**Title**
INFLUENCE OF SMALL PT ADDITIONS ON Al2O3 SCALE ADHERENCE



**Author**
Allan, I.M.

**Publication Date**
1979-05-01

LBL-9180
Preprint

# Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

Submitted to Oxidation of Metals

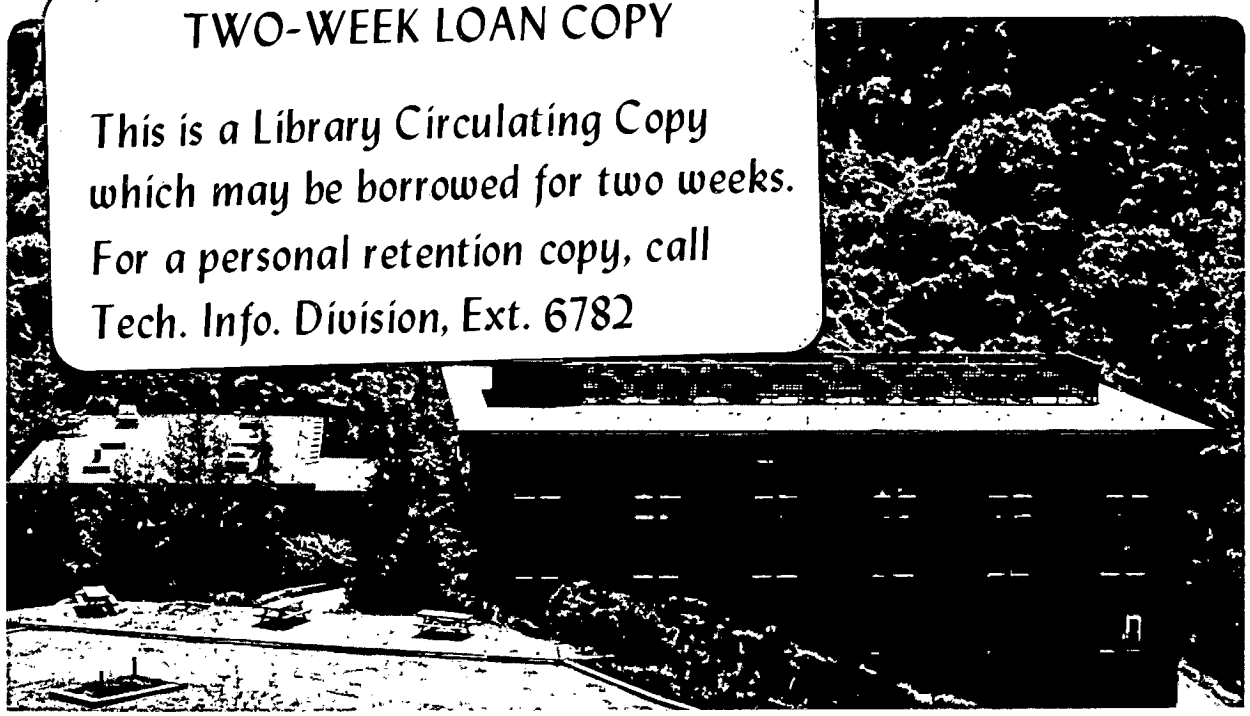
INFLUENCE OF SMALL PT ADDITIONS ON $Al_2O_3$ SCALE ADHERENCE

I. M. Allam, H. C. Akuezue, and D. P. Whittle



May 1979





Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

## DISCLAIMER

# INFLUENCE OF SMALL PT ADDITIONS ON $Al_2O_3$ SCALE ADHERENCE

I. M. Allam*, H. C. Akuezue*, and D. P. Whittle*

May, 1979

## ABSTRACT

The effects of small Pt additions (1 or 3 wt.%) on the oxidation behavior of Co-10 Cr-11 Al and a similar alloy containing Hf have been studied. An intermetallic phase was present in the alloy containing Hf and Pt but not in that containing Pt alone. The size and distribution of the intermetallic was comparable to that of similar alloys containing oxide dispersions produced by a controlled internal oxidation treatment. As a consequence it promoted the formation of inwardly growing $Al_2O_3$ pegs that helped key the surface scale to the substrate and improve the scale/metal adhesion in both isothermal and cyclic oxidation tests. The improvement in overall oxidation resistance relative to an addition-free alloy was considerable, and similar to that of the best oxide dispersion-containing alloys.

Key Words: CoCrAl; oxidation, oxide/scale adherence, platinum; rare-earth effects.

---

*Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Formerly Department of Metallurgy and Materials Science, University of Liverpool, Liverpool L693BX, England.

# INTRODUCTION

Adhesion between surface scale and alloy substrate is an essential requirement of a material possessing good overall oxidation resistance. Poor adhesion can lead to exfoliation of the oxide in response to thermal cycling, or mechanically applied stresses, resulting in enhanced oxidation rates. Marked improvements in scale/substrate adhesion, however, can be achieved via the "rare-earth effect" whereby addition of a small amount of a rare-earth element to a heat-resisting alloy produces significant increases in the alloys' resistance to cyclic oxidation conditions. This effect is no longer limited to rare-earth elements: additions of other active elements, or of fine distributions of stable oxides are equally, if not more so, efficient.

Recent work[1,2] has demonstrated that the major factor responsible for the improved scale adherence with $Al_2O_3$-forming alloys is the formation of protrusions of oxide growing into the alloy. These act to key the protective scale to the surface and are more effective when a uniform distribution of small oxide pegs can be achieved at the alloy/scale interface. This is difficult to control with metallic additions since essentially the active element oxidizes internally during high temperature exposure and these internally precipitated oxides form the nuclei around which the protective oxide forms the pegs. Clearly, the distribution of the internal oxides, and hence the subsequent pegs, depends on the exposure conditions and is thus not directly controllable.

Nevertheless, Hf, which is completely soluble up to at least 1.5 wt.% in most CoCrAl and NiCrAl systems, was better than Y which tends to segregate as a grain boundary intermetallic. Additions of finely distributed oxide phases offer a greater potentiality since the dispersion can be controlled independently of the subsequent exposure conditions. It has been shown that a pre-internal oxidation treatment is one, but not very practicable, way of producing a controlled dispersion.[2]

As a further consideration, it appears that the composition of the dispersion is not critical. Nitrides, for example, have been used in austenitic[3] and ferritic[4] stainless steels, although they are not as efficient as oxides. Other possibilities may exist and the following factors seem important:

(1) the dispersion must be very stable so that it does not dissociate or disolve in the matrix, and it is better if it does not oxidize;

(2) it is better also if the dispersoid does not contain the constituent that is going to form the protective scale; and

(3) it is possible to disperse the phase within the matrix in the right configuration.

Several reports have indicated that marked improvements in $Al_2O_3$ scale adherence are also achieved by the presence of Pt in the alloy[5] or from an external source[6] and from Rh.[7] This was partly attributed to a keying-on effect due to the irregularity of the oxide/alloy interface[5] or possibly a decrease in the tendency of the

$Al_2O_3$ to form a convoluted scale.[6] However, it seems possible that the formation of the intermetallic $PtAl_3$ may be involved, and that this might exist as a fine dispersion in the alloy which then acts in the same way as an oxide dispersion.

Thus, the present paper examines the feasability of obtaining similar improvements in scale/alloy adhesion using a dispersion of a stable intermetallic compound. $PtAl_3$ fulfills the first of the criteria mentioned above, although it is not entirely clear whether it will oxidize under these conditions. It does not fulfill the second criterion, but this may not be too important, since the formation of $PtAl_3$ with a 1 wt.% Pt addition should only reduce the effective Al content of the matrix by about 1 wt.%. However, Pt and Hf additions can be made together, and the intermetallic $HfPt_3$ used as the dispersoid. This is even more stable, satisfies the second criterion above, and if it does oxidize would produce a $HfO_2$ dispersion anyway. It remains to be seen whether or not the right distribution of the dispersoid can be achieved.

## EXPERIMENTAL

As in earlier studies[1,2] the principal alloy studied was Co-10Cr - 11Al (wt.%), which forms an external scale of $\alpha$-$Al_2O_3$ over the temperature range studied, although breakdown to a greater or lesser extent of this oxide can result in the formation of other oxidation products. Additions of 1 Pt, 1 Hf-3Pt or 0.3Hf-0.9Pt (all wt.%) were made to this base alloy. Alloy and sample preparation have been described earlier.[1]

Oxidation experiments were of two types: (a) isothermal exposure, and (b) repeated thermal cycles of 20h duration each. Details of these along with techniques of sample examination have been given.[1] As earlier, the detailed morphology of the alloy/scale interface was deemed to be important and this was studied by stripping the scale and examining its underside and, when possible, the exposed surface of the alloy. Scales were stripped either mechanically by quenching in liquid nitrogen, or with particularly adherent scales, the substrate was dissolved away using a 10% bromine in methanol solution.

## ALLOY MICROSTRUCTURE

Figure 1 shows typical cross sections of the as-cast Co-10Cr-11Al alloys containing 0.3 Hf-0.9Pt and 1Hf-3Pt. The microstructures are clearly very similar and consist principally of a dark, dendritic, $\beta$-CoAl phase in a lighter, $\alpha$-Co matrix. There is also a third, very dark precipitate phase which appears to be confined to the $\alpha$-Co matrix only. There is a higher concentration of the dark precipitates in the alloy containing higher Pt and Hf contents, and in addition the particles are larger and more elongated.

EPMA of the precipitate phase and the matrix immediately adjacent to the precipitate was carried out for both alloys in a number of locations and qualitatively the analyses were identical. Fig. 2 shows typical energy dispersive spectra. There is a marked Pt peak in the precipitate phase and not in the adjacent matrix; a similar partitioning of Hf to the precipitates is also noted, although it is not as pronounced. No such precipitate phase was detected in the Co-10Cr-11Al-1Pt alloy.

## ISOTHERMAL OXIDATION KINETICS

Figure 3 shows the effects of Pt and Pt+Hf on the oxidation behavior of the Co-10Cr-11Al alloy under isothermal conditions at 1100°C. The addition of 1% Pt results in a slight decrease in the isothermal oxidation rate. Results for Co-10Cr-11Al and Co-10Cr-11Al-0.3Hf are included for comparision.[1] For the ternary alloy, the slope of a log (wt. gain) vs. log (time) plot, measured over the period 10 to 100 h to avoid the initial transient stages of oxidation, is 0.5 while this is 0.4 for the alloy containing 1 Pt (Fig. 3b). For the Hf-containing alloys the situation was rather different: the Co-10Cr-11Al-0.3Hf had a slope of 0.28 while for the same alloy containing 0.9 Pt the slope was 0.18. In addition, Fig. 3A shows that the initial stages of oxidation were terminated more rapidly with the 0.3Hf-0.9Pt-containing alloy in comparison to the 0.3Hf alloy, and that with both these Hf-containing alloys the transient stage was shorter than the Hf-free alloys. As indicated in the earlier paper,[1] it is difficult to define precisely the end of the transient stage, but typically it lasts for 1/2-1 h. Table I, therefore, compares the weight gains of the four alloys after this period (1 h) and after 120 h exposure. Also included are the data for the alloy showing the lowest overall weight gain under these conditions in the previous study:[2] this was Co-10Cr-11Al-0.3Hf that had been internally oxidized for 300 h at 1200°C.

## THERMAL CYCLING

Figure 4 shows the results of cyclic oxidation tests on the Pt and Pt+Hf-containing alloys: these are 20 h cycles. The thermal cycling resistance of the base alloy is only marginally improved by the addition of 1 Pt, but the improvement becomes very significant with an 0.3 Hf+0.9 Pt addition, being slightly better than the Hf addition alone. The alloy containing 1Hf+3Pt is slightly worse.

## DISCUSSION OF SCALE MORPHOLOGIES

The $Al_2O_3$ scale which formed on the alloy Co-10Cr-11Al-1Pt after 265 h oxidation at 1200°C was not adherent and spalled from the alloy on cooling. Typical features are shown in Fig. 5. The oxide is multi-layered in many locations, particularly at the corner of the sample, and the outer layer of oxide at the gas/scale interface was heavily wrinkled. Similar features were observed with the ternary Co-Cr-Al alloy of the same composition oxidized under similar conditions, as reported earlier.[1] The formation of convolutions in the outer scale layer always seems to be accompanied by scale breakaway and the formation of new oxide below. Figure 6 shows this in some detail.

Surface examination of the alloy Co-10Cr-11Al-0.3Hf-0.9Pt after oxidation at 1200°C, Figure 6, indicated that the scale was tightly adherent to the substrate and spalled during cooling only from very small discrete areas. The major difference between this alloy and a Pt-free alloy but containing Hf[1] was that with the Pt-free alloy, the substrate surface appeared to be more heavily convoluted.

Figure 7 shows the underside of the $Al_2O_3$ scale after the alloy substrate has been dissolved away: this is the Co-10Cr-11Al-1Hf-3Pt alloy, oxidized isothermally for 200 h at 1100°C. This regular distribution of oxide protrusions compares well with those obtained in previous studies.[2] The protrusions do not penetrate so deeply and are not as tortuous in shape as those formed in the case of a Co-10Cr-11Al-0.3Hf alloy, but compare well with those formed when this latter alloy had been given a pre-internal oxidation treatment prior to exposure. This regular distribution of oxide protrusions is the most desirable one in determining oxide/scale adherence. EPMA indicates that the pegs consist primarily of $Al_2O_3$, encapsulating the dispersed phase. Presumably they grow by some form of short circuit diffusion of oxygen along the incoherent interface between the matrix and the dispersoid: as a consequence the composition of the dispersed phase is not critical.

Table II compares the average spacings between the $Al_2O_3$ pegs and those of the dispersion phase in the alloy. These are quite similar for each alloy. and typically have spacings of 3-4 μm along the interface. This is similar to that observed in the internally oxidized Co-CrAlHf alloys studied previously.[2] The length of the peg protruding into the alloy is also important. Typically these are in the range 5-10 μm with the alloy containing 1Hf-3Pt and slightly less than this for the 0.3Hf-0.9Pt alloy. Long protrusions tend to promote scale cracking above the pegs. Figure 8 shows a cross section of the Pt-Hf-containing alloy after 10x20 h cycles at 1100°C. The highly convoluted alloy/scale interface is clearly apparent.

In addition to the Pt-containing alloys a Pt-coated alloy was also investigated. The coating consisted of a 2 μm deposit followed by diffusion annealing for 30 min. in argon at 800°C. There was no real improvement in the scale/alloy adherence. In fact, the Pt-coating may even have had a detrimental effect as indicated in Fig. 9, where loss of contact has occurred between the $Al_2O_3$ and the substrate in some locations. Scanning electron microscopy of the surface of the scale formed on the coated alloy revealed that the Pt deposit collected into globules, which remained on top of the oxide surface.

## CONCLUSIONS

Intermetallic dispersions of Hf and Pt are formed in Co-10Cr-11Al alloys containing 0.3Hf-0.9Pt and 1Hf-3Pt additions. No intermetallics are observed in the same alloy containing Hf and Pt alone. The intermetallic dispersion is comparable in size and distribution to the $HfO_2$ dispersions produced by pre-internally oxidizing Co-10Cr-11Al-Hf alloys and seems to provide an alternative way of producing a dispersed phase in the alloys. The inwardly growing $Al_2O_3$ pegs which develop on subsequent exposure to oxidizing environments seem equally effective in keying the $Al_2O_3$ surface scale to the substrate and thereby improving the oxidation resistance of this type of alloy under both isothermal and particularly thermal cycling conditions.

## ACKNOWLEDGMENTS

This work was originally supported by the University of Liverpool, but completed under the support of the Division of Materials Sciences, Office of Basic Research, U. S. Department of Energy, Contract NO. W-7405-ENG-48.

## REFERENCES

1. I. M. Allam, D. P. Whittle and J. Stringer: Oxid. Met. 12, 35 (1978).

2. I. M. Allam, D. P. Whittle and J. Stringer: Oxid. Met. 13 381 (1979).

3. O. T. Goncel, D. P. Whittle and J. Stringer: Corros. Sci., to be published.

4. O. T. Goncel, J. Stringer and D. P. Whittle, Corros. Sci. 18, 701 (1978).

5. E. J. Felten and F. S. Pettit, Oxid. Met. 10, 189 (1976).

6. J. G. Fountain, F. A. Golightly, F. H. Stott and G. C. Wood, Oxid. Met. 10, 341 (1976).

7. E. J. Felten, Oxid. Met. 10, 23 (1976).

Table I. Weight Gain Data at 1100°C: Isothermal Exposure

| Alloy | Weight Gain, ($mg/cm^2$) | | Rate Index |
|---|---|---|---|
| | 1.h | 100 h | 2-100 h |
| Co-10Cr-11Al | 0.15 | 0.9 | 0.5 |
| Co-10Cr-11Al-1Pt | 0.16 | 0.72 | 0.4 |
| Co-10Cr-11Al-0.3Hf | 0.2 | 0.53 | 0.28 |
| Co-10Cr-11Al-0.3Hf-0.9Pt | 0.1 | 0.2 | 0.18 |
| Co-10Cr-11Al-0.3Hf (internally oxidized) | 0.09 | 0.18 | - |

Table II. Average Spacings of Dispersed Phase and Oxide Pegs

| Alloy | Peg Spacing,μm | Dispersoid Spacing,μm |
|---|---|---|
| Co-10Cr-11Al-0.3Hf-0.9Pt | 6.5 | 1-5 |
| Co-10Cr-11Al-1Hf-3Pt | 3.5 | 1-4 |
| Co-10Cr-11Al-0.3Hf | 9.1 | - |

## FIGURE CAPTIONS

Figure 1. Cross sections of the as-cast alloys, (a) Co-10Cr-11Al-1Hf-3Pt and (b) Co-10Cr-11Al-0.3Hf-0.9Pt.

Figure 2. Energy dispersive analysis of the precipitates in Co-10Cr-11Al-0.3Hf-0.9Pt (a) precipitate and (b) adjacent matrix.

Figure 3. Weight gain/time data for the isothermal oxidation of Co-10Cr-11Al alloys containing Pt and/or Hf at 1100°C.

Figure 4. Weight gain/time data for the cyclic oxidation of Co-10Cr-11Al alloys containing Pt and/or Hf at 1100°C.

Figure 5. Scanning electron micrographs of the surface scale on Co-10Cr-11Al-1Pt oxidized for 265 h at 1200°C.

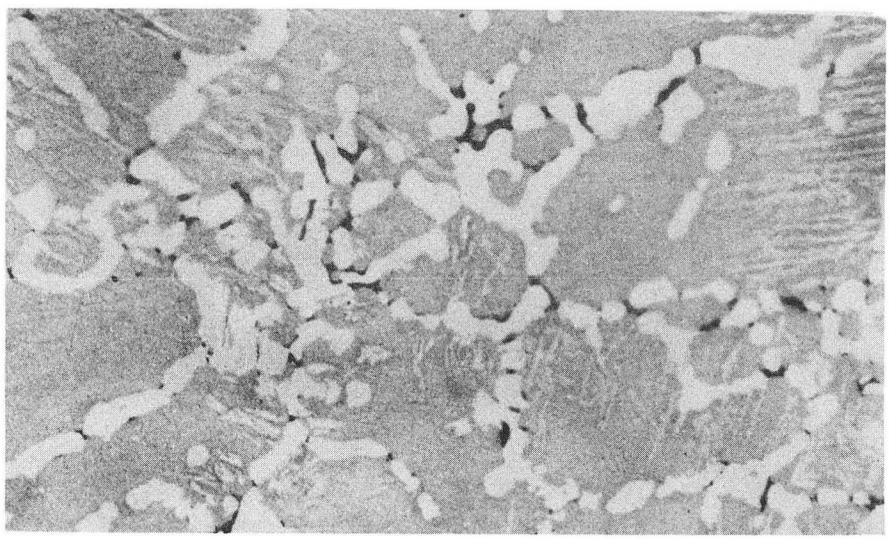
Figure 6. Scanning electron micrographs of the surface scale on Co-10Cr-11Al-0.3Hf-0.9Pt oxidized for 265 h at 1200°C.

Figure 7. Underside morphology of the $Al_2O_3$ formed on Co-10Cr-11Al-1Hf-3Pt after isothermal oxidation of 1100°C for 200 h: alloy substrate has been dissolved away.

Figure 8. Cross section of the scale formed on Co-10Cr--11Al-1Hf-3Pt oxidized at 1100°C for 10 x 20 h cycles.

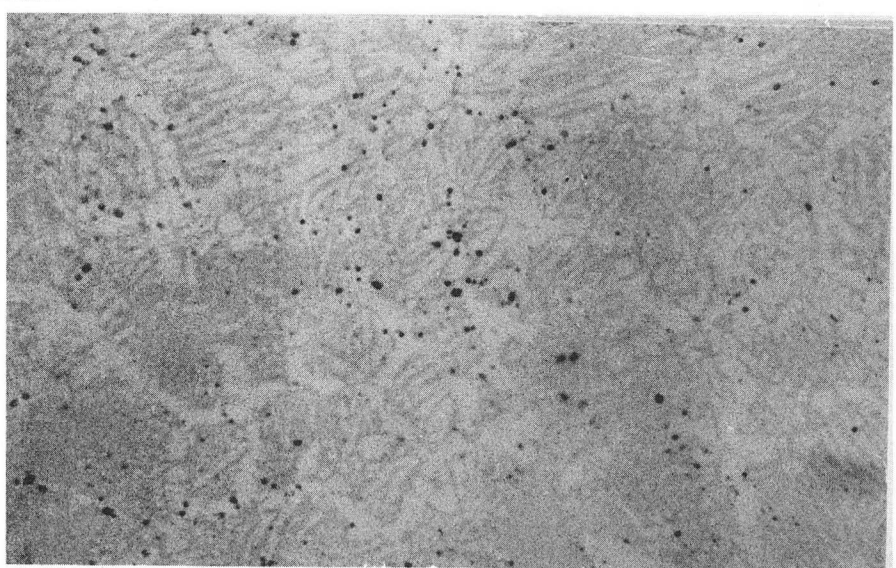
Figure 9. Cross section of the scale formed on Co-10Cr-11Al-1Hf coated with 2 μm Pt, annealed in A for 30 min at 800°C. and then oxidized for 200 h at 1200°C.

(a)



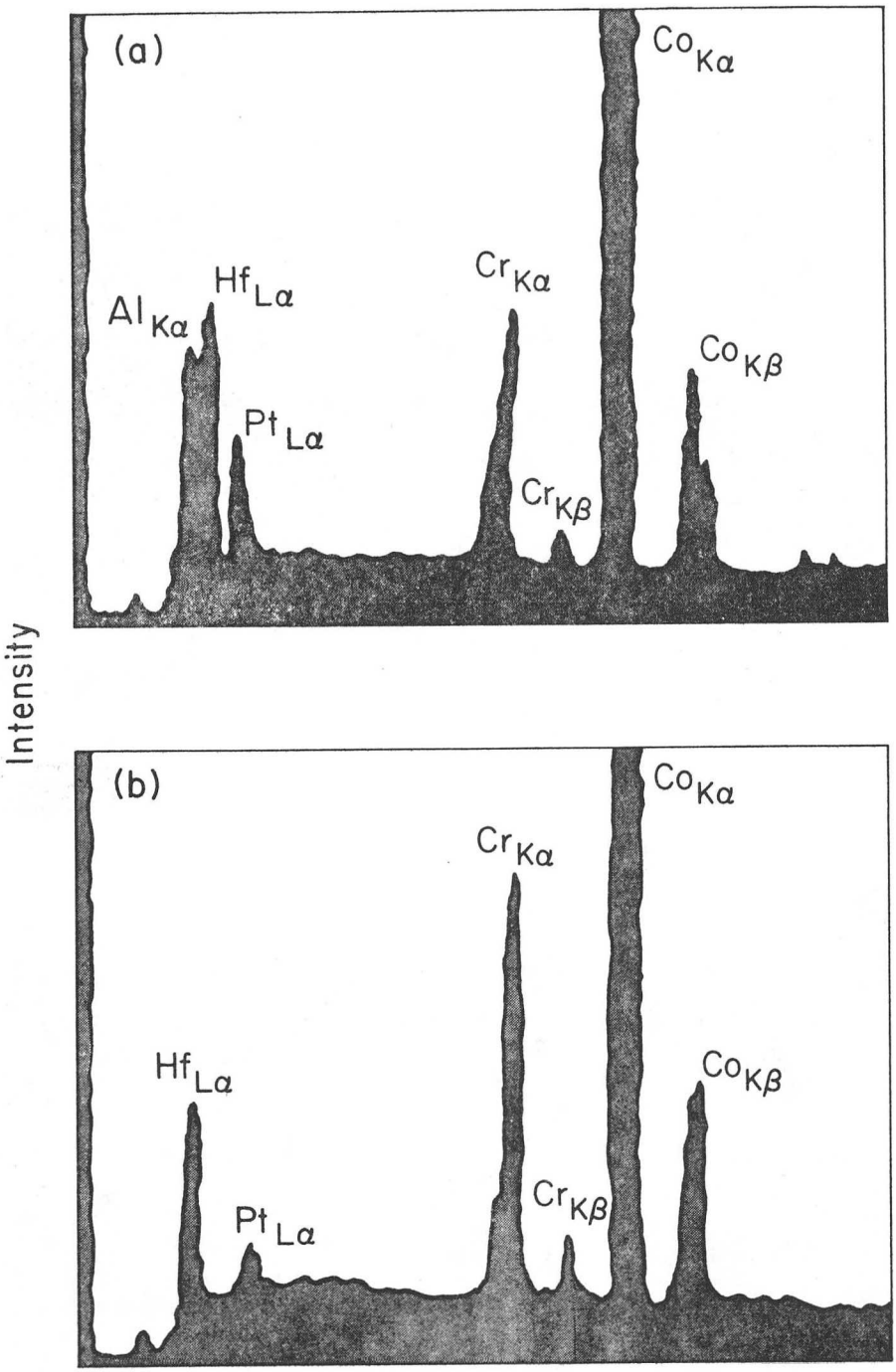
26μ

(b)

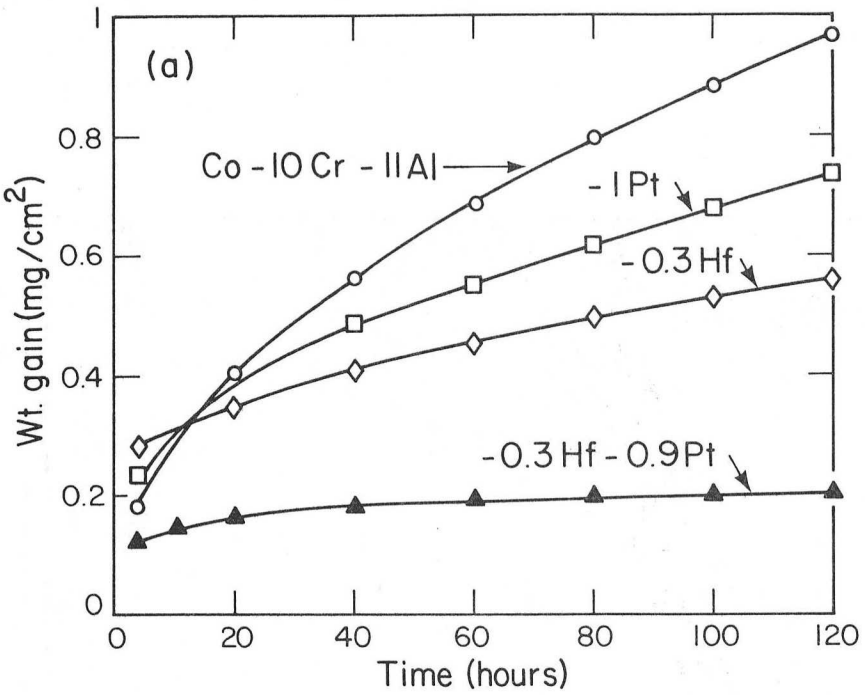


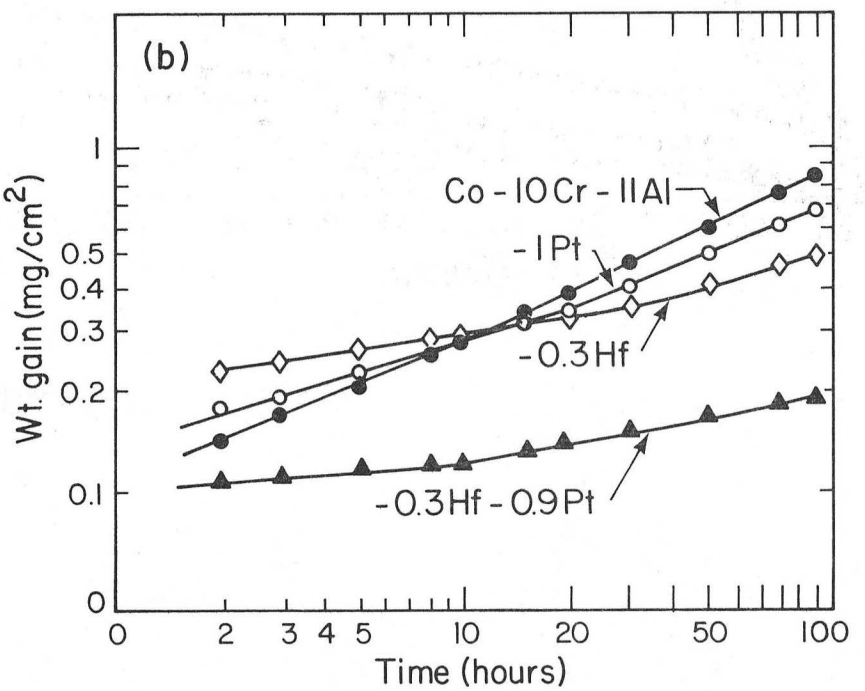
26μ

XBB 798-10391

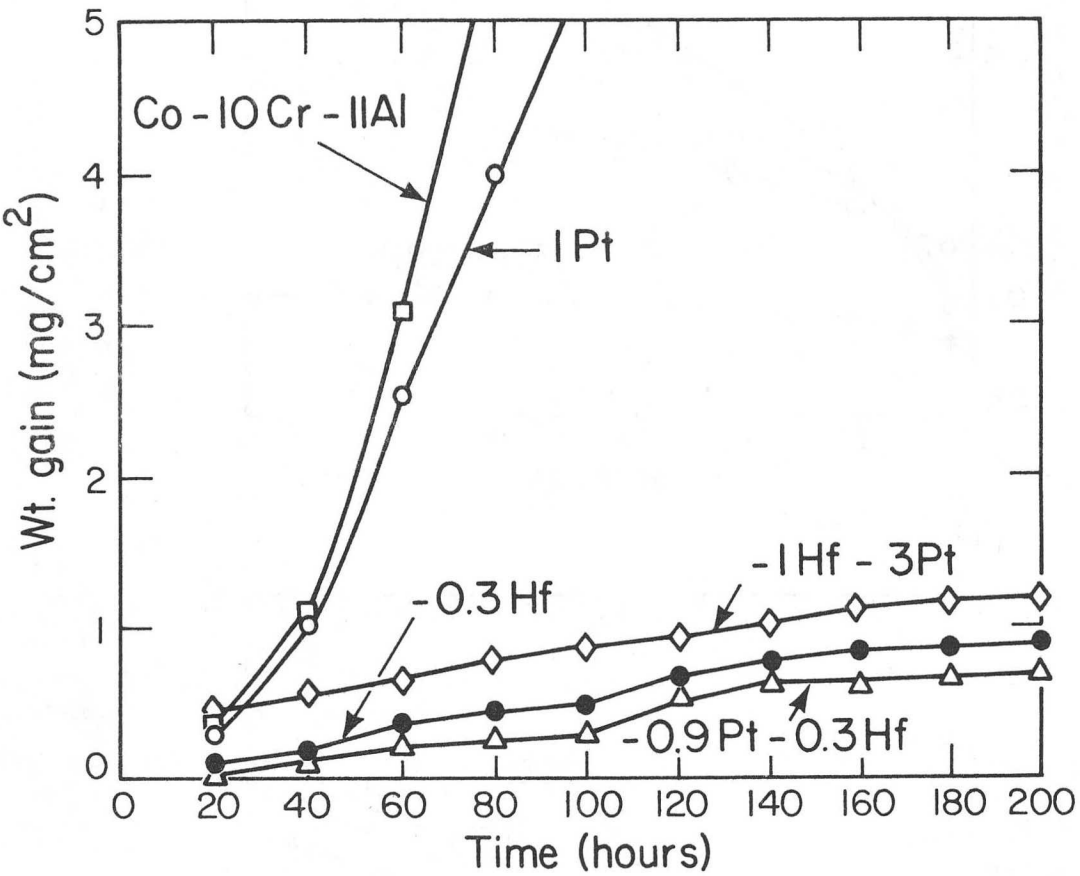

(a)
Co Kα
Al Kα
Hf Lα
Pt Lα
Cr Kα
Cr Kβ
Co Kβ
Intensity
(b)
Co Kα
Cr Kα
Hf Lα
Pt Lα
Cr Kβ
Co Kβ

XBL 798-2393

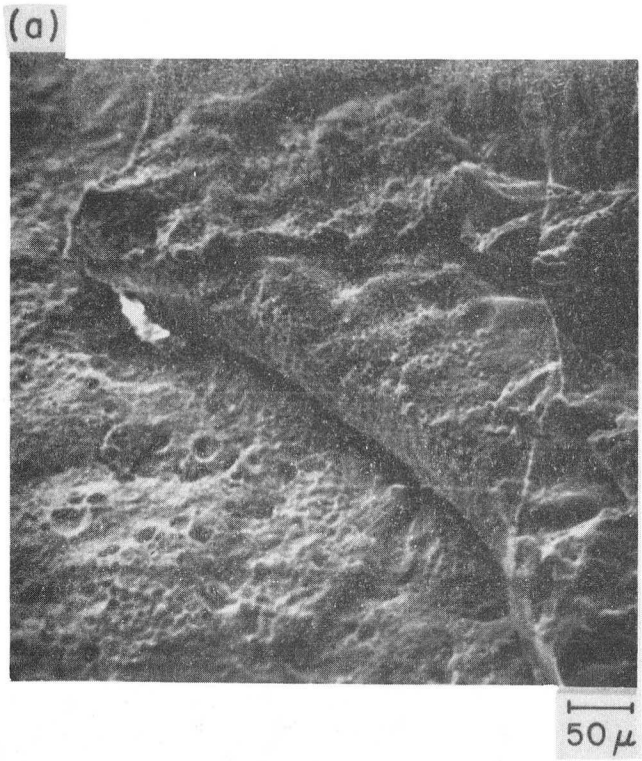

(a)
Co - 10 Cr - 11 Al
- 1 Pt
- 0.3 Hf
- 0.3 Hf - 0.9 Pt
Wt. gain (mg/cm²)
Time (hours)
0
0.2
0.4
0.6
0.8
1
0
20
40
60
80
100
120


(b)
Co - 10 Cr - 11 Al
- 1 Pt
- 0.3 Hf
- 0.3 Hf - 0.9 Pt
Wt. gain (mg/cm²)
Time (hours)
0
0.1
0.2
0.3
0.4
0.5
1
0
2
3
4
5
10
20
50
100

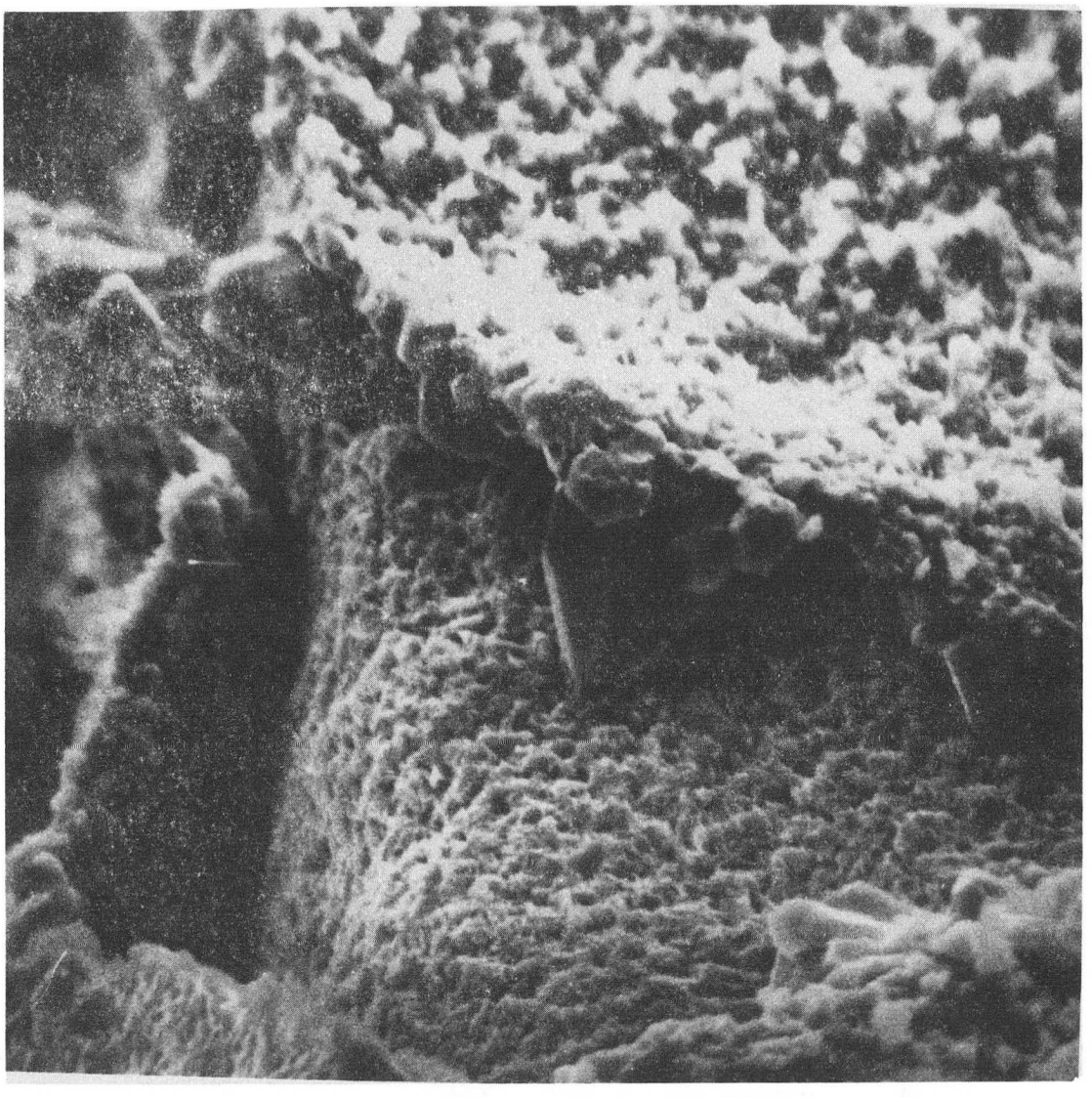
XBL 798-2392


Co - 10 Cr - 11Al
1 Pt
- 0.3 Hf
- 1 Hf - 3Pt
- 0.9 Pt - 0.3 Hf
Wt. gain (mg/cm²)
Time (hours)
0
1
2
3
4
5
0
20
40
60
80
100
120
140
160
180
200

XBL 798-2391

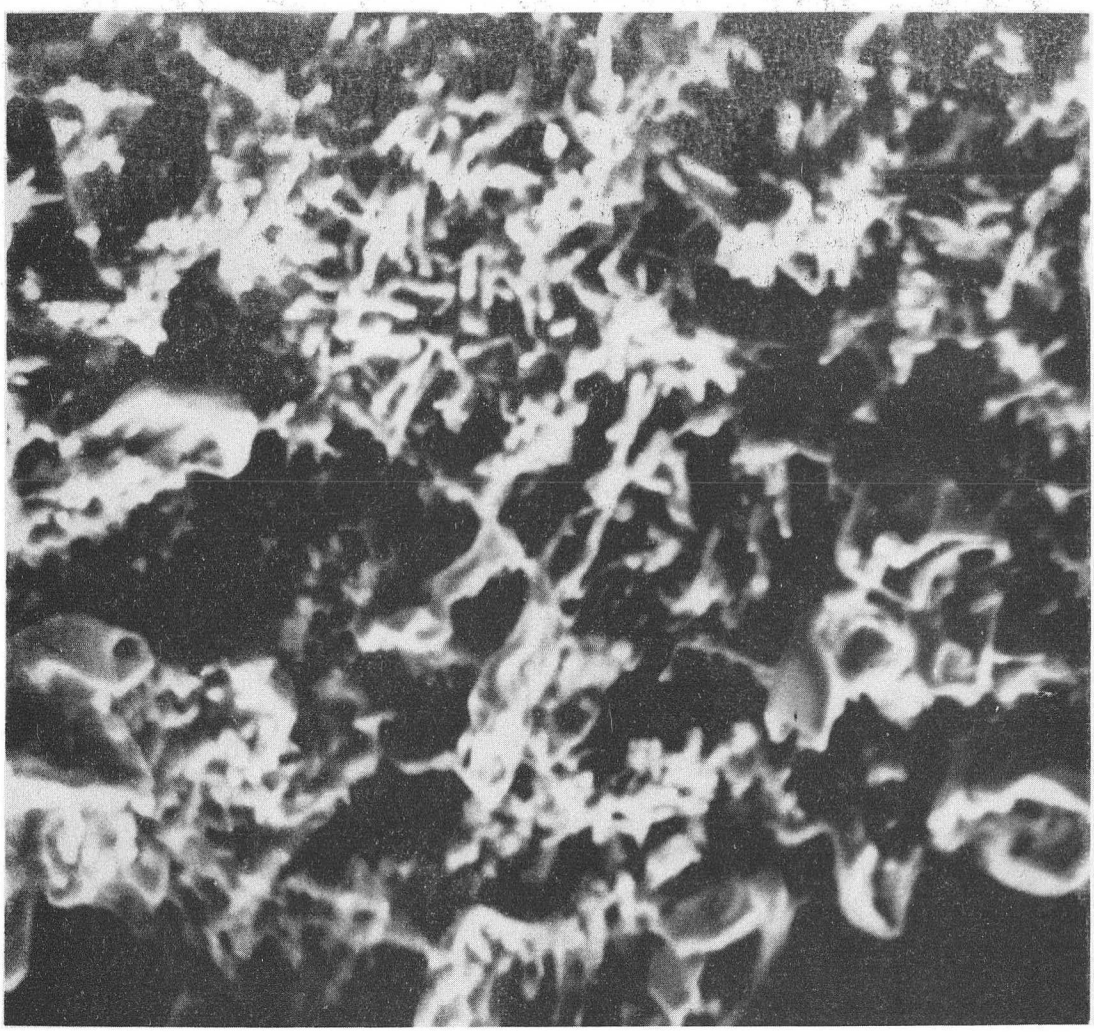



XBB 798-10390



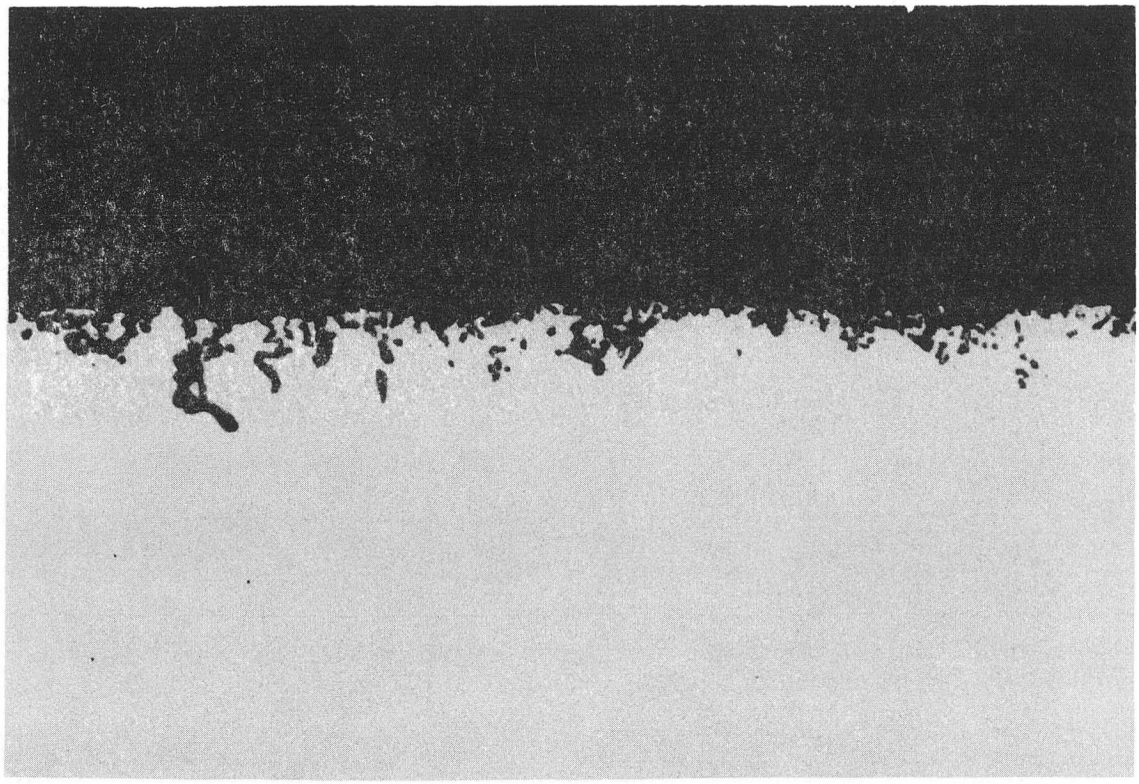
10 μ

XBB 798-10389



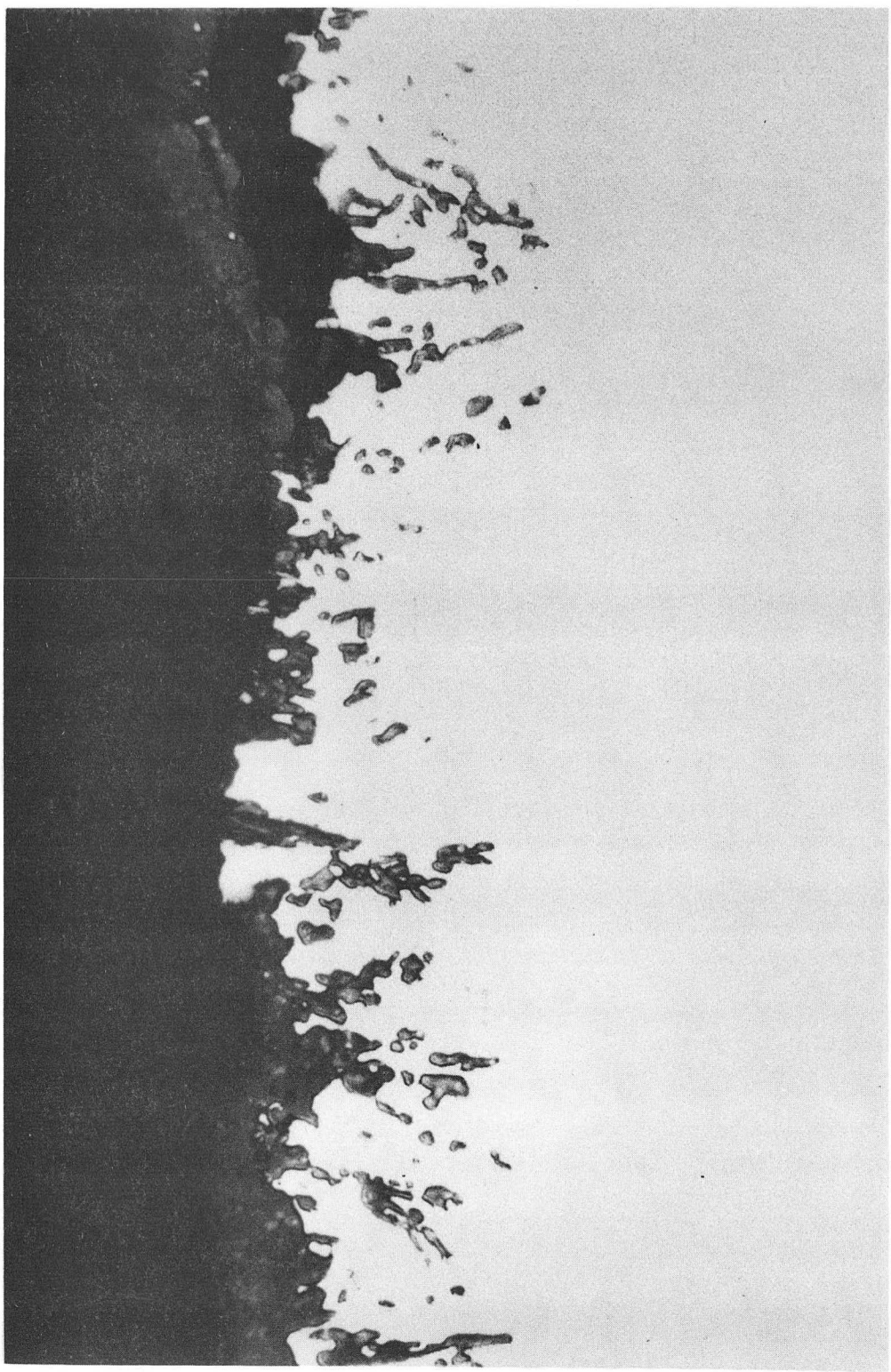
3 μ

XBB 798-10392



26 μ

XBB 798-10394



13 μ

XBB 798-10393

*TECHNICAL INFORMATION DEPARTMENT*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*