powder after $2\frac{1}{2}$ hours at 800° C.

At 1000° C the colors of the scales ranged from a light green at low chromium contents to a dark olive green at the higher chromium contents. With increasing chromium contents, the scales went from thick, disk-like scales which tended to spall on cooling to fairly thin, disk-like scales with a very slight tendency to spall. A brownish overcoat was noted on the dark green scales at chromium contents of approximately 7 percent and higher but not as a distinct layer. X-ray diffraction patterns (table 4) showed that the H-form of Cb_2O_5 was always present with no apparent contraction. The brownish overcoat, when it appeared, was also of the normal H-form of Cb_2O_5. Metallographic examinations again indicated that the scales were all single layered and fairly nonporous.

At 1200° C oxidation rates and scale character were very poor and only one group of specimens (group 2) was studied. Although very high chromium contents might give good oxidation resistance, such alloys would be brittle, as mentioned earlier.

Figure 4 shows the continuous weight gain against time curves at 800° and at 1000° C for all three groups of specimens. Although the oxidation rates vary from one group to another depending upon the fabrication technique (which are discussed later) the effect of changing the chromium concentration on the oxidation rate is similar in all three groups. At 800° C and low chromium concentrations, oxidation is rapid and the curves approach linearity. As the chromium content is increased, oxidation becomes slower and the curves tend to become parabolic. The results for groups 2 and 3 indicate that an optimum chromium concentration exists for best oxidation resistance, and that if the chromium concentration is increased beyond this point, oxidation becomes more rapid. According to the results for group 2, the optimum concentration is within the range from 1.58 to 9.9 atomic percent chromium, and, according to the results for group 3, the range is further narrowed to between 6.34 and 9.15 atomic percent chromium. Referring back to the results for group 1, the optimum concentration must be above 7.23 atomic percent chromium. Thus the optimum chromium content for low scaling rates at 800° C appears to be about 8 atomic percent. The decrease in oxidation resistance at higher chromium concentrations was associated with a tendency of the scales to become powdery in texture, as is very evident in the photographs in Fig. 3. From the standpoint of scale character, the soundest scale was that on the specimen in group 2 containing 4.86 atomic percent chromium. The scaling rate of this specimen was also quite low.

The results at 1000° C indicated that the oxidation resistance was continually improved as the chromium content was increased and that no optimum concentration existed within the range studied. The improvement in oxidation rates due to chromium was more pronounced in group 3 than in the other two groups. The oxidation rates at 1000° C are not widely different from the rates at 800° C.

Only specimens in group 2 were run in oxidation tests at 1200° C. At this temperature, the oxidation curves were essentially linear and the rates were very close to that of pure columbium.

DISCUSSION

On the basis of the free energies of oxidation of columbium and chromium, it was expected that the primary oxide formed on columbium-chromium alloys (in the composition range studied) would be Cb_2O_5. It was further expected that any chromium that oxidized would be in the scale as the Cr^{+3} ions, and because of the similarity in size between the Cr^{+3} ion and the Cb^{+5} ion, the chromium would dissolve in the scale by substituting for the columbium. These effects are confirmed by the observed color changes, the chemical analyses, and the X-ray diffraction analyses of the scales.

At 800° C the dissolved chromium had two effects on the scale structure. First, at all chromium compositions, it contracted the Cb_2O_5 lattices (table 3); and secondly, above about 4 atomic percent chromium, it promoted the formation of the H-form of Cb_2O_5 as well as the more normal L-form (in the low and unalloyed columbium used in this study only the L-form of the scale was evident at this temperature). In the composition range of 4.5 to 9 atomic percent chromium there appears to be a critical ratio of the H and L oxide structures which results in a hard, mechanically sound, and adherent scale. Below this range of compositions only the L-form existed and this was porous and not protective. Above this composition range, there was apparently an excessive amount of the H-form and the scale became powdery. The best appearing scale observed in this study occurred in this composition range, between 4.5 and 9 atomic percent (a group 2 specimen containing 4.86 atomic percent chromium).

At 1000° C only the H-form of Cb_2O_5 was found. As in the case of several of the scales at 800° C, dissolved chromium apparently altered the lattice enough to make the scale more stable and mechanically sound. Increasing amounts of chromium within the range studied improved the character of the scale and reduced oxidation rates. However, the best scale formed at 1000° C was not so tough as the scale formed at 800° C on the 4.86 a/o chromium specimen.

At 1200° C although the chromium dissolved into the Cb_2O_5 lattice to about the same degree as at 800° and 1000° C, it was of little value. The scales were porous and obviously unprotective. The lack of improvement obtained here by chromium additions, as compared to the slight improvement obtained in the screening studies at 1200° C (Ref. 1), may have been due to the fact that in the screening studies the moisture content of the oxidizing air was controlled, while in the studies reported herein the air was not dried.

Fabrication technique was found to influence the rates of oxidation; e.g., specimens of group 3 generally had lower rates of oxidation than group 2. This might have been due to chromium enrichment or depletion at the surface due to the high volatility of chromium during sintering, to the degree of porosity, or the degree of homogeneity. Chemical analyses indicated no difference in chromium concentration in the surface layers of of sintered specimens in groups 2 and 3 from that in the body of the same specimens. Metallographic examinations showed that porosity had no effect on the rate of growth of the oxide scale since the oxide interface did not advance faster through the pores. More complete homogenization in the group 3 specimens (resulting from the larger sintering time at 3500° F) may have accounted for the generally lower oxidation rates as compared to those of the specimens in the other two groups. Improvement in fabrication techniques might further improve the oxidation resistance of columbium-chromium alloys.

Figure 5 summarizes the improvement obtained in the oxidation resistance of columbium by additions of chromium and compares the rate of oxidation to that of several familiar materials, iron, nickel, and nichrome. The curve for unalloyed columbium has a slope of unity, indicating that the oxidation rate is linear and the scale is nonprotective. The curves for the remaining materials have slopes of close to one-half indicating that the oxidation rates are nearly parabolic and the scales are protective (i.e., oxidation is diffusion controlled). The alloy containing 4.86 atomic percent chromium, which had the most mechanically sound scale and one of the lowest oxidation rates of the columbium-chromium alloys, has an oxidation rate very close to that of pure iron and 600 times that of commercial nichrome.

The oxidation rates for the columbium-chromium alloys were not significantly greater at 1000° than at 800° C, probably due to the sintering of the scale. Thus, the oxidation rate of the best columbium-chromium alloy at 1000° C (11.6 atomic percent chromium, group 3) was roughly 110 times that of nichrome. This is a considerable improvement over the relative rates at 800° C.

SUMMARY OF RESULTS

This investigation has shown that a mechanically sound oxide scale can be produced on columbium by the addition of small amounts of chromium. At 800° C an optimum chromium concentration for the soundest scale and lowest oxidation rate was found to exist at about 5 to 8 percent. At 1000° C both the scale characteristics and the oxidation rates improved with increasing concentrations of chromium. However, the chromium content may be limited by fabrication difficulties associated with the brittleness of alloys containing more than about 7 a/o chromium. At 1200° C chromium had no appreciable effect in the range of compositions studied.

Although the oxidation rates for the columbium-chromium alloys were less than for pure columbium, the rates were still too high for the prolonged use of columbium-chromium alloys at elevated temperatures.

CONCLUDING REMARKS

Because the scales on the best columbium-chromium alloys are mechanically sound and diffusion controlled further improvement by lowering the ionic diffusion rates by the addition of other elements should be possible. Third and fourth alloying elements might also be of value by forming spinels or protective underscales. Although it is difficult to assess the feasibility of achieving a high degree of oxidation resistance, it appears reasonable to presume that an alloy can be developed that could be clad without the danger of catastrophic failure in case the cladding ruptures.

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TABLE I. - PROCESSING DATA FOR SINTERED Cb-Cr ALLOYS

Group	Nominal atomic percent Cr	First press, psi	First sinter	Second press, psi	Second sinter	Actual atomic percent Cr	Percent theoretical density
1	1	100,000	3100°F, $\frac{1}{2}$ hour, vacuum	150,000	3500°F, $\frac{1}{2}$ hour, vacuum	0.8	----
	2					1.75	----
	5					3.9	----
	10					7.23	----
	17					8.2	----
2	2	100,000	3100°F, $\frac{1}{2}$ hour, argon*	150,000	3500°F, $\frac{1}{2}$ hour, argon*	1.58	92.4
	5					4.86	91.0
	10					9.9	86.8
	17					10.2	87.9
3	4	100,000	3100°F, $\frac{1}{2}$ hour → 3500° $\frac{1}{2}$ hour, argon*	150,000	3500°F, $\frac{1}{2}$ hour, argon*	3.85	90.0
	6.5					6.34	88.2
	8.5					8.35	84.8
	9.5					9.15	84.0
	12					11.6	85.0

*Purified by continuous flow through a cold trap of dry ice and varsol and through a titanium chip furnace at 900° F.

TABLE II. - DATA ON Cb·Cr ALLOY SCALES

Oxidizing temperature, °C	Group	Actual composition of alloy, a/o Cr	Color of scale	Type of scale	X-ray analysis	Chemical analysis of scale	
						w/o Cr	w/o Cb
800	1	0.8	Tan	Thick, disk like, adherent	L-Cb_2O_5*	0.15	62.6
		1.75	Brown	Thick, disk like, adherent	L-Cb_2O_5*	.43	64.7
		3.9	Brown	Thick, disk like, adherent	L-Cb_2O_5*	.72	65.7
		7.23	Dark brown	Thin, disk like, adherent, powdery texture	L-Cb_2O_5* + H-Cb_2O_5*	1.14	63.1
		8.2	Dark brown	Thin, disk like, adherent, powdery texture	L-Cb_2O_5* + H-Cb_2O_5*	.86	66.3
	2	1.58	Brown	Thick, disk like, adherent	L-Cb_2O_5*	.77	68.2
		4.86	Brown	Thin, very disk like, very adherent	L-Cb_2O_5* + H-Cb_2O_5*	1.57	71.0
		9.9	Dark brown	Completely powder	L-Cb_2O_5* + H-Cb_2O_5*	3.89	68.7
		10.2	Dark brown	Completely powder	L-Cb_2O_5* + H-Cb_2O_5*	3.89	69.6
	3	3.85	Brown	Thick, disk like, adherent	L-Cb_2O_5*	1.54	63.8
		6.34	Brown	Thin, very disk like, adherent	L-Cb_2O_5* + H-Cb_2O_5*	----	64.7
		8.35	Dark brown	Thin, disk like, slightly powdery	L-Cb_2O_5* + H-Cb_2O_5*	----	----
		9.15	Dark brown	$\frac{1}{2}$ Specimen powder, $\frac{1}{2}$ thin disk like	L-Cb_2O_5* + H-Cb_2O_5*	3.67	69.3
		11.6	Dark brown	$\frac{1}{2}$ Specimen powder, $\frac{1}{2}$ thin disk like	L-Cb_2O_5* + H-Cb_2O_5*	4.35	65.0
1000	1	0.8	Light green	Thick, disk like	H-Cb_2O_5	0.26	65.2
		1.75	Light green	Thick, disk like	H-Cb_2O_5	.38	64.2
		3.9	Green	Thick, disk like	H-Cb_2O_5	.79	65.3
		7.23	Green, brownish overcoat	Thin, disk like, adherent	H-Cb_2O_5 + overcoat of H-Cb_2O_5	1.04	61.4
		8.2	Green, brownish overcoat	Thin, disk like, adherent	H-Cb_2O_5 + overcoat of H-Cb_2O_5	.93	64.1
	2	1.58	Green	Thick, disk like	H-Cb_2O_5	.80	67.4
		4.86	Green	Thin, disk like	H-Cb_2O_5	1.63	64.6
		9.9	Green, brownish overcoat	Thin, disk like, adherent	H-Cb_2O_5 + overcoat of H-Cb_2O_5	3.82	65.7
		10.2	Green, brownish overcoat	Thin, disk like adherent	H-Cb_2O_5 + overcoat of H-Cb_2O_5	3.81	65.5
	3	3.85	Green	Thick, disk like	H-Cb_2O_5	1.12	67.4
		6.34	Green, brownish overcoat	Thin, very disk like, edge spalling	H-Cb_2O_5 + overcoat of H-Cb_2O_5	2.41	63.5
		8.35	Green, brownish overcoat	Thin, very disk like, edge spalling	H-Cb_2O_5 + overcoat of H-Cb_2O_5	3.06	63.4
		9.15	Green, brownish overcoat	Thin, very disk like, edge spalling	H-Cb_2O_5 + overcoat of H-Cb_2O_5	3.15	64.4
		11.6	Green, brownish overcoat	Thin, very disk like, edge spalling	H-Cb_2O_5 + overcoat of H-Cb_2O_5	3.82	61.8
1200	2	1.58	Olive	Large, porous, blossom like	H-Cb_2O_5	0.76	63.1
		4.86	Olive drab	Large, porous, blossom like	H-Cb_2O_5 + complex columbite	1.77	63.1
		9.9	Brown	Large, porous, blossom like	H-Cb_2O_5 + complex columbite	3.52	62.0
		10.2	Brown	Large, porous, blossom like	H-Cb_2O_5 + complex columbite	3.31	63.3

*Contains certain d values consistently smaller than pure Cb_2O_5.

TABLE III. - d VALUES OF OXIDE SCALES FORMED ON COLUMBIUM AND COLUMBIUM-CHROMIUM ALLOYS DURING $2\frac{1}{2}$ HOURS IN AIR AT 800° C.

[Intensity: S = strong, M = medium, W = weak; d values in angstrom units and obtained with CuKα radiation.]

Pure Cb			a/o Cr in Cb-Cr alloys													
L-Cb_2O_5 (This study)	L-Cb_2O_5 (Ref. 2)	L-Cb_2O_5 (Ref. 2)	0.8	1.58	1.75	3.85	3.9	4.86	6.34	7.23	8.2	8.3	9.15	9.9	10.2	11.6
3.95 S	3.93 S	------	3.92	3.92	3.91	3.88	3.92	3.91 S	3.93 S	3.92 M	3.91 S	3.90 S	3.90 S	3.91 S	3.91 S	3.92*W
------	------	3.66*S	----	----	----	----	----	3.60*W	------	------	3.62*W	------	3.62*W	3.64*M	3.62*M	------
------	------	3.33*S	----	----	----	----	----	3.29*M	3.28*W	3.33*W	3.31*W	3.29*M	3.30*M	3.29*M	3.30*M	3.31*S
3.15 S	3.14 S	------	3.14	3.13	3.13	3.12	2.13	3.12 S	3.14 S	3.14 S	3.14 S	3.13 S	3.14 S	3.13 S	3.13 S	3.14 S
3.08 S	3.08 S	------	3.08	3.08	3.07	----	3.08	3.08 M	------	------	3.08 M	3.07 M	3.08 M	3.08 W	3.09 M	------
------	------	2.98*M	----	----	----	----	----	2.97*W	------	------	------	------	2.97*W	2.97*W	2.97*W	2.96*W
------	------	2.69*S	----	----	----	----	----	------	------	------	------	------	------	------	------	------
------	------	2.51*M	----	----	----	----	----	2.51*S	2.52*M	2.53*	2.53*W	------	2.50*	2.50*W	2.52*M	2.50*M
2.45 S	2.46 M	------	2.45	2.45	2.45	2.43	2.45	2.44 M	2.44 S	2.45 M	2.45 M	2.44 M	2.45 M	2.45 M	2.44 M	2.45 M
2.42 M	2.43 M	------	2.43	2.42	2.42	----	----	------	------	------	2.42 M	------	------	------	------	------
2.35 W	------	------	----	----	----	----	----	------	------	------	2.31 W	------	2.33 W	------	------	------
------	------	------	----	----	2.21	----	2.26	------	------	------	------	------	2.22 W	------	2.24 W	------
------	------	------	----	2.107	----	----	----	------	2.12 W	2.13 W	------	------	------	------	------	------
2.00 W	------	------	----	2.00	2.00	----	----	------	------	------	2.00 W	------	------	------	------	------
1.96 M	1.97 M	------	1.96	1.96	1.96	1.95	1.96	1.95 W	1.95 M	1.96 M	1.96 W	1.96 W	1.96 W	1.95 W	1.96 W	1.95 W
------	------	1.91*W	----	----	----	----	----	------	------	------	------	------	------	------	------	------
1.85 W	1.83 W	------	1.83	1.82	1.82	----	----	1.82 W	1.82 S	1.83 S	1.82 W	1.82 W	1.82 W	1.82 W	1.82 W	------
1.77 W	1.79 W	------	1.79	1.79	1.79	----	1.79	1.79 W	1.79 W	1.80 M	1.79 W	1.79 W	1.79 W	1.79 W	1.79 W	1.79 M
------	------	1.71*M	----	----	----	----	----	------	1.70*W	1.71*W	------	1.70*W	1.71*W	1.71*W	1.70*W	1.71*M
1.66 W	1.66 W	------	1.66	1.65	1.65	1.65	1.65	1.65 W	1.65 M	1.66 M	1.66 W	1.65 W	1.66 W	1.65 W	1.66 W	1.66 W
------	------	------	----	----	----	----	----	------	------	------	1.65 W	------	------	------	------	------
1.63 W	1.63 W	------	1.63	----	1.62	1.63	1.62	1.63 W	------	------	1.63 W	1.63 W	------	------	------	------
1.57 W	------	------	1.57	----	1.57	1.57	1.57	1.57 W	1.57 M	1.57 M	1.57 W	1.56 W	------	------	------	------
1.54 W	------	------	----	----	----	----	----	------	------	------	------	------	------	------	------	------
1.46 W	------	------	1.46	----	1.46	1.46	1.46	------	1.46 M	1.46 W	1.45 W	------	------	------	------	------
------	------	------	----	----	----	----	1.40	------	------	------	------	------	------	------	------	------
------	------	------	1.34	----	----	----	----	------	------	1.33 W	------	------	------	------	------	------
1.32 W	------	------	1.32	----	----	1.32	1.32	------	------	------	1.32 W	------	------	1.32	------	------
1.23 W	------	------	----	----	----	----	----	------	1.19 W	------	------	------	------	------	------	------

*H-Cb_2O_5 values.

TABLE IV. - d VALUES OF OXIDE SCALES FORMED ON COLUMBIUM AND COLUMBIUM-CHROMIUM ALLOYS DURING $2\frac{1}{2}$ HOURS IN AIR AT 1000° C

[Intensity: S = strong, M = medium, W = weak; d values in angstrom units and obtained with CuKα radiation.]

Pure Cb		a/o Cr in Cb-Cr alloys													
$H-Cb_2O_5$ (Ref. 2)	$H-Cb_2O_5$ (This study)	0.8	1.5	1.75	3.85	3.9	4.86	6.34	7.25	8.2	8.35	9.15	9.9	10.2	11.6
5.14 M	------	----	----	----	----	----	----	----	----	----	----	----	----	----	----
4.67 M	------	----	----	----	----	----	----	----	----	----	----	----	----	----	----
3.75 S	3.72 S	3.72	3.71	3.73	3.70	3.73	3.76	3.72	3.73	3.73	3.76	3.74	3.73	3.74	3.74
3.65 S	3.63 S	3.62	----	3.61	----	----	----	----	----	3.63	----	----	----	----	----
------	------	----	3.55	3.56	3.53	3.58	3.59	3.55	3.56	----	3.59	3.57	3.55	3.55	3.57
3.49 S	3.48 S	3.50	----	3.48	3.46	3.42	----	3.42	----	3.48	----	----	----	----	----
3.36 M	------	3.35	----	3.33	----	----	----	----	----	----	----	3.34	3.28	3.28	----
3.16 W	------	----	----	----	----	----	----	----	----	----	----	----	----	----	3.11
2.83 M	2.82 M	2.82	----	2.82	----	2.82	----	----	----	2.82	----	----	----	----	----
2.78 M	2.76 M	2.79	2.76	----	2.75	2.78	2.79	2.77	2.79	2.77	2.79	2.78	2.77	2.78	2.78
2.71 M	2.70 M	2.71	----	----	----	----	----	2.69	2.70	2.71	----	----	----	----	----
------	2.54 M	2.54	----	2.53	----	2.53	----	2.52	2.53	2.54	2.53	2.53	2.52	2.52	2.53
------	2.49 M	----	----	----	----	----	----	----	----	----	----	----	----	----	----
------	2.25 M	2.31	2.30	2.30	----	2.31	2.31	2.30	2.31	2.31	2.31	2.32	2.31	2.31	2.31
------	------	----	----	----	----	----	----	----	2.12	----	----	----	----	----	----
------	2.07 M	2.07	2.05	2.05	2.04	2.04	2.06	2.04	2.05	2.07	2.05	2.05	2.05	2.04	2.05
------	2.03 W	2.03	----	----	----	----	----	----	----	2.03	----	----	----	----	----
------	1.91 S	1.90	1.91	1.91	1.90	1.91	1.91	1.90	1.90	1.91	1.91	1.91	1.91	1.91	1.91
------	1.78 W	1.78	1.78	1.78	----	----	1.79	1.78	1.78	1.78	1.78	----	1.78	1.78	----
------	------	1.74	----	1.74	----	----	----	----	----	----	----	----	----	----	----
------	------	----	----	1.73	----	----	----	----	----	1.73	----	----	----	----	----
------	1.68 M	1.68	1.68	1.68	1.67	1.68	1.68	1.67	1.68	1.68	1.68	1.69	1.68	1.68	1.68
------	1.58 W	1.58	----	1.57	1.58	1.58	1.58	1.57	1.57	1.58	1.57	1.57	1.57	1.57	1.57
------	1.55 W	1.55	----	----	----	----	----	----	----	----	----	----	----	----	----
------	------	----	----	----	----	1.45	----	----	1.46	----	----	----	----	----	----
------	------	1.40	1.40	1.40	----	1.39	1.40	1.39	1.40	----	----	----	----	----	----
------	1.30 W	1.30	----	----	1.34	----	----	----	----	----	----	1.31	1.30	1.30	----
------	1.28 W	----	1.27	----	----	----	----	----	----	----	----	----	1.27	1.27	----

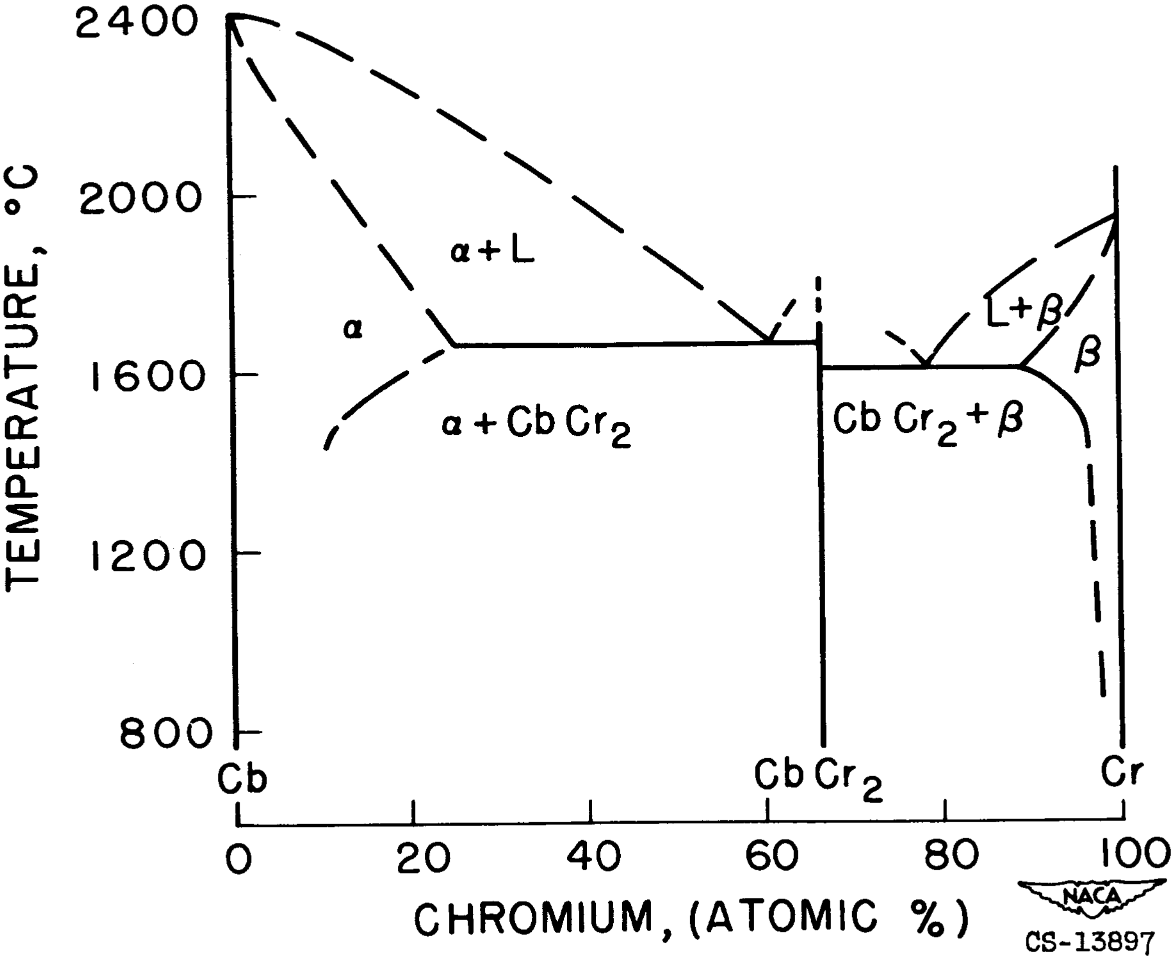

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Fig. 1. - Equilibrium diagram for the columbium-chromium binary system (from Ref. 11).

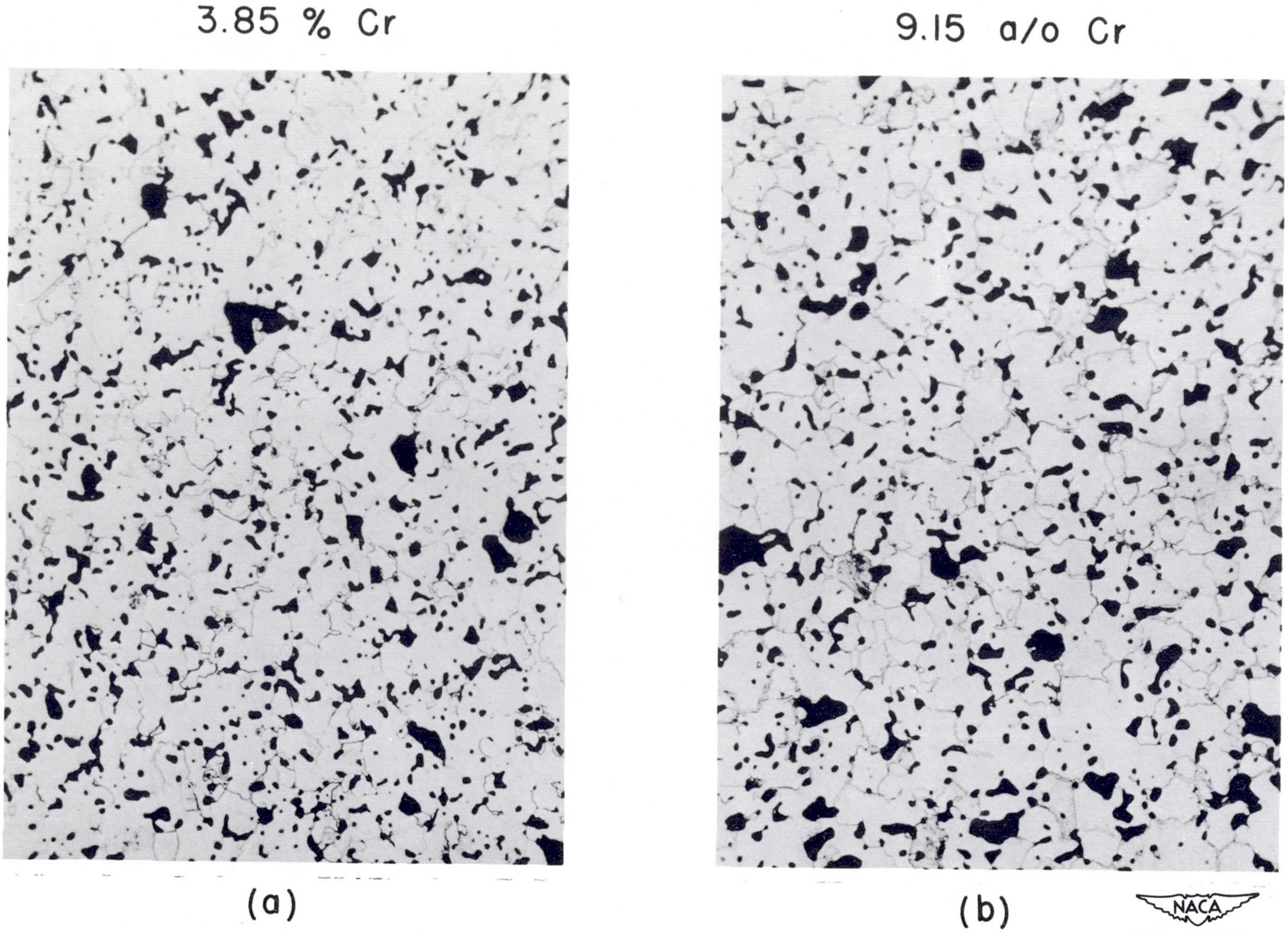

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Fig. 2. - Sintered Cb-Cr alloys at low and high Cr contents.

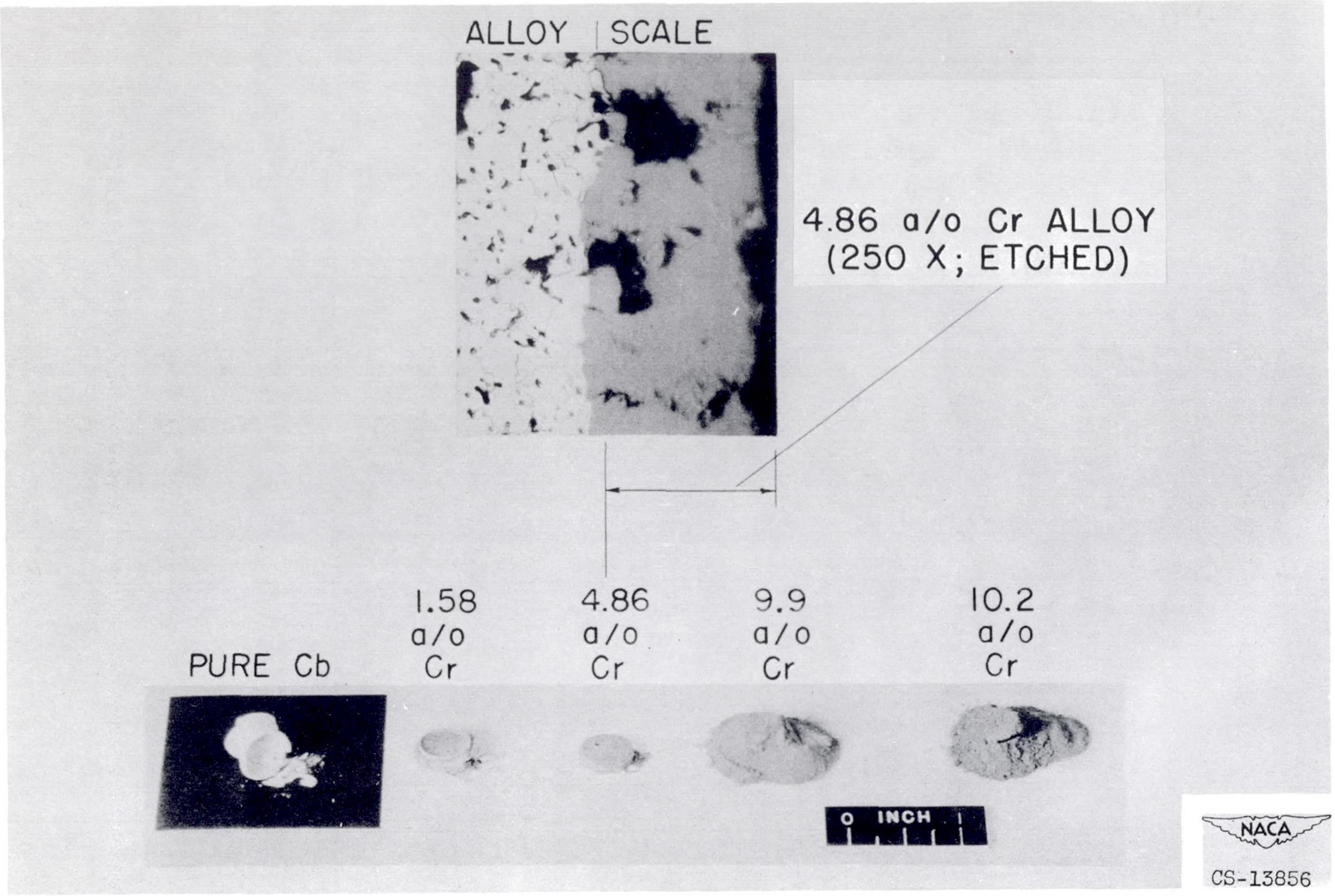

Fig. 3. - Cb-Cr alloys scaled in air at 800° C for 2.5 hours.

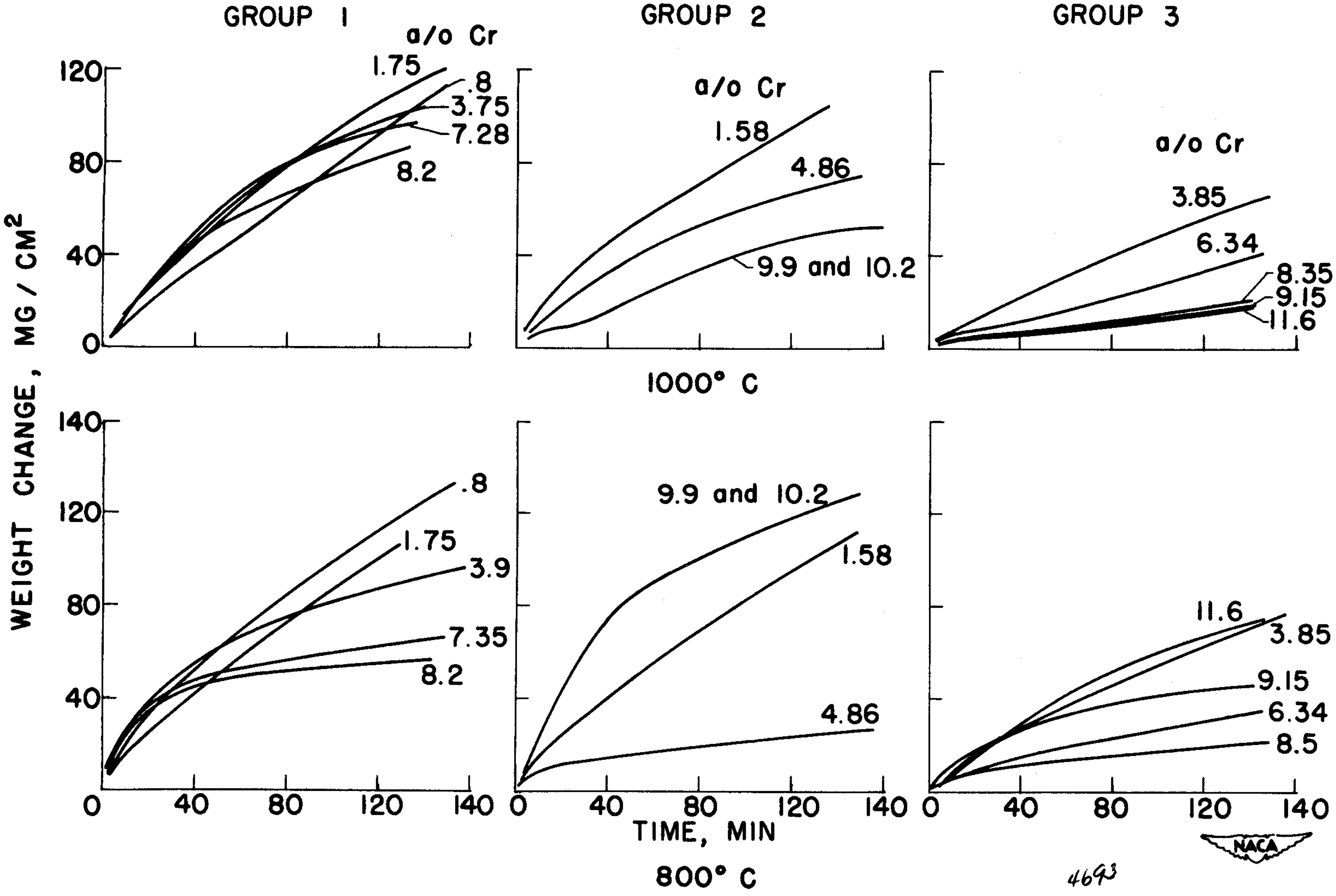

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Fig. 4. - Effect of chromium content on oxidation rate for three groups of columbium-chromium alloys at 800° and 1000° C.

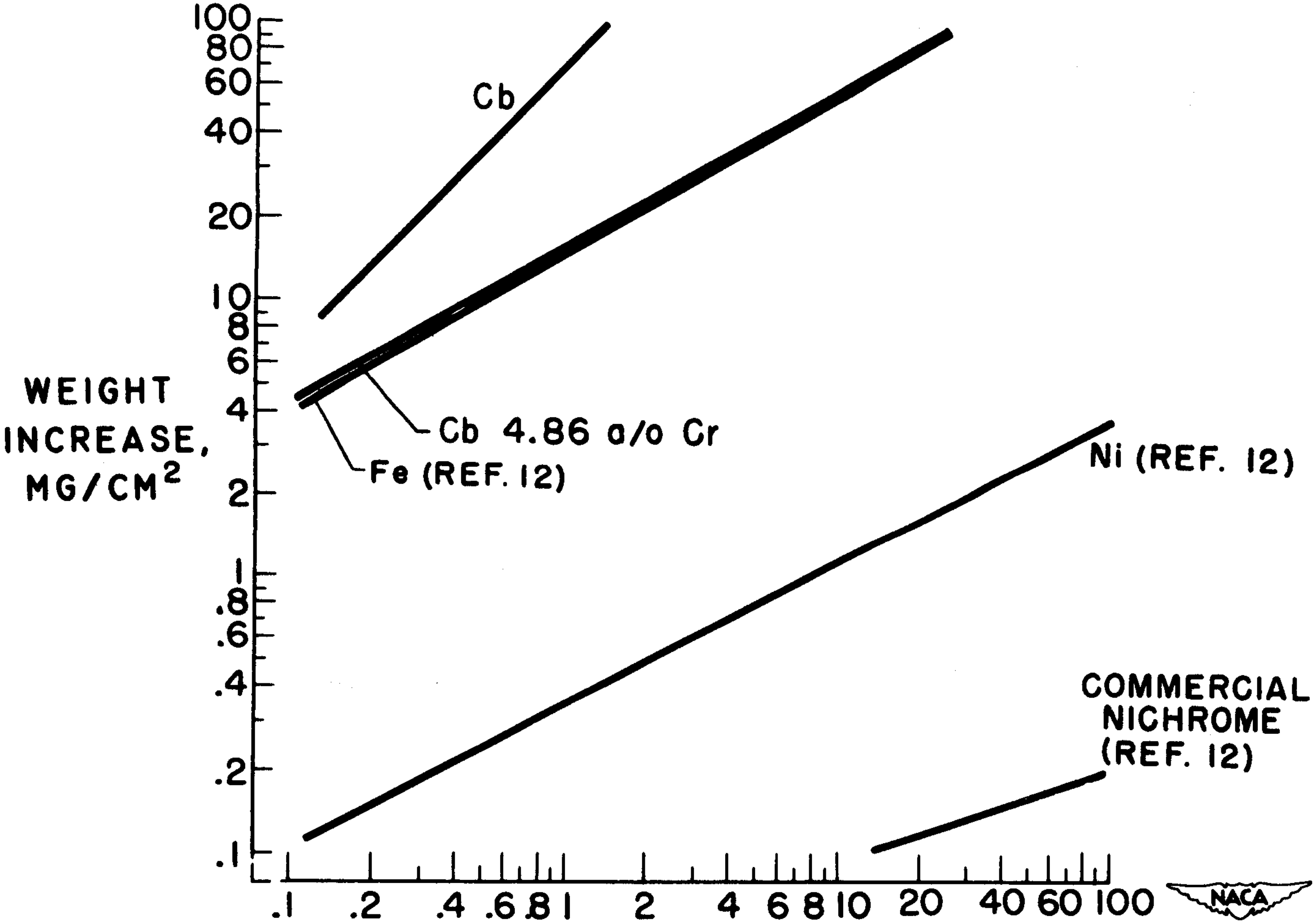

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Fig. 5. - Comparison of oxidation rates in air at 800° C of columbium and a columbium-chromium alloy with other metals and alloys.