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Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY, CA

Materials & Molecular Research Division

Presented at the 81st Annual Meeting of the
American Ceramic Society, Cincinnati, Ohio,
April 28 - May 2, 1979

GAS/SOLID REACTIONS: HYDROGEN REDUCTION OF COBALT FERRITES AND Al^{3+} CONTAINING COBALT FERRITES

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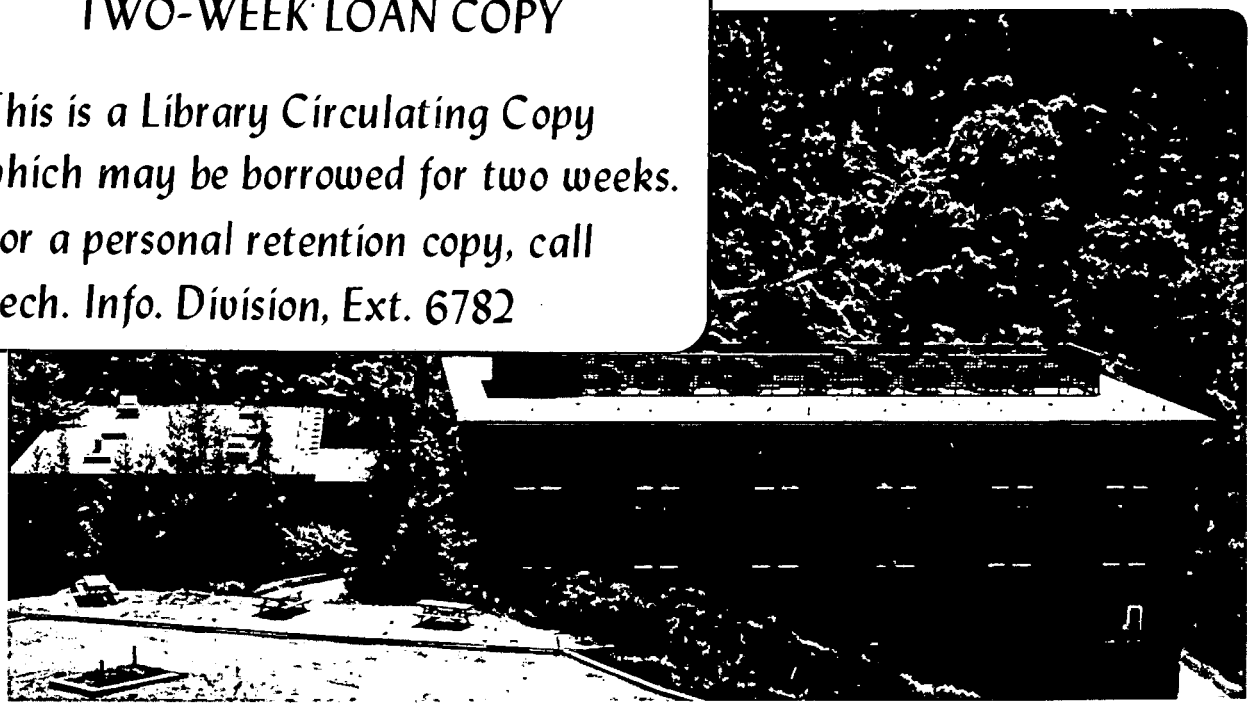

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Abstract

The various mechanisms in the gas/solid reaction of hydrogen with Al^{3+} containing cobalt ferrites was studied between 500 and 800°C at 1 atmosphere and at 400 Torr of hydrogen. The compositions were $Co\ Fe_2\ O_4$. In all cases did a porous metal scale form, approximately in a topochemical way. A reaction rate maximum was found for the first two compositions. The reaction kinetics indicate that at the lower temperatures studied interface reactions are rate limiting. With increasing temperature the gas transport through the porous product layer becomes a more important reaction step. The reaction maxima that were observed were associated with the formation of a wüstite type subscale, and not with changes in the scale micromorphology.

Gas/Solid Reactions:

Hydrogen Reduction of Cobalt Ferrites and Al^{3+} Containing Cobalt Ferrites

In this paper we discuss the hydrogen reduction of cobalt ferrites and aluminum doped cobalt ferrites, containing up to 5 cation percent of Al^{3+} in solid solution, between 500 and 1000°C. The purpose of the study was to examine the various mechanisms that contributed to the control of the reduction kinetics, and to establish how hard-to-reduce solid solution ions such as aluminum, would effect the reduction behavior. Cobalt ferrites were chosen for this study since they are relatively easy to reduce by hydrogen. Also, lightly doped cobalt ferrite, $CoAl_{0.02}Fe_{1.98}O_4$, and heavily doped cobalt ferrite, $CoAl_{0.1}Fe_{1.9}O_4$, were used. When these oxides are exposed to hydrogen in the temperature range indicated, a porous reaction layer will develop in a topochemical fashion from the surface. To determine which reaction mechanisms were dominant or contributed to the reaction kinetics, the reduction was studied by means of thermogravimetrical analysis and by various microscopy techniques.

In our experiments, cubes of dense, polycrystalline cobalt ferrites with a size of approximately .5 x .5 x .5 centimeters were used. These cubes were subjected to a stream of flowing hydrogen at temperatures between 500 and 1000°C. The rate of scale formation was determined by means of optical microscopy on samples that had been reduced for varying amounts of times. Additionally, thermogravimetrical work was carried out on similar specimens. For the reduction of the bulk specimens the total pressure was 1 atmosphere while for the thermogravimetrical work the total pressure was about 400 Torr. The rates at which reduction reactions proceed has been studied and modeled by many workers. One model that applies reasonably well to our observations is the shrinking core model[1]. Here the reduction process is modeled with three successive steps. The first step is a mass transport resistance in

which gases are transported through the stagnant film on the outside surface of the specimen. The second is gas transport through the porous reaction layer. The third is an interfacial step in which a variety of gas/solid reactions can occur. This treatment is useful so long as the reaction product takes the form of a fairly well defined layer with an identifiable interface. There are, however, conditions under which the interface is not well defined. This is, e.g. the case for a distributed interface[2]. The shrinking core model can still be useful in this case, however, even if the interface is to some degree distributed: this is when the distributed interface has a characteristic width that is significantly smaller than the sample dimension and remains constant throughout the duration of the experiment.

Under certain gas flow conditions hydrogen starvation may occur in the bulk of the gas stream. Such a condition is not characteristic of the sample itself and is therefore not of interest here. Experimentally one assures that the gas flow is sufficient to avoid such massive gas starvation. A graph of the reduction rate versus the gas flow rate is shown in Figure 1. At low flow rates the reduction rate increases approximately linearly with increasing gas flow rate, after which a plateau is reached. In our experiments we worked at flow rates of approximately 2,000 cm^3 per minute. This brings the experiment well outside of the range of massive gas starvation, but of course does not eliminate the possibility of a surface mass transfer layer contributing to the overall reaction resistance. It should be noted that if this mass transfer layer were a dominant resistance to the proceeding of the reduction, the kinetics would be linear with time for samples of any geometry. This permits the distinction of the external interface resistance from that of the matrix/product layer interface.

The results of the layer thickness measurements for cobalt ferrite and lightly doped cobalt ferrite are shown in Figure 2. Note that a so-called Hedvall effect[3] is observed in the reduction of these oxides. For the undoped ferrite a maximum in the reaction rate is observed around 650°C. For the lightly doped cobalt ferrite this maximum seems to be displaced to around 750°C. These effects could be followed more clearly by thermogravimetrical analysis. This is shown for pure cobalt ferrite in Figure 3, and in Figure 4 for lightly doped cobalt ferrite. For the pure cobalt ferrite, Figure 3, it is evident that the magnitude of the Hedvall effect depends on the reduction time. For the longer reduction times the Hedvall effect appears more pronounced. The temperature above which the decrease in the reaction rate occurs seems to be unaffected by the reduction time, however. This kind of effect has been explored by Porter and De Jonghe in more detail by thermogravimetrical analysis[4]. The calculated layer thickness as a function of time and temperature for lightly doped cobalt ferrites is shown in Figure 4. Here the reaction rate increases monotonically with temperature until it reaches a maximum at 750°C. We believe that the Hedvall effect is in both cases associated with the possibility of wüstite formation between the porous metal layer and the unreduced spinel. An alternative explanation might be that sintering effects in the porous product layer are responsible for the decrease in the reaction rate. To eliminate this possibility the scale structure had to be examined in more detail. Therefore, samples were cut perpendicular to the reaction zone and polished, leaving a fairly damaged surface layer so that the pore structure could not really be examined in the scanning electronmicroscope. This problem could be eliminated by R. F. sputter - etching the surface of the polished samples for approximately two to three hours. Sufficient material was then removed to permit

a clear study of the pore structures of the reaction product layer. While significant differences could be observed in the pore structure of the scales, depending on the temperature at which the reduction had been carried out, it was not possible to correlate these changes with the changes in the reduction rate. For the undoped cobalt ferrite the most drastic changes in the scale structure occur between 600°C and 650°C which is below the maximum reaction rate temperature, as shown in Figure 5. The same is true for the lightly doped cobalt ferrite. Again the most drastic changes in the pore structure of the product layer were observed between 600°C and 650°C, as shown in Figure 6. Optical micrographs of the interface region at 700°C for the undoped material are shown in Figure 7 and for lightly doped material at 800°C in Figure 8. Note that here a wüstite layer is visible ahead of the porous metal. The wüstite layer is identifiable by etching with hydrochloric acid. We associate this wüstite with the Hedvall effect. It is interesting to compare the scale structures of the lightly doped and the undoped cobalt ferrite with the scale structure of the heavily doped cobalt ferrite. In heavily doped cobalt ferrite no coarsening could be observed in the scale up to temperatures as high as 800°C. The scale consists at all times of a dual pore network in which the largest pores are at the original ferrite grain boundaries, and the relic grains are very finely porous. Presumably the presence of alumina in sufficient concentration leads to the formation of dispersed unreduced aluminum oxides or iron aluminate spinels that prevent further coarsening of the scale after its formation. In the heavily doped cobalt ferrite a reaction maximum was also observed. However, anomously high reaction rates at lower temperatures were associated with profuse cracking of the specimen during reduction. Such cracking decreased with increasing temperatures leading to an apparent

Hedvall effect. Comparison of the reduction data collected at 750 Torr, Figure 2, and 400 Torr, Figures 3 and 4, shows that the maximum reaction rate for the undoped and the lightly doped cobalt ferrite is not very sensitive to the total hydrogen pressure. For the lightly doped and for the undoped cobalt ferrites no shift in Hedvall temperature could be observed between the 400 and 750 Torr data. There is general qualitative agreement in the kinetic trends obtained from direct measurements of layer growth and from conversion of weight loss data. There are, however, differences to the magnitude of the reaction rate decrease above the Hedvall temperatures at different hydrogen pressures. One striking difference is that at one atmosphere of hydrogen pressure the 700°C rate does not fall below the 600°C one. At 400 Torr of hydrogen, however, both the 700°C and the 750°C rates fall below the 600°C rate.

In this paper we have associated the Hedvall temperature with the appearance of a intermediate wüstite phase at approximately 650°C for the undoped cobalt ferrite and at approximately 750°C for the doped cobalt ferrite. Phase diagrams of iron oxide indicate that the first temperature at which wüstite can be stable is 570°C[5]. The presence of cobalt in wüstite is expected to stabilize the wüstite to an even lower temperature. We believe that the absence of wüstite below the Hedvall temperatures (which are well above the equilibrium wüstite stability temperature) is of a kinetic nature. The argument considers that the hydrogen/water ratio adsorbed on the specimen surface is kinetically determined while the reaction rate is determined by the hydrogen partial pressure and may not permit the formation of a continuous wüstite layer. This point has been examined in greater detail by Porter and De Jonghe[4] and will be discussed in a later paper.

Acknowledgements

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Figure 1: Reduction rate of $CoFe_2O_4$ versus gas flow rate. For the experiments flow rates of approximately 2,000 cm^3/min were used (∿1.3 cm sec^{-1} at the specimen). XBL 791 8164

Figure 2: Scale thickness versus time for $CoFe_2O_4$ and for $CoAl_{0.02}O_4$ $Fe_{1.98}O_4$ reduced at 1 atm of hydrogen. XBL 791 8165

Figure 3: Thermogravimetrical data of reduction of $CoFe_2O_4$ reduced in 400 Torr of flowing hydrogen. The weight loss data have been recalculated to show metal scale thickness versus temperature after 5, 10 and 13.5 minutes of reduction. The Hedvall effect at 650°C is more pronounced for longer reductions. XBL 791 8161

Figure 4: Thermogravimetrical data of reduction of $CoAl_{0.02}$ $Fe_{1.98}O_4$ reduced in 400 Torr of flowing hydrogen. The Hedvall temperature has been shifted to about 750°C by the Al^{3+}. XBL 791 8162

Figure 5: Scale morphology of $CoFe_2O_4$ after polishing and RF sputter-etching; observed in the SEM. The most notable microstructural changes occur between 600°C and 650°C. XBB 794 5001

Figure 6: Scale morphology of $CoAl_{0.02}Fe_{1.98}O_4$ as a function of temperature. The most notable microstructural changes occur again below 650°C. XBB 794 5000

Figure 7: Optical micrograph of scale/matrix interface region $CoFe_2O_4$, reduced at 700°C. XBB 794-4998

Figure 8: Optical micrograph of scale/matrix interface region. $CoAl_{0.02}Fe_{1.98}O_4$, reduced at 800°C. XBB 791 1040

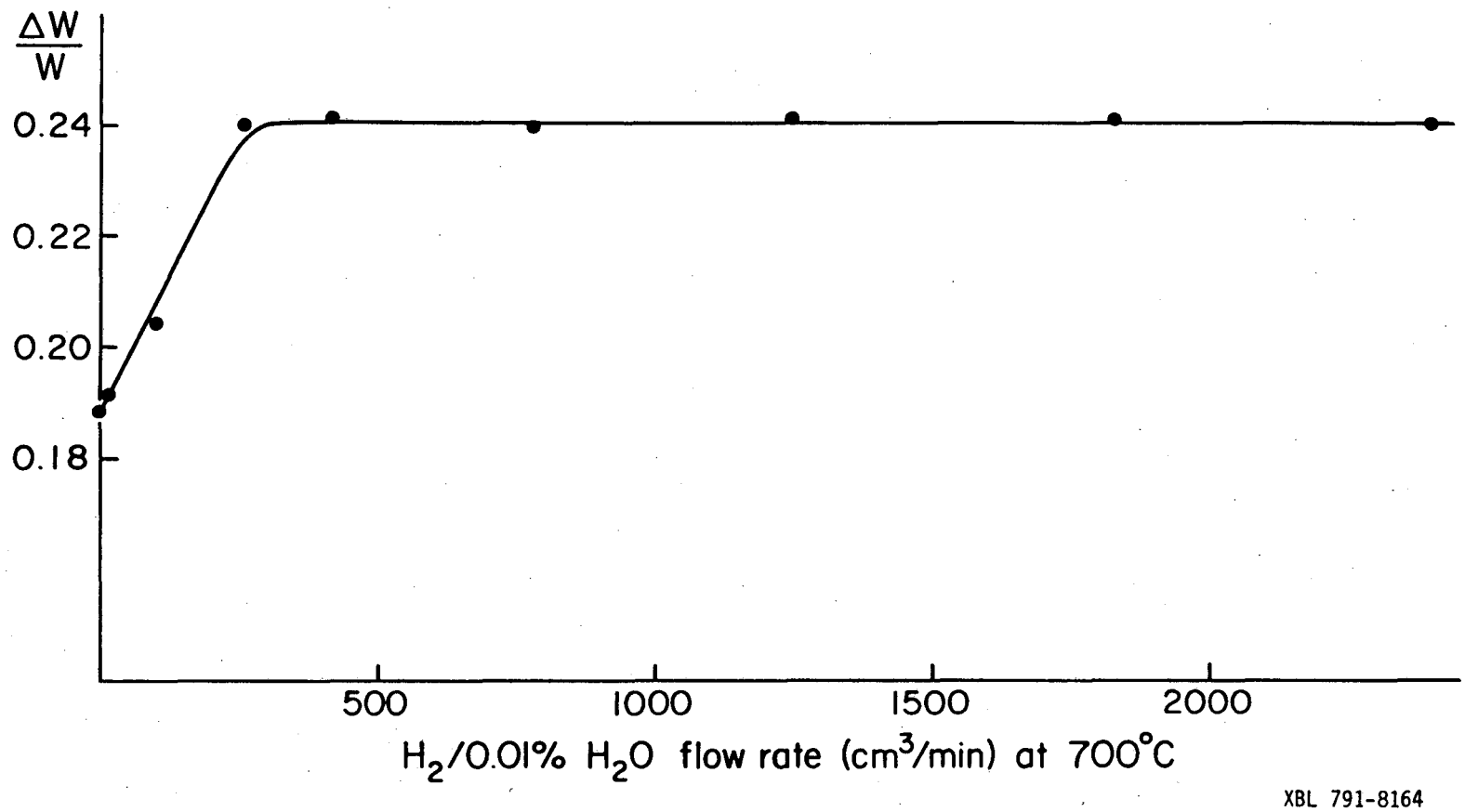
ΔW/W
0.24
0.22
0.20
0.18
500
1000
1500
2000
H2/0.01% H2O flow rate (cm3/min) at 700°C
XBL 791-8164

Figure 1.

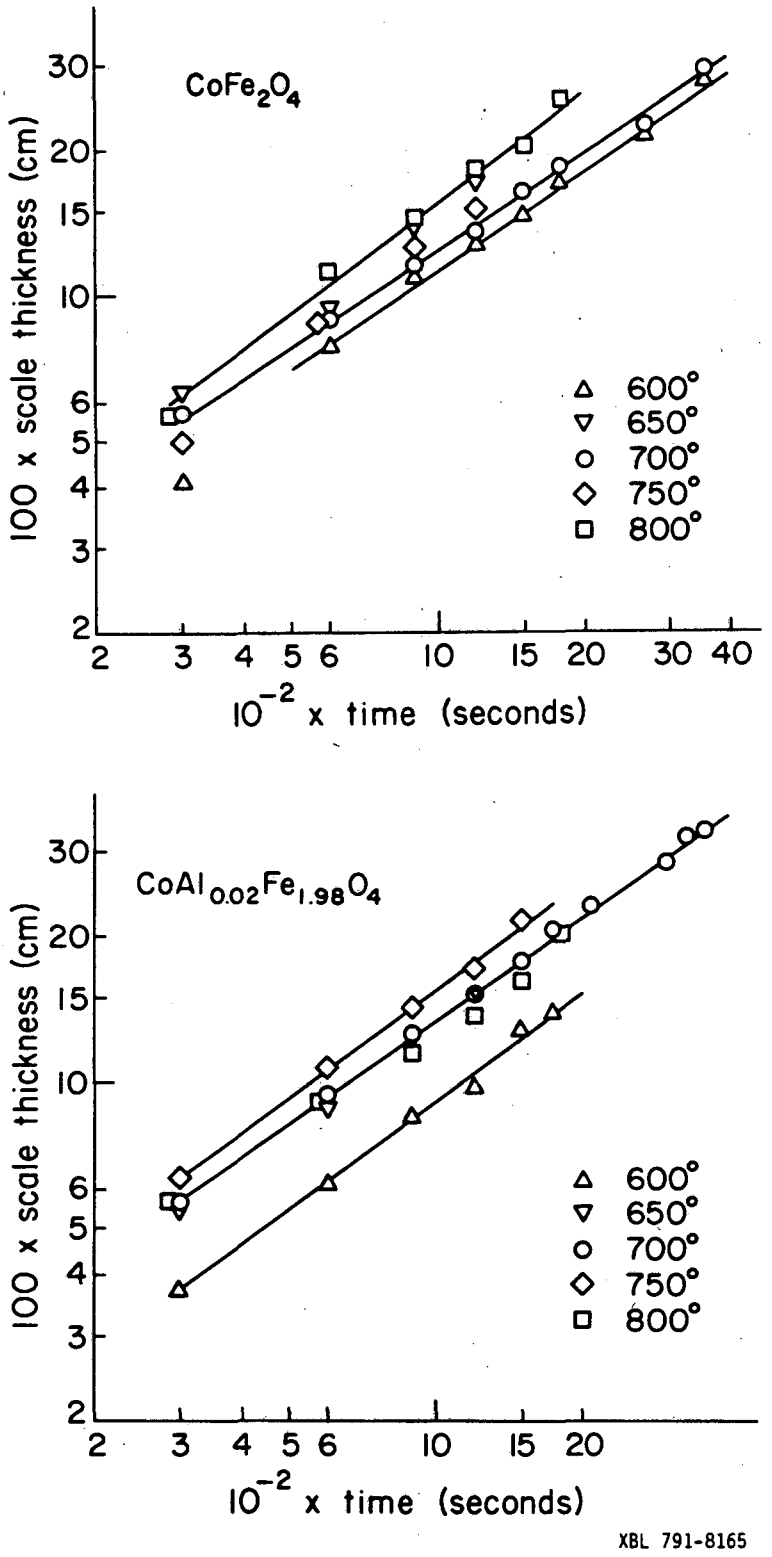
CoFe2O4
100 x scale thickness (cm)
10^-2 x time (seconds)
600°
650°
700°
750°
800°
CoAl0.02Fe1.98O4
100 x scale thickness (cm)
10^-2 x time (seconds)
600°
650°
700°
750°
800°
XBL 791-8165

Figure 2.

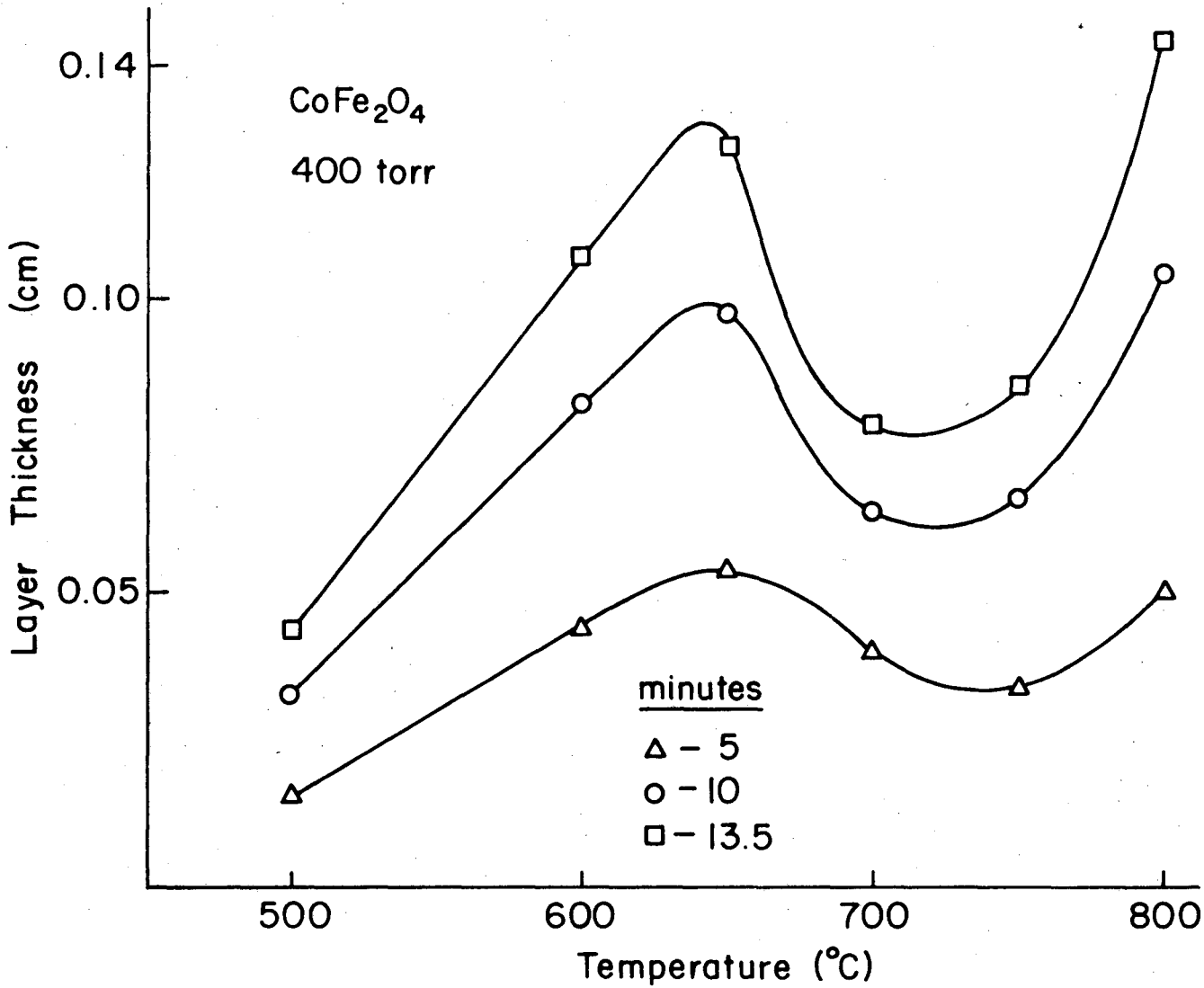

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Figure 3.

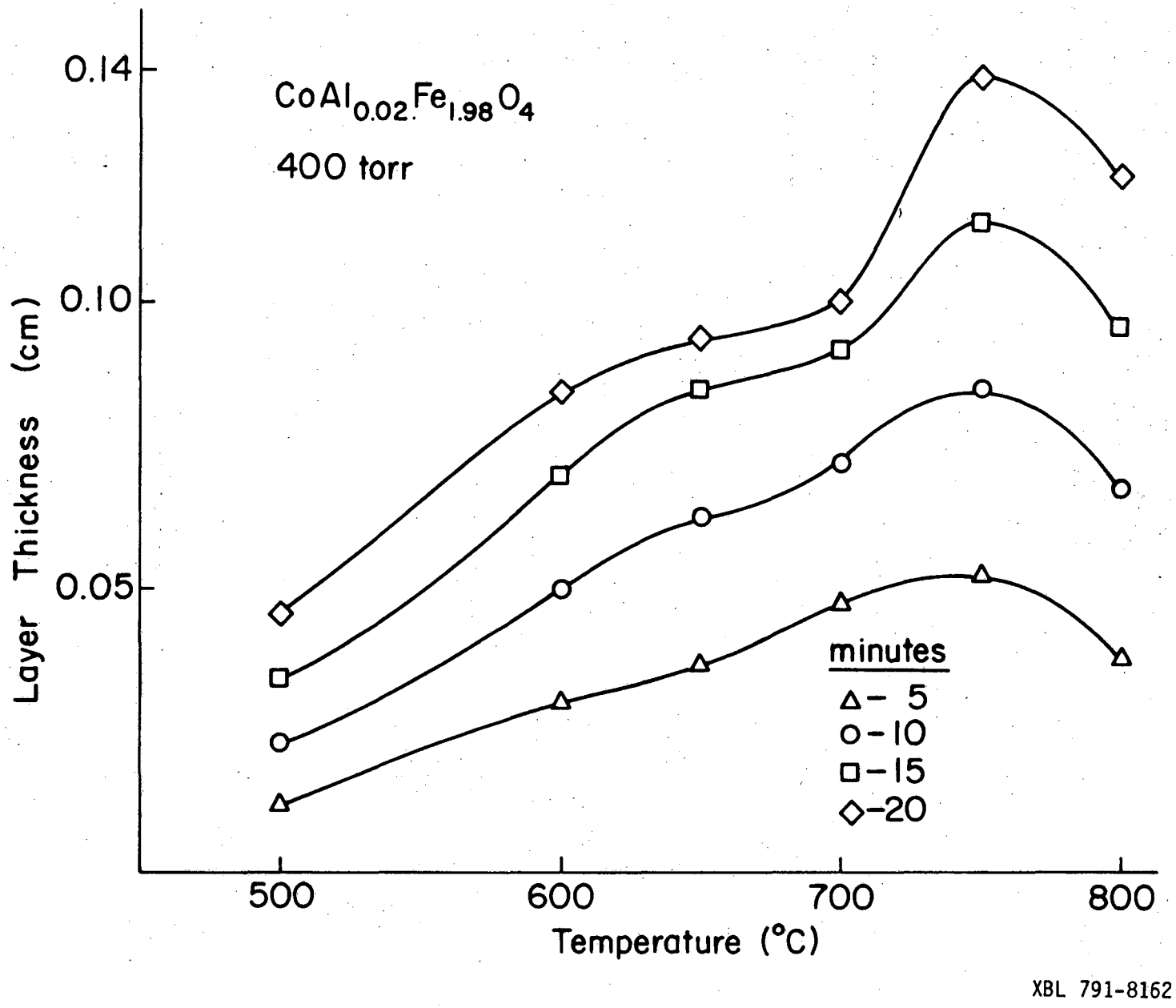
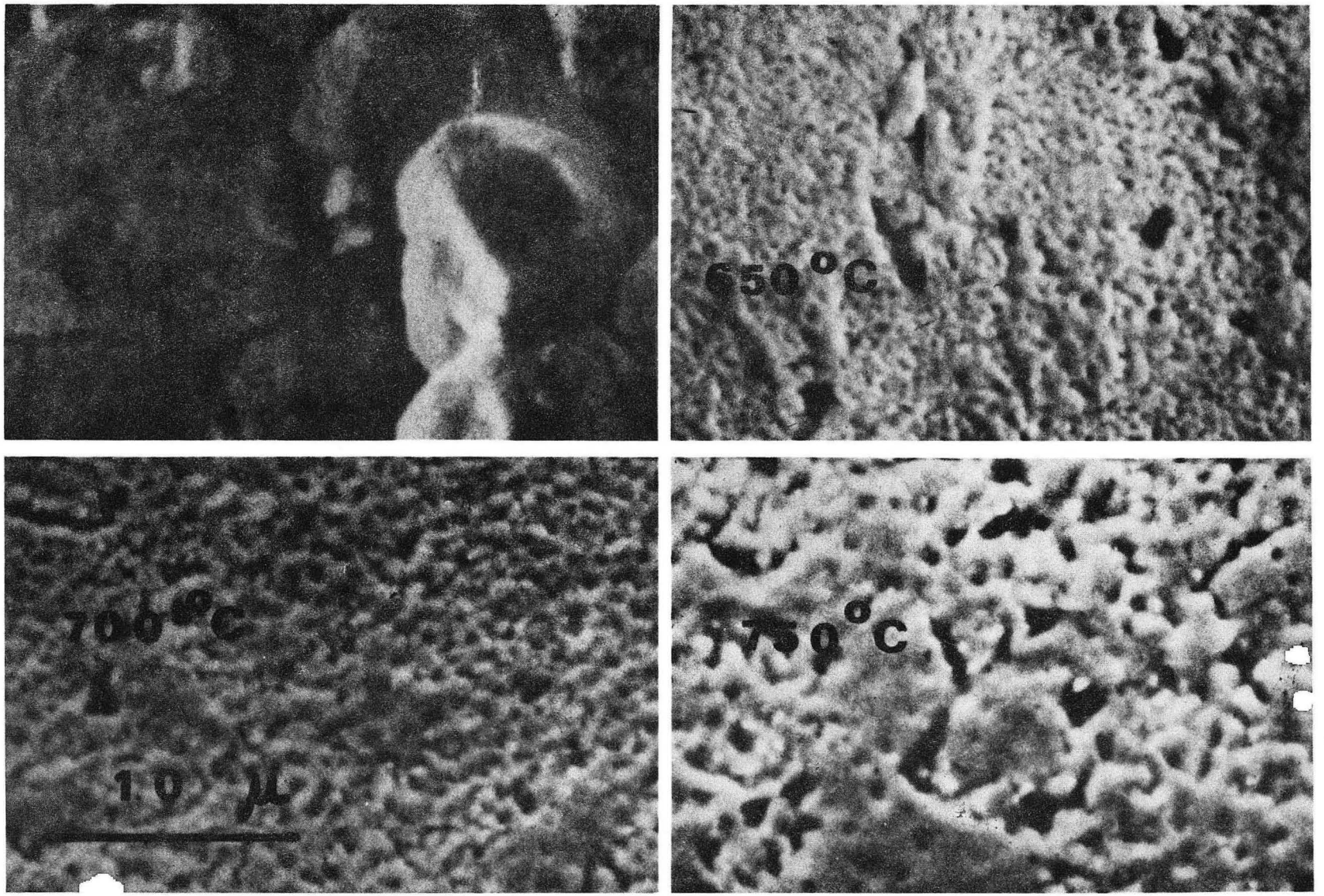
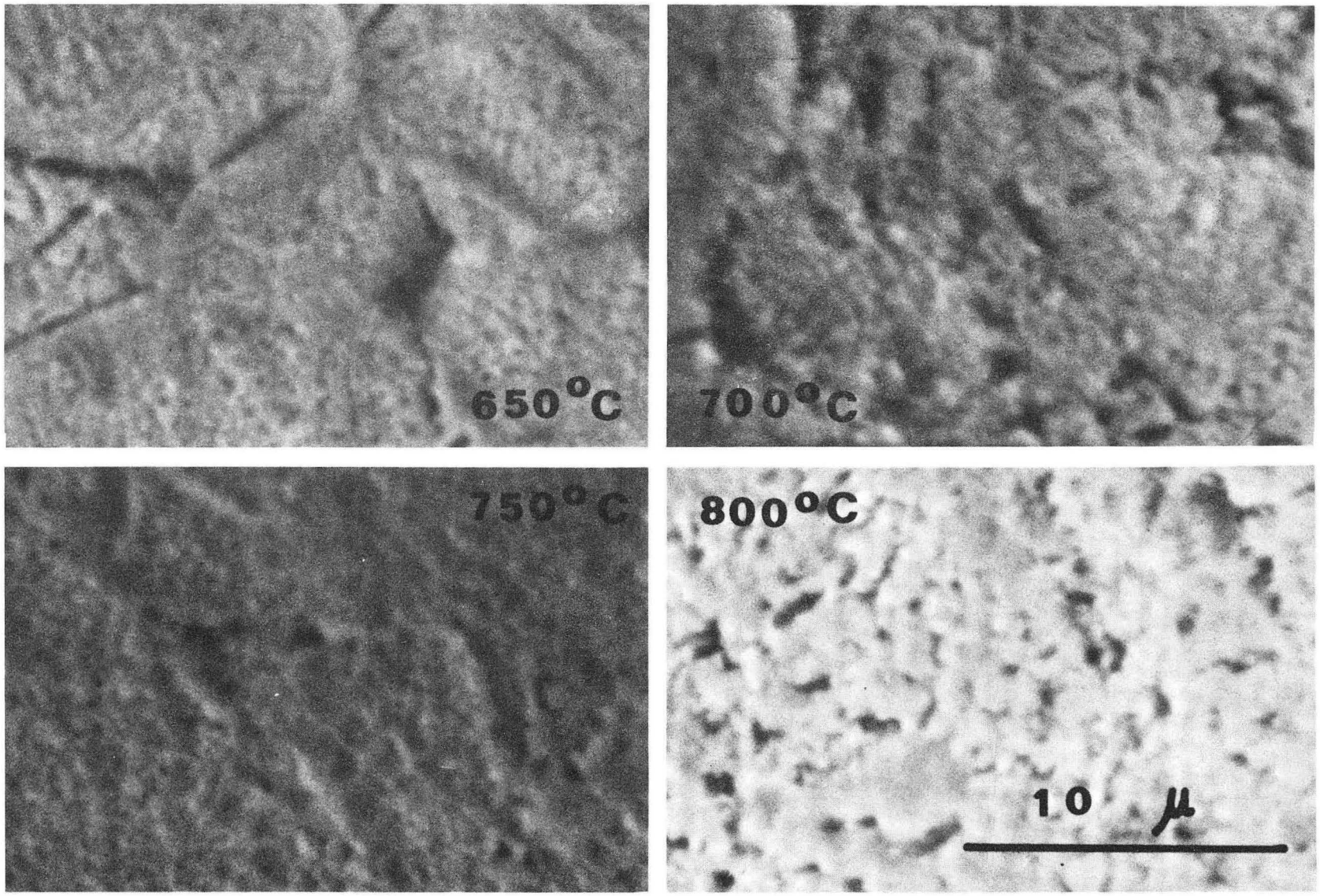

$CoAl_{0.02}Fe_{1.98}O_4$
400 torr
0.14
0.10
0.05
Layer Thickness (cm)
500
600
700
800
Temperature (°C)
minutes
Δ- 5
o-10
□-15
◇-20
XBL 791-8162

Figure 4.



XBB 794 5001

Figure 5.



XBB 794 5000

Figure 6.

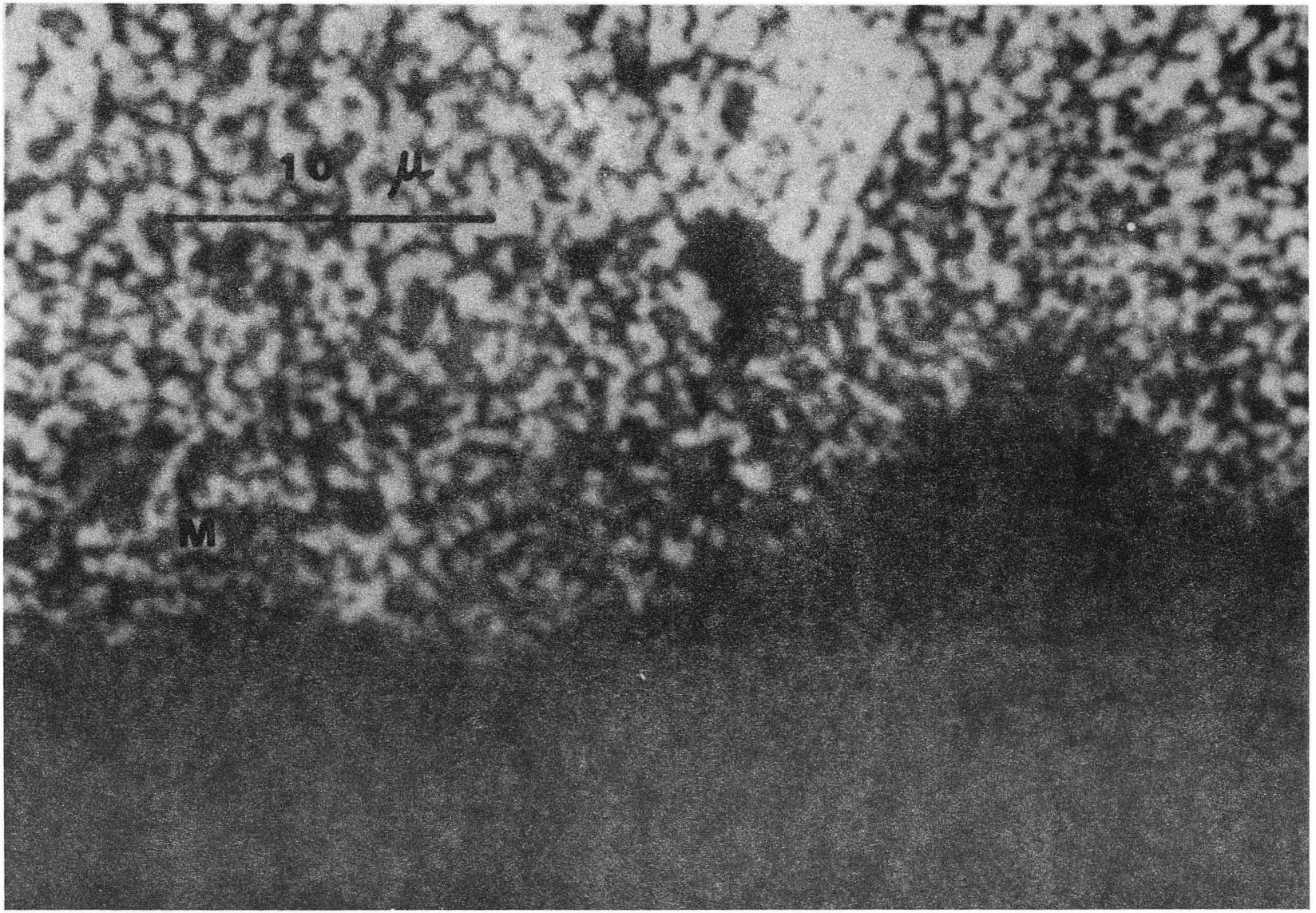


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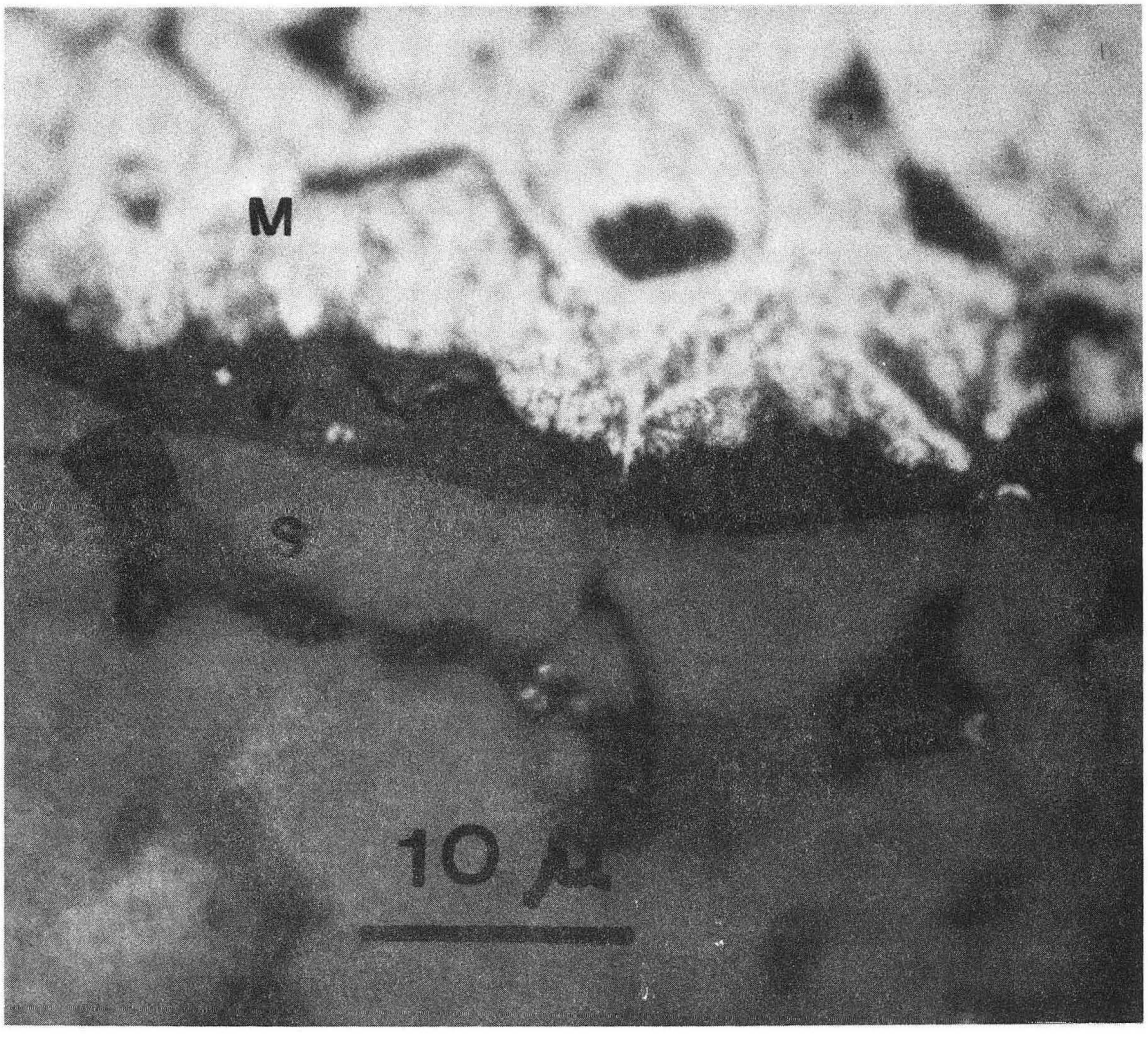
Figure 7.



XBB 791 1040

Figure 8.

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