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A METALLOGRAPHIC EVALUATION OF SOME COATED  
COLUMBIUM ALLOYS.

by

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SUMMARY:

The results of a metallographic study of two coated columbium shuttle candidate materials are presented. Optical and scanning electron microscopy examinations were conducted on coating R512E and VH109.

## I. Coated Columbian Alloys

INTRODUCTION:

Two types of coatings were available and were examined. They were R512E and VH109 and Table I summarizes the designations and compositions of the coatings and substrates.

TABLE I.

Coating and Substrate Compositions.		
Coating designation	R512E	VH109
Coating developed by	Sylvania Corning	Vac-Hyd
Coating nominal composition	Si-20Cr-20Fe	1st cycle; Si-20, Hf-65, Ta-15 2nd cycle; Si-70, Hf-20, Cr-5, Fe-5
Substrate Alloy	Cb 752	C129Y
Alloy developed by	Union Carbide	Wah Chang/Boeing
Nominal Composition	Cb-10W-2.52r	Cb-10W-10Hf-0.1Y

The coatings are typically applied as slurries of the nominal composition in a lacquer vehicle. The slurry is fused in a vacuum (inert gas may be used) at temperatures of around 2400<sup>o</sup>-2600<sup>o</sup>F. The coating fuses and the finished coating is generated by liquid-solid intermetallic diffusion. It is important to observe that once the coating is established any difference in thermal expansion coefficient between the coating and substrate will lead to the generation of stress in both coating and substrate. The situation is complicated by the variation

in composition (and hence thermal expansion coefficient) across the coating thickness arising from the interdiffusion process.

One aim of the coating developer is to obtain a coating which matches as closely as possible the expansion coefficient of the substrate. As is evident in later photographs the as-received coatings exhibit cracks and this is evidence that the coating expansion coefficient is slightly greater than the substrate alloy. The cracks are also evidence of the brittleness of the coating and microhardness results, given later, confirm that the coating is very hard.

It has been observed that the coatings usually fail at edges or at defects whose exact nature is unknown.

During exposure at anticipated service temperatures, ie up to around 2400<sup>o</sup>F, the coating is subject to oxidation. The nature of the oxidation process will depend upon the prevailing oxygen partial pressure as well as other variables. Cracks of thermal stress origin will tend to have closed up again at temperatures approaching the formation temperatures, so that the coating should tend to oxidize in a more or less straight forward fashion. Where, however, a crack or defect tends to expose the substrate, the coating is intended to be self-healing via the formation of a glassy phase.

In the work reported here optical metallography and electron microscopy (SEM and REM) studies were made of R512E and VH109 coatings in the as received, furnace cycled, and

furnace cycled, and arc-jet tested (R512E only) conditions.

SAMPLE PREPARATION:

In conducting optical metallography the first problem encountered and a severe one, is to prepare a polished section representative of the sample. It was found that mounting samples with a conventional mounting press lead to considerable cracking. The technique finally adopted was to wire together at least two identical samples with coated faces in contact, placing these between small pieces of glass reinforced circuit board and vacuum casting around these pieces an epoxy mounting compound loaded with polishing alumina. 1-um alumina in a volume ratio of about 1 alumina to 3 to 4 epoxy was used.

The reasoning behind the above is that R512E etches much more slowly than VH109 so the different coatings should not be placed in the same mount. To permit high magnification examination of the coating it must be polished flat and this is best accomplished by mounting samples face to face. The coating is sufficiently hard that the glass circuit board as well as the epoxy loaded alumina will polish away more rapidly than the coating inducing thereby a rounding of any coating which is not face to face with another coating. Vacuum casting ensures filling of small voids between the face to face specimens and also generally good contact between the epoxy and coating. Epoxy was used

because of its convenience and also because it could be formulated for an oven-bake cure which provided minimum shrinkage. This mounting procedure did not introduce cracks.

Polishing was performed on wet 180 through 600 grit, silicon carbide paper followed by vibratory polishing first with 15-um Diamond and finally with a slurry of 3-um Diamond, 1-um  $Al_2O_3$  and chrome oxide. The combination provided a good polish of the coating but left many scratches in the substrate columbium alloy. The vibratory polish was slow and at least an overnight period on the polisher was necessary.

An important detail of the rough polishing with silicon carbide papers is that contrary to normal practice it is important that all polishing be carried out in a direction parallel to the coating. The sample was not rotated between papers. This action minimizes the likelihood of small chunks of coating tearing out and scratching the specimen. The usual etches for columbium and its alloys acted very rapidly and vigorously on the coating and it did not prove possible to etch for simultaneous examination both the coating and its substrate. Instead, only the coating was etched, but only lightly, since the variation of composition across the coating made for varying rates of attack of the coating by the etchant. In particular the phase visible in the center of the VH109 coating was especially prone to rapid removal.

The etchant used was composed as follows:

HF 4ml

$HNO_3$  30ml

Lactic Acid 150ml

Optical metallography was performed under polarized light since it was observed that the grain structure of the coating could be discerned only with nearly fully crossed polarizer and analyzer. The etchant delineated second phase within the coating but did not contribute to contrast of the grains.

Cracks were visible in all polished sections, whether they were introduced by the polishing procedure or were originally present in the sample is not definitely known. It is suspected (without adequate proof) that the visible cracks were originally present. Some Microhardness traverses across the coatings and substrate at 200 gram load with a Knoop indenter were made on the polished sections. Some samples of coatings were examined by scanning electron microscopy (SEM). Some samples were examined in the natural state and some polished sections prepared as above were viewed. SEM samples were cemented to a specimen holder with conductive paint.

RESULTS AND DISCUSSION:

Representative optical metallography sections of R512E, and VH109, both as received, are shown respectively in Plates 1 and 2. R512E is shown etched in Plate 1A and in Plate 1B it is shown through deeply crossed polarizer/analyzer and essentially unetched. These do not show the same field but nonetheless the difference between the two is quite striking. The polarized light micrograph 1B, reveals the grain structure of the coating and reveals generally a very fine grain size next to the substrate (bottom) and a large grain size near the outer surface (top). Different layers are visible but fine cracks are not readily discerned. The etched sample shows cracks readily and also shows different composition layers and apparent second phase. Cracks in the coating do not follow the grain boundaries; they usually do not penetrate the substrate but 1B is an illustration of a crack which has penetrated the substrate. The cracks are usually wider at the outer surface than at the substrate; this and other characteristics generally suggest that they were induced by thermal (tensile) stresses set-up during cooling from the formation temperature. Cracks are also seen in optical and SEM micrographs of the surface (see for example Plate 4 & 5).



Plate 2 shows VH109; 2A and 2B are of the same area, etched, in bright field and in polarized light. The etchant has eaten away second phase leaving small pits which appear as very bright areas under polarized light. 2C is another field under polarized light, this sample etched very lightly relative to 2A.

Plate 3 shows dark field micrographs of R512E and VH109. Although both 3A and 3B have surface cracks they are not readily visible in these photomicrographs and generally these plates illustrate the desirability of higher magnifications such as are possible via SEM.

Plate 4 shows SEM micrographs of as received R512E and Plate 5 shows SEM micrographs of as received VH109. These micrographs illustrate the superior rendition of surface detail that the SEM makes possible. Both coatings are seen to be cracked, the variation in texture of the surface from point to point is clearly visible particularly in Plate 4 of R512E at 500X. The cause of this texture is unknown. Plate 4D, at 10,000X shows features suggesting grain boundaries. The diameter of these "grains" corresponds very roughly with the grain size one might estimate from polished cross sections. The crack visible in Plate 4 crosses these grains more or less randomly suggesting a crack which opened up under a tensile stress.

The surface structure of VH109 shown in Plate 5 is seen to be different in detail and is presumably due to the different composition and method of application. Plates 6, 7 and 8 show optical metallography sections of coatings after cycling to elevated temperature. Plates 6 and 7 show R512E. Plate 6 is after furnace cycling, 5 times, in air to 2400<sup>o</sup>F and Plate 7 is sample R1 (Ecord), which has been arc-jet tested to a similar temperature. Plate 8 shows VH109 after furnace cycling. The polished sections show little change except that a columnar morphology may be deleterious if it offers easy crack paths through the coating. The reason for the development of the columnar structure is unknown.

SEM micrographs of the above samples are shown in Plate 9 (R512E, Furnace Cycled), Plate 10, (R512E, Arc-jet, tested) and Plate 11 (VH109, Furnace Cycled). All samples are very similar in appearance. Cracks are visible in both R512E and VH109. Whether the number of cracks per unit area is changed cannot be positively stated since this question was not investigated. Plate 10 (R512E, Arc-jet, tested) shows the appearance of an artificial defect which has been introduced by drilling a 0.01" hole through

the coating to the Cb 752 substrate. It may be seen that the defect has healed and is not greatly different in appearance from the surrounding coating. Unfortunately the SEM micrographs of Plate 10 were taken with a different instrument at different settings so that no photographs are available to properly compare the coating by appearance of R512E after furnace cycling as compared with Arc-jet testing. To the unaided eye there was little difference. Optical dark field micrographs, Plate 12 suggest a greater difference than was apparent. It is thought that a detailed and careful investigation will be necessary to ascertain what the differences really are. Since Arc-jet testing is slower and more expensive such a study may be worthwhile.

The metallographic studies were supplemented by microhardness measurements performed on the polished sections and by X-ray fluorescence scans of polished sections via the SEM X-ray spectrometer accessory.

The microhardness measurements were conducted with a 200g load and revealed that the coating is extremely hard. The Knoop indenter which was used caused cracks to appear at the indentations thereby inducing hardness numbers which are probably erroneously low. The microhardness tester could not load at less than 100g and even this load caused cracking. Some data obtained is presented in Table 2.

TABLE 2

Microhardness values, (KHN, 200g load) on polished Coating Sections

Specimen	Cb Substrate	Coating
R512E on Cb 752 as received	Average = 203	1000 to 1300
VH109 on Cb 129Y as received	220	600 to 1200
R512E on Cb 752 Furnace cycled	200	1100 to 1300
VH 109 on Cb 129Y Furnace cycled	210	1000 to 1200
R512E on Cb 752 Arc-jet, tested	196	1100 to 1200

It can be seen that the coating is very hard and will be therefore rather brittle. The hardness is not affected by the exposure to furnace cycling or arc-jet testing. There are probably variations in hardness across the thickness associated with the variation in composition but cracking of the test indentations prevented a quantitative assessment.

X-ray spectrometer scans across the polished coating sections were conducted in the SEM. These were somewhat cursory and revealed more or less what might be anticipated

given the chemical composition of the coating and the thermal treatment. Examination of the charts from the SEM X-ray spectrometer did not lead to any insight concerning the behaviour of the coatings so they are not discussed further. A more careful study using the capability of the SEM would no doubt be capable of revealing differences between the as received and cycled coatings.

This opinion is significant insofar as the metallographic results generally do not show any difference between the furnace cycled and arc-jet tested samples. Even the differences between as received and furnace-cycled samples are very small as revealed by metallographic sections. The SEM micrographs show obvious differences between the as received and furnace cycled samples (including the arc-jet tested sample). Hence if furnace cycling is to be considered as a quicker and more convenient way of testing coatings than arc-jet testing it will be important to characterize more carefully what differences do exist between specimens tested via the two methods. It seems likely the SEM work with X-ray scans will be an approach which will work.

CONCLUSIONS:

- 1). Metallography of coated columbium is difficult. Great care is necessary to avoid the introduction of cracks during specimen preparation.
- 2). Scanning electron microscopy provides a superior method of examination of surface features.
- 3). Changes in microstructure occur as a result of simulated service tests.
- 4). More X-ray spectrometer work will be needed if it is desired to elucidate the compositional changes which occur in the coating during testing.

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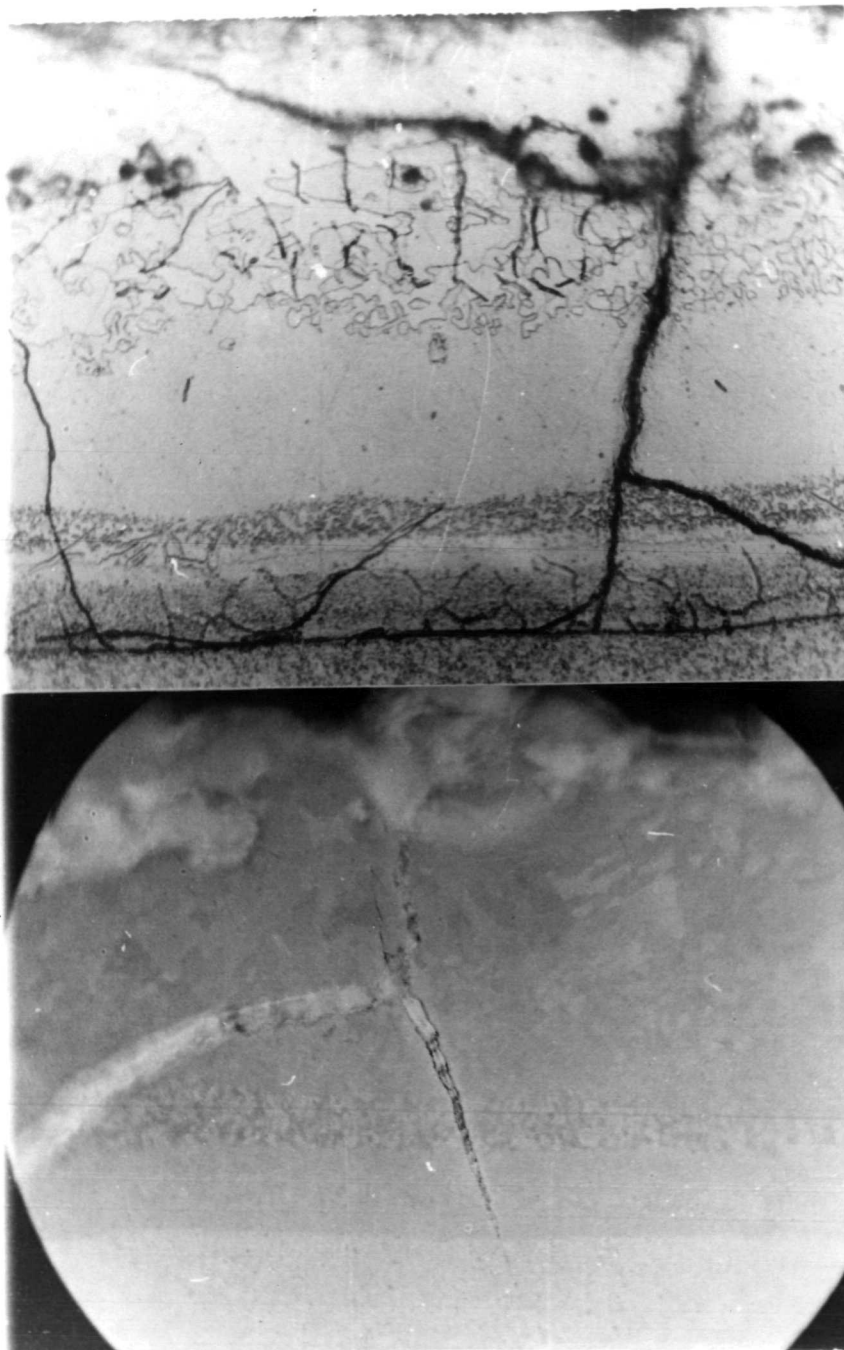


Plate 1A) R512E coating deeply etched bright field substrate at bottom. Note cracks and evidence of differing composition across coating. 425X B) R512E, etched, crossed polarizer/analyzer. Grains structure of coating is visible. 425X



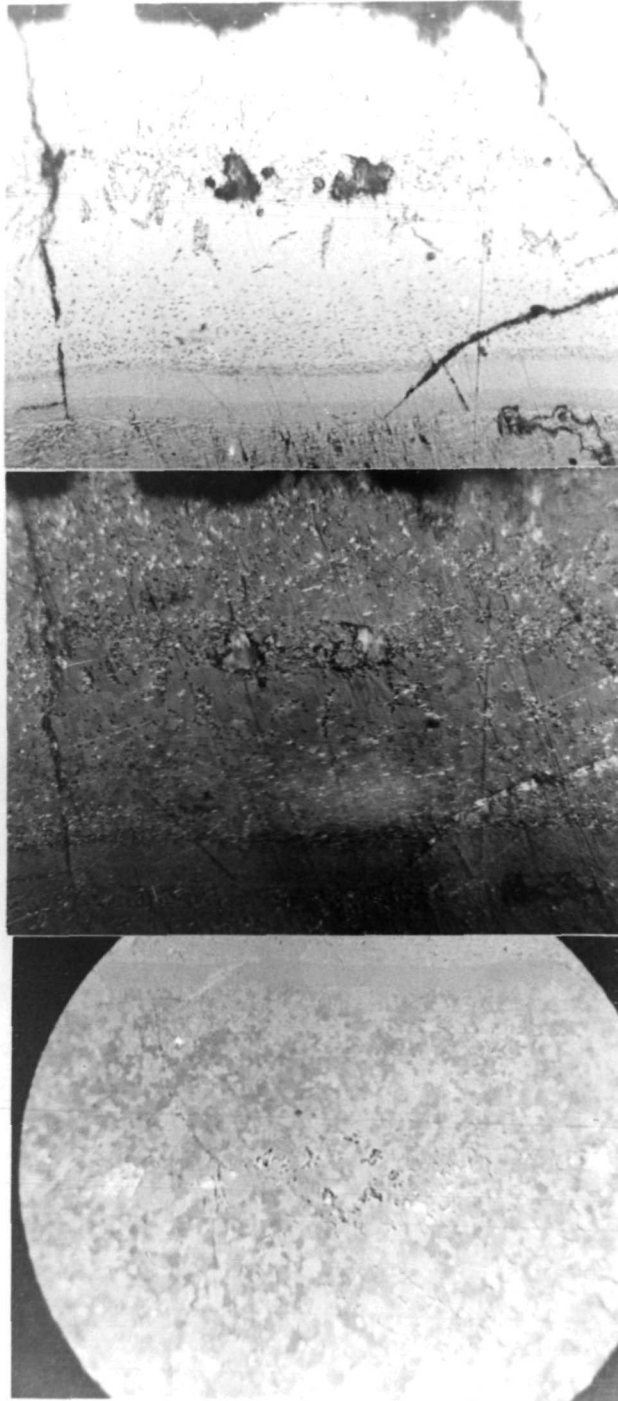


Plate 2 A & B (top & middle) show same area. VH109, bright field & polarized light respectively. C shows another area, polarized light. All at 425X.

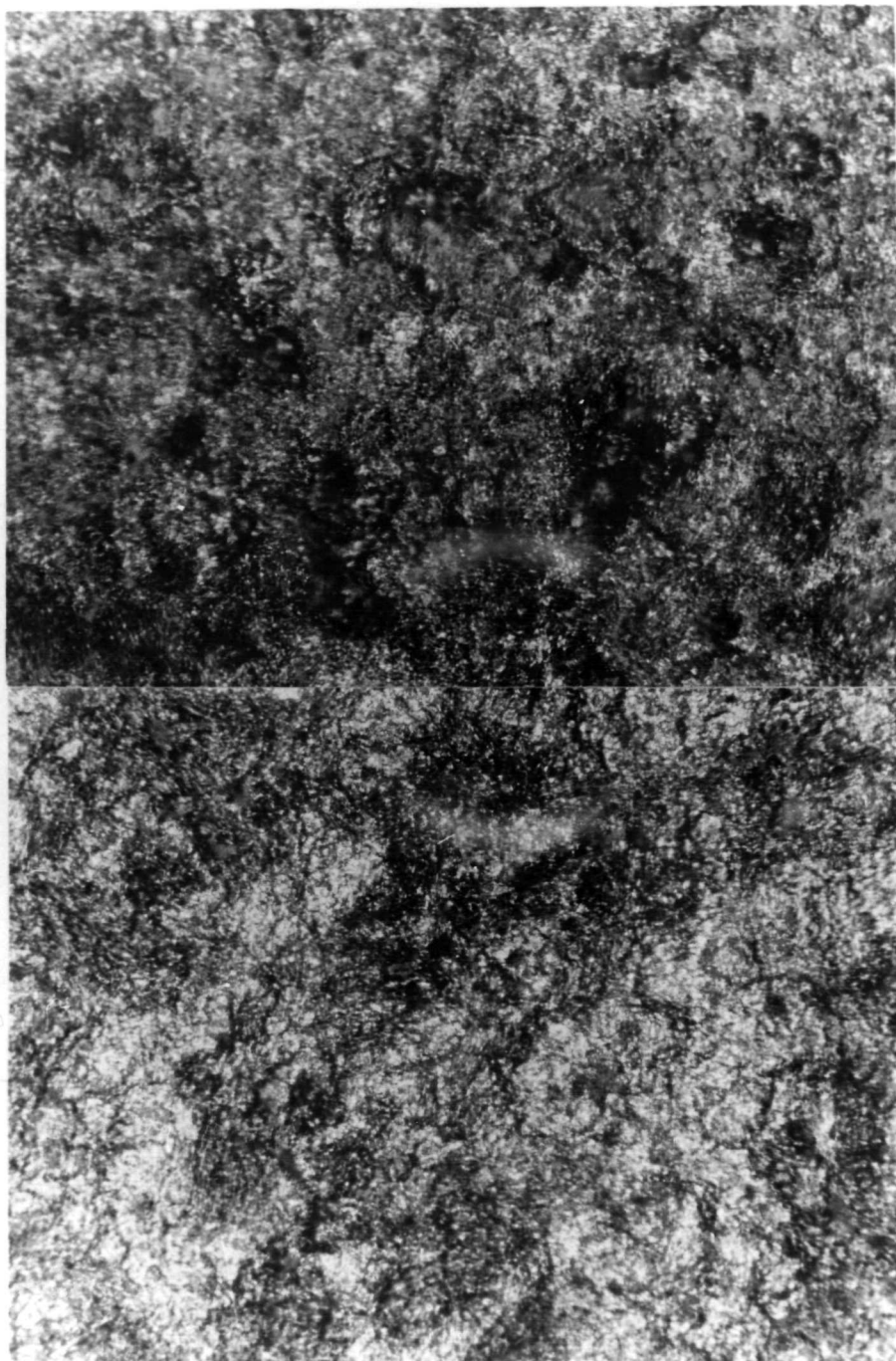


Plate 3 A) Bottom, dark field optical micrograph of outer surface of R512E at 90x. B) Top, same but VH109. Both show surface cracks.

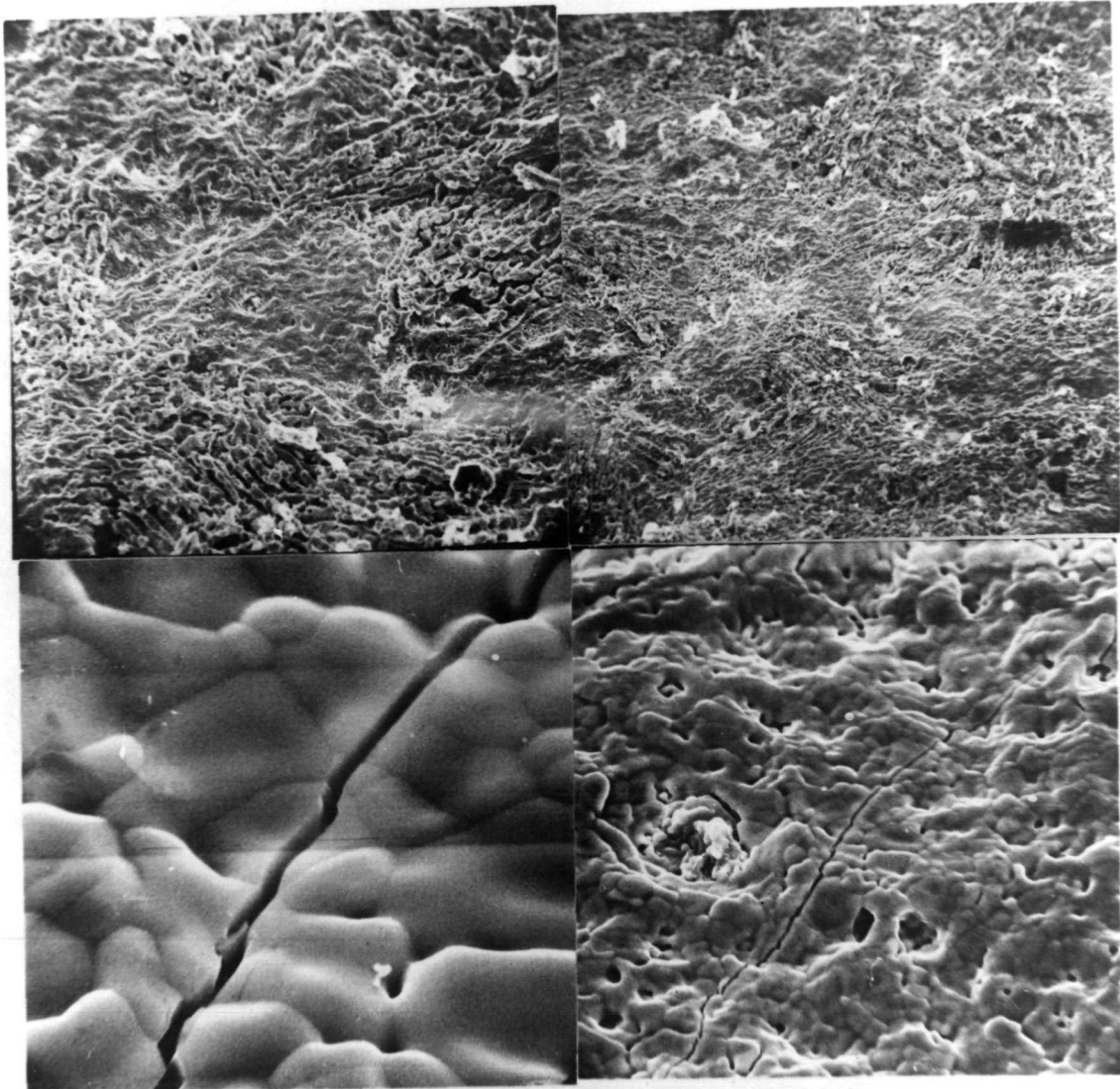


Plate 4 SEM micrographs of R512E. All are of same area. Upper right 200x, upper left 500x, lower right 2000x, lower left 10,000x. Note surface cracks and varying texture in 200x and 500x photos. Compare with Plate 3A. Features in 10,000x photo are thought to represent grains.

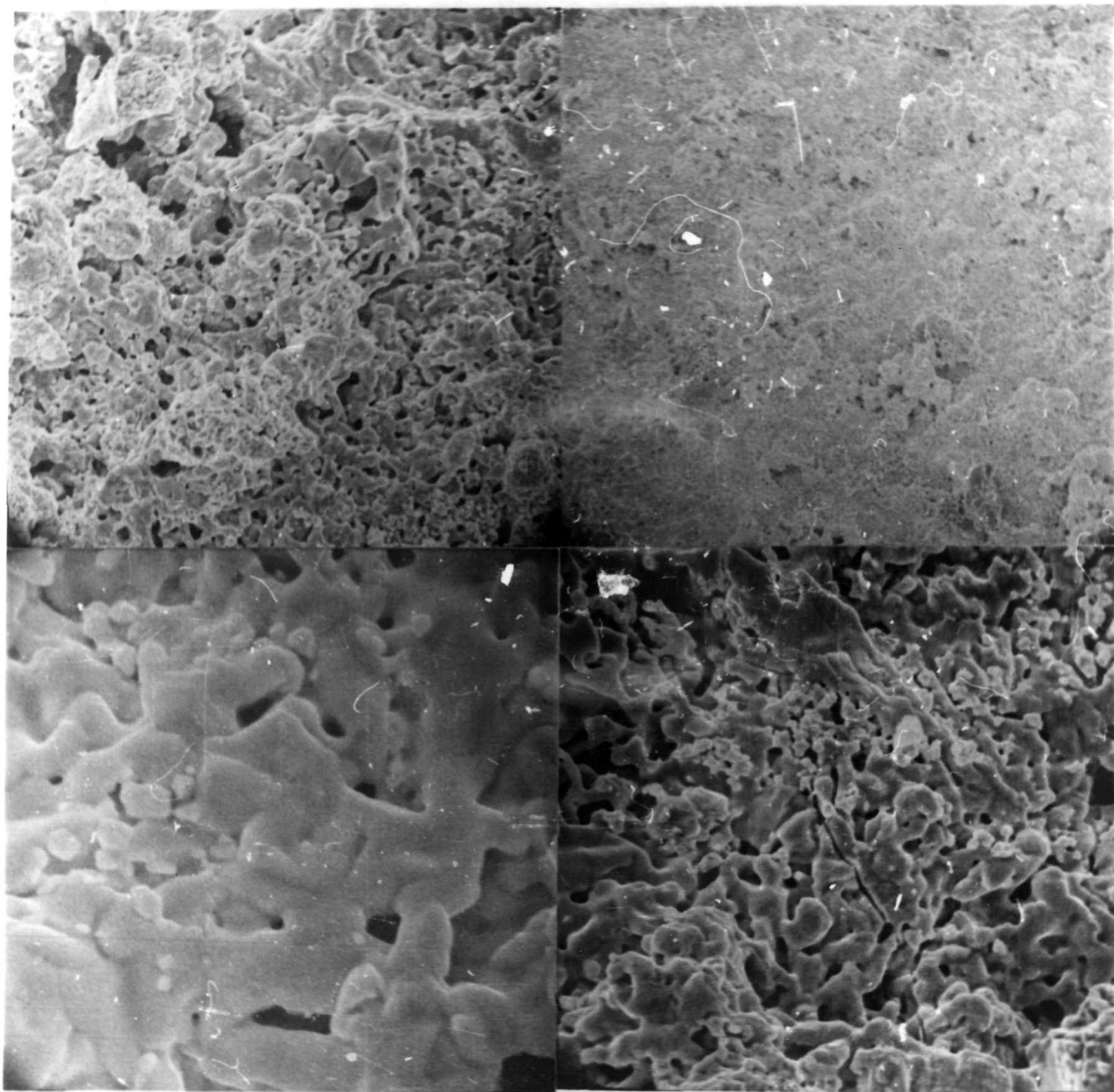


Plate 5 SEM micrographs of VH109. All are of same area. Upper right 200x, upper left 1000x, lower right 2000x, lower left 5000x. Surface cracks are also present here.

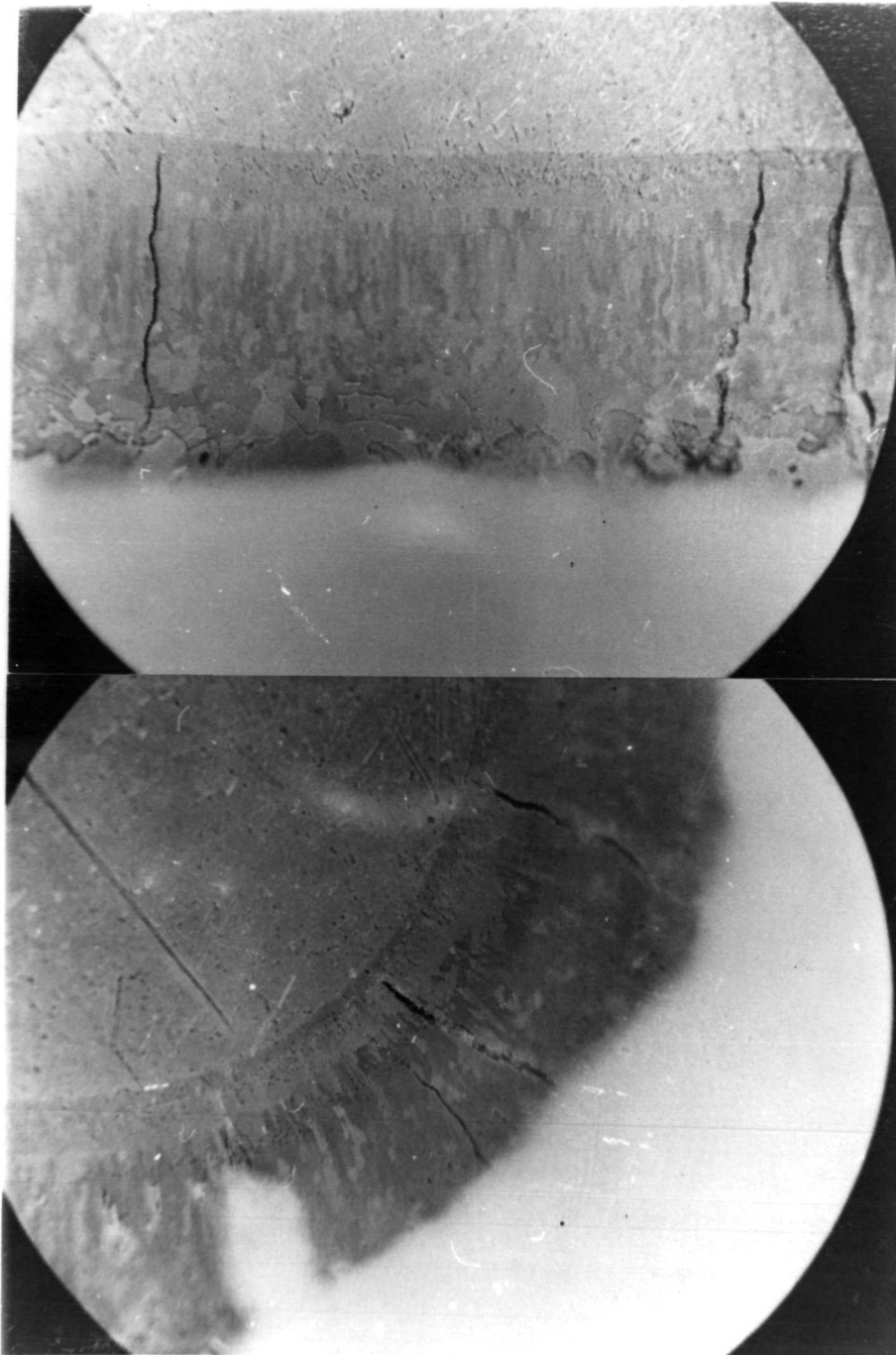


Plate 6 R512E after furnace cycling, 5 times, in air, to 2400<sup>o</sup>F. The coating has developed a columnar morphology but no other changes are discernible. Polarized light, 425x.

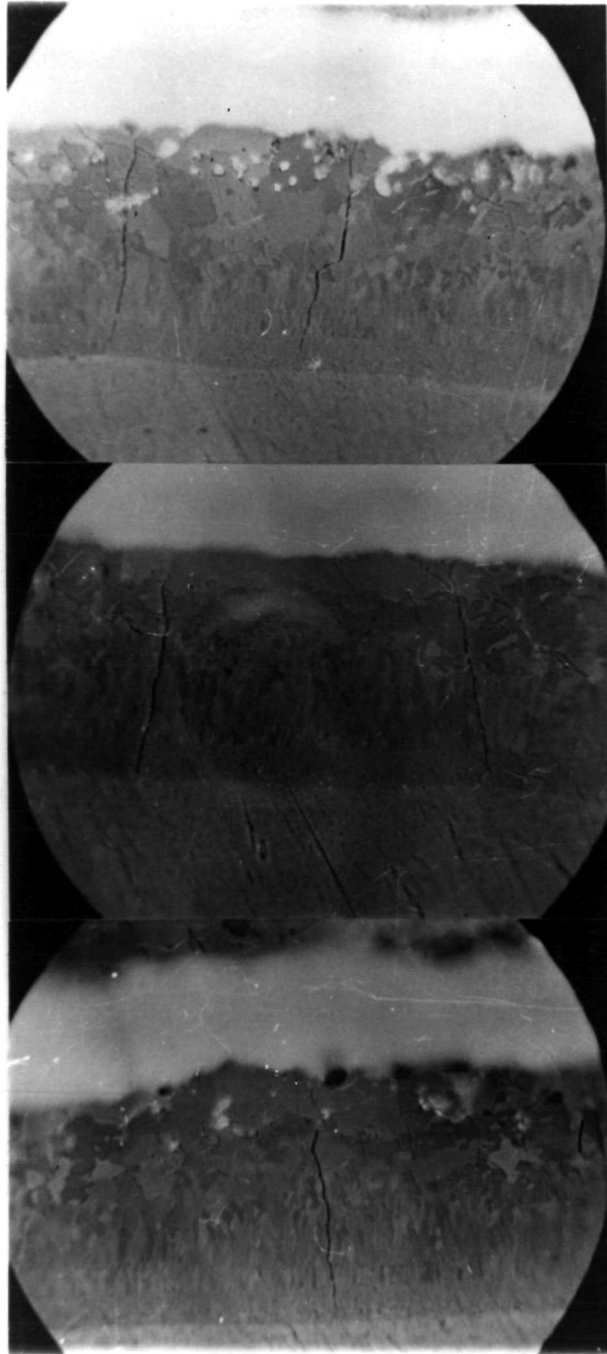


Plate 7 R512E after 5 cycles of arc-jet testing to nominal 2400<sup>o</sup>F. Columnar coating morphology. Similar to Plate 6. Polarized light, 425x.





Plate 8 VH109 after furnace cycling, 5 times, in air to 2400° F. Coating has developed columnar morphology. Top & center photo show same area, bright field and polarized light respectively. 425X (bottom), 660x (center & top).



Plate 9 SEM micrographs of R512E, furnace cycled in air, 5 times to 2400° F. All same area. Upper right 200x, upper left 500x, lower right 1000x, lower left 2000x.



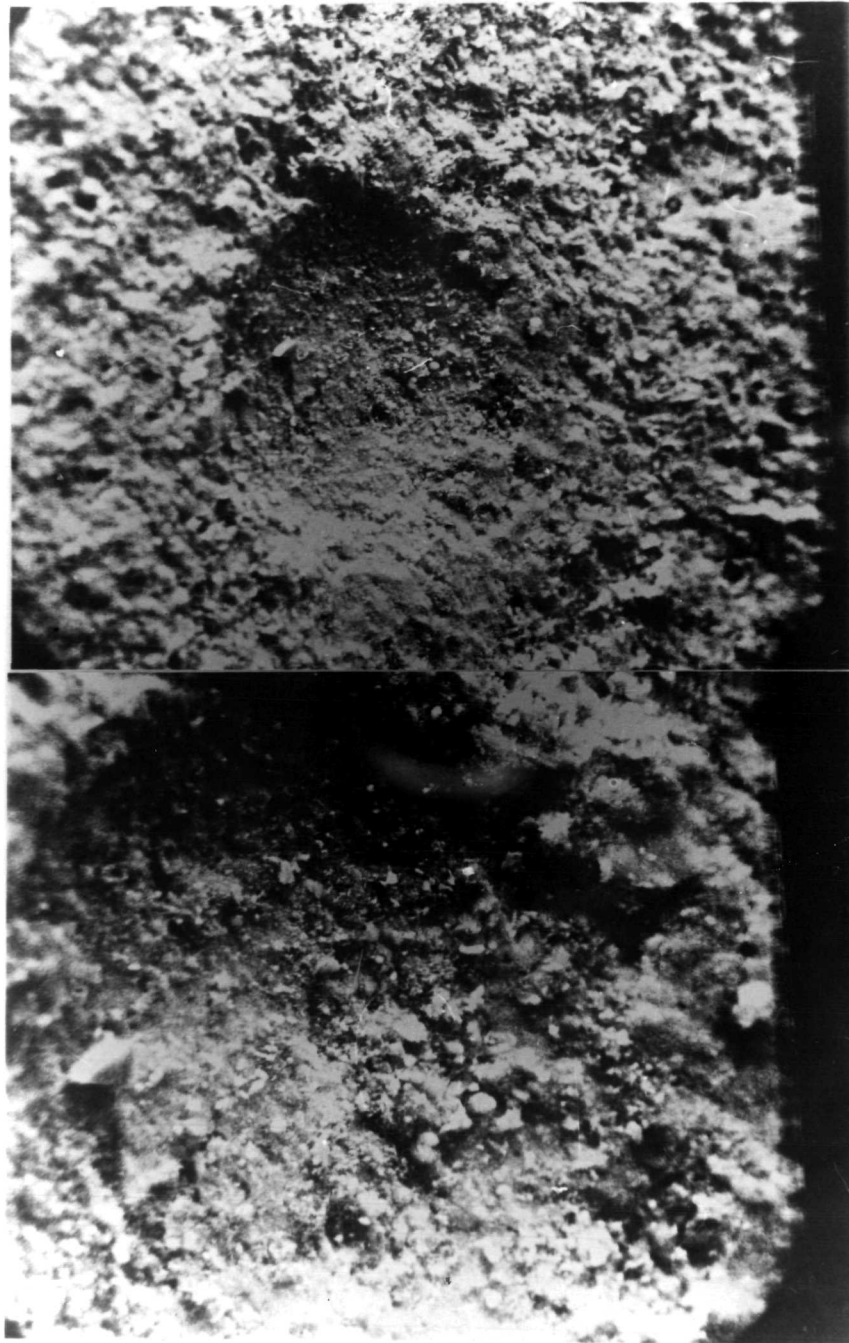


Plate 10 R512E after arc-jet testing (see plate 12)  
This is an SEM micrograph of a synthetic defect (a 0.01"  
hole to the substrate) after testing. Upper 190x, lower  
440x.

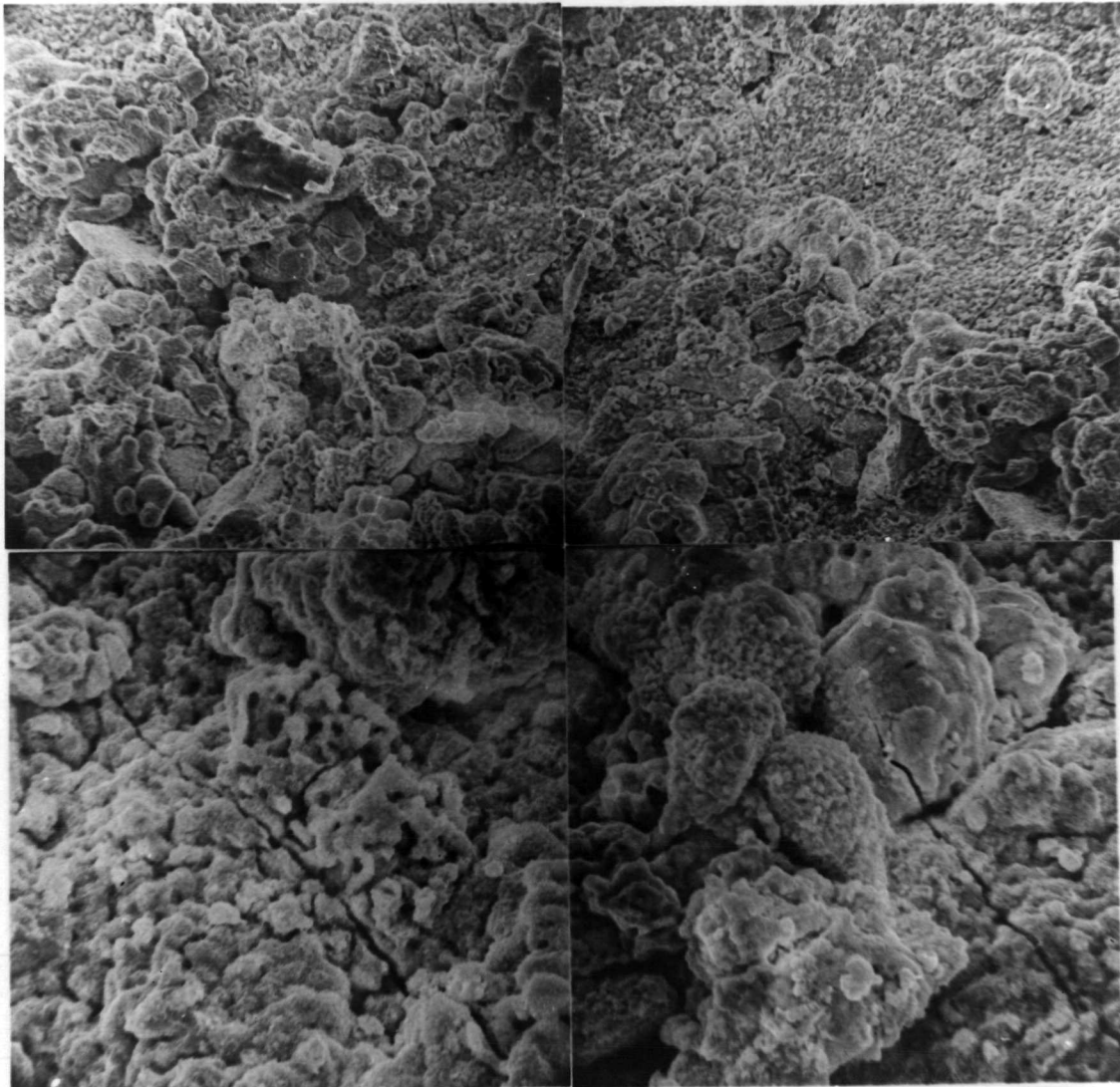


Plate 11 SEM micrographs of VH109 after furnace cycling, 5 times, in air to 2400 F. All same area. Upper left & right, 500x. Lower left & right, 2000x.

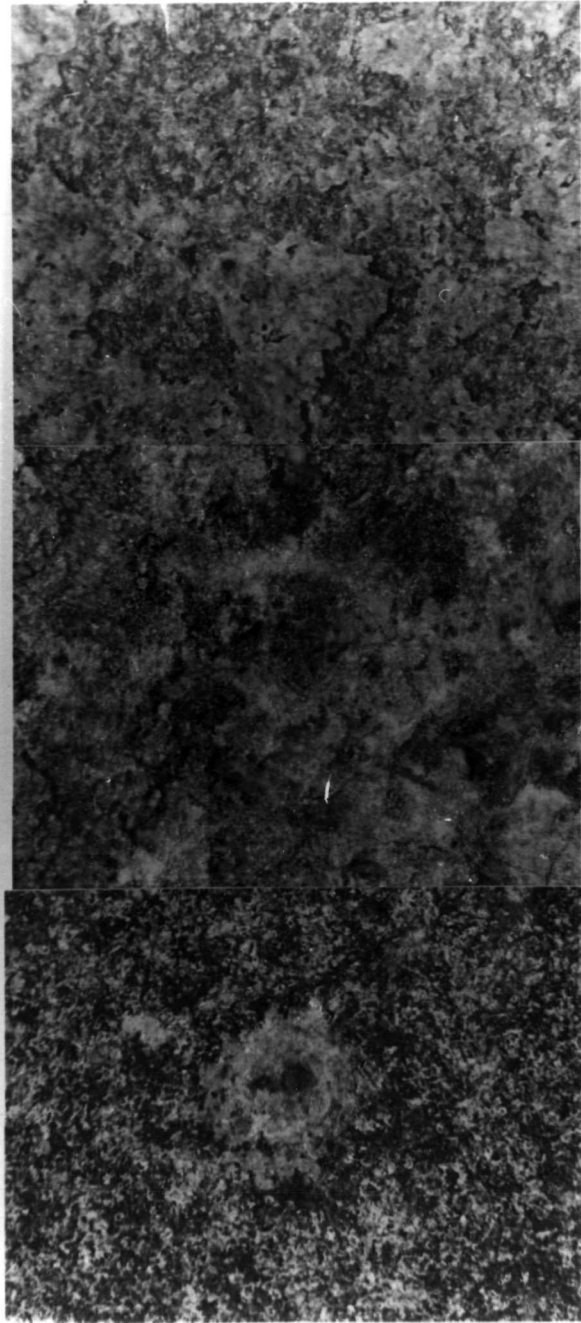


Plate 12 Optical dark field micrographs. Top, 90x, R512E after furnace cycling. Center, 90x, VH109 after furnace cycling. Bottom, 75x, R512E arc-jet tested, synthetic defect in center.

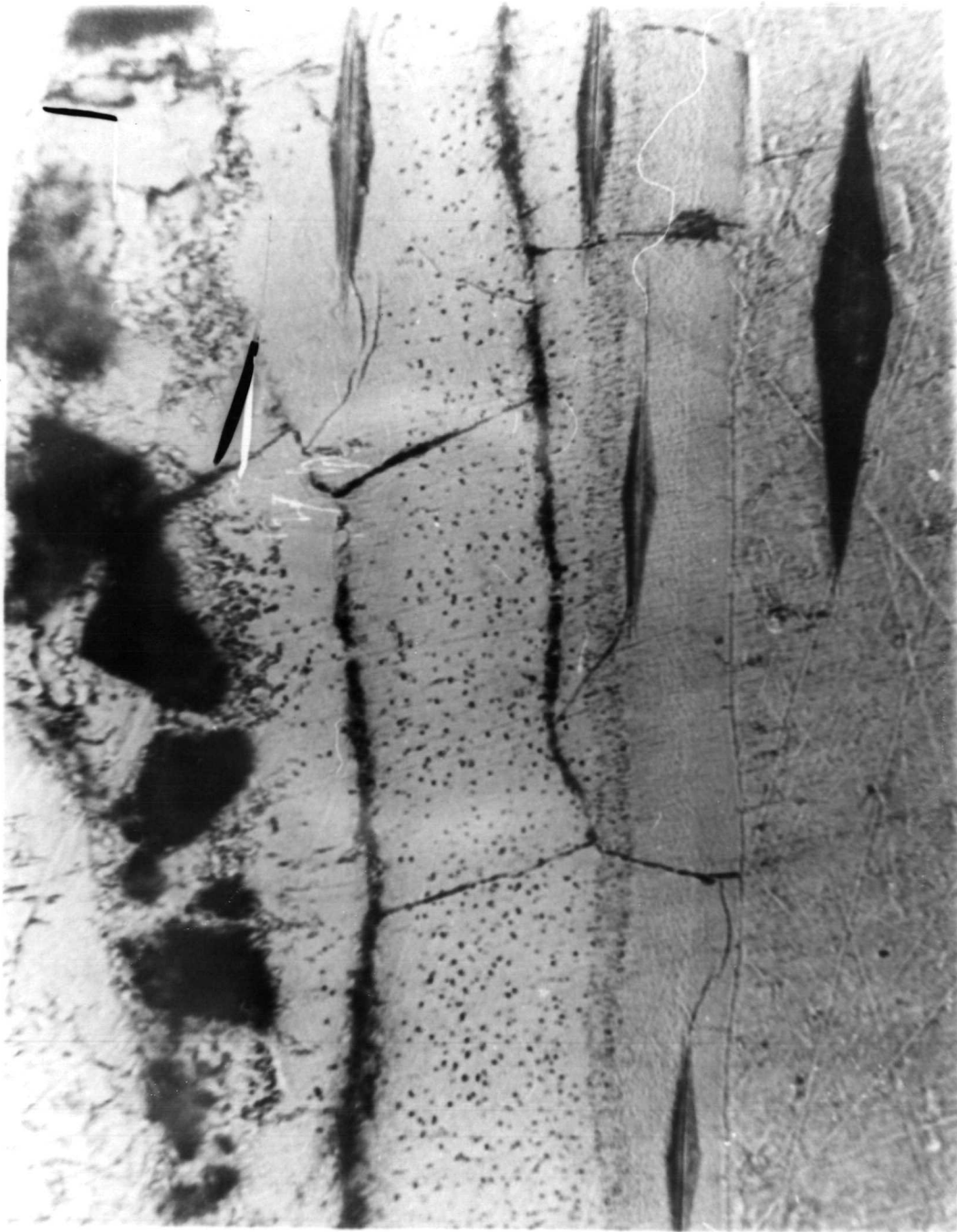


Plate 13 Microhardness indentations in R512E. Substrate at right. Note cracked indentations in coating. 425x (enlarged twice in reproduction)