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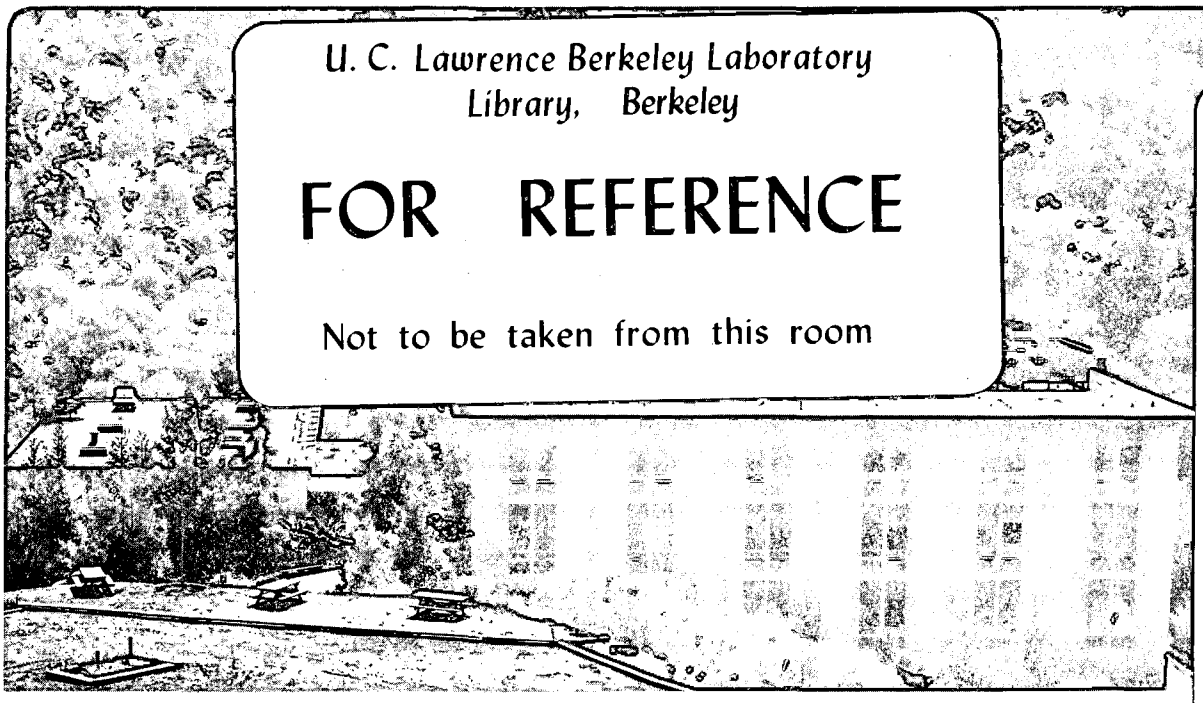

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The Oxidation Behavior of Co-15wt%Cr Alloy Containing Dispersed Oxides Formed by Internal Oxidation*

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ABSTRACT

Internal oxidation pretreatments of Co-15wt%Cr and Co-15wt%Cr-1wt%Ti were carried out using a Rhines pack in quartz, in mullite and in alumina. A dispersion of titanium oxide particles formed in the Ti-containing alloy as a result of the internal oxidation. However, silicon also diffused into all treated specimens when the pretreatments were carried out in quartz or in mullite. The effect of various pretreatments on the subsequent oxidation of these alloys was studied at 1000°C, and compared with that of a Co-15wt%Cr-1wt%Si alloy. The main purpose of this study was to determine the relative effectiveness of the dispersed oxide particles and the contaminated silicon on the selective oxidation of chromium. It was found that the oxidation behavior of both treated alloys were strongly affected by the degree of silicon contamination. Selective oxidation of chromium to form a nearly continuous protective Cr_2O_3 scale was achieved with greater than 0.4wt% silicon. The presence of dispersed particles reduced initial oxidation rate, but was ineffective in promoting Cr_2O_3 scale formation.

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INTRODUCTION

One of the beneficial effects of minor alloying additions of reactive elements or their oxides on Cr_2O_3-forming alloys is the selective oxidation of chromium[1]. For alloys which can form a continuous Cr_2O_3 scale after an initial transient stage, the additions shorten the transient period, resulting in a rapid development of the protective chromia layer and largely eliminates the formation of base metal oxides. For alloy systems which normally do not have enough chromium to form a continuous Cr_2O_3 scale, the addition can promote its development, thus greatly reducing the oxidation rate. For this purpose, a dispersion of the reactive metal oxide is believed to be more effective than the corresponding reactive metal[2].

The ability of reactive metals or their oxides to promote selective chromium oxidation was first attributed by Davis et al.[3] to an enhanced chromium diffusion in the alloy. Earlier studies[4,5] showed that the diffusivity of chromium in a dispersion-containing (ThO_2 or CeO_2) Ni or Ni-Cr alloy was an order of magnitude higher than that of a dispersion-free alloy. Since the transition between external scale development and internal oxidation is dependent upon the interdiffusivity of the scale/forming species, an increase in the diffusivity of chromium in the alloy (D_{Cr}^{alloy}) would naturally enhance the external Cr_2O_3 scale development. However, later diffusivity measurements carried out by Seltzer et al.[6,7]on Y_2O_3- and ThO_2-containing Ni-Cr and Co-Cr alloys showed that the presence of dispersoids alone did not enhance the diffusivity of chromium in the alloy, but that D_{Cr}^{alloy} increased with decreasing alloy grain size. Although a high dislocation substructure resulting from alloy preparation using mechanical alloying technique could further increase D_{Cr}^{alloy}[7], this enhancement did not seem to have much effect on subsequent oxidation kinetics. These observations were in accord with other studies[8,9], which showed that in binary Cr-containing alloys Cr_2O_3 developed more readily over alloy grain boundaries than over the bulk of the grains. Furthermore, selective oxidation to form

continuous external Cr_2O_3 could occur at lower chromium concentrations over cold-worked surfaces, which recrystallized to form smaller grains, but not on coarse-grained polished surfaces[8].

Since the addition of either the reactive metals or their oxide dispersions tend to stabilize a fine alloy grain size[10], the enhanced D_{Cr}^{alloy} observed by the early diffusion studies[4,5] could be due to a finer grain size that resulted from the incorporation of oxide dispersions. Therefore, it is possible that the presence of the reactive metals or oxides decreases alloy grain size, which in turn increases D_{Cr}^{alloy}, and aids in the development of the Cr_2O_3 scale. However, Whittle et al.[2] have found that while Co-10 and 15 wt% Cr alloys containing 1 wt% Ti, Zr or Hf failed to form even a healing layer of Cr_2O_3, a continuous external Cr_2O_3 scale was promoted after an internal oxidation pretreatment converting the Ti, Zr or Hf metal to its oxide. There was believed to be no change in alloy grain size as a result of the internal oxidation; even if there were, the grain size would be larger due to grain growth. Their work implies that the enhanced chromium diffusivity in the alloy caused by a decreased grain size cannot be the explanation for the selective oxidation of chromium. Rather, the evidence supports the mechanism suggested by Stringer et al.[11] that the oxide dispersions reduce spacings between the first formed nuclei on alloy surfaces and thus promote a continuous Cr_2O_3 scale formation.

The internal oxidation carried out by Whittle et al.[2] was a commonly-used procedure, in which an oxygen activity is generated that will internally oxidize the reactive minor constituent, but is insufficient to form the oxide of any of the less-reactive elements in the alloy. This oxygen activity was produced by the use of a powder pack, often called a Rhines pack, composed of Cr_2O_3 and either chromium metal or a Co-Cr alloy having a chromium activity equal to that of the alloy to be internally oxidized, to avoid vapour-phase chromium transport. The powder pack and the specimens were sealed in a

dumbell-shaped quartz capsule to physically separate the powders from the specimens. The internal oxidation pretreatments were generally performed between 1100° and 1300°C for times up to 350 hours. Heat-treatments of this kind in quartz above 1100°C have recently been demonstrated by Hou and Stringer[12] to cause silicon contamination in the specimens, resulting in a dramatic change in the subsequent oxidation behavior, even when internal oxide particles were absent. Since Whittle et al. only carried out their internal oxidation pretreatment on the Ti, Zr and Hf-containing ternary alloys, but did not test its effect on any binary Co-Cr alloys, it becomes unclear if their observed effect on selective chromium oxidation was indeed a result of particle formation, or was due rather to silicon contamination, or perhaps a combination of the two.

In light of the importance of this earlier work in determining the mechanisms involved in the reactive element effect, it seemed necessary to repeat the experiments under conditions which preclude any possibility of silicon contamination. The purpose of this study then is to investigate the oxidation behavior of Co-15wt%Cr and Co-15wt%Cr-1wt%Ti alloys after internal oxidation pretreatments. Both alloys were pretreated in sealed quartz, mullite or alumina. The effect of silicon contamination and the effect of particle formation are examined in detail. For comparison, the oxidation behavior of a Co-15wt%Cr-1wt%Si alloy was also studied.

EXPERIMENTAL METHODS

Alloy Preparation

Actual compositions of the three alloys, nominally Co-15%Cr, Co-15%Cr-1%Ti, and Co-15%Cr-1%Si (all in weight %), are given in Table 1. The alloys were made by induction melting and casting from high-purity materials, followed by a homogenization anneal at 1100°C in vacuum for 24 hours. Specimens 15 mm x 10 mm x 1 mm were cut from the center of the homogenized ingots to avoid surface contamination. All three alloys were

single-phased, and consists of uniform but elongated grains approximately 350μm wide for Co-15Cr, and 250μm wide for Co-15Cr-1Ti and Co-15Cr-1Si, with an overall average length of 0.9 mm. Each specimen was polished to 1200 SiC grit and thoroughly washed ultrasonically prior to subsequent pre-oxidation and oxidation treatments.

Pre-oxidation Treatment

The Rhines pack for the internal oxidation (IO for short) treatment usually consisted of Cr and Cr_2O_3 powders. Only during one particular run a mixture of Co-15Cr powder and Cr_2O_3 was used. Heat treatments were carried out in quartz, in a commercial grade mullite tube or in a 99.8% pure alumina tube. In all cases, Co-15Cr as well as Co-15Cr-1Ti specimens were included. The tubes containing the specimens and the powder pack were first evacuated to about 10^{-4} Torr, back-filled with helium, then pumped and back-filled again for several times before sealing. Sealing of the quartz tube was done by closing it under a flame. The mullite and the alumina tubes were sealed by high temperature O-rings with stainless steel fittings. In the alumina and the mullite tubes, the specimen and the powders were placed in separate alumina boats (again 99.8% purity) to avoid physical contact between the two. In quartz tubes, the specimens and the powders were normally placed directly in the quartz, separated by the narrow neck of the dumbell-shaped capsule. Only in one run were the powder and the specimens placed in separate small alumina tubes, having one closed end, before sealing them in the quartz capsule.

The internal oxidations were performed at either 1100°C for 200 hours or at around 1200°C for 160 hours. The entire quartz capsule was put inside a box furnace, while the mullite and alumina tubes were placed in a tube furnace with their fittings-end being at room temperature. Some specimens were subjected to a similar heat treatment in quartz,

but without the presence of the powder pack. Table 2 summarizes these various internal oxidation pretreatments. A name for each type of run is given for easier identification throughout this paper and indicated in Table 2.

At least one Co-15Cr-1Ti and one Co-15Cr specimen from each pre-oxidation treatment was mounted for cross-sectional observations under an optical microscope, followed by electron probe microanalysis (EPMA) for quantitative assessment of silicon, chromium, aluminum, titanium, oxygen and cobalt. The surface chemistry of a Co-15Cr specimen after an IO pretreatment was determined using Auger spectroscopy, particularly to verify the presence of segregated sulfur[12]. X-ray diffraction was used to identify the internal particles found in these treated alloys.

Oxidation Treatment

The treated specimens were always polished on SiC papers prior to the subsequent oxidation at 1000°C. The thickness removed from each face was carefully determined using a micrometer. Depending on the specimen surface condition after the pre-oxidation treatment, 2-15μm could be removed. Occasionally, a larger depth was ground away in order to specifically examine the effect of silicon or particles. In any case, the specimen surface was always finished on 1200 grit SiC paper and ultrasonically cleaned before the oxidation test.

All oxidation tests were performed isothermally in 1 atm dry oxygen at 1000°C. A Cahn 2000 microbalance was used for kinetics measurements. Specimens were loaded into the apparatus and equilibrated with oxygen before the furnace was turned on. The heating rate of the radiation furnace was such that the desired temperature could be

achieved in 10 minutes. After oxidation, the furnace was turned off and specimens were cooled in O_2 to room temperature in about 30 min, during which time the weight lost due to any spallation could be measured on the microbalance.

Analyses of oxidized specimens involved first a phase identification using X-ray diffraction. A few specimens were observed under the scanning electron microscope (SEM) in plan view, but most specimens were cross-sectioned for optical microscopy or SEM observations. Some selected scale cross-sections were examined under an electron microprobe (EPMA) for quantitative analysis of their composition.

RESULTS

Pre-oxidation Treatments

As reported before[12], internal oxidation pretreatments carried out in quartz resulted in a) a shallow, less than 3 μm thick, surface enrichment in chromium, b) a surface segregation of sulfur to only a few nanometer in depth and c) an inward penetration of silicon. All these results were observed consistently in this study, but as expected, the chromium surface enrichment did not occur when the powder pack consisted of Co15Cr and Cr_2O_3. Although in most cases, the chromium enrichment is only within a very narrow surface region, during two particular runs carried out in quartz at 1200°C, the treated specimens were found to have a chromium contamination that penetrated about 100 μm deep.

Since the silicon contamination was previously found[12] to influence subsequent oxidations, the amount of silicon in specimens after each pretreatment was carefully examined using electron microprobe analysis. Figure 1 shows some typical microprobe results. All samples treated in quartz, whether there was a powder pack or not, and regardless of the temperature, had a relatively high silicon content, which penetrated about

200 μm at 1200°C and between 100-150 μm at 1100°C. Specimens treated in mullite also contained a small amount of silicon, but those treated in alumina did not show any silicon contamination, at least not within the sensitivity of the microprobe, which was about 30 ppm. Within each run, the amount and the degree of silicon penetration was similar for the Co-15Cr and the Co-15Cr-1Ti alloys. Since silicon contamination was found whether the specimens were in direct contact with the quartz or not, its transport to the specimen surface must be via a gas phase specie. This is particularly obvious with IOcap, because the amount of silicon in this case varied from specimen to specimen depending on its position within the small alumina tube. The one closest to the open end had the heaviest silicon contamination, and the one closest to the closed end had the lowest level of contamination.

Internal oxide particles formed in Co-15Cr-1Ti specimens after each IO pretreatment. Figures 2(a) and (c) show typical microstructures developed at 1100°C and 1200°C respectively. Some surface Ti-rich oxide, whose diffraction pattern corresponded to that of Ti_3O_5, developed on these treated specimens either as islands or as a thin surface film. At 1100°C, only within a shallow depth, no more than 3 μm thick, were oxide particles found within the alloy. At 1200°C, two types of internal particles were apparent: an outer band of denser oxide particles, as seen in Fig. 2(b), and an inner band of particles that were actually TiN. The depth of the layer containing the oxide particles was about 30 μm, with particle sizes between 0.1-7μm and an average spacing of 2.5μm. The nitride particles penetrated some 250-300 μm deep, but the particles were much further apart with an average spacing of 30 μm. These nitride particles most likely formed from air diffusing through the quartz at these high temperatures. In no cases were any particles found in the Co-15Cr alloy. Heat treatments in quartz without any powder pack resulted in heavier

external oxidation of the Ti-containing alloy, which in turn caused the development of a shallow depth of internal oxide particles, as seen in Fig. 2(d); these specimens however, did not develop any nitride particles.

Oxidation Kinetics

The influence of various pretreatments on the oxidation kinetics of the Co-15Cr alloy is shown in Figure 3. Even though none of these specimens developed any kind of internal particles, their oxidation behavior was greatly affected by the heat treatments. Comparing the silicon content in these specimens after they were treated in alumina, in mullite or in quartz (Fig. 1), it is seen that the oxidation rate shown here is strongly related to the silicon content. Table 3 summarizes the effect of silicon on the initial oxidation rate, taken as the weight gain after 5 hours, and on the steady state oxidation rate (k_p), evaluated from 10 hours on, of this alloy. Although the oxidation behavior was seldom truly parabolic, k_p was still found to be the best way to describe and compare the steady state behavior.

The amount of silicon in Table 3 was taken as the silicon content on the specimen surface after slight cleaning by polishing prior to the oxidation tests. It is clearly seen that both the initial and the steady state rates were strongly depended upon specimen silicon concentration. Surface enrichment of chromium reduced only the initial rate, but had no effect on the steady state rate. If all of the material contaminated with the Si was removed by polishing away a large depth from the specimen surface, the oxidation rate became identical to that of the untreated alloy. The Co-15Cr-1Si alloy, which had the highest Si content, oxidized the slowest, and its oxidation rates, both initial and steady state, were considerably lower than that of the binary Co-15Cr alloy. The steady state rate is plotted against specimen surface Si content in Figure 4. The drop in rate was very sensitive to the Si content until a concentration of about 0.3 wt% was reached, after which the reduction in rate became more gradual.

The oxidation kinetics of different pre-treated Co-15Cr-1Ti specimens are presented in Figure 5. The untreated ternary alloy oxidized at a slightly lower rate than the binary alloy, and with a wider scatter. Consequently, the treated specimens also showed a larger variation in subsequent oxidation behaviors. In general, the treated Co-15Cr-1Ti behaved like the Co-15Cr that underwent the same pre-treatments, indicating a similar effect due to silicon contamination. The only exception however, was with specimens pre-treated in the alumina tube. Even though from EPMA examinations these specimens did not have a detectable silicon concentration, their oxidation rates were always slightly slower than that of the untreated.

The effect of pretreatments was more complicated in the case of the Ti-containing alloy due to the presence of both silicon and internal particles. A surface layer of internal oxide particles always existed even in situations where a powder pack was lacking. This arose from the development of the thin Ti-rich external oxide layer, which formed by the reaction of outwardly diffused titanium and the residual oxygen in the pretreatment vessel. In order to eliminate the presence of particles, specimen surfaces had to be polished to a certain depth until no more particles were observed. Table 4 summarizes the oxidation results after various heat treatments in order to clarify the effects of particles and of specimen silicon contents. Particle densities were considered high if the outer oxide particles were present prior to oxidation tests. A low particle density implies that the surface was in the inner layer containing nitride particles. Zero particle density resulted from specimens that did not have any nitride particles and their outer oxide particles were removed by polishing; this usually took off 80-90 μm.

From Table 4, it is again seen that both the initial and the steady state rates of the treated specimens were a strong function of silicon content. The rates decreased with increasing silicon concentration at the specimen surface. However, unlike the binary Co-Cr

alloy, these treated specimens never resumed the fast oxidation rate of the untreated state, not even with specimens treated in the alumina tube. Within a detectable silicon concentration of less than 0.2wt%, all of the treated specimens oxidized about 2-3 times slower than that of the untreated. This was so whether the specimen had a relatively high density of particles or not. Particle density did not affect the steady state rate in any way, but had a slight effect on the initial rate. Comparing silimar silicon contents, it is seen that the higher the particle density, the lower the initial rate; the reduction was about 30-40%.

Oxide Morphology and Composition

Both untreated Co-15Cr and Co-15Cr-1Ti alloys developed duplex scales that are typical in binary Co-Cr alloys with this composition[13-16]. The outer layer was mainly CoO with a very small amount of Co_3O_4; the inner layer consisted of CoO, Cr_2O_3 and $CoCr_2O_4$. This type of scale is believed to grow by the outward transport of cobalt[13,15]. Local establishment of a thin and partial Cr_2O_3 layer sometimes took place at the scale/alloy interface (Fig. 6), thus slowing down the scale growth rate in the region, but this healing layer often broke down to allow thickening of both the inner and the outer portion of the scale, and fast scale growth resumed in the region. The observed oxidation kinetics were then an average record of all these local behaviors.

Different pre-oxidation treatments affected the subsequent oxidation rates differently. However, not until there was more than 0.4wt% silicon on the surface of Co-15Cr-1Ti and 0.5 wt% on Co-15Cr was a somewhat continuous Cr_2O_3 formed with little CoO formation. Other specimens with lower Si content, whether in the Co-15Cr or in the Co-15Cr-1Ti, and regardless of high or low particle densities in the ternary alloy, developed Co-rich duplex scales with different degrees of Cr_2O_3 healing layer coverage; the higher the silicon content, the higher was the percentage. Figure 7 shows the micrograph of such

a duplex structure along with an EPMA trace across the scale. Small amounts of silicon were detected within the entire inner layer, but most silicon concentrated at the scale/alloy interface immediately beneath the chromia healing layer.

With a surface silicon concentration at about 0.4 wt% in the Ti-containing alloy, the development of a Cr_2O_3 layer was nearly complete (Fig. 8), with the exception of several large duplex, Co-rich nodules. These nodules are believed to have grown from local breakdown of the thin protective scale. Composition of the thin scale examined by EPMA showed that the scale consisted of a thin outer layer of mainly CoO, beneath which was a layer of Cr_2O_3. In between the two layers was a high concentration of titanium; this should be attributed to the internal titanium oxide particles formed in the specimen by the IO pretreatment. However, the local enrichment of titanium within the scale was not believed to have much influence on scale development, because other EPMA examinations have found the same degree of enrichment on scales that are totally non-protective. A small amount of silicon was detected in the Cr_2O_3 layer, but a noticeable concentration was found at the scale/alloy interface. Silicon however, was never detected on specimens which had been pretreated in the alumina vessel.

The oxide scale formed on the Co-15Cr-1Si alloy was the only one that showed extensive spallation during cooling. After 50 hours at 1000°C, the entire scale had spalled, leaving only specks of oxides on the metal surface which was full of voids. Auger analysis was performed on the metal surface and found only a thin layer of CoO which probably developed during cooling; nowhere was any appreciable amount of silicon detected. Scales that formed after 24 hours spalled only 50%, and Figure 9 shows the morphology of such a scale. While most part of the specimen developed Cr_2O_3 scales, some Co-oxide duplex scale with a Cr_2O_3 healing layer was also present. The magnified view in Fig. 9(b) indicated the presence of a different oxide, which appeared dark in the backscattered image, at the

scale/alloy interface. From the results of EPMA analysis, this oxide should be silicon rich, and this was indeed confirmed using energy dispersive X-ray analysis. It is not clear in what form this silicon oxide existed. Although it was found to be present at most interfacial areas, this layer was not completely continuous.

DISCUSSION

One of the original aims of the present work was to verify the results reported by Whittle et al.[2] on the effectiveness of dispersed particles formed by internal oxidation on the selective oxidation of chromium in Co-Cr alloys. Their titanium oxide particles formed after internal oxidation pretreatments at 1200°C ranged between 0.6-15 μm in diameter, spaced some 8 μm apart, and penetrating about 50 μm into the alloy. Finer particles with a deeper penetration resulted with a higher pretreatment temperature. In all cases, their treated specimens oxidized at a much slower rate than the untreated alloys and developed Cr_2O_3 scales, regardless of the distribution and size of the dispersed particles. This was true even with specimens which had developed 'dispersion free zones' either near to the alloy surface or within the internal oxide zone. In the present study, the internal oxide particles developed in Co-15Cr-1Ti at 1200°C had a very similar morphology to those obtained by Whittle et al., except the penetration depth was slightly shallower. The possible effect of these particles will be discussed later, but all results acquired here pointed to a strong effect of silicon on the selective oxidation of chromium.

Silicon diffused into the treated alloys as a contaminant from the quartz vessel in which the internal oxidation pretreatment was carried out. Even with pretreatments carried out in mullite, a small concentration of silicon was also detected in the alloy. The binary Co-15Cr alloy never developed any internal oxide particles, as one would expect. However, its subsequent oxidation behavior was greatly affected by the pretreatments, depending strongly on the amount of silicon that was introduced into the alloy during the

process. Only when the Co-15Cr was pretreated in an alumina tube, which resulted in specimens free from silicon contamination, was the subsequent oxidation rate not affected. Furthermore, by removing all of the silicon from a contaminated specimen surface by polishing, the oxidation rate would return to that of the untreated alloy.

Impurity levels of silicon have been suggested by Jones and Stringer[17] to change the oxidation of Co-25wt%Cr alloy from a fast oxidation rate, where a duplex, Co-rich scale developed, to a slow rate where a Cr_2O_3 scale formed. For the Co-15wt%Cr studied here, the amount of silicon in the alloy surface had to reach about 0.4wt% before considerable Cr_2O_3 scale development would occur. Alloying the binary Co-Cr with 1wt% Si did not significantly change the alloy grain structures, but the Co-15Cr-1Si alloy oxidized to form Cr_2O_3 scales instead of Co-rich scales. The addition of silicon definitely promotes Cr_2O_3 scale formation in these alloy systems, although the effect was not as strong as that due to alloying of reactive element dispersions[11,18].

It is not entirely clear by what mechanism the silicon was effective, since many factors may be involved in a complicated system like this. However, Johnston[19] has reported that the addition of silicon to Ni-Cr alloys increased chromium diffusivity in the alloy, and that D_{Cr}^{alloy} increased with increasing silicon concentration. Furthermore, selective oxidation of chromium in binary Ni-Cr alloys has been shown[8,9] to occur at alloy grain boundaries or on cold-worked surfaces, due to a faster transport of chromium from the alloy to the oxidizing surface. Incorporation of silicon in the Co-based alloys then may also enhance chromium diffusivity, thus promoting the selective oxidation of chromium. As the alloy silicon content increased, the oxidation rate decreased quickly until a nearly complete layer of Cr_2O_3 scale developed. Further reductions in oxidation rate were more gradual, and probably involved the accumulation of silicon at the scale/alloy interface. An amorphous silica layer, which was believed to act as a diffusion barrier to reduce

oxidation rates, has been detected[20-22] at oxide/alloy interfaces in alloys containing Si, and the presence of such a silica layer also increased scale spallation[21]. In the present study, the silica layer was never found to be continuous. From the fact that no silicon could be detected by Auger spectroscopy on the underlying metal surface, spallation of the oxide layer must have taken place at the silica/alloy interface.

The oxidation behavior of the Ti-containing ternary alloy was also affected by the presence of silicon contamination; the rate decreased with increasing silicon content. However, unlike the binary Co-Cr alloy, these treated specimens never resumed the fast oxidation rate of the untreated state. Between a detectable silicon concentration of 0-0.1wt%, all of the treated specimens oxidized about 2-3 times slower than that of the untreated. This was so whether the specimen had a relatively high density of particles or not. Even when particles were all removed by polishing, taking away approximately 90 μm from each face, the steady state rate was still low. It is not clear why this lowering of the oxidation rate should occur with a simple heat treatment, especially when similar behavior was not observed with the binary alloy treated under the same conditions, and the lowering apparently was not related to the presence of internal particles. Perhaps the ternary alloy was more sensitive to impurity levels than the binary alloy. Since the alumina tube and the alumina boats used were not of a very high purity, some very small amount of silicon, whose concentration may be too low for the sensitivity of the microprobe, could still be incorporated into the specimen.

Although the presence of dispersed particles did not affect the steady state oxidation rate, it did reduce the initial rate (within the first 5 hours) by about 40%. This reduction however, was not enough to cause any selective oxidation of chromium in this alloy. Since the particle size, distribution and depth were quite similar to those reported in the work of Whittle et al.[2], the selective oxidation observed in their work must also have been due

to a strong silicon contamination, rather than the presence of internal oxide particles. This is especially so because most of their internal oxidation pretreatments were carried out in quartz at temperatures as high as 1300°C, and silicon contamination from quartz is known to increase with increasing heat treatment temperature and time[12].

A significant implication from the work by Whittle et al.[2] was that the presence of dispersed particles, without a modification of alloy grain sizes or dislocation substructures, could facilitate the establishment of a continuous protective Cr_2O_3 scale at much lower alloy chromium levels. These dispersoids were envisaged as nucleation sites[11] for the initially-formed oxide, reducing the spacings between oxide nuclei and hence promote a continuous Cr_2O_3 scale formation. In light of the results obtained from the present study, which strongly question the validity of the work by Whittle et al., it becomes important to re-examine the effect of reactive element dispersions on the selective oxidation of chromium more carefully, particularly in alloys that normally would not form a continuous chromia scale on their own.

CONCLUSIONS

Heat treatments carried out in quartz above 1100°C and in mullite at 1200°C all resulted in silicon contamination, the amount being higher with quartz. Subsequent oxidation at 1000°C of the treated Co-15Cr and Co-15Cr-1Ti alloys was greatly affected by the presence of silicon. Oxidation rate decreased with increasing silicon content in the alloy, and the presence of silicon promoted chromia scale formation. The oxidation behavior of a Co-15Cr-1Si alloy confirmed the effectiveness of silicon in the selective oxidation of chromium in this alloy system.

The presence of internal titanium oxide particles reduced the initial oxidation rate by approximately 40%, but the particles themselves are ineffective in causing the estab-

lishment of a protective chromia layer. These results indicated that the selective oxidation observed by Whittle et al.[2] after internal oxidation pretreatments of their reactive element containing alloys in quartz at above 1200°C must also be due to a strong silicon effect. The effectiveness of dispersoids in promoting chromia scale formation on alloys which normally would not form a steady state Cr_2O_3 layer warrants more careful evaluation.

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FIGURE CAPTIONS

Figure 1: Silicon content in Co-15Cr or Co-15Cr-1Ti after pre-oxidation treatments in quartz, mullite or alumina.

Figure 2: Optical micrographs showing internal particles formed in Co-15Cr-1Ti after pre-oxidation heat treatments. (a) IO at 1100°C, (b) IO at 1200°C, (c) magnified view of outer oxide particles on IO1200 specimens and (d) IO at 1200°C in quartz without powder pack.

Figure 3: Effect of various pretreatments on the oxidation kinetics of Co-15Cr alloy at 1000°C in 1 atm oxygen. The behavior of a Co-15Cr-1Si alloy was also presented for comparison.

Figure 4: Effect of silicon content on the steady state oxidation rate of Co-15Cr.

Figure 5: Effect of various pretreatments on the oxidation kinetics of Co-15Cr-1Ti alloy at 1000°C in 1 atm oxygen. All of these treated specimens contained internal oxide particles within 20-30 μm in depth.

Figure 6: Optical micrograph of oxide scale developed on untreated Co-15Cr-1Ti after 24 hours at 1000°C, showing a portion of the scale that had a partial Cr_2O_3 healing layer.

Figure 7: (a) Optical micrograph of oxide scale formed at 1000°C for 50 hours on Co-15Cr pretreated in quartz at 1200°C, [Si]=0.43,and (b) EPMA analysis across the scale.

Figure 8: Optical micrograph of oxide scale formed at 1000°C for 50 hours on Co-15Cr-1Ti pretreated in quartz at 1200°C, [Si]=0.43,(b) EPMA analysis across the thin portion of the scale shown in (a).

Figure 9: Backscattered SEM images of oxide scales formed on Co-15Cr-1Si after oxidation at 1000°C for 24 hours. (b) is a magnified view of (a).

Table 1: Alloy Composition (in weight %)

Alloy Type	Co	Cr	Ti	Si
Co-15Cr	bal.	15.35	-	-
Co-15Cr-1Ti	bal.	15.23	0.82	-
Co-15Cr-1Si	bal.	15.14	-	0.88

Table 2: Summary of Pre-oxidation Treatments

Run Name	Description of Experimental Procedures
IO1100	Internal oxidation at 1100°C for 200 hours in quartz.
IO1200	Internal oxidation at 1200°C for 160 hours in quartz. (Several runs were performed under this condition).
IOcc	Internal oxidation at 1200°C for 160 hours in quartz, using Co-15Cr/Cr_2O_3 powder pack instead of Cr/Cr_2O_3.
IOcap	Internal oxidation at 1200°C for 160 hours in quartz, but specimens and powders were placed in separate alumina tubes having one closed end.
IOmul	Internal oxidation at 1185°C for 165 hours in mullite.
IOal	Internal oxidation at 1185°C for 165 hours in alumina.
HT	Heat treatment (no powder pack) at 1200°C for 160 hours in quartz.

Table 3: Summary of Oxidation Behavior of Co-15Cr after Pre-oxidation Treatments

Pretreatment Conditions	Silicon Concentration (wt%)	Weight Gain after 5 hours (mg/cm^2)	Steady State Oxidation Rate ($mg\ cm^{-2}\ h^{-1/2}$)
untreated	-	22.55	6.67
IOal	0	24.59	6.38
IO1100*	0	23.26	7.69
IOmul	0.04	19.12	4.87
IOcap	0.05	12.87[a]	3.65
IOmul	0.09	18.87	2.68
IOmul	0.13	18.89	2.33
IOcc	0.18	11.89	1.00
IO1100	0.25	8.81	0.62
HTqz	0.32	14.10	0.11
IO1200	0.43	7.87	0.21
IO1200	0.58	0.60[b]	0.29
Co-15Cr-1Si	0.88	2.54	0.07

* An IO1100 specimen, after removing 150 μm from each surface.
[a] Surface slightly enriched with chromium: about 10% higher.
[b] Surface enriched with chromium: 40% higher.

Table 4: Summary of Oxidation Behavior of Co-15Cr-1Ti Alloy After Pre-oxidation Treatments

Pretreatment Conditions	Silicon concentration (wt%)	Particle density+	Weight Gain after 5 hours (mg/cm^2)	Steady State Oxidation Rate ($mg\ cm^{-2}\ h^{-1/2}$)
untreated	0	0	16.6±0.7	5.7±1.1
IOal	0	high	15.4	2.3
IOal*	0	low	20.7	1.2
IOal*	0	0	19.7	2.9
IOmul	0.06-0.12	high	15.6-11.1	3.0-1.1
HT*	0.14	0	18.1	2.9
IOcc*	0.15	low	11.0	2.7
IOcc	0.17	high	7.5	2.1
IO1100	0.25	0	11.8	1.2
HT	0.32	high	4.5	1.1
IO1200*	0.37	low	7.5	0.6
IO1200	0.43	high	2.4	0.2
IO1200	0.55	high	1.7[a]	0.1
Co-15Cr-1Si	0.88	0	2.5	0.1

+ High density refers to the outer oxide layer; low density refers to the inner nitride layer.

* Specimen surfaces polished 40-100 μm to reach different particle densities.

[a] Specimen surface was also enriched with chromium.

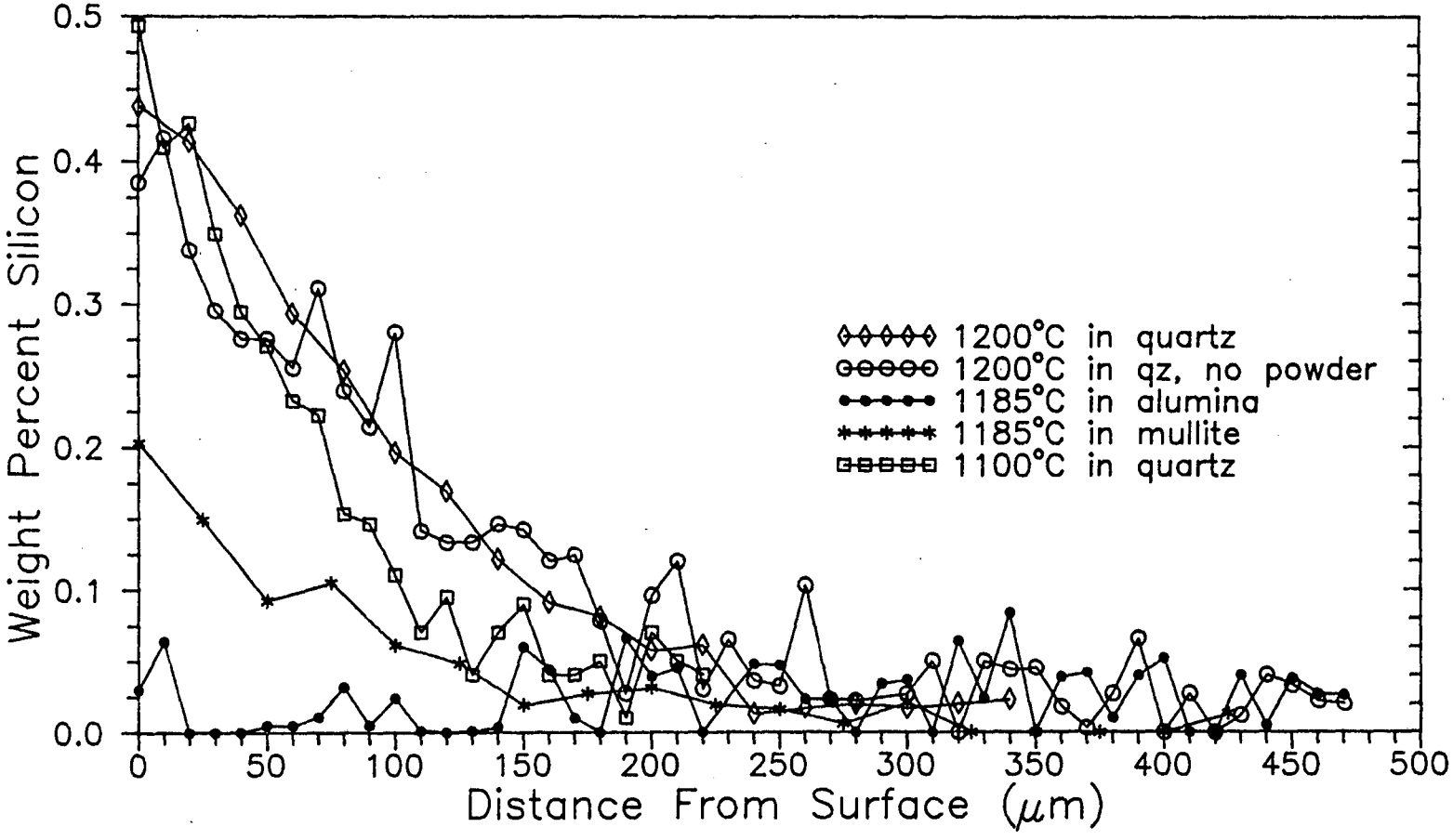

Weight Percent Silicon
0.0
0.1
0.2
0.3
0.4
0.5
0
50
100
150
200
250
300
350
400
450
500
Distance From Surface (μm)
1200°C in quartz
1200°C in qz, no powder
1185°C in alumina
1185°C in mullite
1100°C in quartz

Figure 1

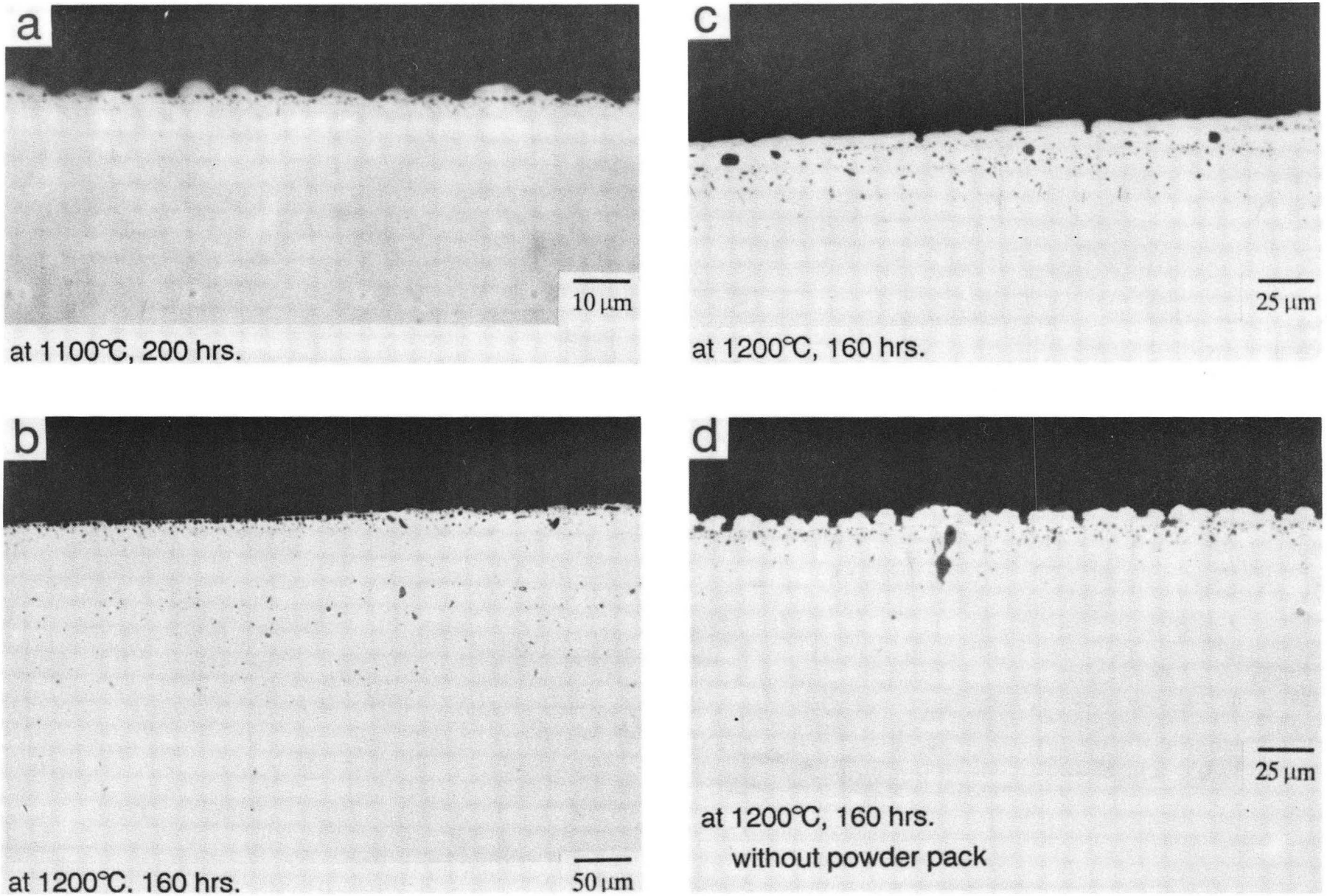


Figure 2: XBB921-129

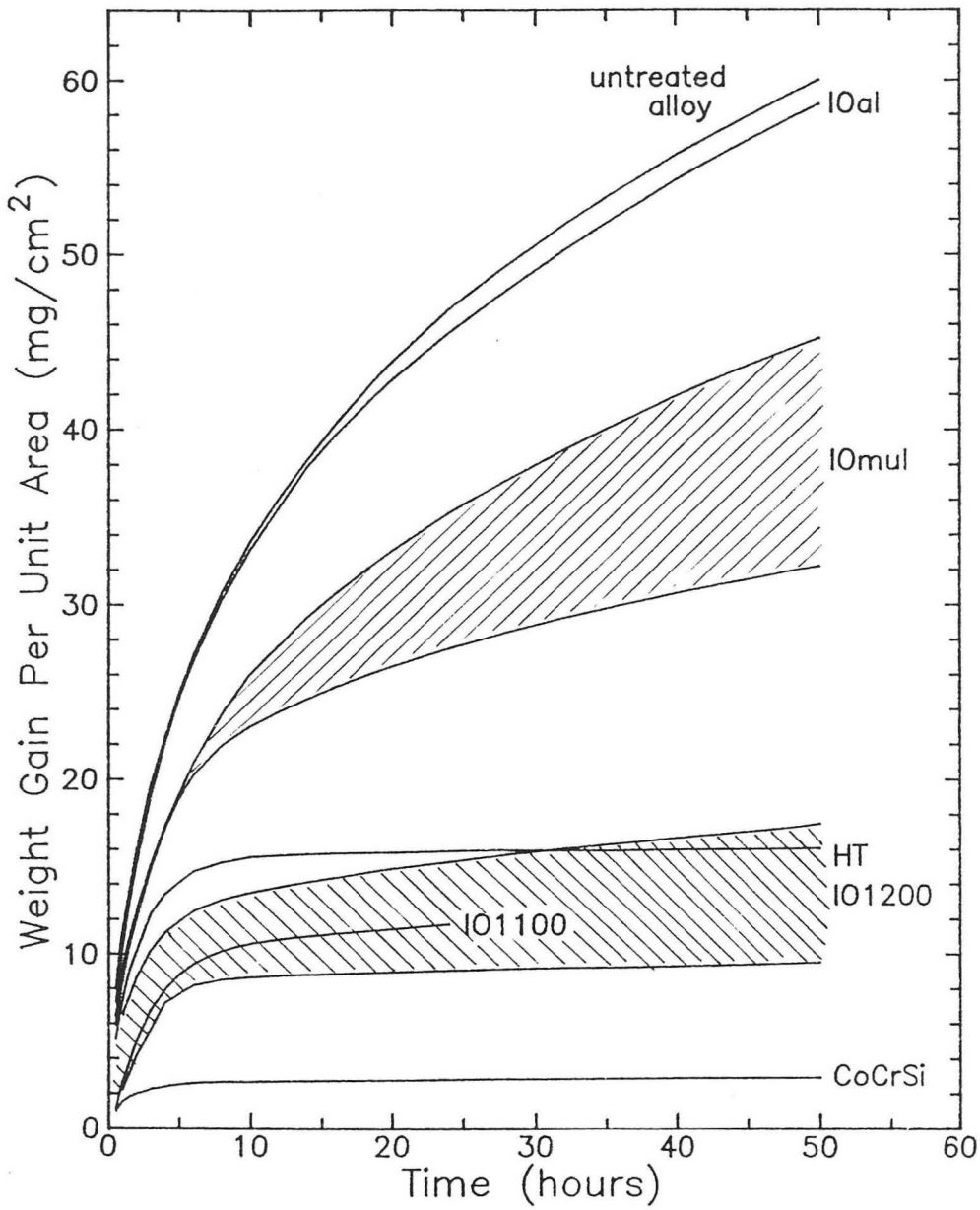

untreated
alloy
10al
10mul
HT
101200
101100
CoCrSi
Weight Gain Per Unit Area (mg/cm^2)
Time (hours)
0
10
20
30
40
50
60

Figure 3

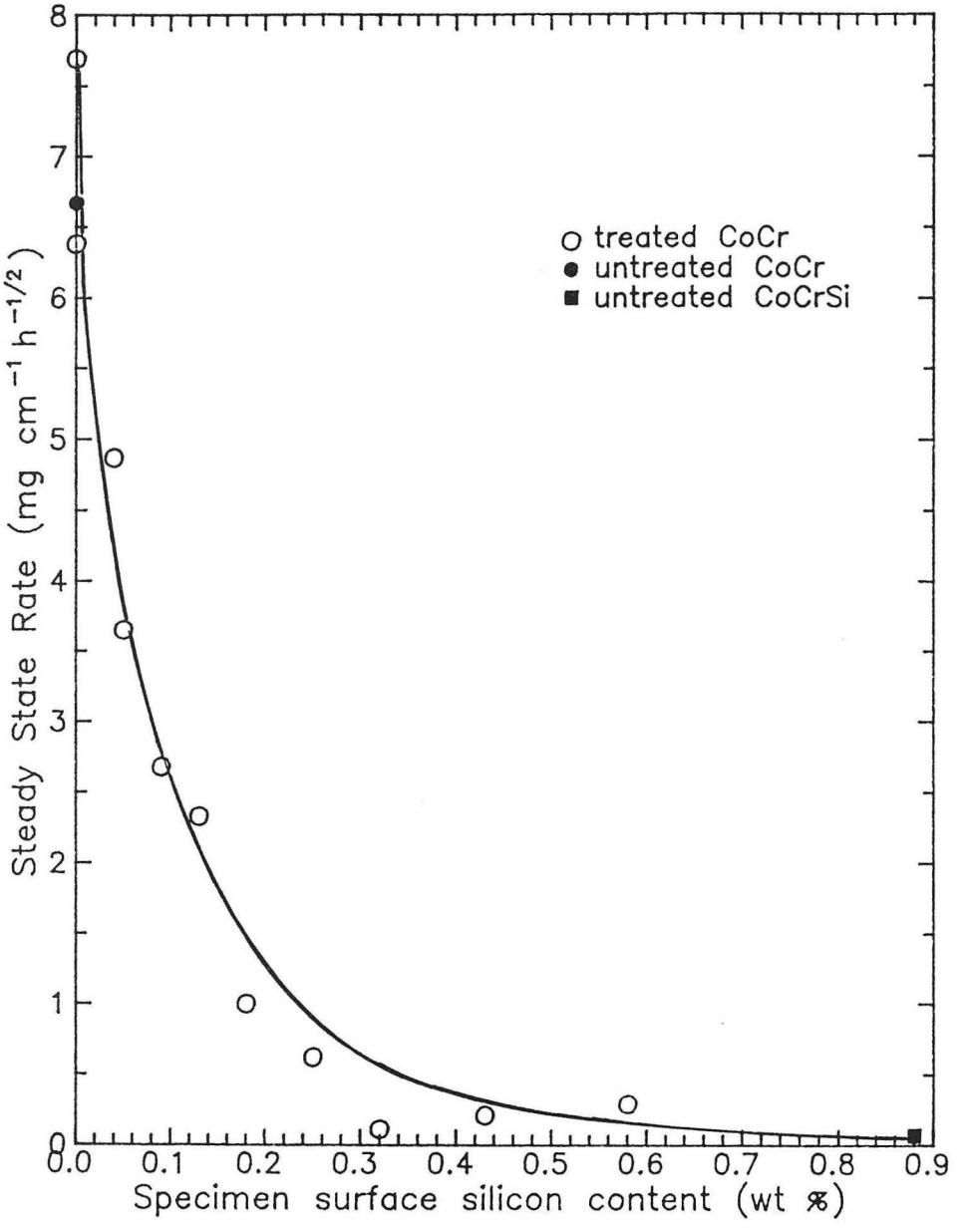

Steady State Rate (mg cm^{-1} h$^{-1/2}$)
Specimen surface silicon content (wt %)
treated CoCr
untreated CoCr
untreated CoCrSi
0
1
2
3
4
5
6
7
8
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

Figure 4

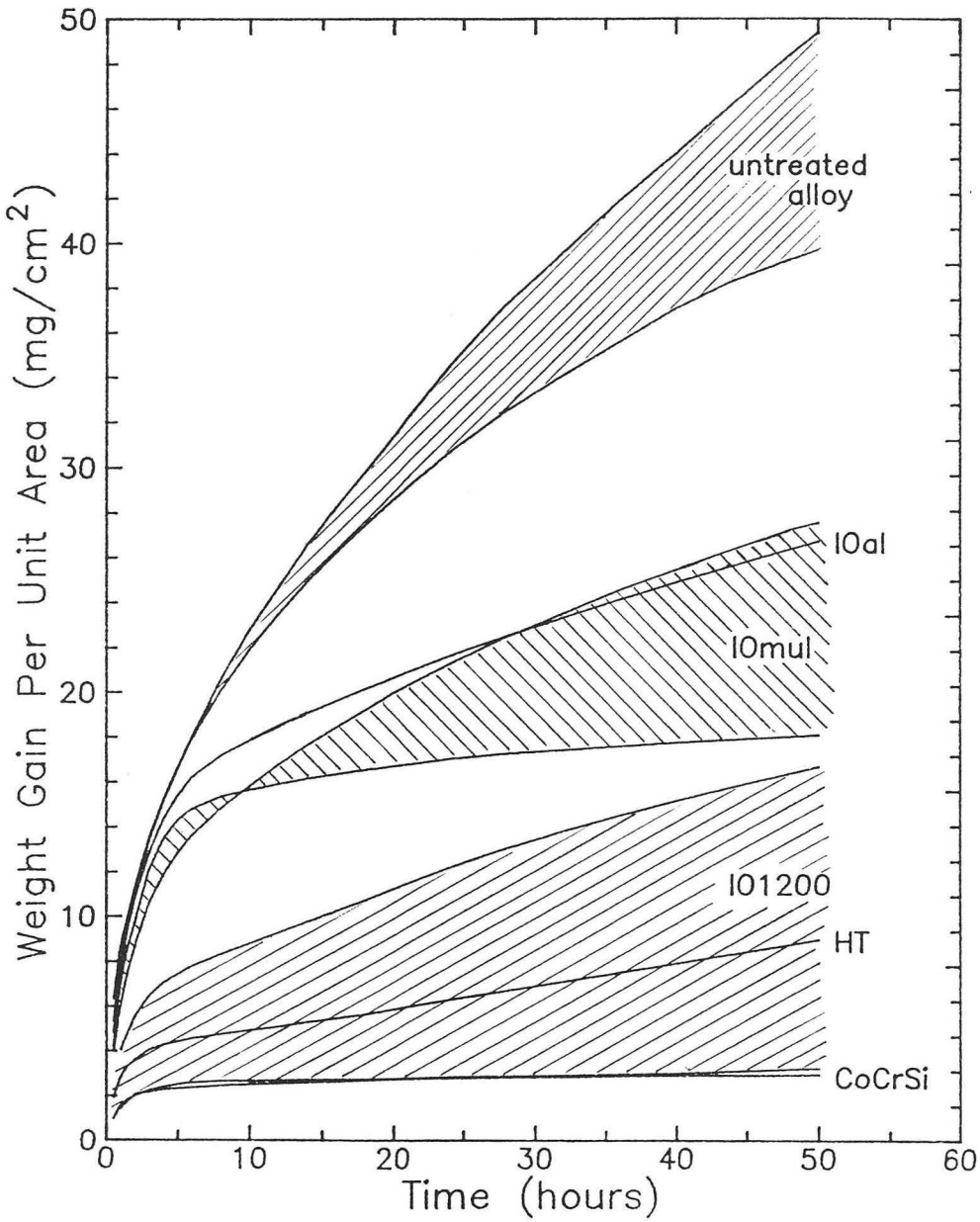

Weight Gain Per Unit Area (mg/cm^2)
Time (hours)
0
10
20
30
40
50
60
untreated alloy
10al
10mul
101200
HT
CoCrSi

Figure 5

Co-15Cr-1Ti, 1000℃, 24h.

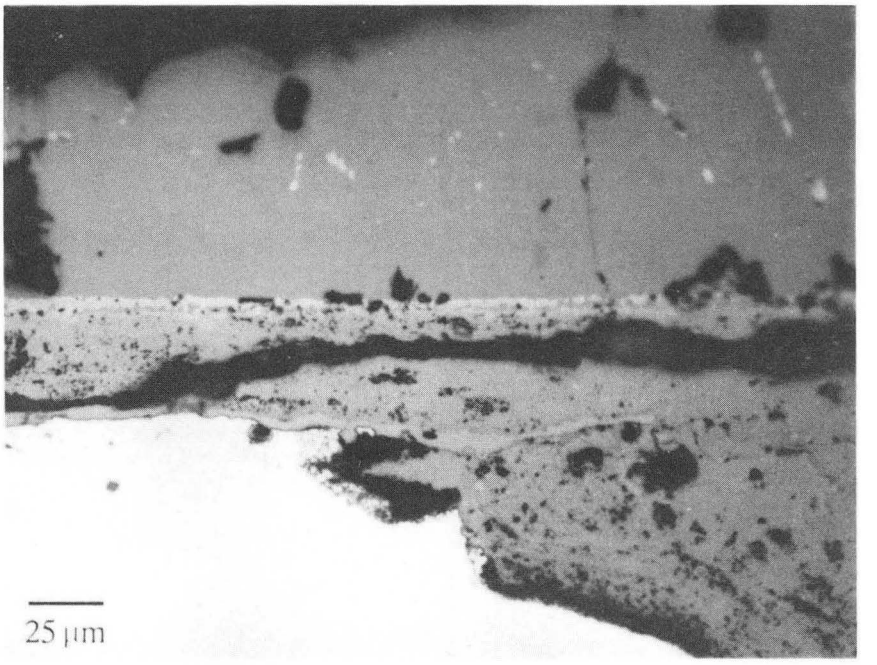
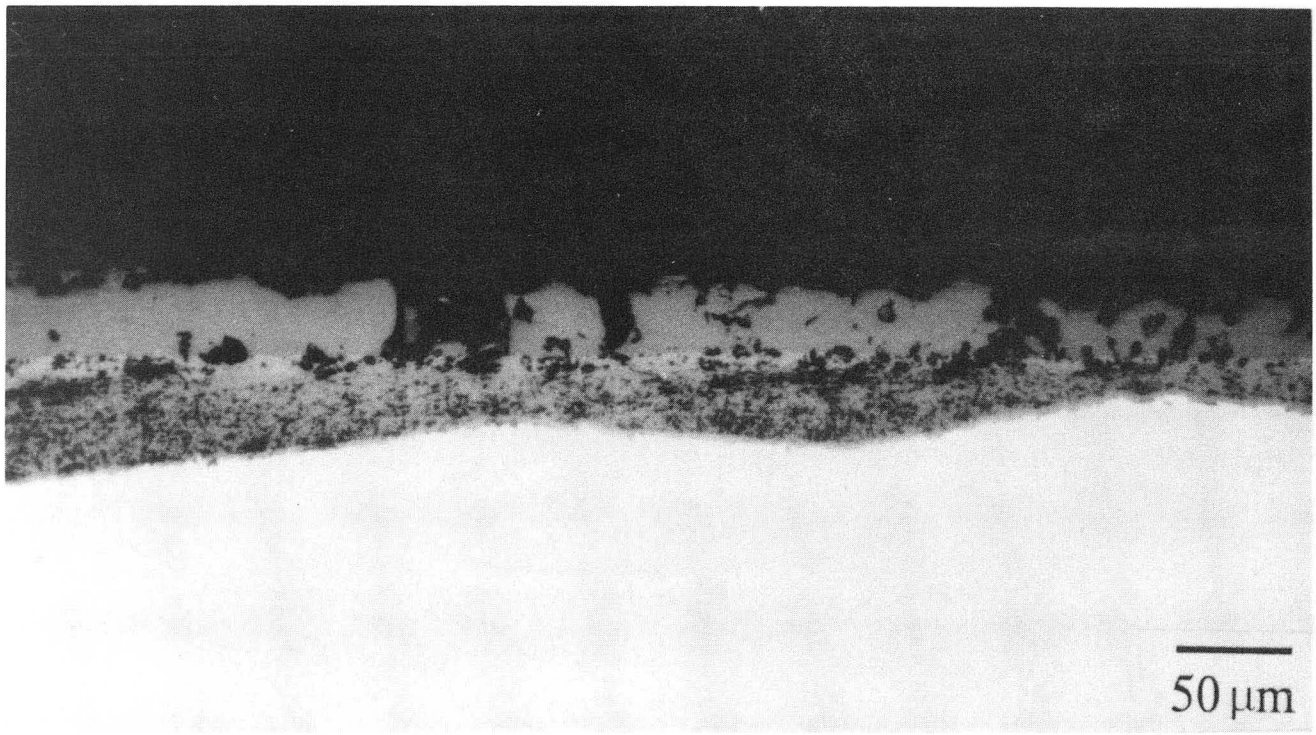


Figure 6 XBB 921-105



XBB921-128top

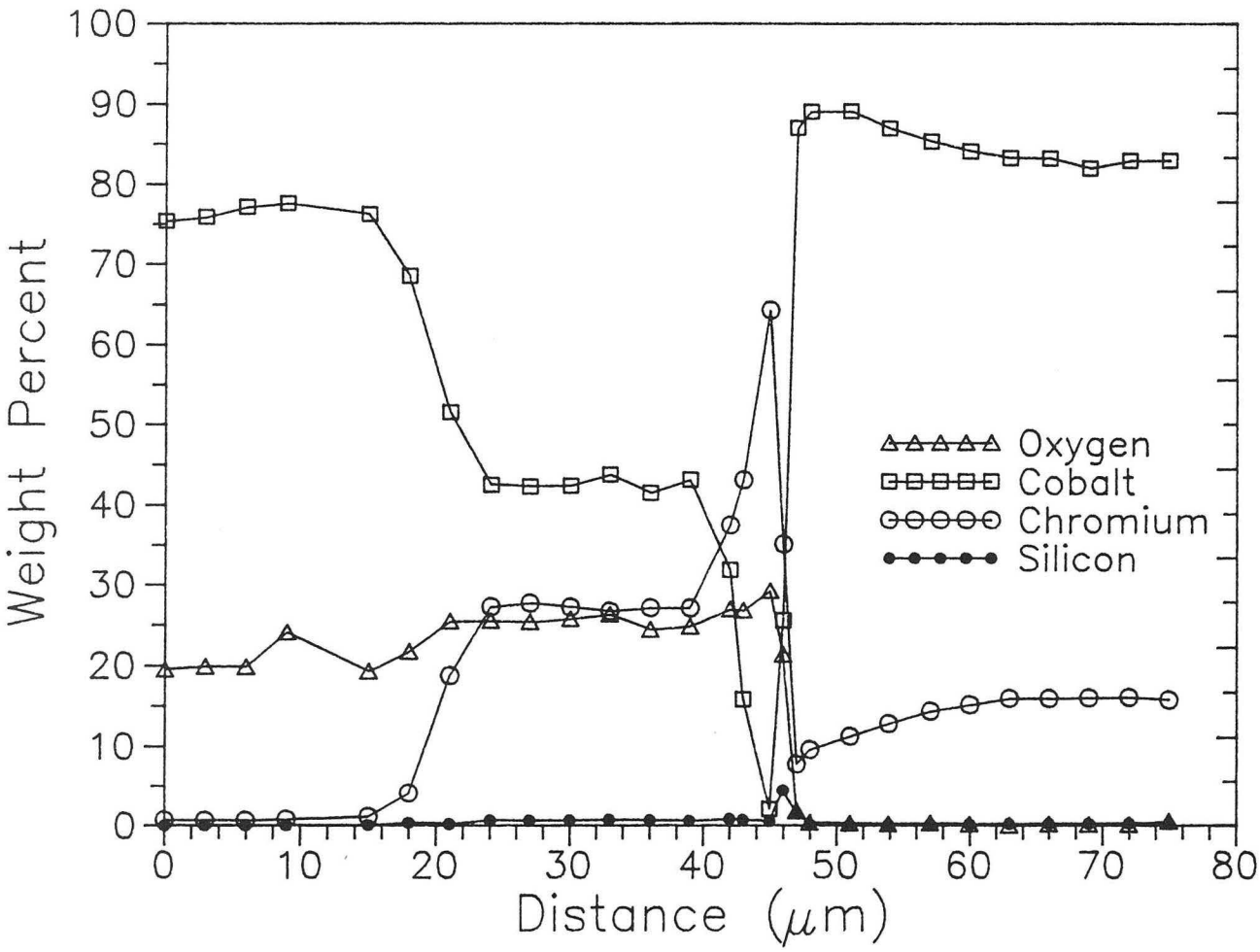
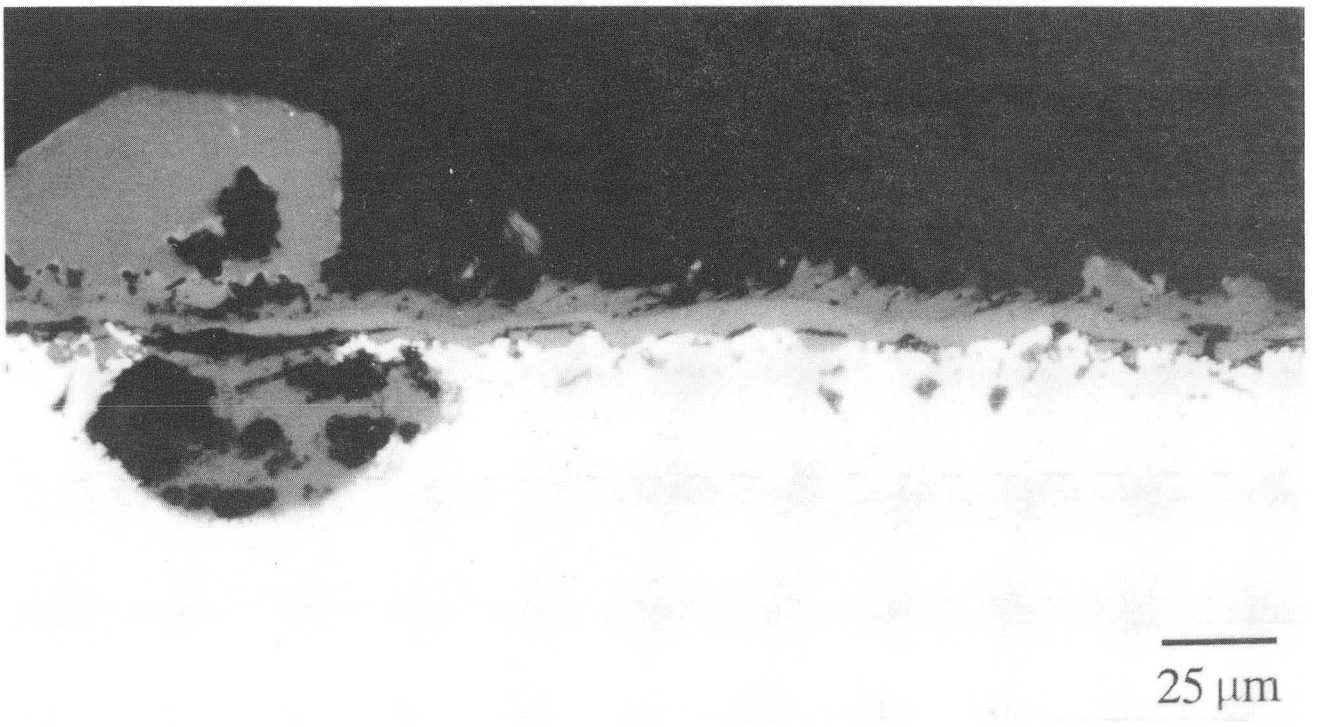


Figure 7



XBB921-128bottom

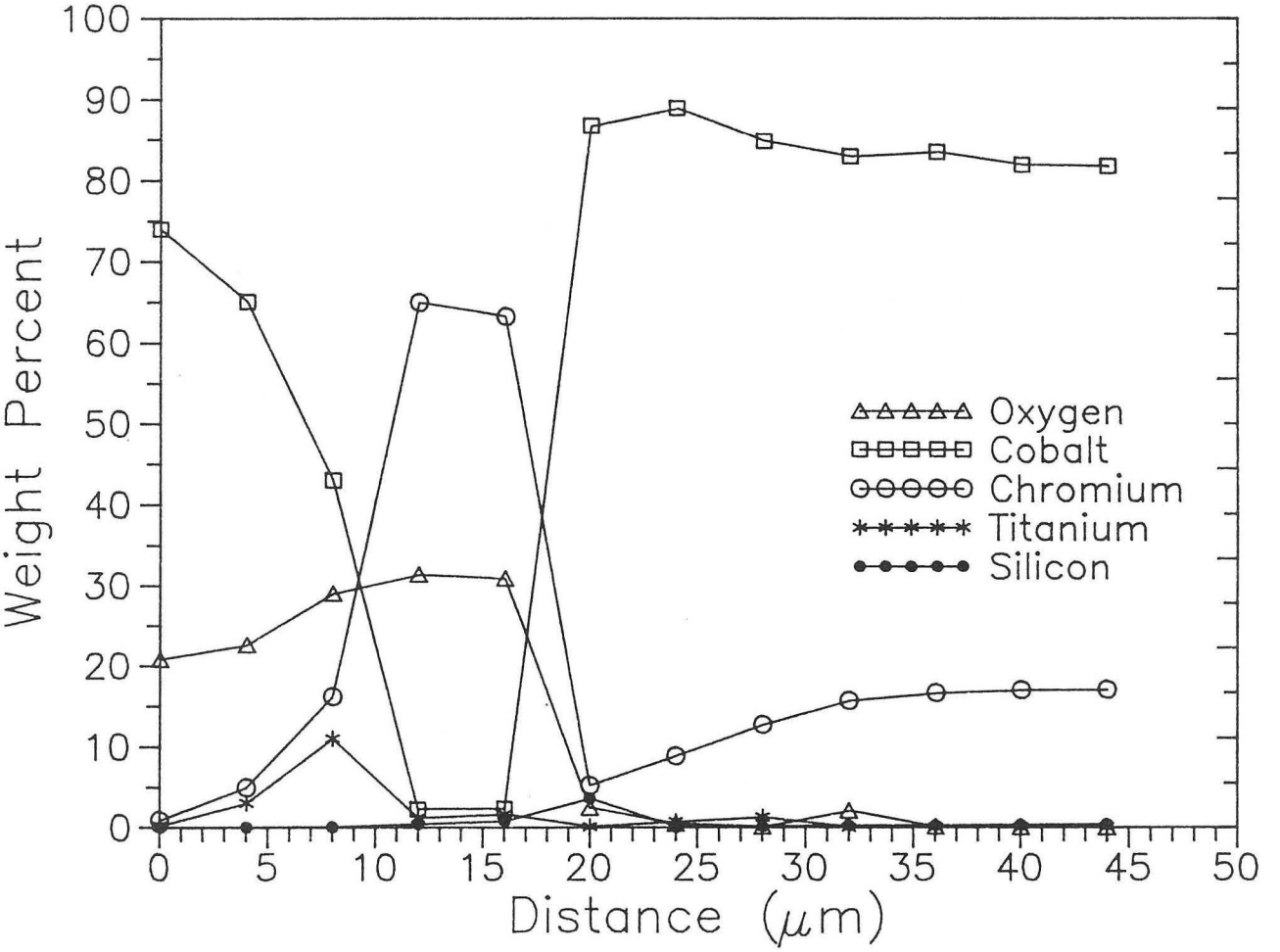


Figure 8

Co-15Cr-1Si, 1000°C, 24h.

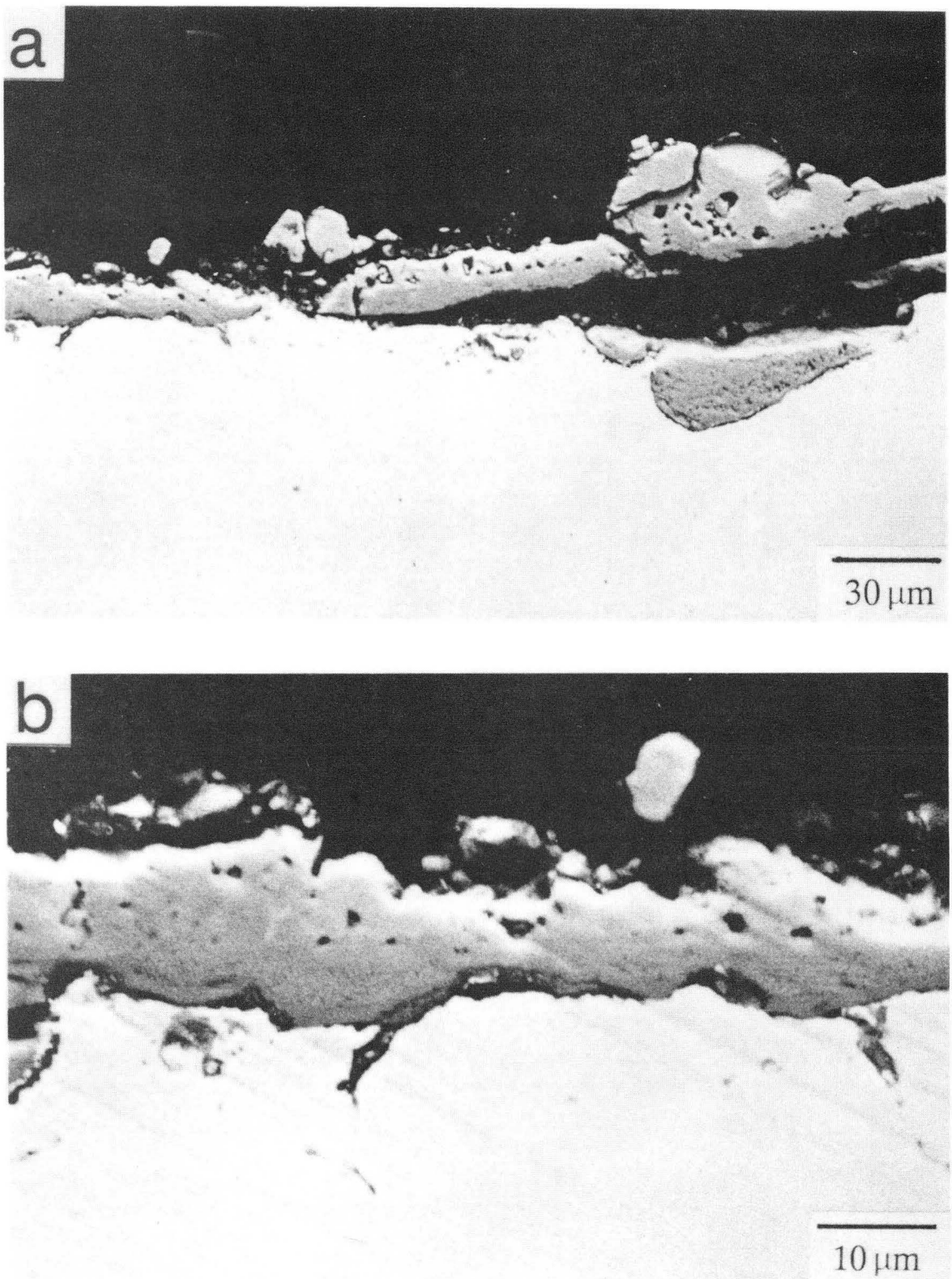


Figure 9 XBB921-127

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