CHARACTERIZATION OF RSI COATINGS

by

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INTRODUCTION

The Ceramic Engineering Division at the University of Washington has been involved since April 1, 1971, in study of RSI materials under contract NAS2-6541, administered by Ames Research Center. Studies of the coating systems used by the various suppliers were initiated in the fall of 1971.

The coating work was divided into two tasks: (1) to study the "as received" coatings with respect to their chemistry and morphology, and (2) to investigate the effect of thermal cycling upon the chemistry and morphology.

This presentation will outline the significant data and conclusions drawn from studies to date of coatings of three suppliers; General Electric, McDonnell Douglas, and Lockheed.

EXPERIMENTAL TECHNIQUES

Specimens of each of the RSI coatings tested were cut from panels provided by the suppliers in such a way as to leave the coating intact with respect to the tile. One specimen of each material was reserved, and two were subjected to thermal treatment; one with a maximum hot-face temperature of 1100°C (200°F) and the other 1250°C (2300°F). The cycling was conducted as follows. The specimen was placed in a window of a furnace with the coating face inward at a furnace temperature of 815°C (1500°F), the furnace temperature was rapidly (less than one minute) raised to the maximum temperature and held there for 15 minutes, then the furnace power was cut off. The furnace and specimen allowed to cool to 815°C, at which time the specimen was taken from the furnace to ambient air and another specimen put in its place and the cycle repeated. The cycling was normally done with pairs of specimens.

Specimens were then cut from the specimens for examination by X-ray diffraction, electron microprobe, SEM, optical microscope, and in some cases, for X-ray spectrographic analysis and porosity determinations. The details of sample preparation will not be discussed here; however, the general method for examination of coating cross-sections was to infiltrate the specimen with methyl methacrylate, polymerize to polymethylmethacrylate, section, and polish. The PMM was then removed by heating at 540°C (1000°F). In the cases of the MDAC MOD III coating, this treatment resulted in loss of the outer layer of the complex coating, but these effects were recognized and accounted for.

The porosity data reported were obtained by two methods, water absorption and mercury intrusion. The water absorption procedure was to immerse the coatings in boiling water for 24 hours and then to weigh them in air and suspended in water. From these data and the original weight of the specimen, the porosity that was filled during immersion was calculated. The mercury intrusion data were obtained using a mercury porosimeter capable of intruding mercury into a 15 nm pore.

In discussing these data it must be remembered that water can penetrate open porosity as small as 1.5 nm (15Å) while the mercury data only shows open porosity larger than 15 nm (150Å).

EXPERIMENTAL RESULTS

The results of these studies will be presented for each of the three contractors' materials. Since the time for presentation is rather limited, only the most significant data will be presented with comments as to its significance.

GE REI COATINGS--CRYSTALLINE SPECIES BY X-RAY DIFFRACTION

(Figure 1)

Figure 1 shows the results of the X-ray diffraction analyses of GE-REI materials in the as-received condition as well as after the cycling tests. There are two important factors to note here: (1) the rather dramatic increase in cristobalite in MOD I after the 1250°C cycling, and (2) the lack of this result in the MOD IA material.

GE REI Coatings

Crystalline Species by X-ray Diffraction

Specimen	As-received	Cycled 10 times 1100°C (2000° F)	Cycled 10 times 1250°C (2300°F)
Mod I	mullite, 5% cristobalite, nickel aluminate	no change	cristobalite increases to 15%
Mod IA	same as above trace cristobalite	no change	no change

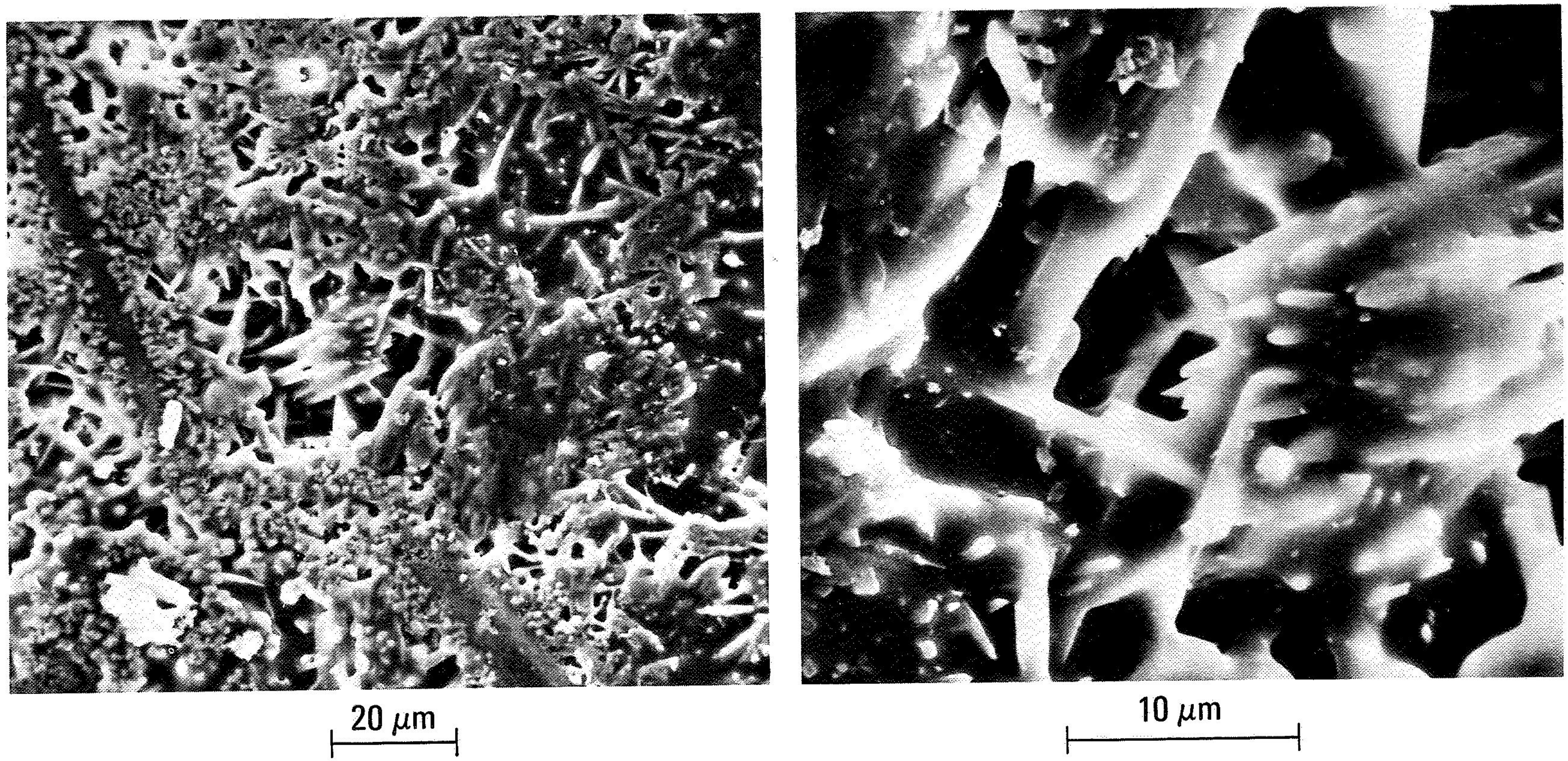
Figure 1

GE MOD I COATING AS RECEIVED--SEM VIEW OF SURFACE

(Figure 2)

Figure 2 shows the surface of the MOD I coating at two different magnifications. The coating appears porous in figure 2(a), but at the higher magnification (2(b)) it is seen that the crystals are well sealed by the glassy phase.

GE Mod I Coating
As Received
SEM View of Surface



(a) (b)

Figure 2

GE MOD I COATING - AS RECEIVED

CROSS-SECTION OF COATING AND INTERFACE

(Figure 3)

Figure 3 shows a cross-section of the MOD I coating. It appears reasonably dense, with only occasional large porosity.

GE Mod I Coating
As Received
Cross-section of Coating and Interface

Figure 3

GE MOD I COATING

10 CYCLES TO 1250°C (2300°F)

MACROPHOTOGRAPH SHOWING GREEN STAIN PENETRATION

(Figure 4)

Figure 4 shows the results of 10 cycles to a maximum temperature of 1250°C. A green-colored stain appears to penetrate the tile after the cycling test. X-ray spectroscopy of the stained region in tile showed only an increase in the silicon content. X-ray diffraction showed no additional phases. It is concluded that the glassy phase, with enough nickel to stain it green, penetrated the tile during the test. Similar tests on the MOD IA coating showed no sign of this behavior.

GE Mod I Coating
10 Cycles to 1250°C (2300°F)
Macrophotograph Showing Green Stain Penetration

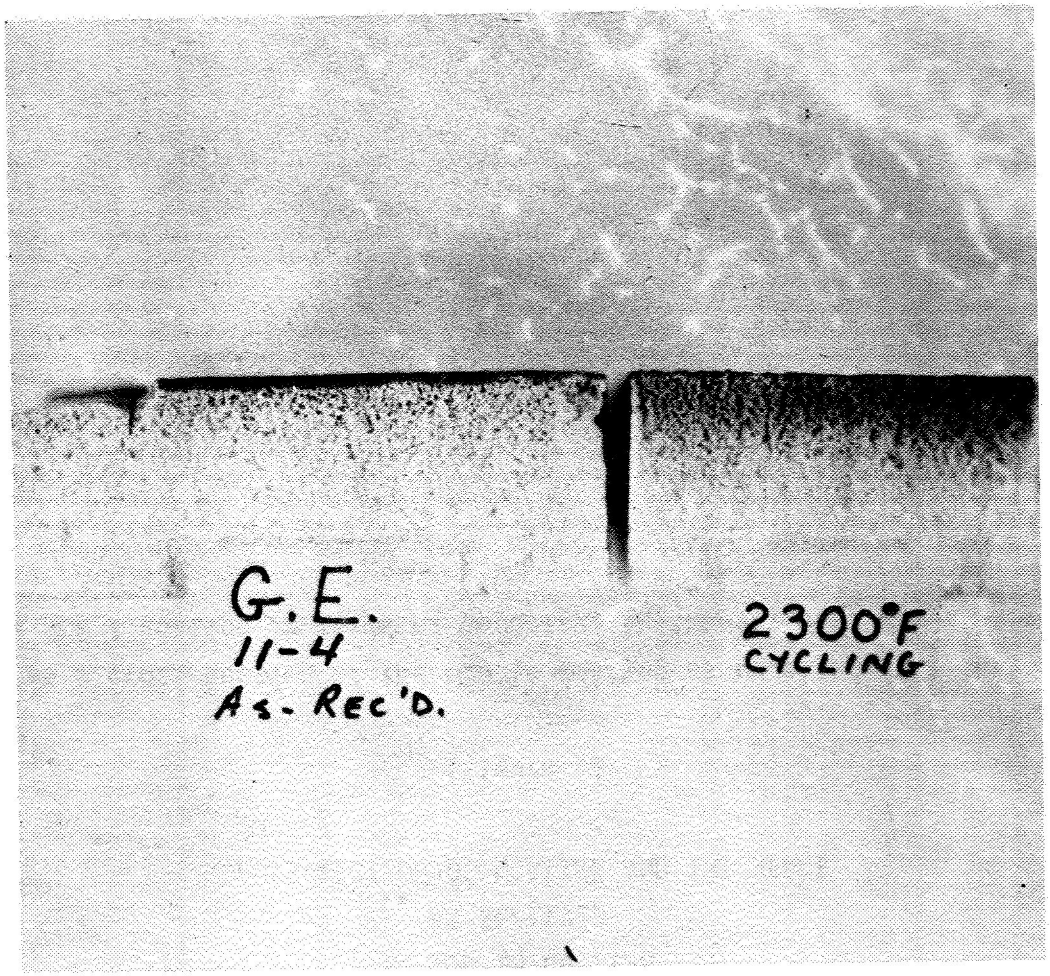


Figure 4

GE MOD IA COATING

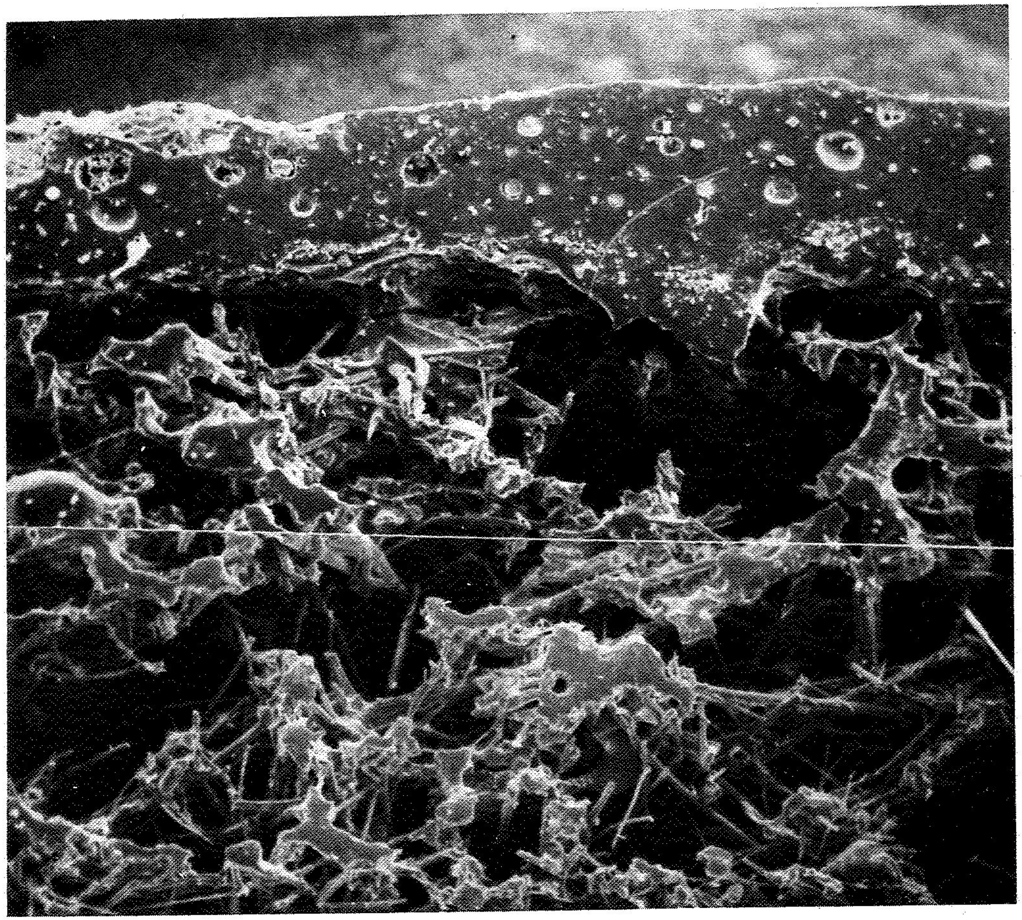
AS RECEIVED

CROSS-SECTION OF COATING AND INTERFACE

(Figure 5)

Figure 5 shows a cross-section of the MOD IA coating as received from the supplier. It appears similar to the MOD I coating in terms of porosity, thickness, etc.

GE Mod IA Coating
As Received
Cross-section of Coating and Interface



400 μm

Figure 5

GE MOD IA COATING

10 CYCLES TO 1250°C (2300°F)

(Figure 6)

Figure 6 displays a cross-section of the MOD IA coating after 10 cycles to 1250°C. No significant changes are seen.

GE Mod IA Coating
10 Cycles to 1250°C (2300°F)
Cross-section of Coating and Interface

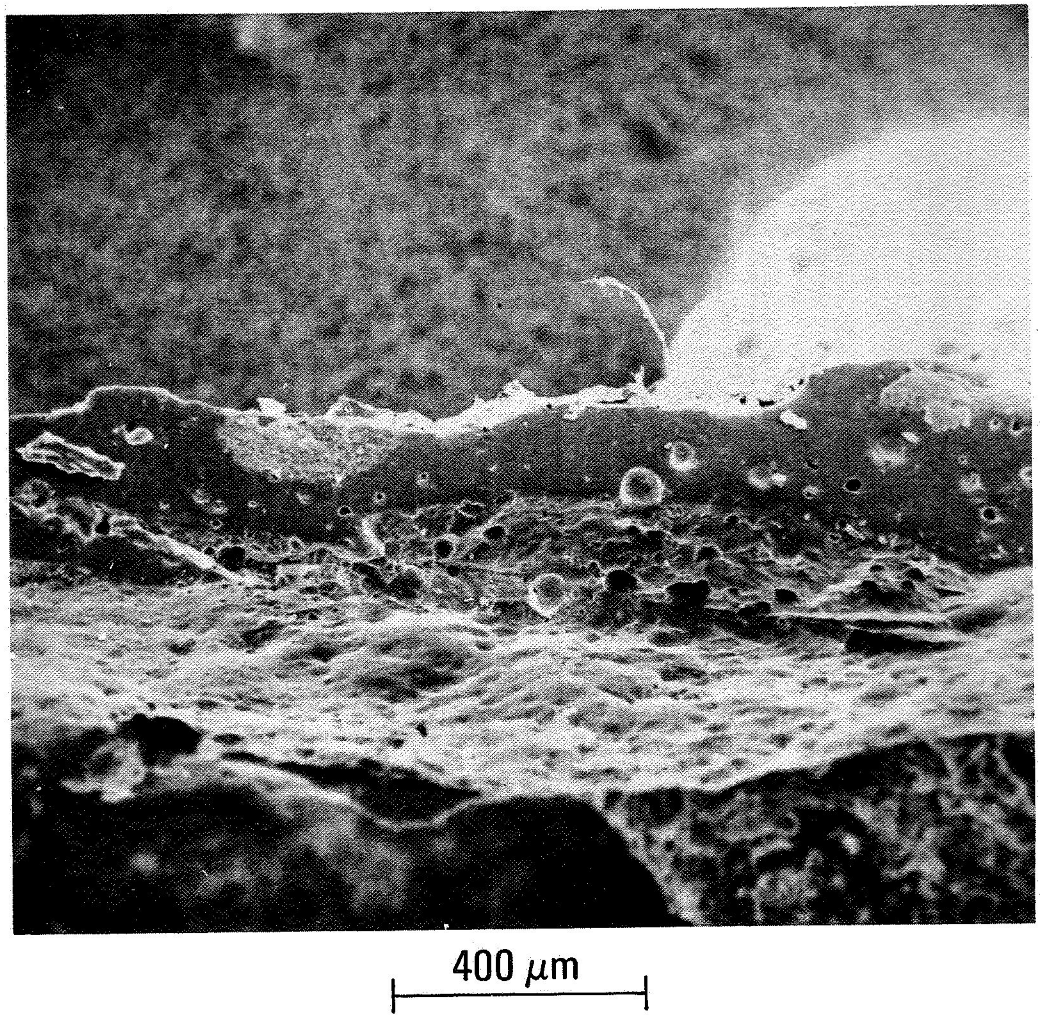


Figure 6

POROSITY DATA
GE MOD IA COATING

(Figure 7)

Figure 7 summarizes the porosity data for MOD IA. These data are felt to be in error as much as five percent for the water method and two percent for the mercury method. The values shown indicate that the porosity is little affected by cycling to 1250°C and that the pores are mostly smaller than 15 nm.

Porosity Data
GE Mod IA Coating

Thermal Treatment	Porosity, % (H_2O method)	Porosity, % (Hg method)
As received	19.4	4.3
10 cycles 1100°C	16.6	4.6
10 cycles 1250°C	18.2	4.5

Figure 7

GE REI

SIGNIFICANT CONCLUSIONS

(Figure 8)

This figure summarizes the most important results of the tests on REI coatings.

GE REI

SIGNIFICANT CONCLUSIONS

1. Mod I shows considerable increase in cristobalite in 1250°C cycling tests. Mod IA shows no change.

2. Mod I shows penetration of glassy phase into the tile in 1250°C cycling. Mod IA shows no change

3. Porosity remains essentially constant for Mod IA under 1100°C and 1250°C cycling. (10 cycles)

Figure 8

MDAC HCF COATINGS
CRYSTALLINE SPECIES BY X-RAY DIFFRACTION

(Figure 9)

Figure 9 is a summary of the crystalline phases determined by X-ray diffraction in McDonnell Douglas HCF coatings. The only changes noted after cycling was the slight increase in cristobalite in the MOD III coating after the 1250°C cycling.

MDAC HCF Coatings

Crystalline Species by X-ray Diffraction

Specimen	As-received	10 Cycles to 1100°C (2000°F)	10 Cycles to 1250°C (2300°F)
Phase I	Cristobalite, quartz, Cr_2O_3	no data	no data
Mod I	Cristobalite, quartz, Cr_2O_3 (Co,Fe,Cr)O_x	no change	no change
Mod III	Same as Mod I + $AlPO_4$	no change	no new phases, slight cristobalite increase

Figure 9

MDAC MOD I COATING

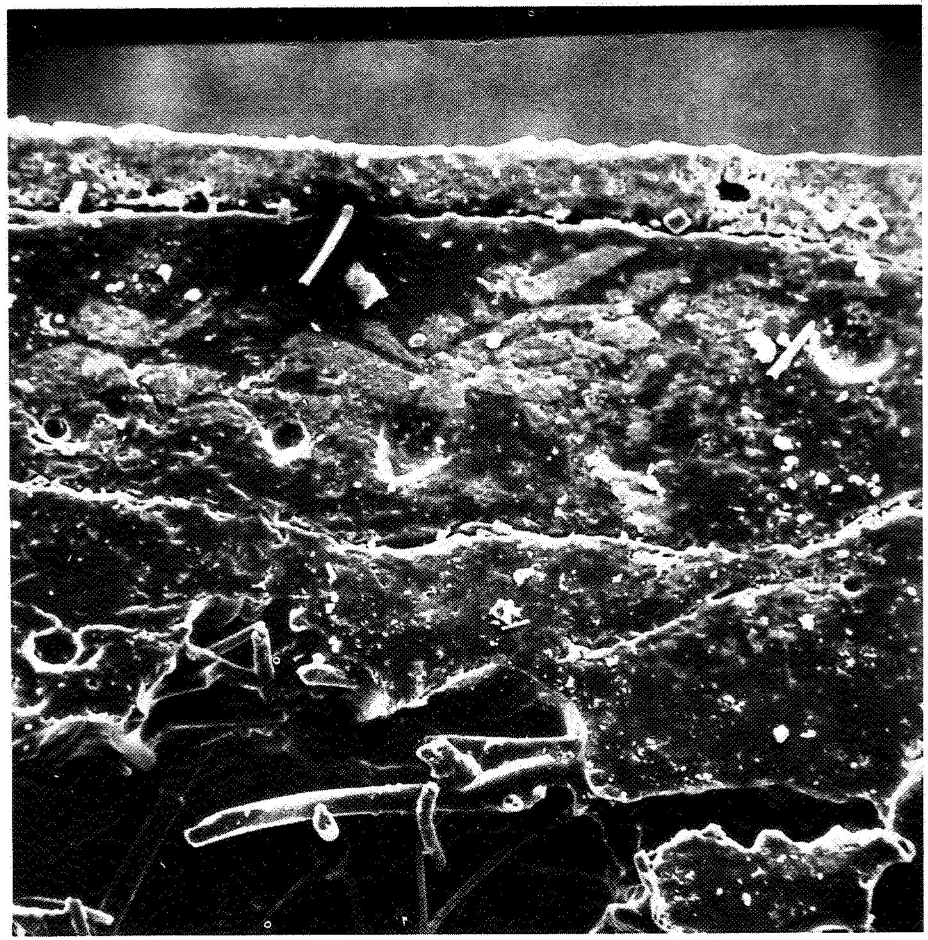
AS RECEIVED

CROSS-SECTION OF COATING AND INTERFACE

(Figure 10)

Figure 10 shows a cross-section of the MOD I coating as received from the supplier. The complex nature of the coating is evident. Electron microprobe analysis shows the coating contains chromium, cobalt, and iron in the outer layer and chromium only in the grains of the middle layer. It is concluded that the outer layer contains a complex (Co, Cr Fe) oxide while the middle layer contains chromium oxide. The inner layer appears glassy and contains little or none of the heavier metal ions.

MDAC Mod I Coating
As Received
Cross-section of Coating and Interface



100 μm

Figure 10

MDAC MOD I COATING

10 CYCLES TO 1250°C (2300°F)

CROSS-SECTION OF COATING

(FIgure 11)

Figure 11 shows the results of cycling the MOD I coating ten times to 1250°C. There is a marked increase in porosity, the surface texture of the specimen becomes rougher and the color changed from black to dark gray.

MDAC Mod I Coating
10 Cycles to 1250°C (2300°F)
Cross-section of Coating

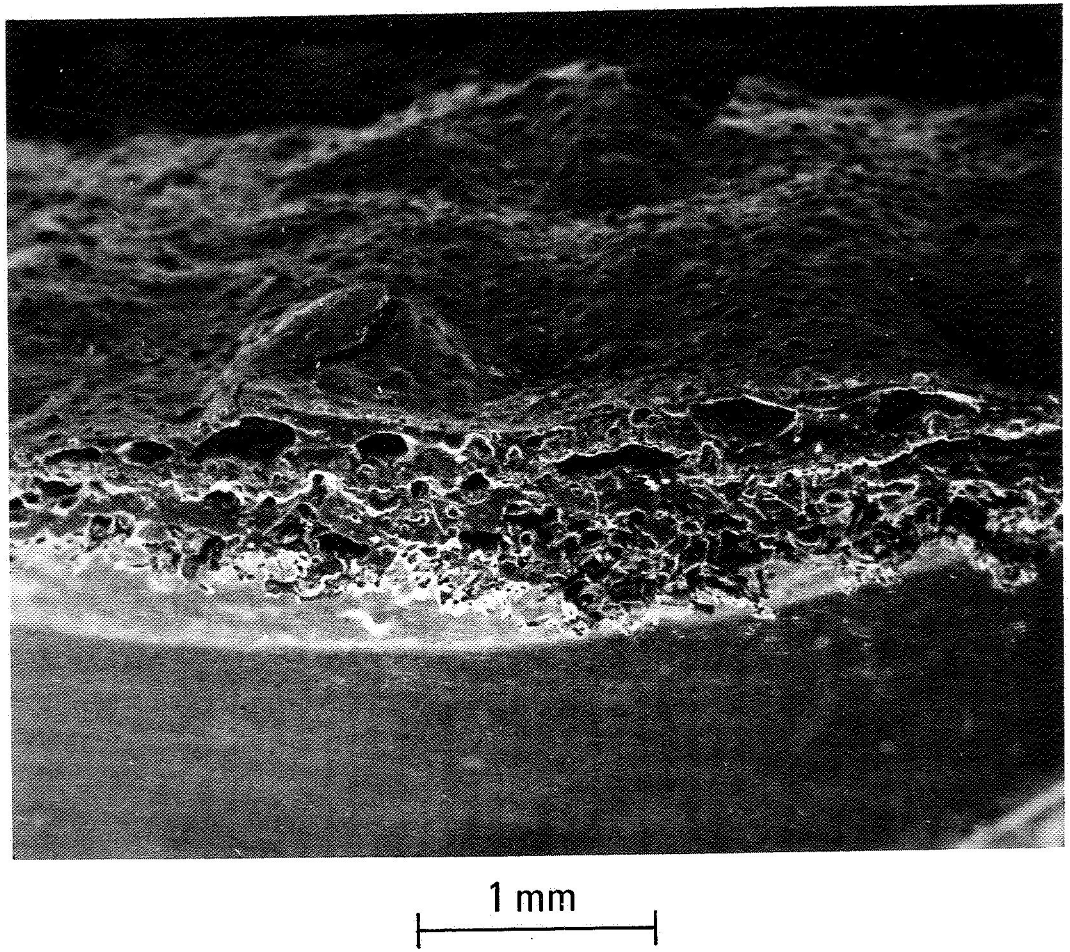


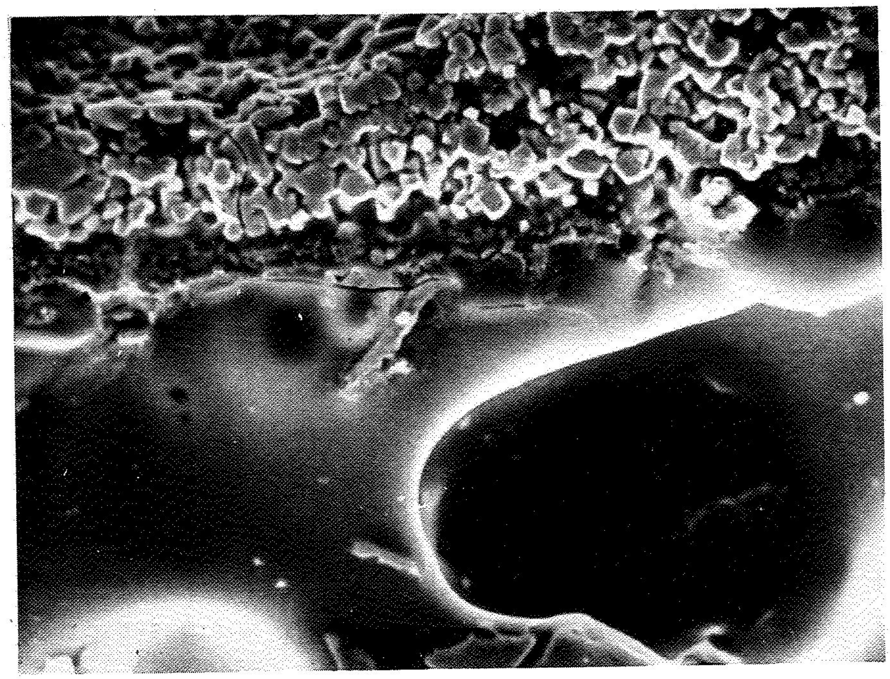
Figure 11

MDAC MOD I COATING
10 CYCLES TO 1250°C (2300°F)
CROSS-SECTION OF COATING

(Figure 12)

This SEM photo shows, at higher magnification, a cross-section of the MOD I coating after 10 cycles to 1250°C. Note the small crystals between the outer layer and the middle layer (the reaction zone). These are newly nucleated crystalline species not seen in the as-received material. Electron microprobe scans show that cobalt and iron have migrated into and beyond the interfacial area between the two layers. Chromium does not appear to move under these conditions.

MDAC Mod I Coating
10 Cycles to 1250°C (2300°F)
Cross-section of Coating



40 µm

Figure 12

MDAC MOD III COATING

AS RECEIVED

CROSS-SECTION OF COATING

(Figure 13)

Figure 13 is a cross-section of the as-received MOD III coating. It appears similar to the MOD I except that the crystalline material (Cr_2O_3) is not so evident in the intermediate layer as in MOD I. Note that the top layer was spalled off during sample preparation.

MDAC Mod III Coating
As Received
Cross-section of Coating

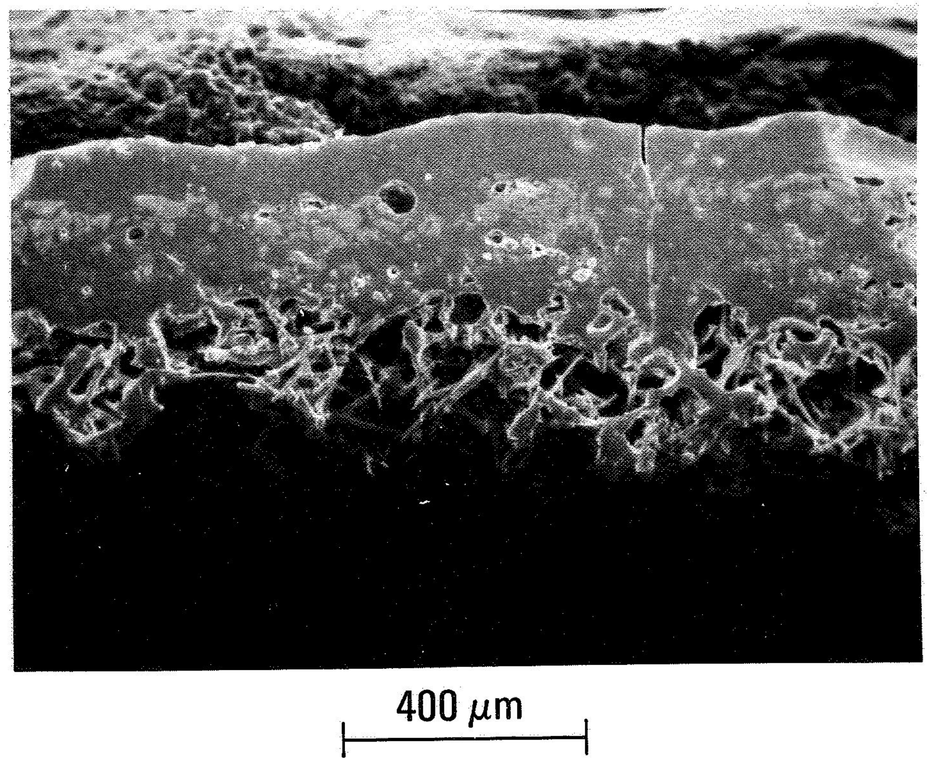


Figure 13

MDAC MOD III COATING
10 CYCLES TO 1250°C (2300°F)
CROSS-SECTION OF COATING

(Figure 14)

This figure shows the results of 10 cycles at 1250°C on the MOD III coating. Again the top layer was spalled off during sample preparation. The innermost layer shows a dramatic increase in porosity as compared with the previous figure. Suspecting that sample preparation might have had some effect on this result, we looked at fracture sections of the same specimen and found similar porosity. The microprobe analysis of this material, however, showed no migration of cobalt and iron as in MOD I.

MDAC Mod III Coating
10 Cycles to 1250°C (2300°F)
Cross-section of Coating

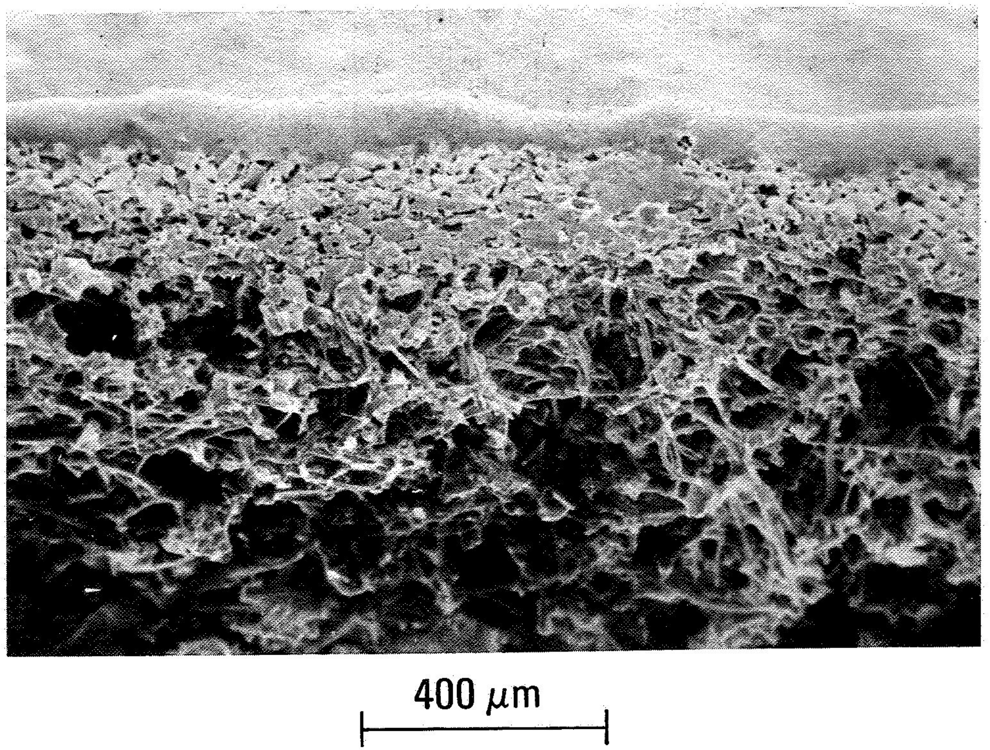


Figure 14

MDAC MOD III COATING

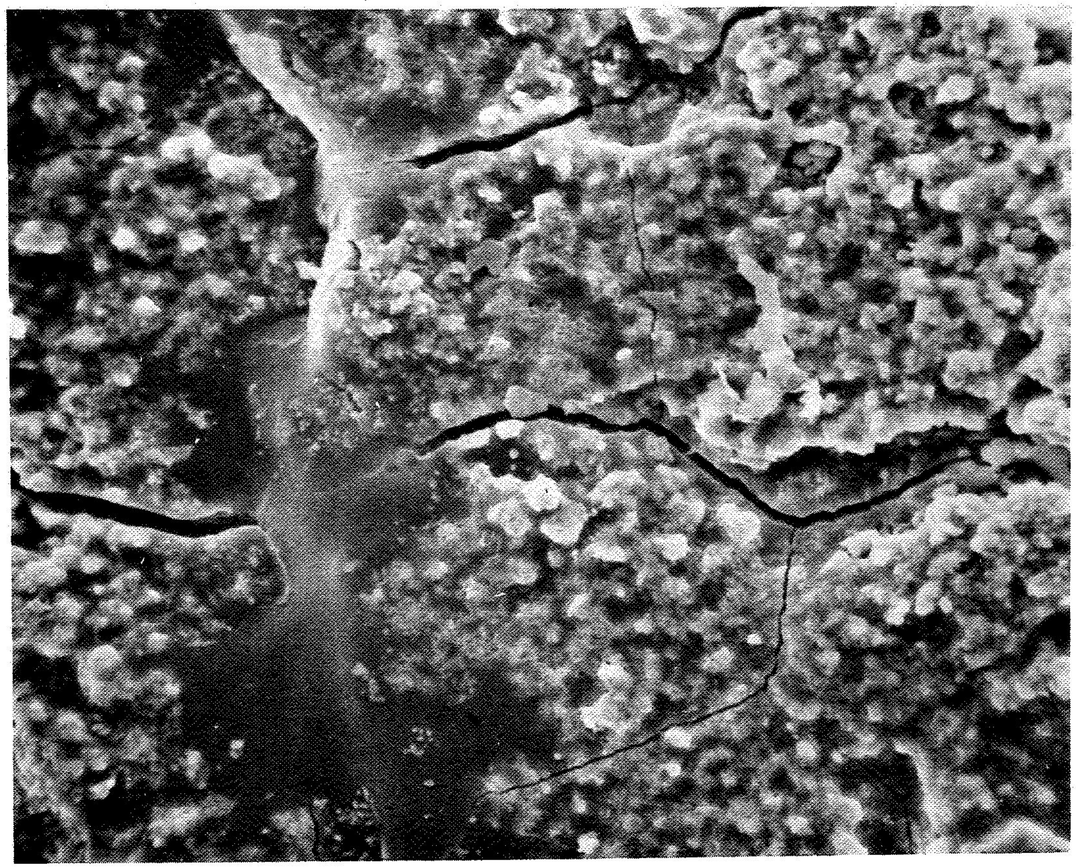
AS RECEIVED

REMNANT OF SURFACE LAYER

(Figure 15)

Figure 15 is a view of the surface of the MOD III coating as received from the vendor. The cracking may be an artifact of sample preparation.

MDAC Mod III Coating
As Received
Remnant of Surface Layer



20 μm

Figure 15

MDAC MOD III COATING

10 CYCLES TO 1250°C (2300°F)

REMNANT OF SURFACE LAYER

(Figure 16)

Figure 16 shows the coating surface after exposure to 10 cycles to 1250°C. It appears that much of the glassy phase present in the as-received material is absent here.

MDAC Mod III Coating
10 Cycles to 1250°C (2300°F)
Remnant of Surface Layer

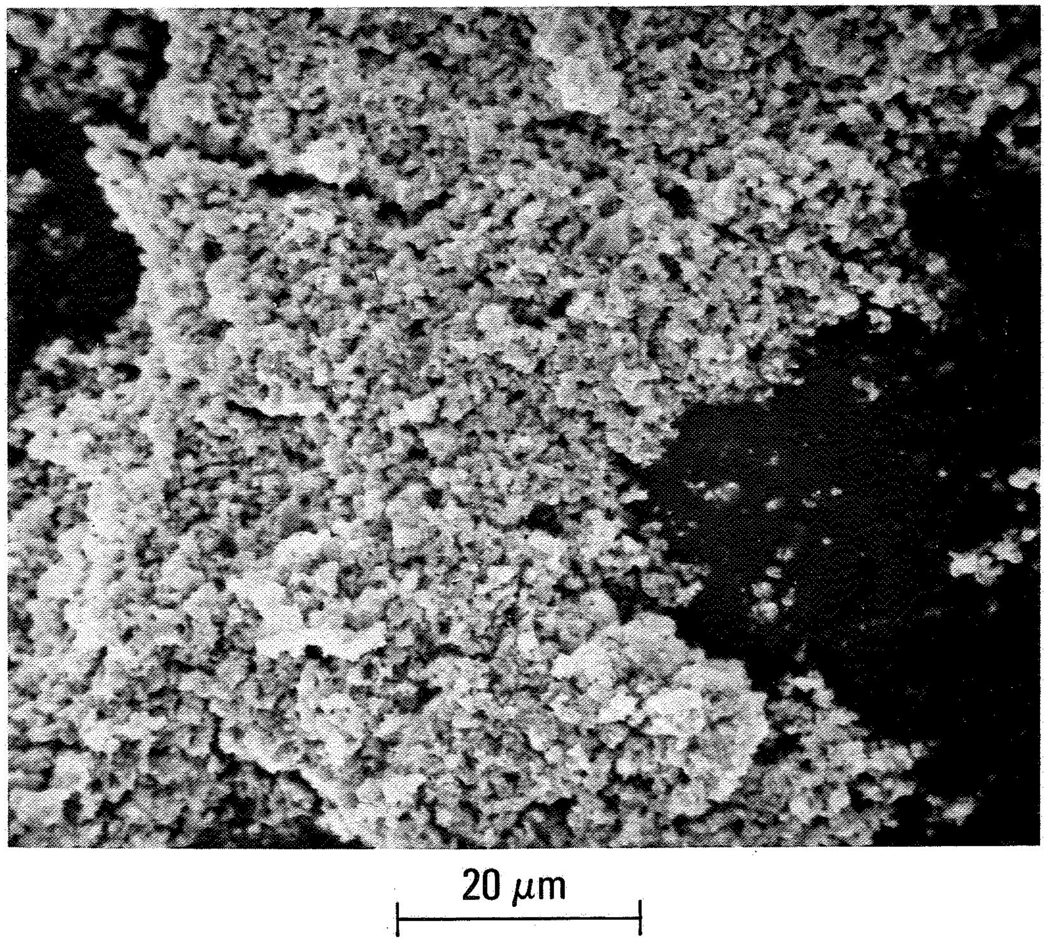


Figure 16

POROSITY DATA
MDAC MOD III COATING

(Figure 17)

This figure presents the porosity data for MOD III. The data would indicate that the total porosity remains essentially constant upon cycling, while the porosity larger than 15 nm decreases. These data are not consistent with the SEM studies. More work must be done.

Porosity Data
MDAC Mod III Coating

Thermal Treatment	Porosity, % (H_2O method)	Porosity, % (Hg method)
As received	25.4	21.1
10 cycles to 1100°C	24.3	18.1
10 cycles to 1250°C	28.0	15.5

Figure 17

MDAC HCF COATINGS

SIGNIFICANT CONCLUSIONS

(Figure 18)

This figure summarizes the important results of the work on MDAC HCF. Probably most important is the increased porosity upon cycling.

MDAC HCF Coatings

Significant Conclusions

1. Mod I shows migration of cobalt and iron with nucleation of new phase after 10 cycles to 1250°C.

2. Mod III shows no migration under same conditions as Mod I.

3. Both Mod I and Mod III show increased porosity after 10 cycles to 1250°C.

4. Water absorption and mercury intrusion porosity data inconsistent with SEM evidence.

Figure 18

LMSC LI-1500 COATINGS

CRYSTALLINE SPECIES BY X-RAY DIFFRACTION

(Figure 19)

Figure 19 summarizes the X-ray diffraction analysis of the LI-1500 coatings, LI-1525 and LI-1542.

LMSC LI-1500 Coatings

Crystalline Species by X-ray Diffraction

Specimen	As received	10 cycles to 1100°C (2000°F)	10 cycles to 1250°C (2300°F
LI-1525	glass, Cr_2O_3	~ 15% cristobalite, Cr_2O_3	~ 25% cristobalite, Cr_2O_3
LI-1542	alpha-SiC	SiC, ~3% cristobalite	SiC, ~8% cristobalite

Figure 19

LMSC LI-1525 COATING

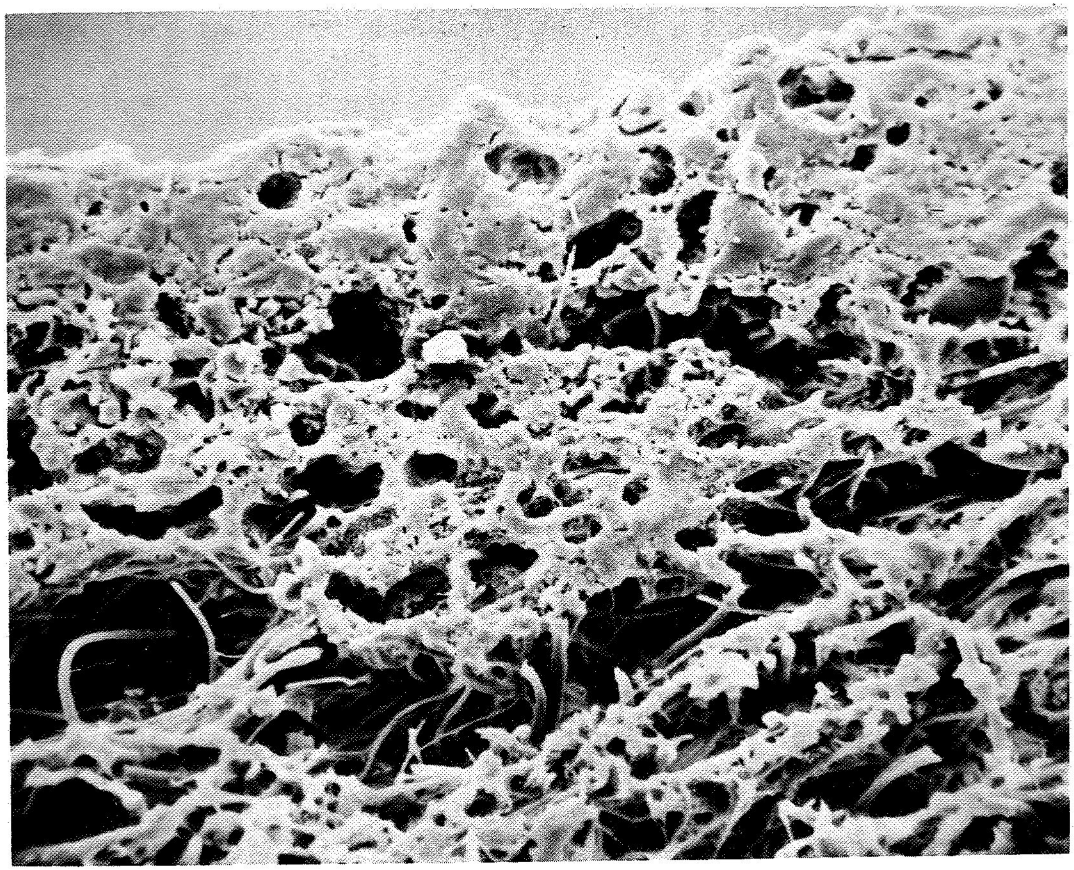
AS RECEIVED

CROSS-SECTION OF COATING AND INTERFACE

(Figure 20)

This figure shows a cross-section of the LI-1525 coating as received. Considerably porosity is evident, however, and good penetration into the transition zone is apparent.

LMSC LI-1525 Coating
As Received
Cross-section of Coating and Interface



100 μm

Figure 20

LMSC LI-1525 COATING
SURFACE OF AS-RECEIVED COATING

(Figure 21)

Figure 21 is a view of the LI-1525 surface. The surface appears well sealed by the glass phase.

LMSC LI-1525 Coating
Surface of As-received Coating

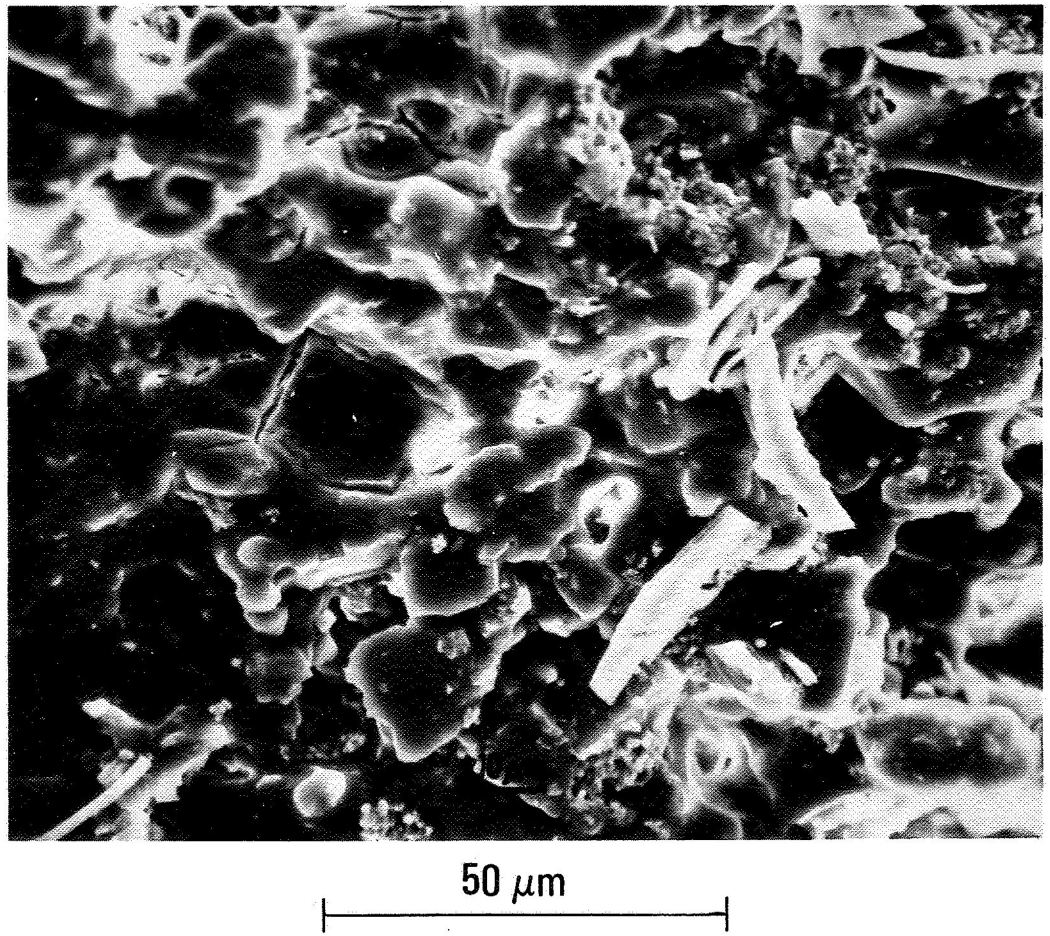


Figure 21

LMSC LI-1542 COATING

AS RECEIVED

CROSS-SECTION OF COATING AND INTERFACE

(Figure 22)

Figure 22 is a cross-section of the li_1542 coating as received. Note the high degree of porosity in the outer half of the coating.

LMSC LI-1542 Coating
As Received
Cross-section of Coating and Interface

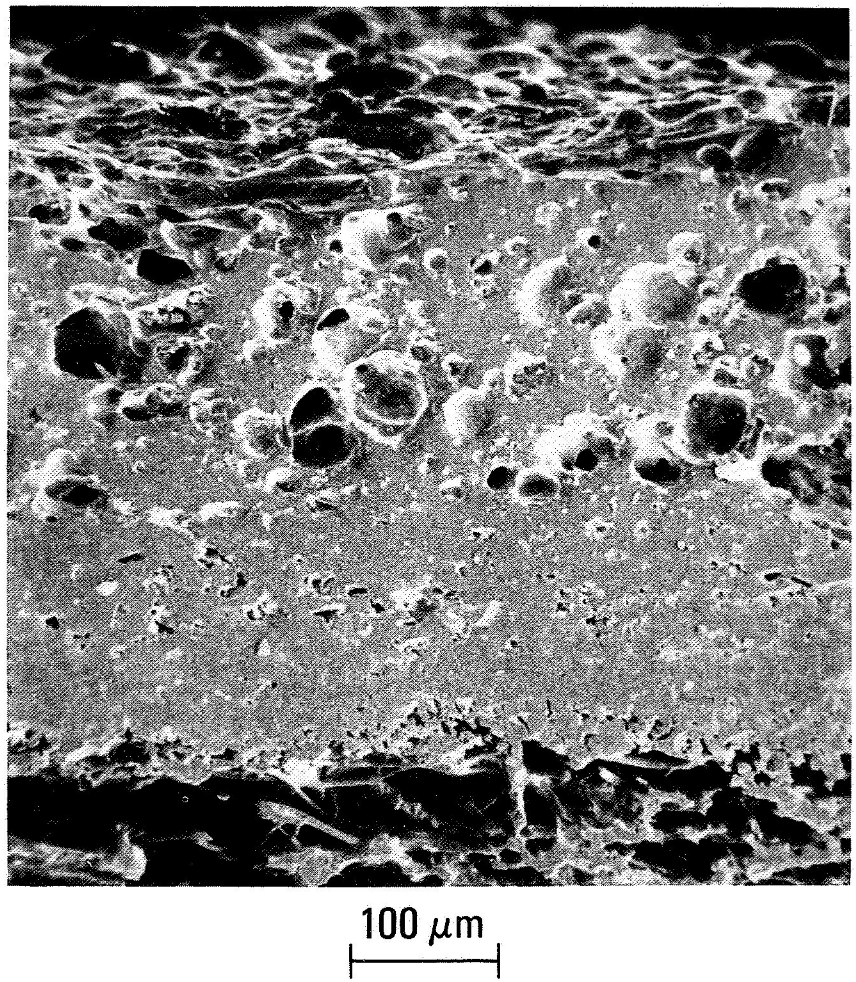


Figure 22

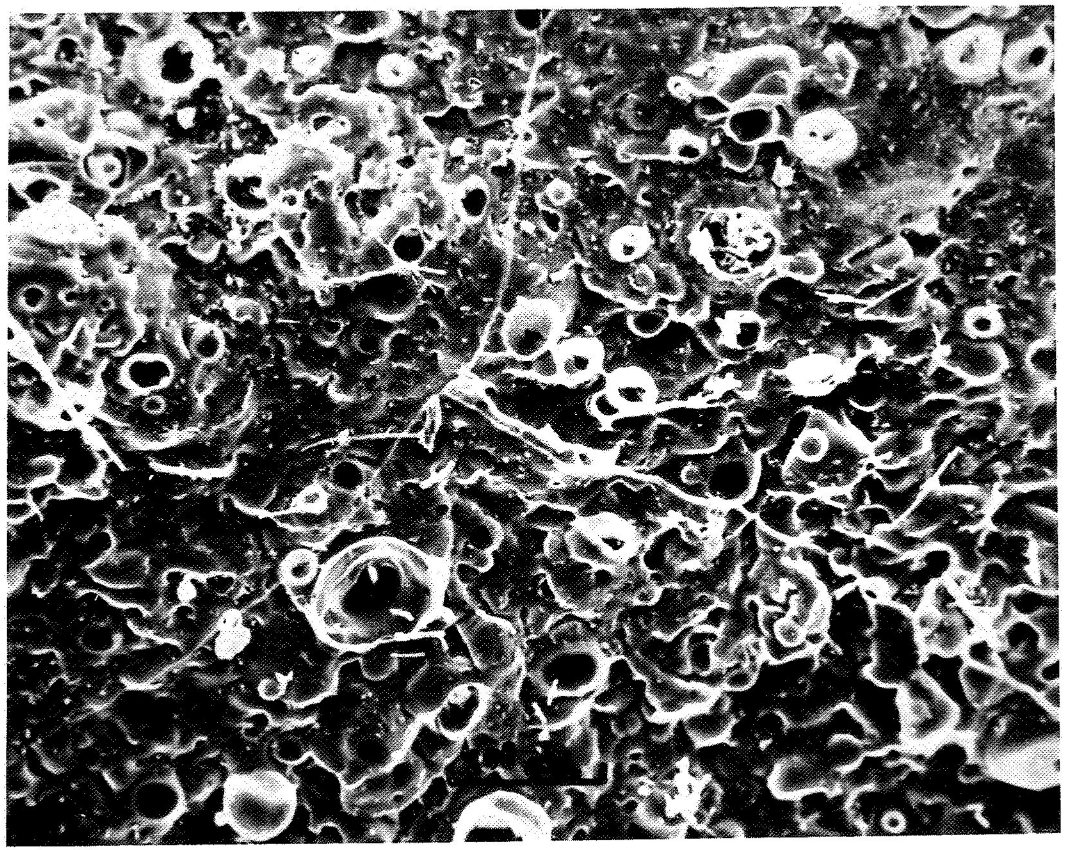
LMSC LI-1542 COATING

SURFACE OF AS-RECEIVED COATING

(Figure 23)

This SEM photo shows the surface texture of the LI-1542 coating; again the porosity is evident.

LMSC LI-1542 Coating
Surface of As-received Coating



100 μm

Figure 23

LMSC LI-1542 COATING

10 CYCLES TO 1250°C (2300°F)

CROSS-SECTION OF COATING

(Figure 24)

This cross-section of the LI-1542 coating shows the results produced by 10 cycles to 1250°C. Note the extreme growth of porosity in the outer layer.

LMSC LI-1542 Coating
10 Cycles to 1250°C
Cross-section of Coating

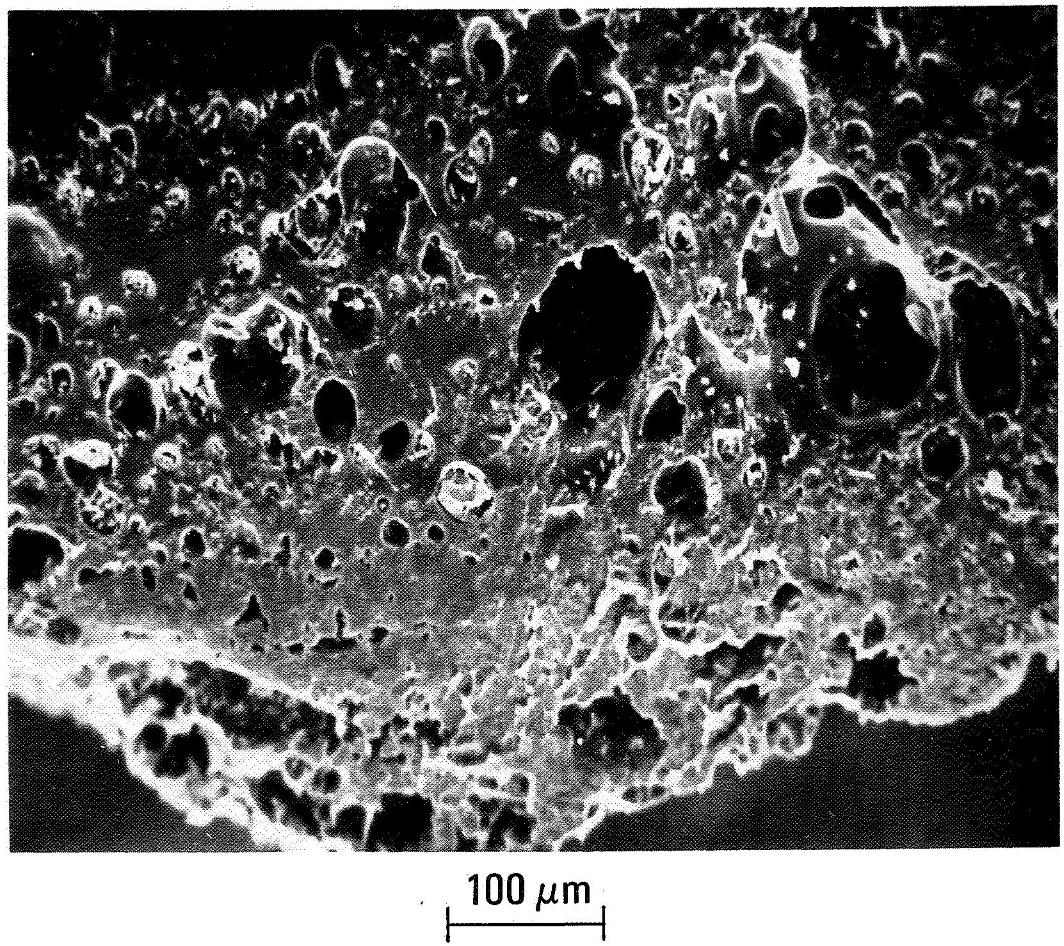


Figure 24

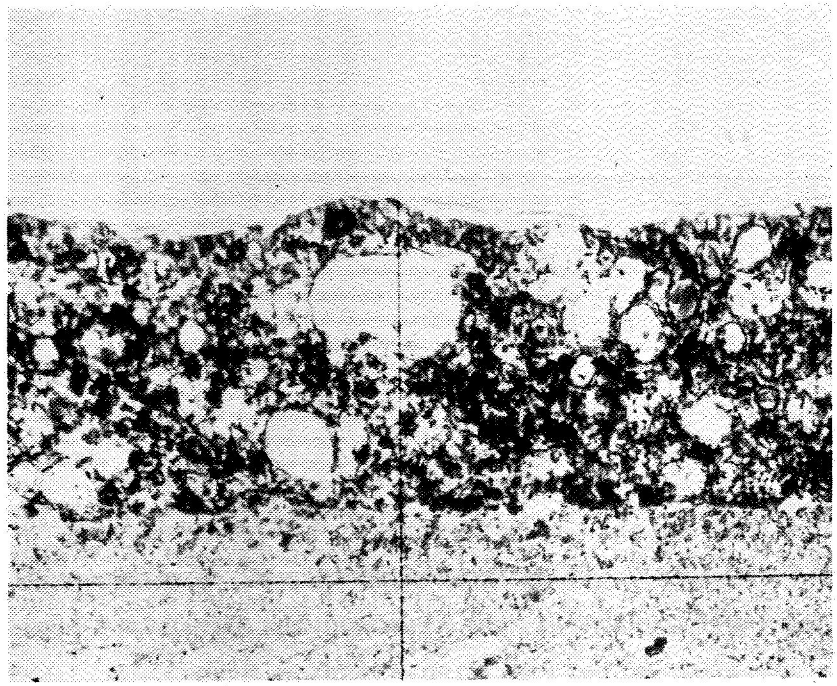
LMSC LI-1542 COATING
CROSS-SECTION, OPTICAL THIN-SECTION

(Figure 25)

Figure 25 shows a comparison of the 1250°C cycled LI-1542 coating with the as-received material. These optical thin sections show a growth of approximately 100 percent in the thickness of the coating as a result of cycling to 1250°C.

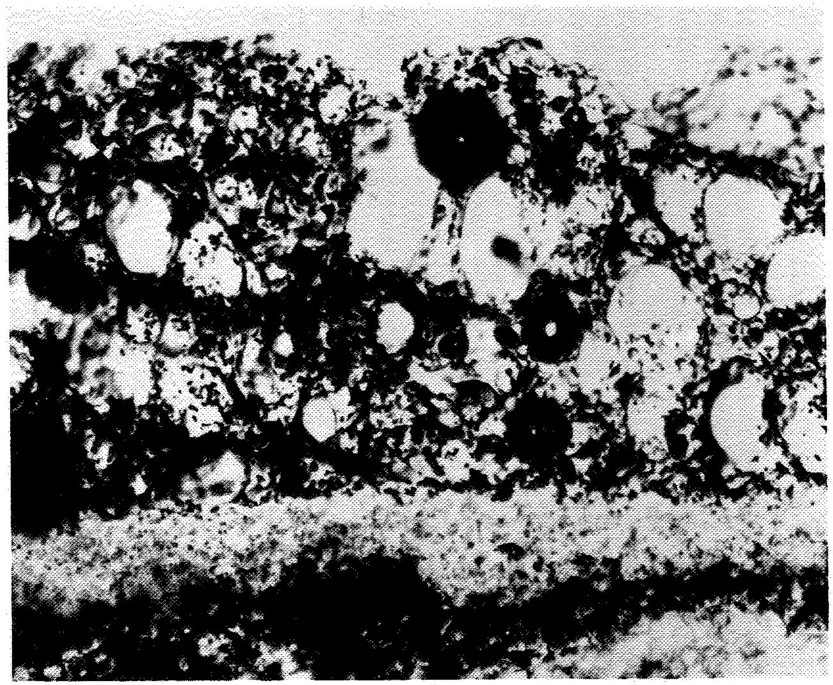
LMSC LI-1542 Coating
Cross-section, Optical Thin-section

As Received



100 μm

10 Cycles to 1250°C



100 μm

Figure 25

LMSC LI-1542 COATING

POROSITY DATA

(Figure 26)

These porosity data on LI-1542 coatings support the SEM and optical microscope data. After 1250°C cycling the porosity has increased approximately 100 percent. There is reasonably good agreement between the two methods indicating the porosity is all larger than 15 nm.

LMSC LI-1542 COATING

Porosity Data

Thermal Treatment	Porosity, % (H_2O method)	Porosity, % (Hg method)
As received	11.3	13.8
10 cycles, 1100°C	14.3	14.3
10 cycles, 1250°C	24.7	29.7

Figure 26

LMSC LI-1500 COATINGS

SIGNIFICANT CONCLUSIONS

(Figure 27)

The most important of the points summarized here is the large increase in porosity in the LI-1542 coatings.

LMSC LI-1500 Coatings

Significant Conclusions

1. LI-1525 shows a strong tendency to precipitate cristobalite during 10 cycles to 1250°C. LI-1542 much better in this respect.

2. Both LI-1525 and LI-1542 show considerable porosity in as-received condition.

3. 10 cycles to either 1100°C or 1250°C results in significant increase in porosity and dimensional instability for the LI-1542 coating.

4. Both mercury intrusion and water absorption porosity determinations support SEM data on porosity increase under cycling tests on LI-1542.

Figure 27

CONCLUSION

While these data are by no means complete, it is hoped that, together with results obtained by other investigators, they may help to provide the information necessary for a valid analysis of coatings for the various RSI materials.