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Authors

Hou, P.Y.
Stringer, J.

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ION-IMPLANTATION OF REACTIVE ELEMENTS IN IMPROVING THE ADHESION OF THERMALLY GROWN Cr_2O_3 SCALES

P. Y. Hou* and J. Stringer†

* Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

† Electric Power Research Institute
Palo Alto, California 94303

ABSTRACT

The high temperature oxidation behavior of Al, Y and Hf ion-implantation in Ni-25wt%Cr alloy with dosages ranging from 10^{15} - 10^{17} ions/cm² has been studied. Results are compared with the unimplanted alloy, a Xe-implanted alloy and alloys with 0.2wt% Y or 1wt% Al additions. Oxidation tests were carried out at 1000°C and 1100°C in 1 atm. O₂. It is found that the ion-implantation of Y and Hf greatly reduced oxidation rate and improved scale adherence after a critical implantation dosage, $\sim 1 \times 10^{16}$ ions/cm², has been reached. The improved scale adhesion is attributed to both a reduction in growth stress and a strengthened scale/alloy interface, which all developed as a result of a modified scale growth process.

1. INTRODUCTION

It is well known that the addition of reactive metals (such as Y, Hf and Ce) or their oxides to heat resistant alloys forming protective Cr_2O_3 or Al_2O_3 scales significantly improves their oxidation resistance under high temperatures. Studies concerning the effect of minor alloying additions of reactive metals or fine dispersions of their oxides were extensively reviewed by Whittle and Stringer [1]. In summary, the effects on Cr_2O_3 -forming alloys are i) a significant reduction in the amount of chromium required to form a continuous protective Cr_2O_3 layer; ii) a change in transport mechanism through the scale from principally metal transport outward for alloys without the reactive element addition to principally oxygen transport inward; iii) a reduction in scale growth rate at temperatures above approximately 900° and iv) a pronounced improvement in scale adherence.

Several mechanisms have been proposed to account for the enhanced adhesion, and they are briefly summarized here: 1) *Vacancy Sink Mechanism* : This proposed that the loss of scale adhesion is primarily caused by the condensation of vacancies at the metal/scale interface to form voids which nucleate cracking at the interface. The dispersion of reactive metal oxide is then believed to act as receptive sink for cation vacancies, thereby preventing void formation at the alloy/scale interface. If the reactive element is added as the metal to the alloy, it is suggested that it oxidizes internally beneath the external oxides to form a dispersion of reactive metal oxides essentially similar to that resulting from adding the reactive element as their oxides. 2) *Oxide Keying or Pegging* : The reactive elements (RE) whether added as an alloy addition or as an oxide dispersion promotes the formation of intrusions of the external oxide into the metal. It is proposed that these intrusions can key the scale to the alloy substrate, and therefore, increase the scale adherence. 3) *Reduction of Stress in Scales* : Models proposed in this group dealt with mechanisms which may be responsible for reducing stresses in the oxide scale and thus make the scales more adherent. i) The reduced growth rate associated with the RE addition can results in less growth stress. ii) The fine-grained oxide often produced on the RE-containing alloys can plastically deform more easily to eliminate stresses, and iii) the presence of RE changes the oxide growth mechanism to entirely oxygen inward transport and eliminate any cation outward movement which causes lateral growth of oxide within the scale to generate large compressive stress. 4) *Improved Chemical Bonding at the Scale/Alloy Interface* : The reactive elements segregate to scale/alloy interface and strengthen the interfacial bonds [2]. 5) *Impurity Gettering Model* : Segregation of impurities, particularly sulfur, to the scale/alloy interface weakens the interfacial bonds which are intrinsically strong. The reactive metals interact chemically with these impurities, and oxide dispersions of reactive metals provide extra interfaces for segregation. Thus, the additions act as getters and prevent impurities from segregating to the critical scale/alloy interface [3].

Ion implantation is an attractive technique for studying the mechanisms of the reactive element effect, since comparisons can easily be made between implanted and unimplanted regions of the same alloy specimen. Furthermore, the oxidation behavior of the surface implanted specimen

can be directly compared with those containing reactive elements as an alloy addition to better distinguish the different mechanisms that might be responsible for the improved adhesion. In this investigation, various levels of yttrium and relatively high doses of aluminum and hafnium have been implanted in a good Cr_2O_3 -forming alloy, Ni-25wt%Cr. The oxidation behavior of the implanted and the unimplanted alloys at 1000°C and 1100°C in 1 atm. O_2 has been studied and compared with the behavior of alloys containing a nominal 1wt% Al or Y.

2. EXPERIMENTAL PROCEDURE

The Ni-25Cr, Ni-25Cr-1Y and Ni-25Cr-1Al alloys were prepared by induction melting and casting under an argon atmosphere. Except the content of Y, which was only 0.2wt%, actual composition of other components in these alloys was found to be similar to their nominal composition. The ingots were homogenized in vacuum for 24 hours at 1100°C. Resulting grain sizes of these three alloys were $51\text{ }\mu\text{m} \times 460\text{ }\mu\text{m}$, $60\text{ }\mu\text{m} \times 340\text{ }\mu\text{m}$ and $18\text{ }\mu\text{m}$ respectively. Specimens $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$ were cut from the center of the ingots. All specimen surfaces were polished to a 600-grit SiC finish and cleaned with alcohol before ion-implantation or before oxidation tests.

The ion-implantation was carried out in the injector portion of the heavy ion linear accelerator at the Lawrence Berkeley Laboratory. The acceleration voltage of the ions was usually adjusted to 400 keV, and the average current density was about $3\text{ }\mu\text{A}/\text{cm}^2$. A few specimens were preoxidized at 1000°C in 1 atm. O_2 for 15 minutes prior to the implantation process. This preoxidation treatment produced a continuous external scale of Cr_2O_3 approximately $1\text{ }\mu\text{m}$ thick. SIMS analyses indicated that the implanted yttrium concentrated near the outer surface of this thin oxide with a range of about $0.2\text{ }\mu\text{m}$. This range is compatible to the normal $0.15\text{ }\mu\text{m}$ implantation depth observed when the ions were implanted onto unoxidized surfaces. The nominal dosage of yttrium ions used in this study varied from 1×10^{15} - 5×10^{16} ions/ cm^2 . The dosage for Al was 5×10^{16} and 1×10^{17} ions/ cm^2 , and for Hf was 5×10^{16} ions/ cm^2 . The nominal dosages were obtained from the total beam current exposed to the specimen. However, from measurements using Rutherford backscattering (RBS) technique on selected specimens the actual dosages were found approximately half the nominal. This discrepancy is due to the emission of secondary electrons during the

implantation process. In this paper, a "dosage" is always referred to the value obtained from the total current, unless it is stated otherwise. Because ion-implantation can cause surface damage, and to evaluate the importance of this, some implanted specimens were annealed before undergoing any oxidation test. The annealing was done under $\sim 1 \times 10^{-6}$ Torr vacuum in sealed quartz capsules at 700°C for 5 hours. As a further test of the effect of implantation damage, separate from any chemical effects, some specimens were implanted with xenon ions.

Oxidation tests were carried out in dry oxygen at 1 atm. total pressure. A Cahn 2000 electrobalance was used for kinetics measurements at 1000°C and 1100°C. After the desired oxidation time, the specimen was cooled to room temperature in approximately 30 min. During this time the amount of oxide spalled from the specimen could be recorded. This spallation behavior was used as an indication of the relative adhesion of the oxide scales.

Characterization of the oxide scales usually involved X-ray diffraction (XRD) for phase identification, analytical scanning electron microscope (SEM) and optical microscope for structure and composition analyses. Some oxides were also studied using a secondary ion mass spectrometer (SIMS).

3. RESULTS

3.1 Kinetics and Spallation Behavior

The oxidation behavior at 1000°C of various implanted specimens with the unimplanted alloy and the Y- and Al- containing alloys are presented in Figure 1. The spallation of oxide scales grown at 1000°C and at 1100°C after cooling to room temperature is summarized in Table 1. The implantation of Xe is seen to slightly increase the oxidation rate and noticeably increased spallation. The Al-implantation, which did not show any beneficial effect on the growth rate of the oxide also increased spallation, with higher degree of spallation being associated with the higher implantation dosage. However, this excess spallation behavior caused by the Al-implants could be eliminated if the as-implanted specimen had been thermally annealed prior to the oxidation test. The Ni-25Cr-1Al alloy also oxidized without a significant reduction in rate, but showed excellent

spallation resistance in contrast to the Al-implanted specimens.

With Y-implantation, the oxidation rate is reduced progressively with increasing implantation dosage, showing a beneficial effect on oxide growth rate similar to that produced by alloying addition of the yttrium when the implantation dosage reached a nominal 5×10^{16} ions/cm². The same amount of Hf-implant is also seen to greatly reduce the oxidation rate as the Y-implant. When such dosage of Y or Hf is implanted into a thin oxide layer of approx. 1 μ m thick, the subsequent oxidation rate is reduced to the same degree as if the ions were implanted into the alloy directly. Depending on the implantation dosage, Y-implantation improved the spallation resistance of the alloy to varying degrees. The only implant condition which showed a compatible improvement in scale adhesion as with the Ni-25Cr-0.2Y alloy is the one implanted with the highest dosage in the alloy surface, not in a pre-existing oxide layer. With Hf-implantation, the oxide scale adhered as well as the Y-implanted or the Y-alloyed, but again, only when the Hf ions were implanted directly in the alloy surface and not in the preformed oxide layer.

At 1100°C, both the high dose Y-implanted and the Y-alloyed specimens showed noticeably reduced growth rate and good scale adhesion. The Al-implanted specimen showed no difference in behavior as the untreated Ni-25Cr. The scale formed on the Ni-25Cr-1Al alloy however, became much poorer in resisting spallation than when it was formed at 1000°C.

3.2 Scale Morphology and Composition

At 1000°C the untreated Ni-25Cr alloy oxidized to a single layer of Cr₂O₃. At the scale/gas interface was a discontinuous layer of NiO which began to develop after 5-6 hours of oxidation in the form of nodules. With time, the NiO reacted with Cr₂O₃ to form the spinel. At 1100°C, the outer layer of Ni-rich oxides were continuous and were thicker than that found at 1000°C. Specimens implanted with Al or Xe developed oxide scales similar to that of the unimplanted. With Al alloying addition, the external scale developed at both 1000°C and 1100°C was Cr₂O₃ only. The aluminum in the alloy oxidized ahead of the Cr₂O₃ scale as rod-shaped Al₂O₃ internal oxides. As a consequence of the Al₂O₃ internal oxide formation, numerous Cr₂O₃ internal oxides developed giv-

ing rise to a peg-like structure at the scale/alloy interface as seen in Figure 2.

Observation of the spalled areas using SEM indicated that more than half of the spallation on the nonadherent scales were through the scale/alloy interface. Interfacial voids and cavities where there was no scale/metal contact were numerous. The only exception from the above morphology is the one found on the Ni-25Cr-1Al alloy oxidized at 1100°C. Although there was an appreciable amount of spallation, almost none of the spalled areas were through the interface, but was through the oxide scale.

Of all the Y- and Hf-implanted specimens, the only ones which showed significant improvement on scale adhesion were those implanted with the highest dosage in an untreated alloy. The scale morphology of these specimen were very similar to one another and drastically different from the nonadherent scales. Figure 3 compares the typical structure of the adherent and the nonadherent scales. Both of these scales shown here are Cr_2O_3 with approximately equal thickness. The adherent scale is seen to have developed a much tortuous scale/alloy interface with large single grains ($\sim 0.5\text{-}1\text{ }\mu\text{m}$) penetrating into the underlying alloy. The nonadherent scale on the other hand seems to have fine equaxed grains throughout the scale with a rather flat scale/alloy interface. Underside of an adherent and a nonadherent scale is shown in Figure 4. The adherent scale shows a very uniform structure consisted of single grains of Cr_2O_3 ranging from $0.5\text{-}2\text{ }\mu\text{m}$ in cross section. The underside of the nonadherent scale, which is also a single layer of Cr_2O_3 , shows nodular morphology with uniformly sized grains no larger than $0.5\text{ }\mu\text{m}$.

Figure 5 shows the morphology of surface oxides near an 5×10^{16} Hf-implanted/unimplanted interface before and after a "peel-off" experiment. The experiment was done the following way: After 50h oxidation at 1000°C, the specimens, which had both an implanted and an unimplanted region, was mounted in an epoxy resin. After the resin had hardened at room temperature, the specimen was thinned into two halves and then immersed in a liquid nitrogen bath, which allowed the specimen to be pulled away from the epoxy. As seen from Fig. 5b, most of the oxide on the unimplanted area were peeled away at the scale/alloy interface, but very little scale was lost on the implanted side. On localized areas where there was peel-off from the implanted area, the frac-

ture is not seen at the scale/alloy interface, but is seen within the scale. Room temperature peel-off test using adhesive tapes can also remove some oxides from the unimplanted region, but the degree is much smaller compared with that shown in Fig. 5b.

The distribution of Y in all of the Y-implanted specimens was studied using depth profiling by SIMS. The analyses started at the scale/gas interface and followed the changes in composition as the surface was sputtered away using an Ar ion source at a rate of approximately $0.1 \mu\text{m}/\text{min}$. Figure 5 shows the depth profiles of Y, Ni and Cr through the scale formed on the $5 \times 10^{16} \text{ Y}/\text{cm}^2$ -implanted specimen. Due to a strong continuous surface contribution during the sputtering process, all the elements with a high surface concentration developed extensive tailing. Nevertheless, it is still obvious that most, if not all, of the implanted Y concentrated at the scale/gas interface. In contrast, the specimen with $5 \times 10^{16} \text{ Y}$ -implanted in a preformed oxide showed a peak Y concentration near the scale/alloy interface; the specimens implanted with lower dosages of Y showed a flat Y profile across the scale with only a slight enrichment at the outer surface.

4. DISCUSSION

The damaging effect associated with ion-implantation is manifested by an excess degree of spallation of the subsequently formed oxide scale. This enhanced spallation can be eliminated by a short thermal annealing treatment. The reactive element effect, in terms of reducing growth rate and improving scale adhesion, can outweigh any radiation effect as demonstrated by the Y and Hf implants.

Neither Al alloying addition nor Al-implantation showed much effect in reducing the oxidation rate. Nevertheless, the alloy containing 1 wt% Al produced much more adherent scales at 1000°C . This excellent adhesion is believed to be provided by the very irregular peg-like morphology at the scale/alloy interface which made the interface stronger, thus made the scale less accessible to spallation. As the oxidation temperature is raised to 1100°C , more growth stress and thermal stress are present and the scale began to spall during cooling. However, the peg-like interface was still strong and spallation was only observed through fractures within the scale. Since the

peg-like interface was promoted by the Al_2O_3 internal oxide formation, the Al-implanted specimens were unable to develop such a morphology, thus the scales formed were not at all adherent.

The tortuous interface formed on the 5×10^{16} Y- or Hf-implanted specimens was also very strong as shown by the "peel-off" test. However, unlike the Ni-25Cr-1Al, these scales did not spall after oxidation at 1100°C (Table 1). It is not likely that the strength of the two types of interfaces varied much, because occasionally, small areas of spallation on the implanted specimens could be found and the spalled oxide actually fractured at the scale/alloy interface. Therefore, besides a strengthened interface these implanted specimens must also have developed scales with less stress, and both factors contributed to their excellent spallation resistance.

Since the scales on the implanted specimens were formed at a much slower rate, it is possible that the reduced rate greatly reduced growth stresses. However, this is not likely because the scales formed on 1×10^{15} Y-implanted and 5×10^{16} Y-implanted (into preoxidized surface) grew at fast and slow rates respectively (Fig. 1), but both showed the same degree of spallation. From this study, the reduced stress seems to be associated with a modified growth process. From the structure of the adherent and the nonadherent scales and the distribution of implanted Y after oxidation, it was found that the adherent scales formed on the 5×10^{16} Y- and Hf-implanted specimens were the only ones grew with a change in growth direction. Whether this modification is by eliminating lateral oxide growth within the scale as suggested by Golightly *et al.* [4] is unknown and further study is needed.

The stronger interface promoted by the implantation of 5×10^{16} ions/cm² of Y or Hf could not be accounted for by the pegging mechanism, at least not the normal type of long, rod-shaped pegs extending deeply into the alloy. Nevertheless, the tortuous scale/alloy interface, which may have developed due to the altered growth mechanism of the scale, could be considered as a form of peg which can better key the scale to the alloy. Since the implanted reactive element is concentrated at the outer surface of the external oxide scale as indicated by this work and several others [5-7], it is difficult to envisage the implanted RE to act as vacancy sinks, to gather impurities which diffuse from the alloy to the scale/alloy interface, or to strengthen the interfacial bonds by

segregating there. Przybylski and Yurek [8] have suggested that the inward diffusion of the implanted species can be very rapid during the initial stage of oxidation, and a portion diffuses into the alloy which later becomes incorporated in the oxide scale. If the diffusivity of the implanted species were indeed rapid, it is still difficult to envisage the small amount of back-diffused reactive element to act according to the above models after the metal removal depth is more than 80 times the original implantation depth as in the case of these adherent scales after 100 hours of oxidation at 1000°C.

5. CONCLUSIONS

Ion-implantation of Y and Hf can reduce the oxidation rate and improve the adhesion of the oxide scale of Ni-25wt%Cr to the same degree as alloying additions once the implantation dosage has reached a critical value of $\sim 10^{16}$ ions/cm² (actual dosage). The better spallation resistance provided by the implanted species is believed to be provided by a) a reduction in growth stress due to a modified growth mechanism from predominantly cation outward transport to predominantly oxygen inward transport, and b) a stronger scale/alloy interface due also to the change in growth direction resulting in a structurally stronger interface. The strength of the interface may in part be related to its tortuous morphology which can be considered as a form of peg.

ACKNOWLEDGMENT

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TABLE 1: Summary of Oxidation Data

Specimen	1000°C, 50 hrs.		1100°C, 24 hrs.	
	Approx. k_p ($\text{mg}^2 \text{cm}^{-4} \text{sec}^{-1}$)	Spallation (mg/cm^2)	Approx. k_p ($\text{mg}^2 \text{cm}^{-4} \text{sec}^{-1}$)	Spallation (mg/cm^2)
Ni-25Cr	1.1×10^{-5}	0.38	1.3×10^{-4}	0.75
5×10^{16} Xe-imp.	1.0×10^{-5}	0.45		
Ni-25Cr-1Al	5.3×10^{-6}	0.03	2.9×10^{-5}	0.78
5×10^{16} Al-imp.	1.2×10^{-5}	0.36	5.4×10^{-5}	1.28
1×10^{17} Al-imp.	2.1×10^{-5}	0.41		
5×10^{16} Al-imp. after annealing	1.4×10^{-5}	0.24		
Ni-25Cr-0.2Y	9.1×10^{-7}	0.02	7.1×10^{-6}	0.11
1×10^{15} Y-imp.	1.2×10^{-5}	0.17		
5×10^{15} Y-imp.	9.0×10^{-6}	0.18		
1×10^{16} Y-imp.	6.3×10^{-6}	0.11		
5×10^{16} Y-imp.	1.2×10^{-6}	0.01	1.0×10^{-5}	0.15
5×10^{16} Y-imp. on oxide	1.3×10^{-6}	0.13		
5×10^{16} Hf-imp.	1.9×10^{-6}	0.04		
5×10^{16} Hf-imp. on oxide	1.2×10^{-6}	0.13		

FIGURE CAPTIONS

- Figure 1 - The weight gain behavior of Ni-25Cr, Ni-25Cr-0.2Y, Ni-25Cr-1Al and various ion-implanted Ni-25Cr specimens as a function of time at 1000°C.
- Figure 2 - Cross section of scales formed on Ni-25Cr-1Al after (a) 50 hours at 1000°C viewed with backscattered secondary electrons and (b) 24 hours at 1100°C and deep etched using Br₂/MeOH.
- Figure 3 - SEM micrographs of cross-sectioned scales after 50 hrs at 1000°C where the underlying alloy had been etched by Br₂/MeOH. (a) and (b) are scales formed with 5×10^{16} Y-implantation on untreated Ni-25Cr alloy surface and on preoxidized alloy surface respectively. (c) is a magnified view of a fractured section in (b).
- Figure 4 - Underside of the scale formed on (a) 5×10^{16} and (b) 5×10^{15} Y-implanted surfaces after 50 hours of isothermal oxidation at 1000°C.
- Figure 5 - SEM micrographs of interfacial areas between 5×10^{16} Hf-implanted and unimplanted regions (a) before and (b) after an oxide peel-off experiment. The oxidation condition is 1000°C for 50 hours and the peel-off experiment is described in the text.
- Figure 6 - SIMS depth profiles on the 5×10^{16} Y/cm²-implanted specimen after 50 hrs of oxidation at 1000°C. Sputtering rate is approximately 0.1 μm/min.

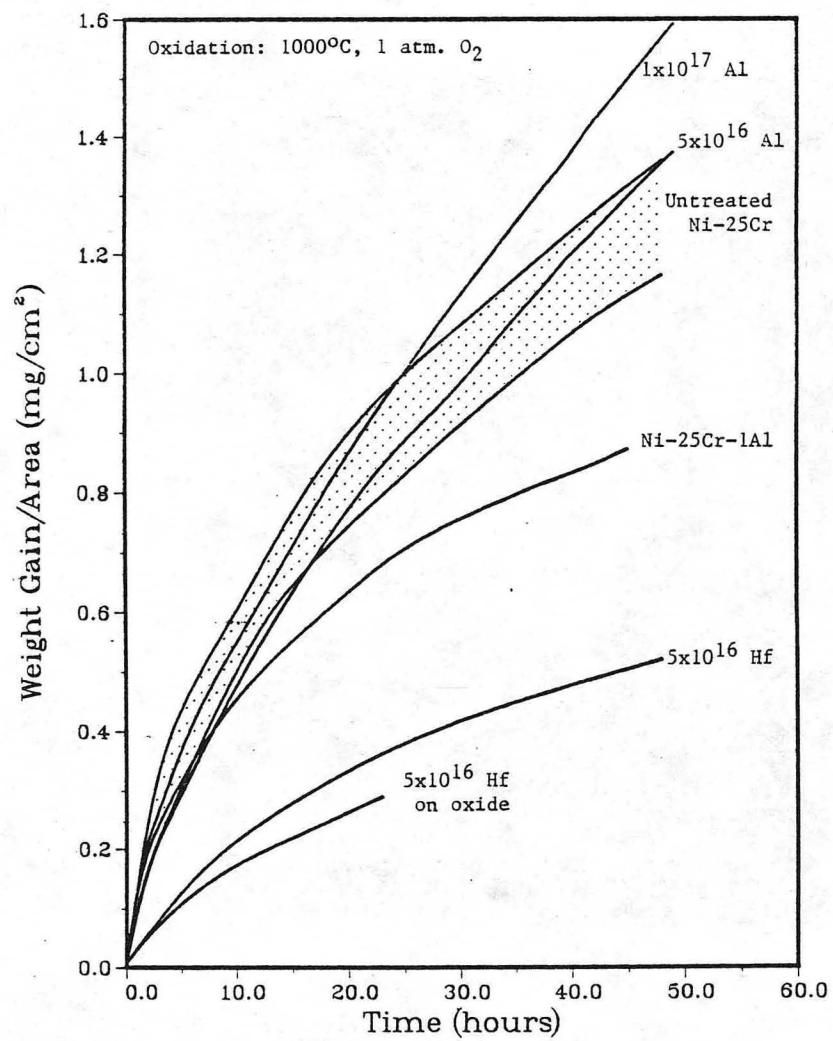
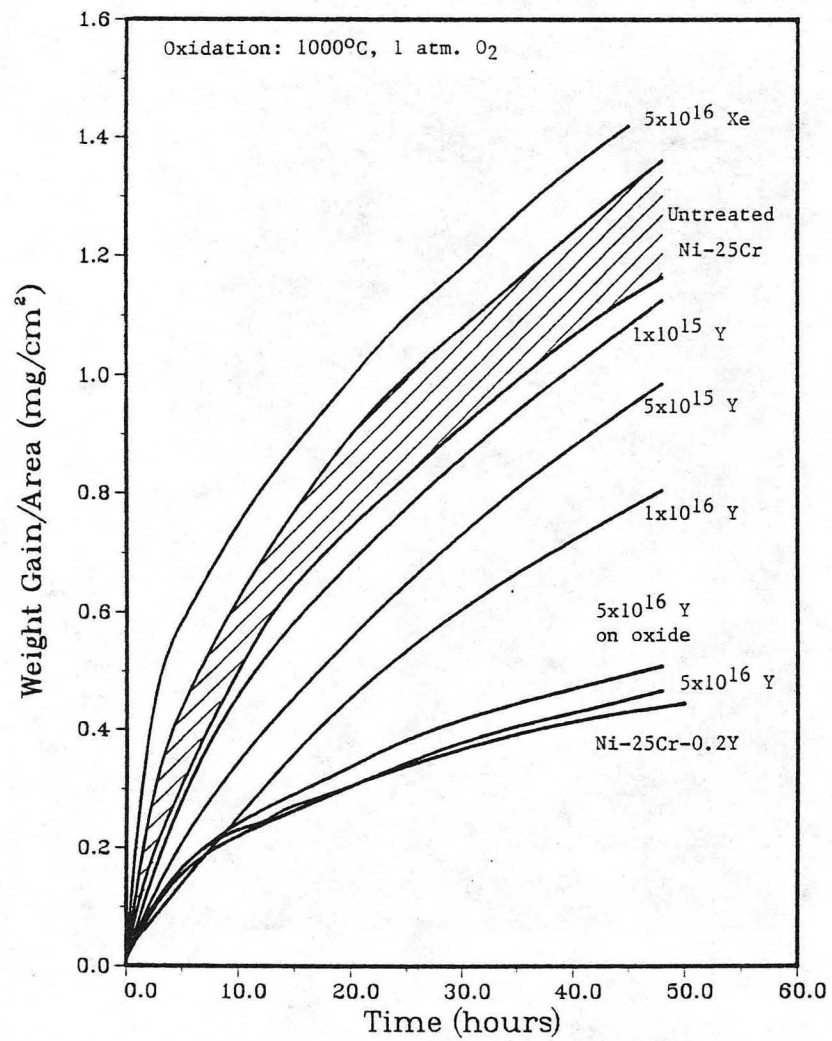
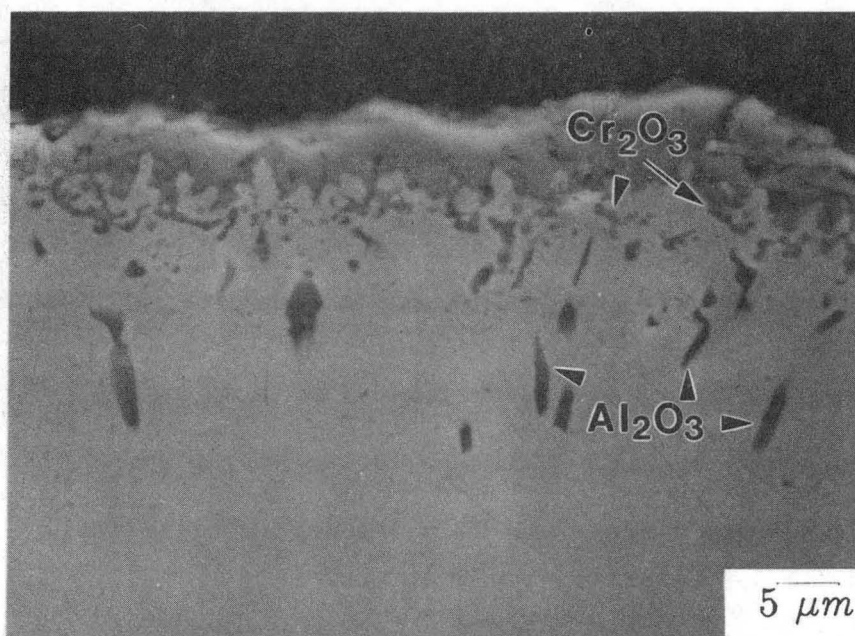
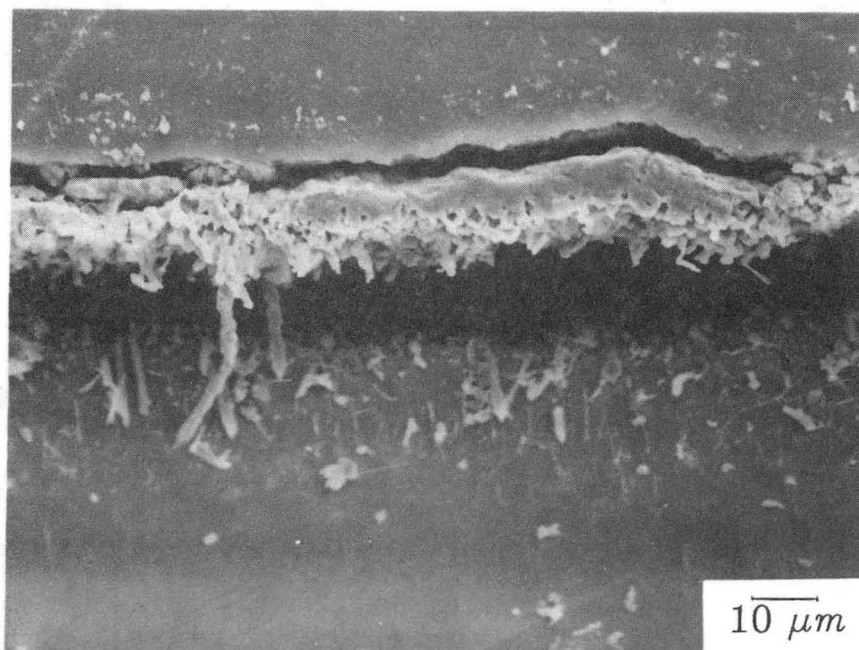


Figure 1



(a) Ni-25Cr-1Al, 1000°C, 50 hrs. BSE-SEM



(b) Ni-25Cr-1Al, 1100°C, 24 hrs. deep-etched

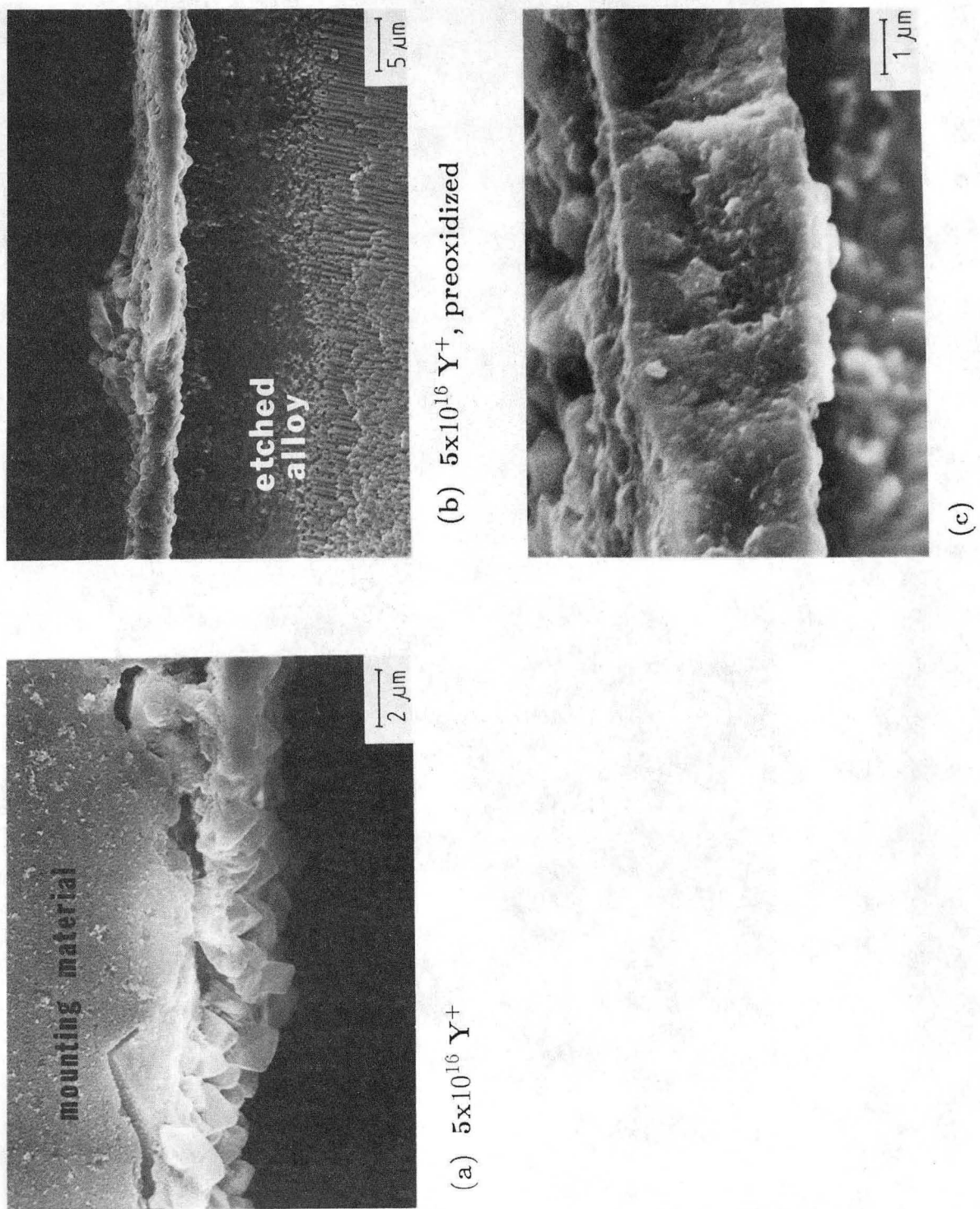
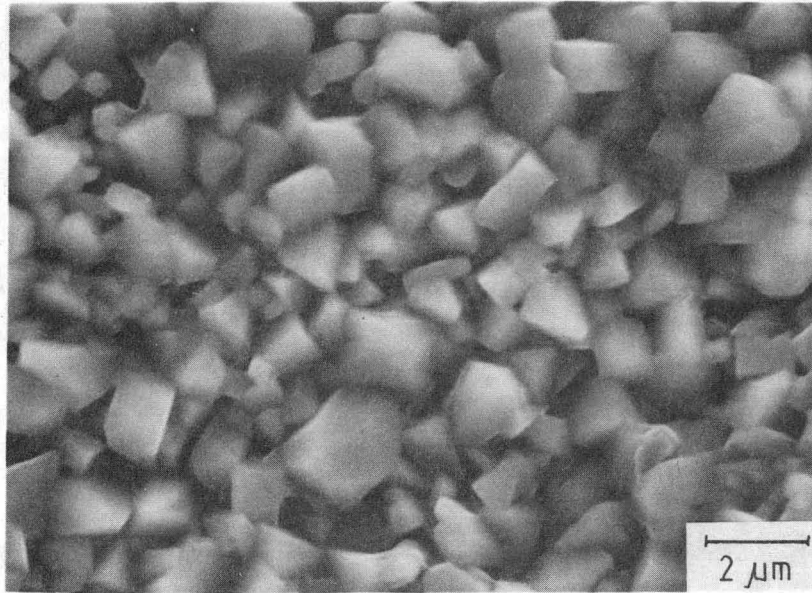
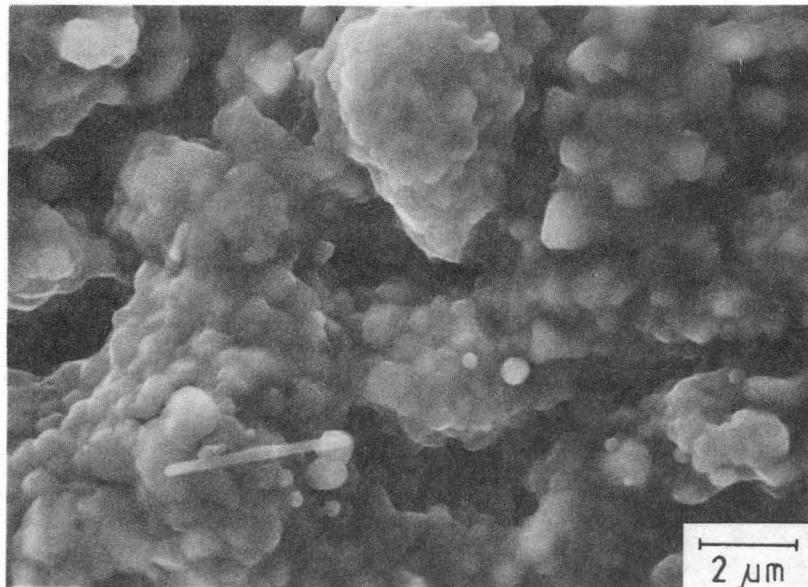


Figure 3

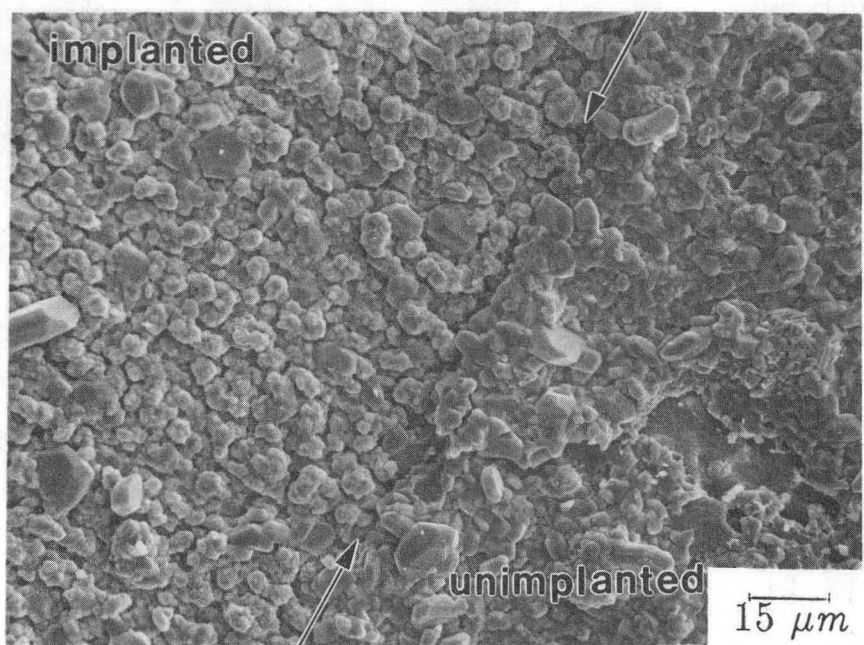
Underside of Scale



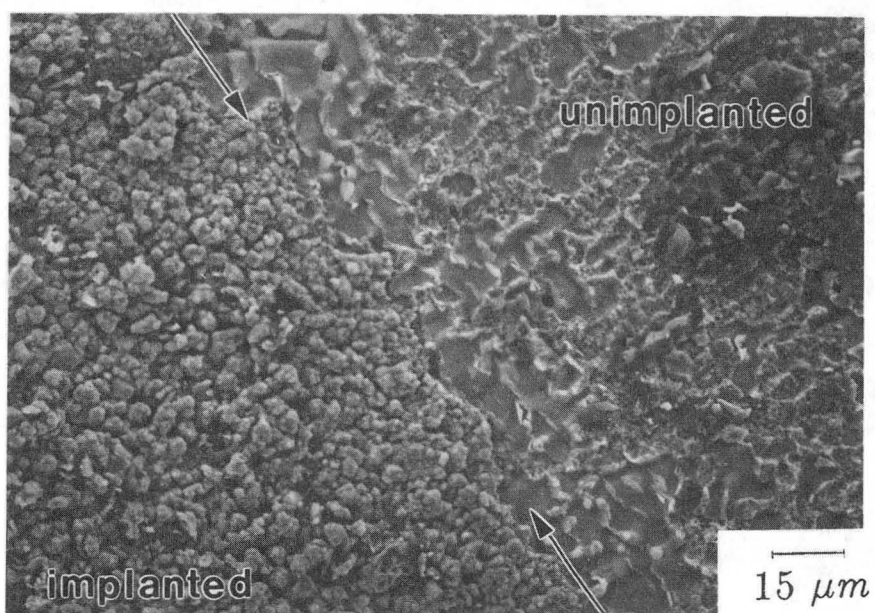
(a) 5×10^{16} Y-imp.



(b) 5×10^{15} Y-imp.



(a) Before LN_2 peel-off test



(b) After LN_2 peel-off test

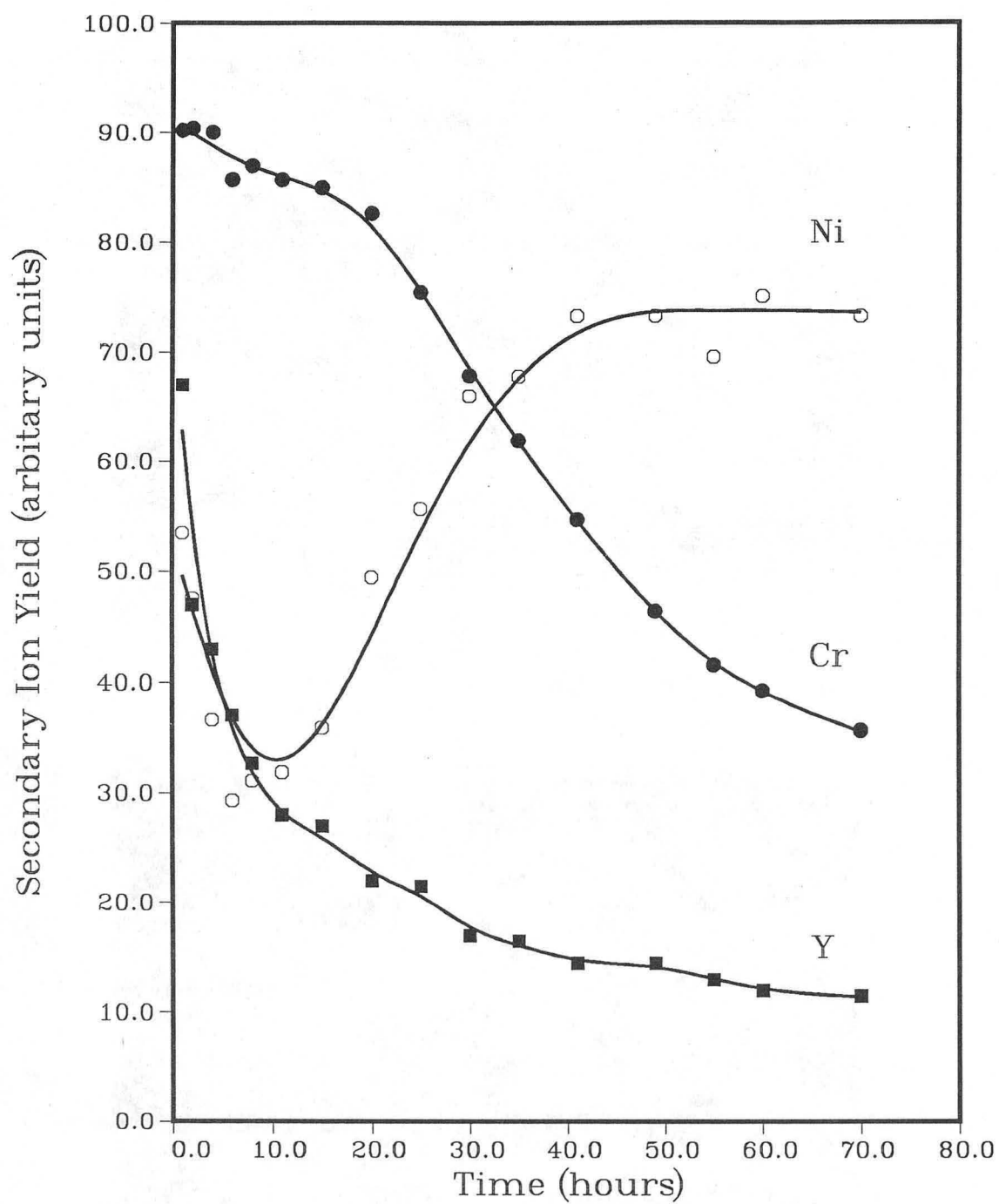


Figure 6

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