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ELECTROPHORETIC DEPOSITION OF GRADATED OXIDATION RESISTANT COATINGS ON TANTALUM-10 TUNGSTEN ALLOY

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SUMMARY AND CONCLUSIONS

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Experimental equipment was successfully tested for the preparation of two-component electrophoretic coatings which are continuously gradated in composition over a thickness of 4-8 mils. A variety of intermetallic compounds and refractory oxides were screened as pellets and as coatings for potential use as gradated coatings for the protection of Ta-10W from oxidation at temperatures above 3000°F. Gradated coatings consisting of $MoSi_2$-CaO-stabilized zirconia and WSi_2-2%TiO_2/CaO-stabilized zirconia were chosen for application to test specimens. Tensile specimens, leading edge specimens, and coupons were coated with each of the chosen systems, and these were sent to NASA for evaluation.

Several problems remain unresolved with these and with similar coating systems and require further study. The most important of these are:

1. Identification of possible reactions which occur among the components of the coating systems upon exposure to high temperature air oxidation.
2. Choice of optimum combinations of intermetallic compounds and refractory oxides for gradated coatings.
3. Methods of obtaining maximum sintered density in the outer, refractory oxide portion of the coatings.
4. Investigation of the effects of coating thickness and composition gradient upon oxidation resistance.

Author

FOREWORD

This is the Final Report under NASA Contract NAS 1-3533, and covers the work performed during the period 1 January 1964 - 31 May 1965 on the application of electrophoretically deposited, gradated intermetallic compound-refractory oxide coatings to tantalum-10 tungsten alloy foil gage specimens.

This program was accomplished under the technical direction of Mr. Bland A. Stein and Mr. Eldon E. Mathauser of the National Aeronautics and Space Administration, Langley Research Center, Structural Materials Branch.

This report has been assigned Vitro Laboratories' internal number VL-2352-7-O.

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INTRODUCTION

The objective of this program was the development of equipment and techniques for producing a thin oxidation resistant coating for tantalum-10 tungsten alloy foil gage material for application at temperatures to 3500°F. The coating was to be applied by electrophoretic codeposition of intermetallic compound and refractory oxide materials to produce a deposit which was continuously gradated in composition from nearly pure intermetallic compound adjacent to the substrate to nearly pure refractory oxide at the coating surface.

A secondary objective of this program was the identification of two intermetallic compound-refractory oxide compositions to provide the required 3500°F capability.

Preliminary screening tests involving sintering and oxidation tests were carried out on several intermetallic-oxide combinations. The two coating systems which were selected, on the basis of these studies, for application to the Ta-10W specimens supplied by NASA were $MoSi_2$-(3.5% CaO stabilized-ZrO_2) and WSi_2-(ZrO_2-2% TiO_2).

Test specimens of the WSi_2-ZrO_2/TiO_2 system survived an average of 3 hours exposure to static air oxidation at 3000°F. When satisfactory coating and sintering procedures were established for each coating system, 22 coupons, 12 sheet tensile specimens, and 10 leading edge specimens were coated with each composition and delivered to NASA for evaluation.

ELECTROPHORETIC DEPOSITION EQUIPMENT FOR GRADATED COATINGS

When a D.C. potential is applied across two electrodes which dip into a dispersion of colloidal or near-colloidal size particles (i.e. 0.2-40 micron) suspended in a non-aqueous medium, the particles are observed to migrate to one of the electrodes where their charge is neutralized and they are deposited. This phenomenon, termed electrophoresis, was first observed in 1809 by Reuss[1*]. Some of the major commercial applications of this process include the deposition of thermionic and insulating materials on electron tube filaments, formation of rubber gloves by electrophoretic deposition of latex onto a mandrel and, more recently, the fabrication of aluminum-clad steel and the painting of steel furniture, partitioning and other components[2-8].

The theory of electrophoresis, which has been discussed by many authors[9-14] is a controversial subject which will be reviewed here only briefly. The most widely accepted theory, due to Stern[15], gives the mobility of the suspended particle (U) as a function of the applied field (E), zeta potential of the adsorbed double layer (z), and dielectric constant (D) and viscosity (n) of the fluid medium as follows:

$$u = {}^{zED}\!/_{4\pi\eta}$$

It will be noted that the mobility is independent of the particle size, shape, and composition so long as the zeta potential and suspending medium are constant. The zeta potential can be made to remain constant through the use of activating agents which are adsorbed uniformly upon the surface of all of the particles in the suspension. This technique is extremely important since mixtures of two or more materials, when dispersed, will deposit upon a substrate in exactly the same ratio that exists in the coating bath. Thus alloys, cermets, and mixed refractory coatings may be prepared by the electrophoretic process to yield deposits wherein the coating composition is indistinguishable from the same material prepared in bulk by conventional powder metallurgical or ceramic techniques.

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[*] Superscripts refer to literature sources listed in the Bibliography

In the electrophoretic process the coating materials are prepared in the form of a fine powder of about 10 micron average particle size. If more than one component is desired in the coating, the individual powders are either prealloyed or are weighed in the required proportion and blended. For the most common coating materials the powders are commercially available in -325 mesh size. If a finer particle size is desired, the powders are jet-milled or ball-milled in alundum, steel, or silicon carbide-lined jars. The powder mixture is then leached to remove impurities, and added to a mixture of isopropanol and nitromethane. The powders generally acquire a static surface charge during ball-milling, and a charge may also be induced on the particle surfaces by the addition of certain proprietary protein-like additives. The resulting dispersion is therefore stabilized by electrostatic repulsion of the charged particles. The dispersion concentration is generally maintained between 1 and 10 wt %, depending upon the coating rate desired.

The coating equipment consists of a stainless steel tank with an overflow at the top and an opening at the bottom. The dispersion is agitated by a recirculating pump whose exhaust is connected to the bottom of the coating tank. The tank serves as an inert electrode and the article to be coated is the second electrode. The electrodes are connected to a D.C. regulated power supply and an external timer which cuts off the power after a set interval. Coating is accomplished at 20-200 V.D.C. and about 5-20 ma. for 0.25-5 minutes depending upon the coating thickness which is desired. After coating, the article is dried in air or under an infra-red lamp and, if the point of electrode contact must also be coated, this area is manually "patched" by applying some of the powdered material of the dispersion with a rounded tool. The coating at this point is about 40% dense and has considerable green strength, however, it is not yet bonded to the substrate or fully densified. To increase the strength of the green coating, the article may then be hydrostatically pressed at 10,000-100,000 psi. This step is required only when the coating must be shipped in the green state or when difficult-to-sinter chemistries are involved. Following hydrostatic pressing the coating is sintered or hot-pressed to increase its density and to bond it to the substrate. It is here that the most variability is encountered in the process. The sintering time, temperature, and atmosphere must be adjusted to the properties of the coating-substrate system. Following sintering, the coating is evaluated by microscopic inspection of the surface and of sections through the specimen, and physical and chemical measurements such as density, porosity, mechanical properties, chemical uniformity, and oxidation or abrasion resistance are also easily obtainable.

Critical variables in the deposition step, which control the uniformity, adherence, and reliability of the coating are:

1. Surface cleanliness and finish of the substrate.
2. Particle size and size distribution of the dispersed powder.
3. Maintenance of the zein and electrolyte concentrations at the proper levels.
4. Purity of the powder.
5. Electrode geometry and deposition voltage.

In the present program, the normal electrophoretic deposition equipment described above was modified so as to permit the deposition of a 2-component intermetallic compound-refractory oxide coating in which the composition of the coating was continuously gradated from a high concentration of the intermetallic adjacent to the substrate to a high concentration of refractory oxide at the outer surface. The gradation in composition was investigated for two reasons; to provide a mechanism for bonding the stable refractory oxide to the substrate, and to overcome the mismatch of coefficients of thermal expansion between the Ta-10W substrate and the oxide outer surface. Heretofore, such gradation in a coating has only been approached by plasma spraying a series of layers of varying composition[16]. A laminar structure of this type, however, would be mechanically weaker than a homogeneously gradated coating.

The simplest method of preparing a gradated oxide-intermetallic compound coating by electrophoretic deposition is to fill a coating tank containing an overflow with a dispersion of the intermetallic compound, and to pump a second dispersion of a refractory oxide into the tank during the application of the coating voltage to the sample. There are two major problems with this system:

1. A large volume of the oxide dispersion is required, and the mixed dispersions must be discarded after each experiment.

2. Assuming perfect mixing of the two dispersions, the concentration of the intermetallic compound in the tank decreases exponentially with time. Control of the concentration gradient in the coating is therefore difficult.

To minimize the volume of dispersion which is required and to obtain positive control of the concentration of the two components during the coating cycle, a special pumping system and a continuous flow coating vessel were designed. The system, shown in Figure 1, consists of two Sigmamotor Type T-8 tubing pumps driven by a 1/2 hp, 1800 rpm motor which is coupled to the pumps through a Vickers variable speed reducer and two variable speed drives connected in opposition. The maximum pumping speed of the tubing pumps is set by the output rpm of the Vickers control. The function of the two variable speed drives is to vary the speed of one pump from 5%-100% of the maximum while the other pump operates between 100% and 5% of the maximum. The equipment was designed and purchased under Vitro's in-house research program.

In the system described above the coating voltage is held constant and the coating time is adjusted by means of the variable speed drives. To insure that a uniform gradation is obtained in the system it is necessary that the coating rate of the two dispersions be approximately equal. The coating rate, in turn, is governed primarily by the concentration of the two dispersions, and is also affected by the particle size distribution of the powders and their surface adsorbing properties.

A calibration curve for the variation in composition of the pump effluents as a function of the setting of the control on the Graham variable speed drive was determined by pumping the fluid used in a standard electrophoretic bath with no solids present. The curve is shown in Figure 2. The composition vs. pump drive setting curve was nearly linear over the range of the control, and the slope of the curve was found to be invariant at input pumping speeds ranging from 210-840 rpm. The average total volumetric flowrate at 210 input rpm was 15± 3 ml/min; the variation of 3 ml/min occurring as the setting on the Graham drive was moved above or below the center position. This variation was probably due to small differences between the pumping rates of the Sigmamotor tubing pumps. As the input rpm to the tubing pumps was increased from 210-840 rpm, the total flowrate increased from 15 to 75 ml/min.

Studies were also carried out to determine the effect of solids concentration upon the coating rate of the various intermetallic compounds and oxides. Before the dispersions were prepared, a sieve analysis was run on 1 gram of a typical oxide ($CaZrO_3$) and intermetallic compound ($MoSi_2$) to check the approximate particle size distributions. The analyses were performed with a standard 325 mesh sieve and with two extremely fine-mesh photoetched screens obtained from the Buckbee-Mears Company. The results indicated that both powders have approximately the same distribution.

Screen Analysis of 1 Gram of $MoSi_2$ and $CaZrO_3$ Powder

	$MoSi_2$	$CaZrO_3$
% -325 mesh	0	0
% on 8-12 micron screen	25	35
% on 3-7 micron screen	50	49
% through 3-7 micron screen	6	0
% recovery	81	84

To prepare uniformly gradated coatings from two dispersions of different compounds at the same concentration it is necessary that the coating rates of the individual dispersions be equal or nearly equal. Accordingly, the coating rates of dispersions containing 1 wt.% of $90ZrB_2$-$10MoSi_2$, $MoSi_2$, WSi_2, 8% Y_2O_3-stabilized ZrO_2, 3.5% CaO-stabilized ZrO_2, $SrZrO_3$, and $CaZrO_3$ were investigated. The dispersions were prepared as follows:

-325 mesh solids	8.5 grams
60% isopropanol-40% nitromethane	850 ml
Zein binder solution	6 ml
Electrolyte solution	0.5 ml

Steel panels were coated from these dispersions at 200 and 300 volts for periods of 1/4, 1/2, 1, 2, 3, and 4 minutes, and the coating thickness and weight increase was recorded as a function of time. The results, shown in Figures 3 and 4 indicated that the coating rates of the $MoSi_2$ and calcia-stabilized zirconia were lower than those of the other materials. The curves for yttria-stabilized zirconia and $90ZrB_2$-$10MoSi_2$ indicate that these dispersions can be made to coat at the same rate at some potential intermediate between 200 and 300 VDC.

Since the principal factor which affects the coating rate is the particle size distribution of the dispersion, a sedimentation experiment was performed on several of the coating materials by the procedure reported by Skinner and Riley[17]. A weighed quantity of nominal -325 mesh powder was slurried in distilled water and poured carefully into the top of a 34 inch high column of deionized water. The slurry was allowed to sediment for 22 minutes, then the material which had settled to the bottom was removed and recycled for a second 22-minute period through an identical column. The coarse and fine fractions were then recovered, dried, and weighed. According to Stokes' Law, the 22-minute sedimentation time will remove all particles larger than 15 microns in diameter, assuming an average particle density of 6 g/cc. The pertinent equation for the time of fall (t), of spherical powder of radius r and density d_1, through a column of liquid of density d_2, height h, and viscosity n, under the gravitational acceleration g is:

$$t = 9hn / 2gr^2 (d_1 - d_2)$$

The results of the sedimentation trials are summarized in Table 1 together with data obtained on several of the same materials after milling at 150 rpm under isopropanol in a steel mill containing several steel spheres for six or forty-eight hours. The milled materials were evaporated to dryness, leached with 250 ml of 50% HCl to remove metallic contaminants, and then washed and dried before use.

The wide variation in the particle size distribution of the nominal -325 mesh powders is evident from the data of Table 1 and, as reported in a later section, had a serious effect upon the sinterability of the coatings. Based upon these results, the remaining oxides and intermetallics were milled to a finer average particle size.

SCREENING OF INTERMETALLIC-REFRACTORY OXIDE COMBINATIONS

A number of intermetallic-refractory oxide combinations were investigated for the purpose of selecting two systems which appeared promising as oxidation-resistant coatings for the Ta-10W specimens.

Physical Property and Analytical Data for the Substrate and Coating Materials. - The physical property data of interest in this program for the Ta-10W substrate and the coating materials to be studied are listed in Table 2.

The sources and forms of the commercially available coating materials are listed in Table 3. The $TaAl_3$ was not available and was synthesized from the elements.

Analytical data for the various intermetallic compounds and refractory oxides used in this program are included in Tables 4 through 8.

Two sources of WSi_2 were used in this program. Source 'A' material was used in the early experimental work and the source 'B' material was purchased during the latter part of the program and was used for the preparation of the final samples for NASA. A spectrographic analysis of the source 'A' WSi_2 is given in Table 8. Analysis of source 'B' material was as follows:

% Tungsten	76.0 %
% Silicon	23.4 %
% Carbon	0.12%
% Iron (Fe)	0.15%
% Oxygen	0.20%

Sintering Studies of Pure Oxides, Intermetallic Compounds and Composite Systems. - To determine the approximate temperature range required to sinter the gradated coatings to be prepared in the program, sintering trials were conducted on pure oxide and intermetallic compounds in the form of pressed discs. Before preparing the discs, all materials were ballmilled to 100% -325 mesh size in a chrome-manganese steel mill, and the resulting powders were leached in dilute hydrochloric acid, washed, and dried to remove metallic contaminants. The powders were then pressed in a steel die at 20,000 psi to 0.5 in. diameter discs, and these samples were sintered under various conditions. Following sintering, the apparent density was determined by weighing in air and in water. The sintering and density data are given in Table 9. The samples were then sectioned, mounted, polished, and photographed. At 1400°C in argon all of the intermetallic compounds except Ta_2Be_{17} could be sintered to apparent densities higher than 80% of theoretical in one hour. In the oxide systems only $SrZrO_3$ reached a reasonable density under these conditions. Calcium zirconate could be sintered to high apparent density at 1700°C for 45 minutes in argon, and an apparent density of 89% was attained with yttria-stabilized zirconia when this material was vacuum sintered at 1900°C. The calcia-stabilized zirconia was more refractory, and yielded an apparent density of only 74% after 45 minutes in argon at 1700°C.

Photomicrographs of cross sections through sintered specimens of $SrZrO_3$, $CaZrO_3$, and 8%Y_2O_3-stabilized zirconia are shown in Figures 5 and 6.

Sintering of Oxide-Intermetallic Powder Mixtures. - To determine the behavior of the oxide-intermetallic systems when in contact, powder blends containing 50wt% of a refractory oxide and an intermetallic compound were prepared. The mixed powders were pressed in a steel die to 0.5 in. diameter discs which were sintered in argon at 1700°C for 30 minutes. The immersion density of the samples was determined and compared to the theoretical value calculated on the assumption that no new phases were formed from the two components. The results are listed in Table 10. The sinterability of the mixtures paralleled that of the pure compounds. The calcia-stabilized zirconia yielded the lowest densities when combined with the various intermetallic compounds, and the tantalum beryllide gave the lowest density of all the intermetallics when combined with the various oxides. The best results, under these sintering conditions were obtained with combinations of $CaZrO_3$ or $SrZrO_3$ and the various silicide compounds. Photomicrographs of composites of $SrZrO_3$ with $TaSi_2$ and $90ZrB_2$-$10MoSi_2$, and of $CaZrO_3$ plus $TaSi_2$ are shown in Figures 7 and 8. The structures appear to be coarse dispersions of the intermetallic compound in a sintered matrix of oxide with no evidence of interaction between the two phases.

Additional work was carried out on the sintering of calcia-stabilized and yttria-stabilized zirconia, alone and in combination with various intermetallic compounds. These systems required further study since, as shown in Table 10 the zirconias were the most difficult of the oxides to sinter to high density at temperatures below 1900°C. In addition previous work on the pure intermetallic compounds showed that synthetic Ta_2Be_{17} could not be sintered to a dense body in 30 minutes at 1400°C. However, when the time at 1400°C was extended to 2 hours and a commercial powder was used, a density of 93% of theory was obtained.

The results of the additional sintering experiments on a variety of materials are summarized in Table 11. The last column of the table refers to the figure number of a photomicrograph of the sample which will be found in subsequent pages of this report.

Based on the data obtained, yttria-stabilized zirconia, calcium zirconate, and strontium zirconate in combination with any of the intermetallic compounds appeared to be the most practicable systems for further study as candidate coating systems.

Studies of Bonding Between Oxides and Intermetallic Compounds. - To study the bonding which occurs between oxide and intermetallic phases, and to explore the possibility of interfacial reactions or eutectic formation, a series of experiments were performed in which 3-layer composites were pressed and sintered together and then examined microscopically. The composites consisted of a sandwich of a 50:50 mixture of oxide and intermetallic between a layer of pure oxide and a layer of pure intermetallic. To prepare the composites, the three types of powders were poured in sequence into a 3/4 in. diameter steel die and unidirectionally pressed at 21,600 psi. The compact was placed in a rubber sheath which was evacuated to remove entrapped gases and was then isostatically pressed at 50,000 psi. The 3-layer discs were finally sintered at 1700°C for 30 minutes under reduced pressure. The compounds selected for study were those which yielded the highest sintered density in earlier work on 50:50 powder mixtures; i.e., $SrZrO_3$-$MoSi_2$, $SrZrO_3$-$ZrB_2/MoSi_2$, $SrZrO_3$-$TaAl_3$, $CaZrO_3$-$MoSi_2$, and $CaZrO_3$-$TaSi_2$. Typical microstructures of these composites are shown in Figures 13through 15. Several common features can be seen in the metallographs. The bonding between the 50:50 mixtures and the oxide layer is better than that between the mixture and the intermetallic compounds in both the $SrZrO_3$-$MoSi_2$ and $SrZrO_3$-$TaAl_3$ systems. This is probably due to the fact that the oxide forms the matrix in the central composite layer and it therefore tends to sinter together with the outer oxide layer of the sandwich. The oxide also occupies more than 50% of the volume of the composite layer since the mixture was prepared on a weight basis and the density of the oxide is lower than that of the intermetallic compound. The photomicrographs of the mixed compositions (Figures 13-15) indicate that the average particle size of the intermetallic compounds is larger than that of the oxides, resulting in a coarse dispersion. The microstructural appearance of the 3-layer composite samples was quite encouraging and indicated that a dense structure could be achieved in a continuously gradated coating.

Oxidation Screening Tests of Intermetallic Compounds. - In previous work it was found that each of the intermetallic compounds under study could be sintered to relatively high density in 1 to 2-1/2 hours at 1400°C in argon. Since none of the compounds was eliminated from further consideration as a coating material on the basis of sinterability, a second screening test was carried out by determining the weight gain or loss of sintered discs of the individual compounds which were subjected to oxidation by heating with an oxyacetylene torch at 1700°-2500°C for various periods of time. Brightness temperatures were determined during the test by sighting on the heated face of the specimen with an optical pyrometer. The measured temperatures were not corrected for emittance. The results of the oxidation trials are summarized in Table 12.

Based upon the results of the oxidation trials, $MoSi_2$ and $90ZrB_2$-$10MoSi_2$ appeared promising for application at temperatures in the neighborhood of 3500°F (1950°C).

COATING STUDIES

Intermetallic Compounds. - The objective of these studies was to determine the optimum conditions for obtaining adherence of the intermetallic compounds and oxides to the Ta-10W alloy substrate, and to investigate factors affecting the ductility of the substrate. The pure intermetallic compounds were studied first since they form the bonding layer of the gradated coating to the substrate. The sintering experiments were carried out in a Globar-heated tube furnace at temperatures to 1400°C and in an induction heated furnace at higher temperatures. All sintering was carried out in a flowing argon atmosphere.

At 1400°C for 1 hour, $TaAl_3$, $TaSi_2$, and Ta_2Be_{17}, coatings on Ta-10W sintered well but were not adherent to the substrate. Under the same conditions, $MoSi_2$ and $90ZrB_2$-$10MoSi_2$ also sintered to high density and exhibited slight adherence. When the temperature was increased to 1700°-1800°C, the $TaAl_3$ coating reacted with the Ta-10W to form a liquid phase. The Ta_2Be_{17} and $TaSi_2$ coatings did not bond to the substrate in this temperature range. After 3 hours at 1800°C, the $MoSi_2$ bonded to the substrate, but only moderate adherence was obtained with the $90ZrB_2$-$10MoSi_2$. In a separate experiment an uncoatedTa-10W panel was exposed at 1700°-1800°C to the argon atmosphere for one hour. After heating, the sample remained bright, indicating that surface oxidation does not occur during sintering of the coatings and is not causing loss of adherence.

In experiments to determine the effect of metallic binders upon adherence, ten weight percent of -325 chromium, nickel, and tantalum powders were added to dispersions of $90ZrB_2$-$10MoSi_2$ and $MoSi_2$, coatings were pressed at 20 tsi and sintered for one hour in argon at 1700°-1750°C. The results, summarized in Table 13 indicate that both chromium and nickel binders caused severe embrittlement of the substrate and that nickel was ineffective in improving adherence of the coatings to the substrate. The tantalum binder had no effect upon either the ductility of the substrate or the adherence of the coating.

In a subsequent experiment to check the effect of the organic binder used in electrophoretic deposition upon the adherence of the coating, a series of coating materials without binder were placed upon the Ta-10W panels, and these samples were heated to 1750°-1800°C in argon for one hour. The results are shown in Figure 16. Tantalum silicide and tungsten silicide plus 10% ZrB_2-$10MoSi_2$ reacted with the substrate to form a molten phase. The remaining materials; pure ZrB_2-$10MoSi_2$, ZrB_2-$MoSi_2$ plus

10%$MoSi_2$ or tantalum, $MoSi_2$, and -10 micron tantalum each sintered, but none adhered to the substrate.

In an effort to improve the sinterability and adherence of the intermetallic compounds, the ZrB_2-10$MoSi_2$, WSi_2, $TaSi_2$, and $MoSi_2$ were screened through -325 mesh and the fines used for coating a set of Ta-10W panels. The panels were then isostatically pressed at 25 tsi and sintered in argon for one to two hours at 1700°-1800°C. The results are summarized in Table 14, and photomicrographs of two of the coatings are shown in Figure 17.

To check the effects of heat-treatment on the ductility of the substrate, an uncoated panel was heated at 1700°-1750°C in argon for one hour and hardness measurements were made of this specimen and of an uncoated, unheated panel. Sections through these samples are shown in Figure 18. After heat-treatment, the substrate microhardness increased from 340 kg/mm^2 to 470 kg/mm^2, however, the sample retained its bright appearance and remained ductile. Other hardness measurements of the coated samples are listed in Table 15. Substrates coated with ZrB_2-10$MoSi_2$ were invariably embrittled after heat-treatment, and diffusion of some component of the coating into the substrate is apparent in Figure 17. The silicide coatings, in general, had little effect upon the substrate ductility as evidenced by the microhardness measurements of Table 15.

Tungsten disilicide was also investigated as a base coating on Ta-10W for possible use in bonding to a gradated WSi_2-refractory oxide coating. This material was prepared for use in electrophoretic dispersions by milling in isopropanol for 48 hours in a steel mill. After milling, the finely-ground powder was leached with a 50% HCl solution, then washed and dried.

Coatings of this material were applied electrophoretically to sandblasted and chemically cleaned Ta-10W substrates. The coatings were densified to 30 tsi, and heat treated in argon at 1400°C for one hour. The resultant coatings appeared quite dense and adherent to the substrates.

An alternate heat-treating procedure, designed to eliminate any free tungsten in the tungsten silicide powder, and to improve the density of the coating, consisted of embedding the coated specimens in silicon metal powder and heating at 1350°C for two hours in an argon atmosphere. Figure 19 shows a cross section of a specimen prepared in this manner. Good bonding to the substrate is evident and the heat treatment did not appreciably affect the ductility of the substrate.

A static oxidation test at 3000°F was made on a coated panel of this type. The coating resisted penetration by oxygen for 30 minutes at this temperature even though it was only one mil thick. Figure 20 shows the specimen after the oxidation test.

Since the test results with this material were very promising, it was therefore anticipated that a WSi_2 coating, prepared in the manner described, would serve as an excellent base for WSi_2-oxide graded coatings on Ta-10W alloy substrates.

Diffusion Barrier Studies

Since the use of a thin layer of $MoSi_2$ or Mo metal coated to the Ta-10W panels beneath the gradated coating appeared promising in improving adherence, further studies of different materials as diffusion barriers were undertaken.

The molybdenum barrier layer was prepared by depositing molybdenum metal on chemically cleaned Ta-10W, pressing isostatically at 20 tsi, and sintering in argon for 2 hours at 1500°C. The molybdenum coating, as shown in Figure 21, was dense and well-bonded and there was no evidence of contamination of the substrate. The hardness of the Mo-coated substrate was 322 KHN (50g load) as compared to 235 KHN for an uncoated, annealed, 20 mil panel.

As complete elimination of embrittlement of the Ta-10W was not achieved with molybdenum, a second material, tungsten, was studied for possible use as a diffusion barrier. Recently, a paper was published[18] indicating that tungsten and rhenium are the best of the available refractory metals (m.p. above 1700°C) for minimizing diffusion of tantalum. In this study, diffusion couples were prepared of tantalum combined with W, Re, Os, Ru, Ir, Hf, V, Cr, and Pt. The couples were annealed for 4 hours at 1700°C or for 3 hours at 1800°C in argon and then examined microscopically to determine the extent of interdiffusion. Of the materials studied, Ta-W and Ta-Re showed minimum diffusion zones under the specified annealing conditions. Iridium and osmium, which also evidenced low diffusion, were rejected because of the formation of very hard brittle phases at the diffusion interface. The experimental results are summarized in Table 16.

Based upon this evidence, tungsten coatings were electrophoretically deposited upon Ta-10W substrates which were previously sandblasted and chemically cleaned. The coated specimens were then densified at 20 tsi and sintered at 1400°C for two hours in an argon atmosphere. A coating of ZrB_2-10$MoSi_2$ was then applied to determine if embrittlement of the substrate could be avoided by the use of a diffusion barrier. After densifying the composite coating at 40 tsi, the specimens were sintered at 1650°C for two hours in argon. This procedure was identical to that used previously for the molybdenum diffusion barriers.

The adherence of these coatings for specimens fired to 1650°C was poor. The coatings were split and pulled away from the substrate. It is likely that the high shrinkage of the tungsten layer was responsible for the poor adherence. Because of this difficulty, no further work was done with the ZrB_2-10$MoSi_2$ intermetallic.

Refractory Oxide Studies

In a parallel NASA program conducted by Vitro[19], studies were made to improve the density of the refractory oxide phase of the gradated coating system by the addition of a fluxing component. The purpose of this material was to provide a liquid phase at temperatures lower than the melting point of the primary refractory oxide. The liquid phase then acts as a sintering aid by promoting material transport, leading to increased densification rates and higher ultimate densities.

Various investigators have studied the effect of metal and oxide additions to zirconia. Ruh, et al[20] note the effect of liquid phase titanium in promoting the sintering of zirconia. In other work, Ruh and Garrett[21] demonstrated the increased sintering of zirconia by additions of chromium in quantities above the solubility limit, i.e. over 1%. This is another example of the beneficial effect of liquid phase formation during sintering.

Additions other than metals may prove more useful for present purposes; for example any one of a number of oxides which combine with zirconia to form eutectics which melt at temperatures below the melting point of zirconia itself. A number of potentially applicable liquidus curves[22] for zirconia and other oxides are shown in Figures 22 and 23.

One experiment was performed in which a pellet composed of 90 w/o $ZrO_2(CaO)$ and 10 w/o TiO_2 was treated at 1700°C for two hours in an argon atmosphere. This pellet was fused and hard and an extensive, even excessive, amount of liquid phase was present during sintering to aid the densification.

Considerable effort was also devoted to the preparation, sintering and study of CaO-stabilized ZrO_2 samples to which various potential fluxing materials were added.

Ten gram batches of each composition were weighed, isopropyl alcohol was added, and the sample was mixed thoroughly in a mortar while the alcohol evaporated. The mixed material was then dry-pressed into 1/2" diameter x 1/8" thick pellets. These pellet specimens were sintered in argon at 1700°C for two hours.

The results of these experiments are listed in Table 17 and applicable photographs of several specimens are shown in Figures 24, 25, and 26. The materials which appeared to have the greatest effect in promoting the densification of CaO-stabilized ZrO_2 at 1700°C were TiO_2 and Al_2O_3.

SINTERING STUDIES OF TWO SELECTED GRADATED COATING SYSTEMS

Based upon the work reported in the previous sections, the following two systems were chosen for application to the Ta-10W substrate specimens:

$MoSi_2$-$MoSi_2$/CaO-stabilized zirconia grade
WSi_2-WSi_2/2%TiO_2-CaO-stabilized zirconia grade

Sintering and oxidation tests performed with these systems are reported in the following paragraphs.

$MoSi_2$-Refractory Oxide Systems. - In all experiments, the Ta-10W substrate was prepared by grit-blasting, then chemical cleaning in an etching bath containing 15 ml lactic acid plus 5 ml of nitric acid, plus 5 ml of hydrochloric acid, and washing in distilled water. Table 18 summarizes the significant experiments which were performed. The data indicated that adherent coatings on Ta-10W could be produced from $MoSi_2$ which had a particle size of approximately 5 microns or less, and that a thin layer of $MoSi_2$ which is sintered on the Ta-10W substrate will bond to the subsequent gradated coating. Improved adherence was also obtained by depositing from a 5% instead of a 1% dispersion.

A photomicrograph of a $MoSi_2$-ZrO_2(CaO-stabilized) coating over a sintered $MoSi_2$ layer is shown in Figure 27. This photograph shows the $MoSi_2$ to Ta-10W bond which has developed after sintering at 1400°C. The gradated layer appears very porous in this photograph because the oxide was soft after sintering at this temperature and could not be polished without causing pull-outs and voids.

Another portion of this same specimen was refired to 1700°C for one hour. The results are shown in Figure 28. Visual inspection of this sample showed that hardness and density were higher than in the 1400°C specimen shown in Figure 27.

To prepare coated Ta-10W specimens for oxidation tests, a base coat of $MoSi_2$ (leached with HCl and ball-milled) was deposited at 100 volts for 1-1/2 minutes, after which it was isostatically pressed at 30 tsi and sintered in argon at 1400°C for one hour. A gradated coating of $MoSi_2$-ZrO_2 was then applied to the $MoSi_2$-coated Ta-10W substrate.

The gradated coatings were isostatically densified at 30 tsi and sintered at 1400° and 1600°C for two hours in an argon atmosphere. Measurement of the coatings indicated that the thickness of the sintered $MoSi_2$ base coat was one mil and that of the $MoSi_2$-ZrO_2 grade was three to four mils.

The coatings sintered at 1400°C were only presintered. Those sintered at 1600°C were improved in density and adherence, and had a hard glass-like surface. Some porosity, however, was still evident in the gradated layer.

Oxidation tests at 3000°F were conducted on the $MoSi_2$-ZrO_2 specimens. Failure occurred almost immediately on specimens which were prepared by sintering at 1400°C. The specimens prepared by sintering at 1600°C survived 15-20 minutes before oxidation effects could be noticed. A photograph of an oxidized specimen is shown in Figure 29.

The poor results on these specimens indicated that improvement in the sintering of the specimens is necessary to obtain better oxidation resistance. The major defect, as shown in the photomicrograph, was the high porosity of these coatings.

WSi_2-Refractory Oxide Systems. - Small panel specimens having gradated coatings on Ta-10W were prepared by electrophoretic deposition and isostatic densification at 20 tsi. The primary objective of this work was to determine the effect of increased sintering temperature on the structure of the coating, and to promote the development of non-porous surfaces for improved oxidation resistance. The gradated coating systems studied and the results of sintering experiments are shown in Table 19.

These experiments indicate that the increase in sintering temperature was beneficial in increasing the densities of the WSi_2-$CaZrO_3$ and WSi_2-Al_2O_3(MgO) gradated coatings. On the other hand, the density of the WSi_2-ZrO_2(CaO) gradated coating was still below 90% of theoretical, and the 1700°C temperature used was apparently still too low by several hundred degrees for complete sintering of the very refractory ZrO_2 component.

Coating, sintering, and oxidation testing were performed for specimens of four different gradated coating systems:

1. $CaZrO_3$-WSi_2
2. Al_2O_3(4 MgO)-WSi_2

3. (3.5%CaO-stabilized ZrO_2-2%TiO_2)-WSi_2
4. (3.5%CaO-stabilized ZrO_2-5%Al_2O_3)-WSi_2

All specimens were prepared by depositing WSi_2 onto a sandblasted and etched Ta-10W panel, densifying, sintering in argon at 1400°C, and siliconizing at 1350°-1375°C to yield a 1.5-2.0 mil-thick WSi_2 layer. Next, the desired gradated coatings were deposited onto the WSi_2, densified, sintered at 1600°C, and siliconized at 1375°C. For comparison purposes, a few specimens were prepared without siliconizing the gradated portion of the coating.

The specimens were oxidation tested in static air as shown in Table 20, which summarizes test conditions and results.

A study of the results of these oxidation tests indicated that the best protection was obtained with the Al_2O_3(MgO)-WSi_2 and 3.5%CaO-stabilized ZrO_2-2%TiO_2)-WSi_2 coatings. Judging from post-test appearance, both types were either solid or very viscous liquids at the test temperature. In both coatings, gas bubbles were apparent under the surface. The cause of these bubbles was not determined. Cross sections of these two coatings are shown in Figures 30 and 31.

PREPARATION OF FINAL SAMPLES FOR NASA EVALUATION

In the final phase of this program, the two gradated coating systems discussed in the previous section were each applied to 12 tensile, 10 leading edge, and 22 coupon-type specimens. Drawings of the three types of specimens are shown in Figure 32. The sample preparation procedure for both coatings was as follows:

$MoSi_2$-CaO-Stabilized Zirconia Gradated Coating on Ta-10W. -The procedure used in preparing these samples was as follows:

1. Grit-blast, hand-radius edges and acid etch in 15-5-5 mixture of lactic acid, nitric acid, and hydrofluoric acid for 10 minutes.

2. Coat with $MoSi_2$ at 100 VDC for 1-1/2.

3. Press at 30 tsi and fire in argon for 1 hour at 1400°C.

4. Coat with silicon, heat 2 hours in argon at 1350°C.

5. Apply $MoSi_2$/CaO-stabilized zirconia gradated coating at 150 VDS for 2-1/2 minutes.

6. Press at 20 tsi and sinter for 1 hour in argon at 1600°C.

WSi_2-(3.5%CaO-Stabilized ZrO_2-2%TiO_2) Coatings on Ta-10W. -

1. Grit-blast lightly with Grade A-10 Al_2O_3 and etch in mixture of $2HF:2HNO_3:1H_2SO_4$.

2. Electrophoretically coat 4 mils of WSi_2.

3. Sinter 2 hours in argon at 1600°C.

4. Embed in silicon powder and heat 2 hours in argon (or at pressure of 0.01 torr) at 1350°C.

5. Apply 5 mils of gradated coating at 100 VDC for about 2-5 minutes.

6. Press at 10 tsi and sinter for 1 hour at 1600°C in argon.

7. Embed in silicon powder and heat treat at about 0.01 torr for 16 hours at 1300°C.

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TABLE 1

SEDIMENTATION TRIALS OF COATING MATERIALS

Material	Preparation	%Coarse (>15μ)	%Fine (<15μ)
WSi_2 (Source A)	As-received -325 mesh	57.3	42.7
$3.5CaO-96.5ZrO_2$	As-received -325 mesh(lot#1)	86.0	14.0
$3.5CaO-96.5ZrO_2$	As-received -325 mesh(lot#2)	13.4	86.6
$3.5CaO-96.5ZrO_2$	Lot #2, milled 6 hours	3.0	97.0
$MoSi_2$	As-received -325	48.7	51.3
$MoSi_2$	Milled 48 hours	6.3	93.7
$SrZrO_3$	As-received -325 mesh	28.8	71.2
$8Y_2O_3-92ZrO_2$	As-received -325 mesh	32	68

TABLE 2

SELECTED PHYSICAL PROPERTIES OF REFRACTORY MATERIALS

	M.P. (°F)	Density (g/cc)	Knoop Microhardness 100g load (kg/mm^2)	Thermal Expansion Per °F x 10^6
Al_2O_3	3720	3.96	2260	4.7 (to 1500°F)
ZrO_2 (cubic)	4760	5.6-6.26	900	4.7 (to 3800°F)
Ta-10W	5495	16.9	230(annealed)	3.9 (1600-2200°F)
Ta_2Be_{17}	3610	5.05	1120*	8.72(to 2750°F)
$TaSi_2$	4350	9.1	1200	4.67(to 2600°F)
$90ZrB_2-10MoSi_2$	4280	6.12(calc.)	1500	3.9
$MoSi_2$	3690	6.24	1260	4.5 (to 2600°F)
$CaZrO_3$	4170	4.78	--	6.4 (to 2400°F)
$TaAl_3$	4950	6.92	--	6.5
$SrZrO_3$	4900	5.48	--	--
3.5%CaO Stabilized ZrO_2	4700	5.65(calc.)	--	--
8%Y_2O_3 Stabilized ZrO_2	4800	5.67(calc.)	--	--
WSi_2	3955	9.8	--	4.4 (to 1958°F)

*Vickers Hardness 2.5 kg load

APPENDIX A

TABLES

TABLE 3

SOURCE AND FORM OF COATING MATERIALS

Material	Source and Form
3.5% Calcia-stabilized, hafnia-free zirconia	Zirconium Corp. of America, Grade CH nominal 5 micron powder
8% Yttria-stabilized zirconia	Zirconium Corp. of America, nominal 5 micron powder
Calcium zirconate	Zirconium Corp. of America, nominal 5 micron powder
Zirconium diboride	A. D. Mackay, -200 mesh powder 99% pure
Molybdenum disilicide	Shieldalloy, 3 micron powder
Alumina (alpha)	Linde Type A, 0.3 micron powder 99.98% pure
Tantalum silicide ($TaSi_2$)	A. D. Mackay, -150+325 mesh powder, 99+% pure
Tantalum beryllide (Ta_2Be_{17})	Brush Beryllium, -200 mesh powder
Strontium zirconate ($SrZrO_3$)	Zirconium Corp. of America, -325 mesh powder. (Typical analysis 0.1% Al_2O_3, 0.1% SiO_2, 0.9% CaO, 1.7% BaO, balance $SrZrO_3$)
Tungsten disilicide	Source A - Shieldalloy -325 mesh powder Source B - Cerac, Inc. -325 mesh powder

TABLE 4

TYPICAL ANALYSES OF ZIRCONIA COMPOUNDS

	3.5%Calcia-Stabilized Zirconia	8%Y_2O_3-Stabilized Zirconia		Calcium Zirconate	
Al	200 ppm	ZrO_2	91.8%*		
B	1	Y_2O_3	8%**	$CaZrO_3$	99 %
Cd	0.5	SiO_2	0.2%	SiO_2	0.5%
Cl	10	Al_2O_3	0.1%	L.O.I.	1 %
Cr	50				
Co	1				
Cu	25				
Fe	500				
Hf	100				
Pb	5				
Mg	200				
Mn	10				
Ni	10				
Si	1500				
Ti	150				
(SO_4)	500				

*ZrO_2 impurities shown in Column 1

**Y_2O_3 is commercial grade, containing about 10% rare earths, compatible with ZrO_2

TABLE 5

SPECTROGRAPHIC ANALYSES OF $MoSi_2$ AFTER DILUTE HCl LEACH

Impurity	%	Impurity	%
Al	0.05	Ni	0.001
B	0.005	Sn	0.001
Ba	0.005	Ti	0.003
Ca	0.2	V	0.01
Co	0.005		
Cr	0.02		
Cu	0.007		
Fe	0.1		
Mg	0.005		
Mn	0.005		

Ag, Be, Bi, Ga, In, Pd, Sr, Zr - Not detected, 0.001%
As, Au, Cd, Hf, Ir, Li, Na, Os, Ru, Sb, Ta, W - Not detected, 0.05%
Ge, Cb, Pb, Rh, Pt - Not detected, 0.005%

TABLE 6

X-RAY DIFFRACTION ANALYSIS OF VITRO-SYNTHESIZED $TaAl_3$

ASTM Standard Data* For $TaAl_3$ "d" Spacing (Angstroms)	Vitro Sample "d" Spacing (Angstroms)
4.26	4.28
3.50	3.50
2.71	2.72
2.28	2.29
2.13	2.13
1.92	1.91
1.75	1.75
1.68	1.685
1.56	1.561
1.47	1.470
1.43	1.427
1.36	1.358
1.29	1.293
1.26	1.262
1.21	1.213
1.17	1.168
1.14	1.145

*ASTM Card 2-1128

TABLE 7

SPECTROGRAPHIC ANALYSIS OF ZIRCONIUM DIBORIDE POWDER

Impurity	%
Ca	0.005
Co	0.02
Cr	0.01
Fe	0.07
Hf	1
Mn	0.001
Mo	0.02
Si	0.003
Ti	0.05

Not Detected, 0.005% - Ag, Al, Ba, Be, Bi, Cu, Ga, In, Mg, Ni, Pd, Sn, Sr, V, Cb, Pb, Pt, Rh, Ge

Not Detected, 0.05% - As, Au, Cd, Ir, Li, Na, Os, Ru, Sb, Ta, Tl, W, Zn

TABLE 8

SPECTROGRAPHIC ANALYSIS OF TUNGSTEN DISILICIDE POWDER (SOURCE A)

SILVER	ND<0.001%
ALUMINUM	0.07%
ARSENIC	ND<0.05%
GOLD	ND<0.05%
BORON	0.01%
BARIUM	ND<0.001%
BERYLLIUM	ND<0.001%
BISMUTH	ND<0.001%
CALCIUM	0.03%
CADIUM	ND<0.05%
COBALT	0.001%
CHROMIUM	0.007%
COPPER	0.005%
IRON	0.1%
GALLIUM	ND<0.001%
GERMANIUM	ND<0.005%
HAFNIUM	ND<0.05%
INDIUM	ND<0.001%
IRIDIUM	ND<0.05%
LITHIUM	ND<0.05%
MAGNESIUM	0.007%
MANGANESE	0.005%
MOLYBDENUM	0.05%
SODIUM	ND<0.05%
COLUMBIUM	ND<0.005%
NICKEL	0.005%
OSMIUM	ND<0.05%
LEAD	ND<0.003%
PALLADIUM	ND<0.001%
PLATINUM	ND<0.005%
RUTHENIUM	ND<0.05
RHODIUM	ND<0.005%
ANTIMONY	ND<0.05%
SILICON	High
TIN	ND<0.001%
STRONTIUM	ND<0.001%
TANTALUM	ND<0.05%
TELLURIUM	ND<0.1%

THALLIUM	ND<0.01%
TITANIUM	0.02%
VANADIUM	0.001%
TUNGSTEN	High
ZINC	ND<0.03%
ZIRCONIUM	0.005%

* * *

(ND< - Not Detected Less Than)

TABLE 9

SINTERING TRIALS OF OXIDES AND INTERMETALLIC COMPOUNDS

Compound	Sintering Conditions*	Apparent Density	
		g/cc	% Theoretical
$3.5CaO-96.5ZrO_2$	a	1.24	22
	b	3.99	71
	c	4.18	74
$8Y_2O_3-92ZrO_2$	a	4.29	76
	b	4.44	78
	d	5.05	89
$CaZrO_3$	a	3.48	73
	b	3.89	81
	c	4.12	86
$SrZrO_3$	a	4.44	81
	b	4.45	81
	c	4.90	89
Al_2O_3	c	3.50	88
$TaAl_3$	a	6.18	89
Ta_2Be_{17}	a	(Powdery, did not sinter)	
$TaSi_2$	a	8.30	91
$90ZrB_2-10MoSi_2$	a	5.82	95

*Conditions:
a) 60 min., 1400°C in Argon
b) Same as (a); then 15 min., 1700°C in Argon
c) 45 min., 1700°C in Argon
d) 45 min., 1900°C, 10^{-6} Torr

TABLE 10

APPARENT DENSITY OF 50-50 BLENDS OF OXIDE-INTERMETALLIC COMPOUNDS AFTER SINTERING IN ARGON AT 1700°C FOR 30 MINUTES

		Intermetallic				
Oxide		$TaAl_3$	Ta_2Be_{17}	$TaSi_2$	$90ZrB_2$-$10MoSi_2$	$MoSi_2$
	calc. density -	6.28	5.35	7.37	5.88	5.94
$3.5CaO$-$96.5ZrO_2$	obs. density -	4.6	1.7	4.34	2.8	2.67
	% Theory -	73%	30%	59%	48%	45%
		6.29	5.36	7.38	5.89	5.95
$8Y_2O_3$-$92ZrO_2$		4.73	-	5.69	3.2	3.78
		75%	-	77%	54%	63%
		5.85	4.92	6.94	5.45	5.51
$CaZrO_3$		4.56	3.25	4.93	4.58	-
		78%	66%	71%	84%	-
		6.20	5.26	7.29	5.80	5.86
$SrZrO_3$		5.15	2.49	5.84	4.35	4.60
		67%	47%	80%	75%	78%
		5.44	4.50	6.53	5.04	5.10
Al_2O_3		1.79	-	3.80	2.87	3.16
		33%	-	58%	57%	62%

TABLE 11

SINTERING TRIALS OF PURE OXIDES, INTERMETALLIC COMPOUNDS, AND COMPOSITE SYSTEMS

(All samples isostatically pressed at 30 tsi before sintering)

Material	Sintering Conditions	Apparent Density (g/cc)	Apparent Density (%Theory)	Figure Number Reference
$90ZrB_2$-$10MoSi_2$	60 min. -1400°C-Argon	5.82	95	9
Ta_2Be_{17}	2-1/2 hrs. 1400°C-Argon	4.7	93	9
$TaAl_3$	60 min. -1400°C-Argon	6.18	89	9
$TaSi_2$	60 min. -1400°C-Argon	8.30	91	9
$8Y_2O_3$-$92ZrO_2$	5 hrs. -1725°C-Argon	4.80	85	10
$8Y_2O_3$-$92ZrO_2$	10 hrs. -1725°C-Argon	4.93	87	10
3.5CaO-96.5ZrO_2	5 hrs. -1725°C-Argon	4.66	83.5	-
3.5CaO-96.5ZrO_2	10 hrs. -1725°C-Argon	5.05	89	-
50(3.5CaO-96.5ZrO_2)-50$MoSi_2$	3-1/2 hrs. -1725°C-Argon	5.9	99	11
50(3.5CaO-96.5ZrO_2)-50$TaSi_2$	3-1/2 hrs. -1725°C-Argon	6.1	83	11
50(3.5CaO-96.5ZrO_2)-50($90ZrB_2$-$10MoSi_2$)	3-1/2 hrs. -1725°C-Argon	5.5	94	-
50($8Y_2O_3$-$92ZrO_2$)-50$MoSi_2$	3-1/2 hrs. -1725°C-Argon	5.64	95	12
50($8Y_2O_3$-$92ZrO_2$)-50$TaSi_2$	3-1/2 hrs. -1725°C-Argon	7.37	99	12
50($8Y_2O_3$-$92ZrO_2$)-50($90ZrB_2$-$10MoSi_2$)	3-1/2 hrs. -1725°C-Argon	5.88	99	12

TABLE 12

OXIDATION TRIALS OF SINTERED INTERMETALLIC COMPOUNDS

Compound	Temperature (°C)	Time (min)	%Wt. Change	Notes
$TaAl_3$	1700-1750	30	+ 2.4	-
	1750-1800	10	+ 6.3	-
	1850	1/6	-	Melted and reacted with Al_2O_3 setter
	1900	1/4	-	Melted and reacted with ZrO_2 setter
Ta_2Be_{17}	1750-1785	15	+ 6.1	Localized melting at 1785°C
	1800	1	+ 6.8	Melting
	2000	3/4	+ 4.2	Melting and vaporization
$TaSi_2$	1700-1750	30	- 15	-
	1800	10	- 16.1	Surface spalling during cooling
	1850	3	-6.1, -4.0	Surface melting
$MoSi_2$	1700-1750	30	- 3.2	-
	1950	6	- 9.9	Surface melting
	2000	3	- 4.0	Surface melting
$90ZrB_2$-$10MoSi_2$	1700	30	- 2.0	Protective oxide surface layer formed
	2000	2	- 4.7	-
	2000	5	- 3.3	-
	2500	1/2	-17.2	Beginning of melting
WSi_2	1700	1/2	-	Surface glaze, no change in dimensions

TABLE 13

EFFECT OF METALLIC BINDERS ON DUCTILITY OF Ta-10W SUBSTRATE AND ADHERENCE OF COATINGS

Intermetallic Compound	Cr	Ni	Ta
ZrB_2-10 $MoSi_2$	Sintered well, good adherence reacted severely with substrate rendering it highly embrittled	Embrittled substrate, did not enhance bonding	sintered well, No adherence to the substrate-substrate ductile.
$MoSi_2$	Melted and reacted with substrate causing severe embrittlement	Sintered well, did not promote better bonding to the substrate. Substrate embrittled.	Coating sintered, no adherence to the substrate. Substrate ductile.

TABLE 14

SINTERING EXPERIMENTS-INTERMETALLIC COMPOUNDS ON Ta-10W

Intermetallic Coating	Sintering Time and Temp. (°C)	Results
ZrB_2-10 $MoSi_2$	1700-1750, 2 hrs	Coating pressed 25 tsi, good sintering characteristics deep diffusion into substrate, good adherence.
ZrB_2-10 $MoSi_2$	1700-1750, 1 hr	Coating not pressed, sintered well, poor bonding to substrate, narrow diffusion zone.
ZrB_2-10$MoSi_2$	temp held steady @ 1800°C - 1 hr	Coating pressed 25 tsi, good sintered coating, good adherence, deep diffusion.
WSi_2	1750-1775 - 1 hr	Coating unpressed, coating material reacted with substrate.
WSi_2	1700-1750 - 1 hr	Coating pressed 25 tsi; coating sintered, slight oxidation, good adherence to substrate.
$TaSi_2$	1700-1750 -2 hrs	Coating pressed 25 tsi, sintered well, slight diffusion, good adherence.
$MoSi_2$	1650-1700, 1 hr	Coating material melted, very slight reaction and bonding to substrate.
ZrB_2-10$MoSi_2$+10%Cr	1700-1750°C, 1 hr	Pressed coating 25 tsi, reacted with substrate, substrate very brittle, coating spalled on cooling.

TABLE 15

KNOOP HARDNESS MEASUREMENTS FOR INTERMETALLIC COATINGS ON Ta-10W SUBSTRATE

Coating Composition	Sintering Conditions	Knoop Hardness Numbers Using a 50 Gram Load		
		Coating	Interface	Substrate
ZrB_2-10 $MoSi_2$	1700°-1750°C, 2 hrs	3630	791-695	468-445
$TaSi_2$	1700°-1750°C, 2hrs	549	4941-1235	385-367
Ta-10W	as received	-	-	361-322
Ta-10W	1700°-1750°C, 1 hr	-	-	473-468
WSi_2	1700°-1750°C, 1 hr	1971	581	361-322
$MoSi_2$	1650°-1700°C, 1 hr	-	-	445
ZrB_2-10$MoSi_2$+10%Cr	1700°-1750°C, 1 hr	-	-	520-473

TABLE 16

EVALUATION OF DIFFUSION BARRIERS FOR TANTALUM[18]

(Diffusion-annealed 4 hrs. at 1700°C or 3 hrs. at 1800°C in Argon)

Couple	Total Diffusion zone thickness(u)	Porosity	Prediminant Diffusion Direction	Diffusion Zone Hardness (KHN)	
				Increment	Maximum
Ta-W(1800°)	20	Some	Into W	450	770
Ta-Re	<50	None	Into Re	200	470
Ta-Re(1800°)	15	Little	Into Re	265	300
Ta-Os	30	None	Equal	600	890
Ta-Ru	45	None	Into Ta	920	1050
Ta-Ir	40	None	Into Ta	990	1350
Ta-Ir(1800°)	40	Some	Into Ta	1175	1480
Ta-Hf	630	None	Into Ta	410	470
Ta-V*	125	Some	Into Ta	415	600
Ta-Cr*	360	Some	Into Ta	200	820
Ta-Pt*	40-100	None	Unknown	880-1030	1250

* 1 Hour annealing at 1700°C

TABLE 17

RESULTS OF SINTERING FLUXED ZrO_2 AT 1700°C

Composition		Appearance
ZrO_2 99%	TiO_2 1%	White, porous
98	2	Light Brown, surface impervious, glassy
95	5	Dark Brown, impervious, glassy
90	10	Dark Brown, impervious, glassy
ZrO_2 99%	Co_2O_3 1%	Pale Green, porous
98	2	Pale Green, porous
95	5	Dark Gray, impervious
90	10	Dark Gray, impervious
ZrO_2 99%	Cr 1%	Gray, porous
98	2	Gray, porous
95	5	Gray, porous
90	10	Gray, porous
ZrO_2 99%	Al_2O_3 1%	White, porous
98	2	White, porous
95	5	White, impervious
90	10	White, impervious
ZrO_2 100%		White, porous

TABLE 18

SINTERING TRIALS OF $MoSi_2$-OXIDE COATINGS ON Ta-10W

	Intermetallic Coating	Oxide Coating	Pressing Pressure (tsi)	Sintering Conditioning	Results
1	$MoSi_2$, particles less than 15 microns	----	20 tsi	1400°C 1hr.	Non-Adherent Soft coating
2	$MoSi_2$, particles less than 5 microns	----	"	"	Adherent soft coating
3	$MoSi_2$, particles less than 15 microns	----	30 tsi	1500°C 2hrs.	Non-Adherent soft coating
4	$MoSi_2$, particles less than 5 microns	----	"	"	Adherent hard coating
5	$MoSi_2$, particles less than 15 microns	$SrZrO_3$, particles less than 15 microns	"	"	Non-Adherent soft coating
6	$MoSi_2$ particles less than 15 microns on sintered Mo barrier coating	$SrZrO_3$, particles less than 15 microns	"	"	Non-Adherent soft coating
7	$MoSi_2$, particles less than 15 microns 5% solids in dispersion	----	"	1400°C 1 hr.	Adherent with fair to good density
8	$MoSi_2$, particles less than 15 microns 1% solids in dispersion	----	"	"	Non-Adherent with high density
9	$MoSi_2$, particles less than 5 microns 1% solids in dispersion, on sintered $MoSi_2$ bond layer	ZrO_2(CaO stabilized) milled 6 hrs.	"	"	Adherent with fair density and hardness
10	$MoSi_2$, particles less than 5 microns, 1% solids in dispersion, no $MoSi_2$ bond layer	ZrO_2(CaO stabilized) milled 6 hrs.	"	"	Non-Adherent
11	No. 9 refired	----	–	1700°C 1 hr.	Adherent, with good density and high hardness

TABLE 19

SINTERING RESULTS ON GRADATED COATINGS

Gradated Coating System	Deposition Data	Sintering Temp	Sintering Time	Results
WSi_2-ZrO_2 (CaO)		1600°C	1 hr.	Coating semi-hard, porous.
WSi_2-$CaZrO_3$		1600°C	1 hr.	Coating hard, dense, reduced and cracked off substrate.
WSi_2-ZrO_2 (CaO)	Grade - 55 sec - 100 volts ZrO_2(CaO) - 45 sec - 150 volts ZrO_2(CaO) - 45 sec - 200 volts	1700°C	1 hr.	Coating harder than that fired at 1600°C but still porous and cracked off substrate.
WSi_2-$CaZrO_3$	Grade - 55 sec - 100 volts $CaZrO_3$ - 45 sec - 150 volts $CaZrO_3$ - 45 sec - 200 volts	1700°C	1 hr.	Coating hard and dense but cracked off substrate.
WSi_2-Al_2O_3 (MgO)	Grade - 50 sec - 100 volts Al_2O_3 - 45 sec - 150 volts Al_2O_3 - 45 sec - 200 volts	1700°C	2 hrs.	Coating hard and quite dense, adherent. Shrinkage cracks at one end of panel.

TABLE 20

RESULTS OF OXIDATION TESTS ON Ta-10W SPECIMENS HAVING GRADATED OXIDE-INTERMETALLIC COATINGS

Gradated Coating	Specimen No.	Siliconizing Treatment	Oxidation Test Temperature	Results
$CaZrO_3$-WSi_2	1	Yes	2912°F	Removed after short time exposure. Surface bubbly and glassy, yellow. Specimen otherwise intact.
	2	Yes	2912°F	Removed after short time exposure. Coating on leading edge deteriorated on entrance to hot zone.
	3	Yes	2912°F	Removed after 10 minutes exposure. Yellow glassy reacted surface, uneven. Movement and flow of material noted during exposure.
Al_2O_3(MgO)-WSi_2	1	Yes	2912°F	Removed after 30 minutes exposure. Surface dark, glassy and wrinkled. Failure site at bottom center where in contact with ZrO_2 setter pellet. No edge failure.
	2	Yes	2912°F	Removed after 30 minutes exposure. Surface dry. Failure at end and patch areas.
	3	Yes	3000°F	Removed after 5 minutes exposure. Failure at one corner.
	Comments:	This coating system was selected for further study because the surface appears to have a high density and high viscosity and the resistance to oxidation (30 minutes) was second best of the four systems studied.		
(3.5%CaO-Stabilized ZrO_2-2%TiO_2)-WSi_2	1	No	2950°F	Removed after 10 minutes exposure. Coating dark, glassy. Failure at corners on both ends.
	2	Yes	3000°F	Removed after 45 minutes exposure. Tight, glassy, adherent coat of yellow cast. Small bubbles on surface. Failure on underside where in contact with ZrO_2 setter pellet.
	3	No	3000°F	Removed after 30 minutes exposure. Failure on one edge and at patch spot.
	4	No	3000°F	Removed after 10 minutes exposure. Failure at ends where in contact with Al_2O_3 setter plate. Remainder of surface did not fail and coating had good adherence.
	Comments:	This coating system was selected for further study because of the high density and viscosity of the surface and because it had the best oxidation resistance of the four systems studied.		
(3.5%CaO-Stabilized ZrO_2-5%Al_2O_3)-WSi_2	1	No	2912°F	Removed after short time exposure. Extreme failure.
	2	Yes	3000°F	Removed after short time exposure. Failure on bottom surface from center to edge.

APPENDIX B

ILLUSTRATIONS

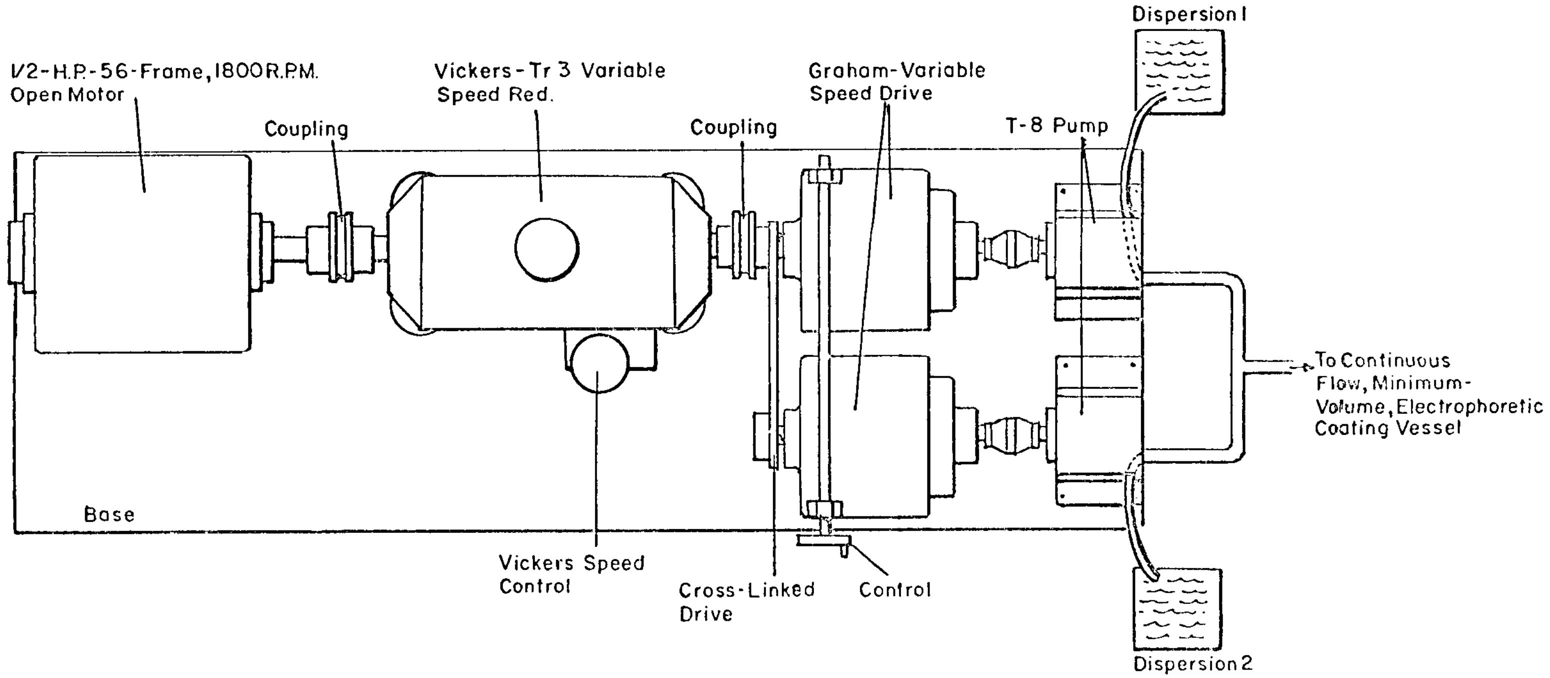


FIGURE 1

PUMPING SYSTEM FOR ELECTROPHORETIC DEPOSITION
OF GRADATED COATINGS

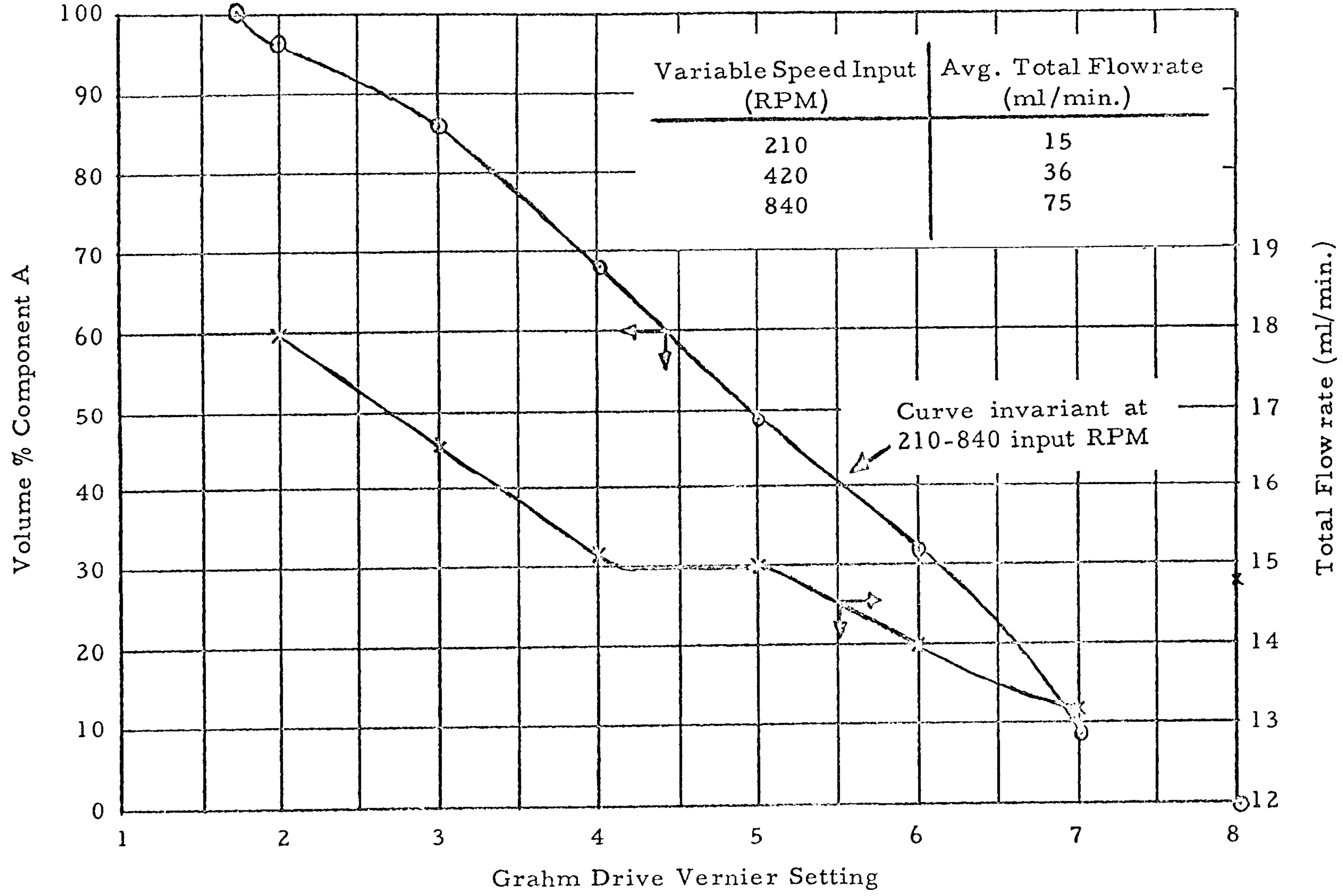


FIGURE 2

EFFLUENT COMPOSITION AND VOLUMETRIC FLOW RATE
VS. PUMPING SPEED FOR 5 MINUTE RUN
THROUGH 1/4 INCH DIAMETER TUBING

(Variable Speed Input = 210 RPM)

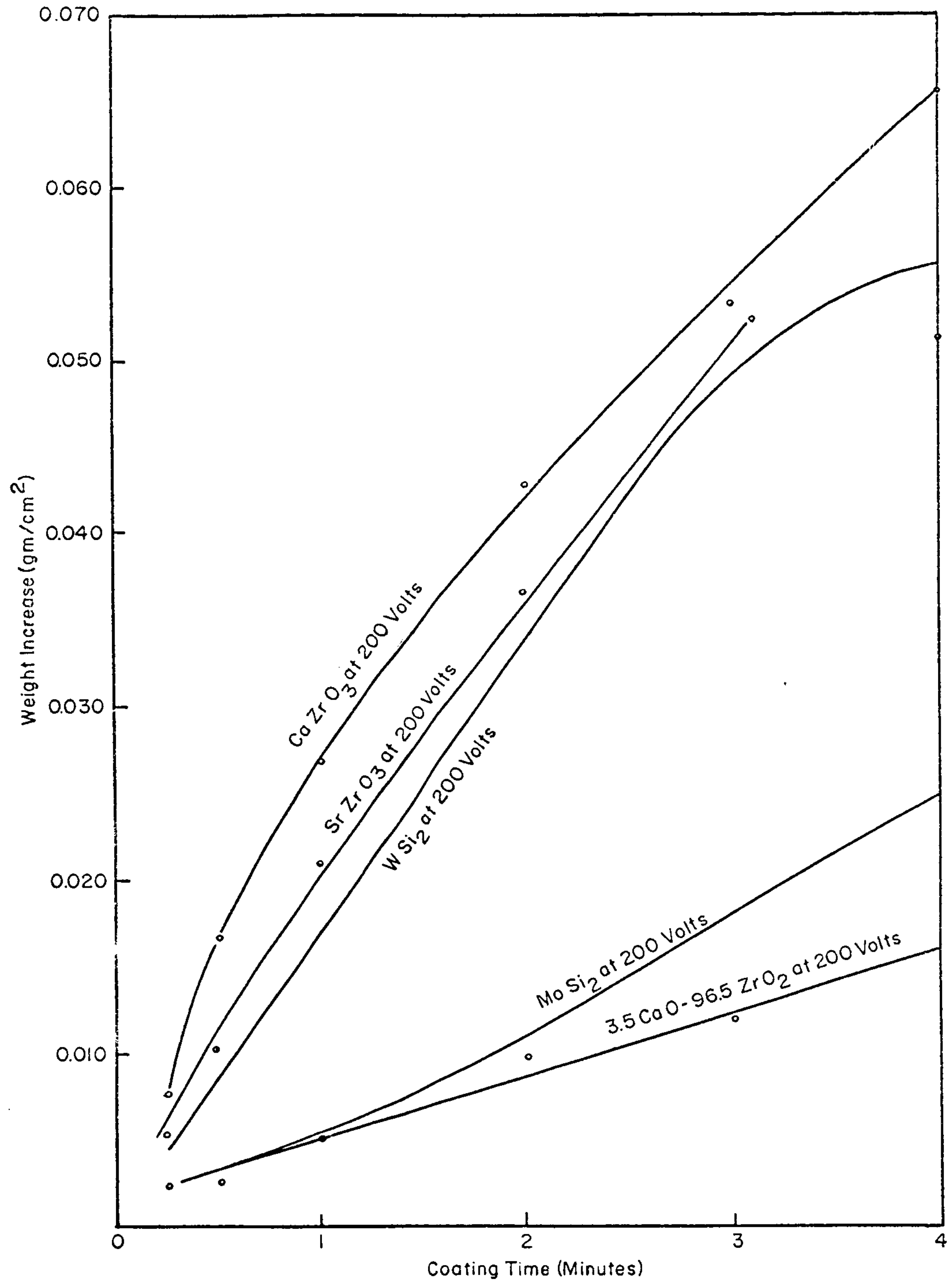


FIGURE 3

COATING RATE OF VARIOUS 1 $^w/_o$ DISPERSIONS

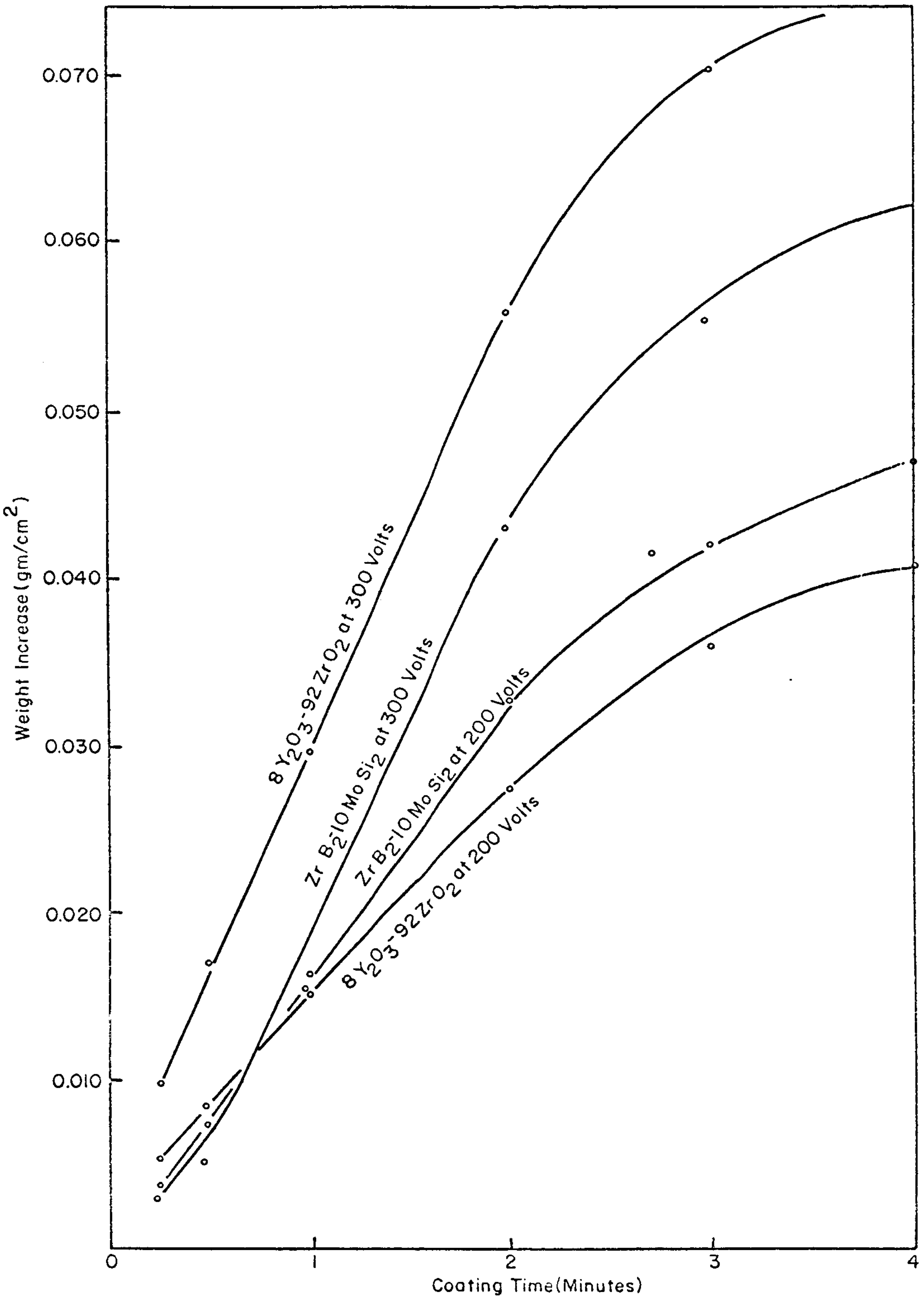
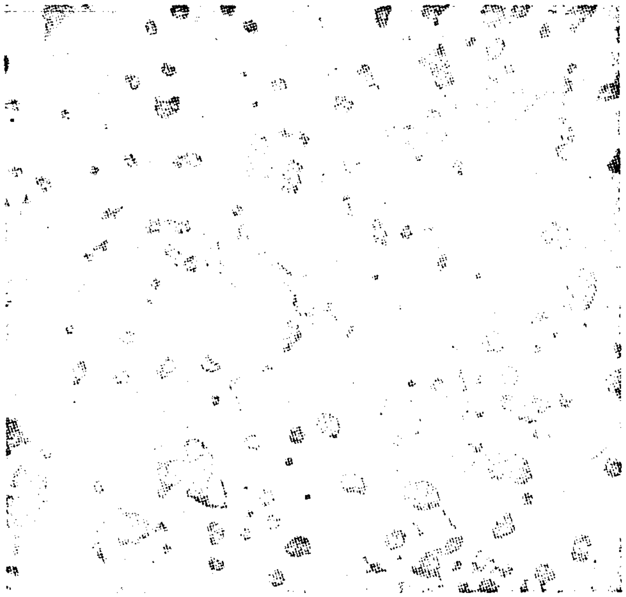
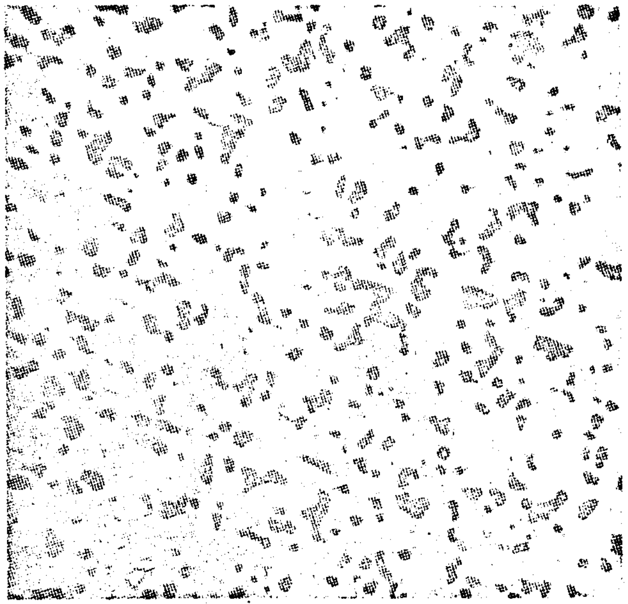


FIGURE 4

COATING RATE OF VARIOUS 1 w/o DISPERSIONS



CaZrO$_3$ 540x Unetched

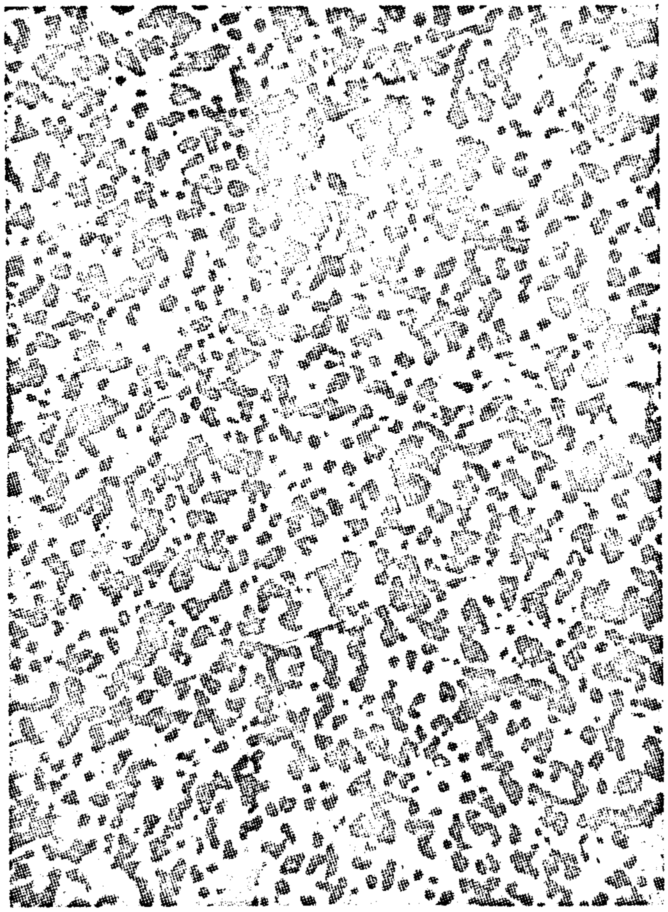


SrZrO$_3$ 540x Unetched

FIGURE 5

PHOTOMICROGRAPH OF SINTERED CaZrO$_3$ AND SrZrO$_3$

(Sintering Conditions - 45 min., 1700°C in Argon)

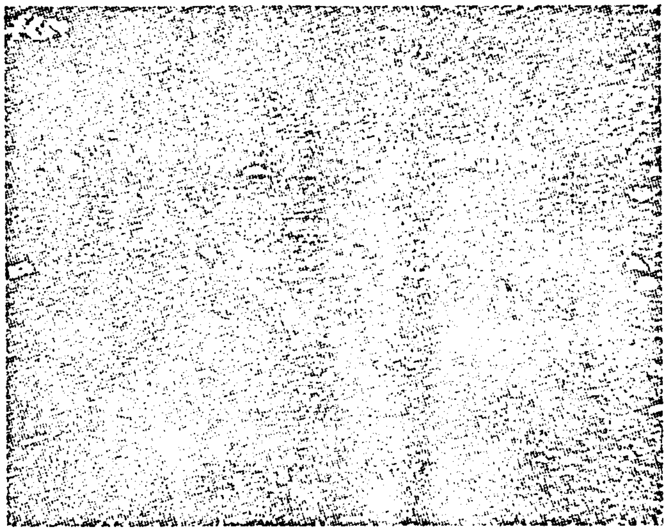


540x
Unetched

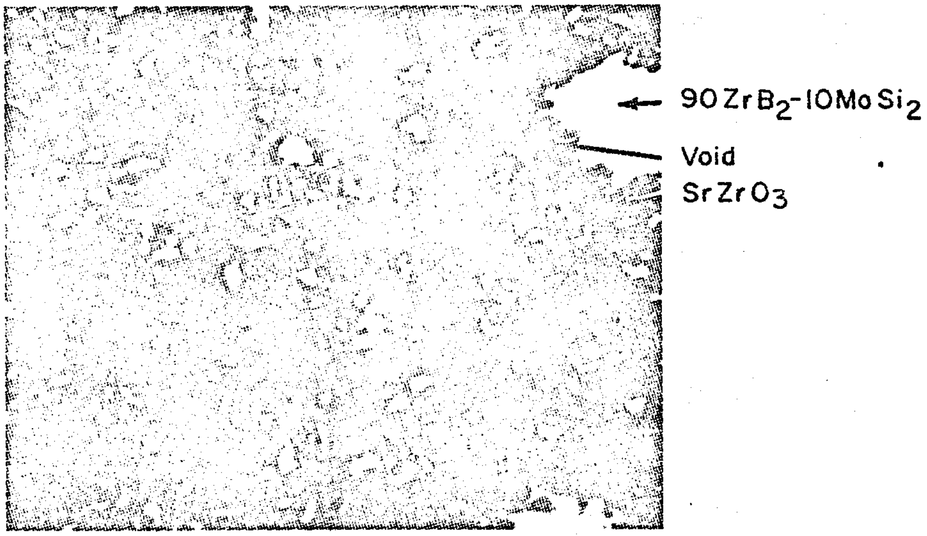
FIGURE 6

PHOTOMICROGRAPH OF SINTERED
8% YTTRIA-STABILIZED ZIRCONIA

(Sintering Conditions - 1900°C,
45 min., 10^{-6} torr)



$SrZrO_3$-$TaSi_2$ 80x
Density=80% Theory Unetched



$50SrZrO_3$-$50(90ZrB_2$-$10MoSi_2)$ 350x
Density=75% Theory Unetched

FIGURE 7

PHOTOMICROGRAPHS OF $50SrZrO_3$-$50TaSi_2$ AND $50SrZrO_3$-$50(90ZrB_2$-$10MoSi_2)$

(Sintered at 1700°C for 30 Minutes in Argon)

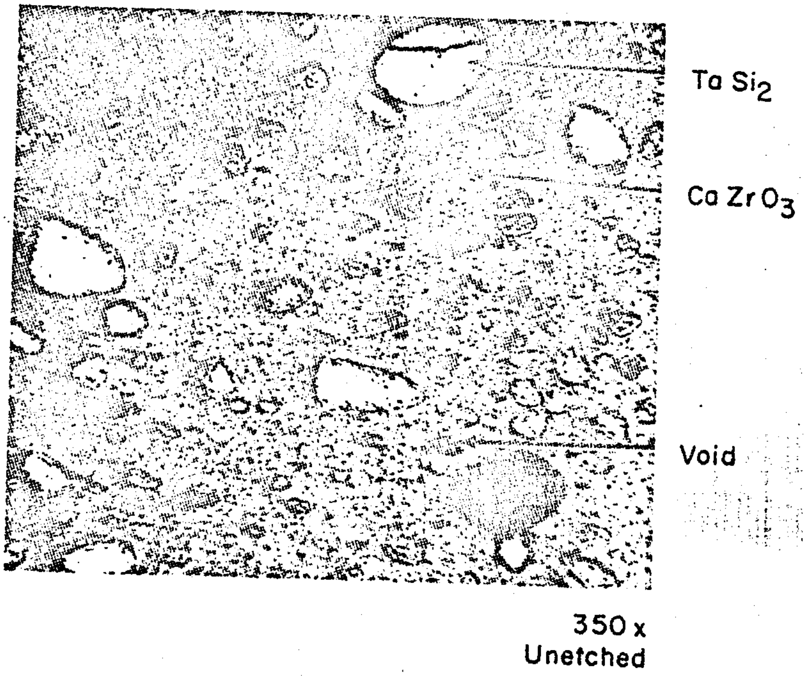
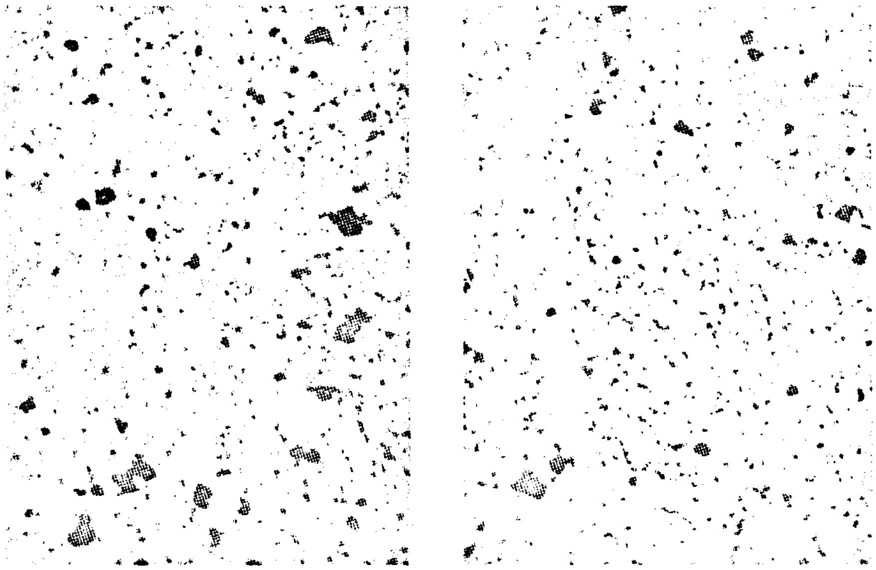


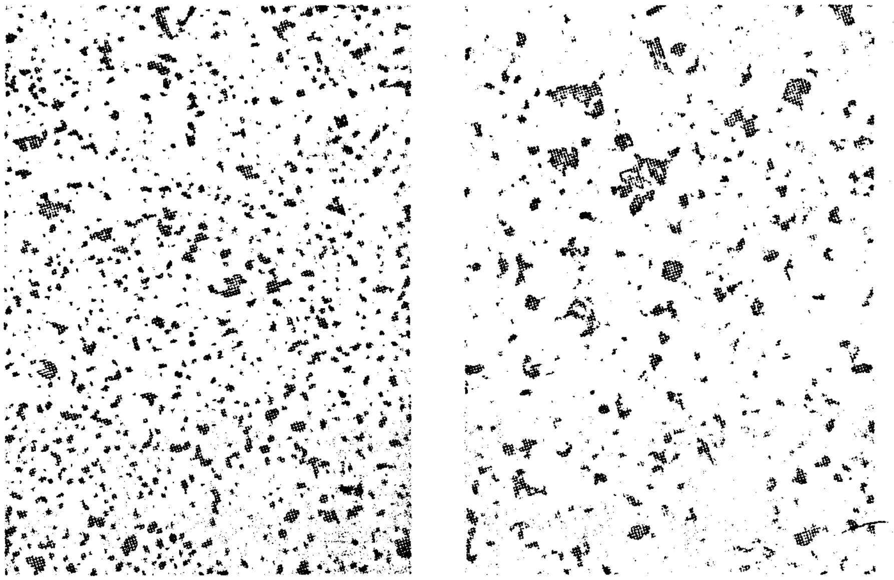
FIGURE 8

PHOTOMICROGRAPH OF 50$CaZrO_3$-50$TaSi_2$ COMPOSITE

(Sintered at 1700°C for 30 min. in Argon)



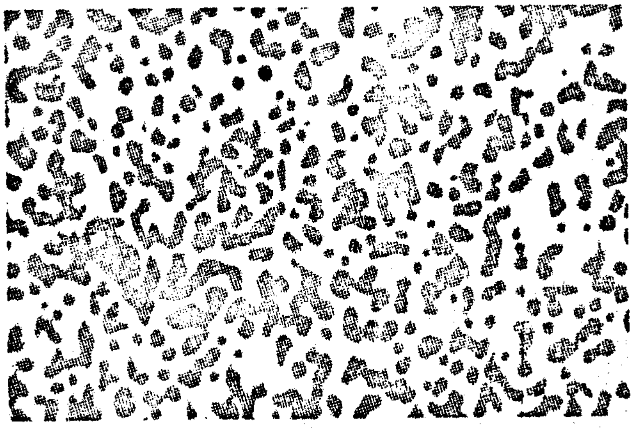
$TaAl_3$ 1 hr., 1400°C, Argon Ta_2Be_{17} 2.5hrs., 1400°C, Argon



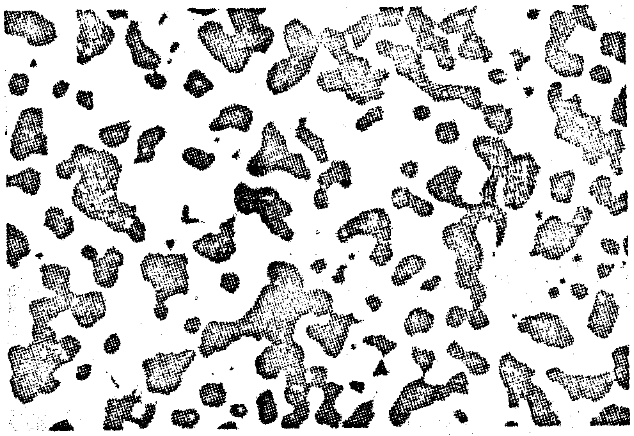
$TaSi_2$ 1hr., 1400°C, Argon   90 ZrB_2-10 $MoSi_2$-1hr., 1400°C, Argon

FIGURE 9

PHOTOMICROGRAPHS OF SINTERED INTERMETALLIC COMPOUNDS
(400X Magnification, Unetched)



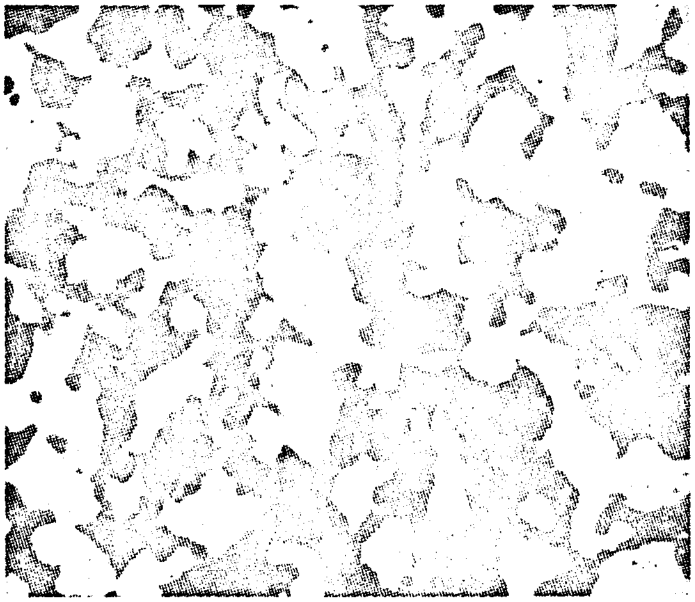
5hrs -1725°C-Argon 400x, Unetched



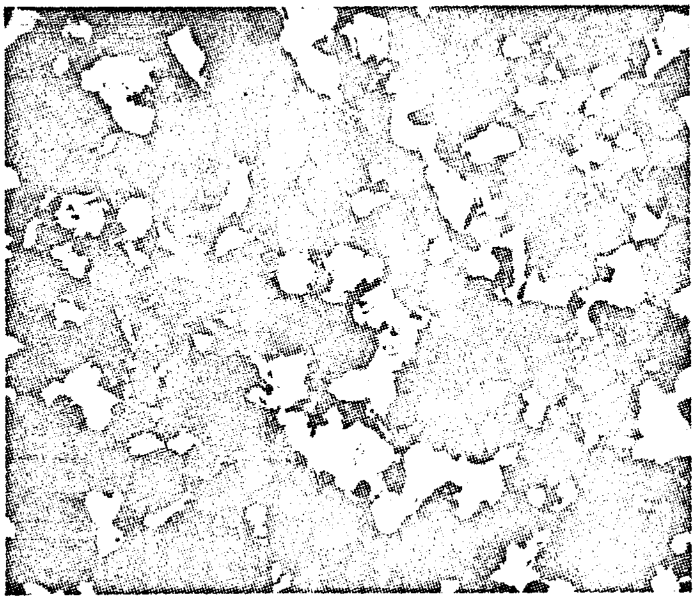
10 hrs-1725°C-Argon 800x, Unetched

FIGURE 10

PHOTOMICROGRAPHS OF SINTERED 8% Y_2O_3-STABILIZED ZrO_2



50(3.5 CaO-96 ZrO_2)-50 $MoSi_2$ 400x
Unetched

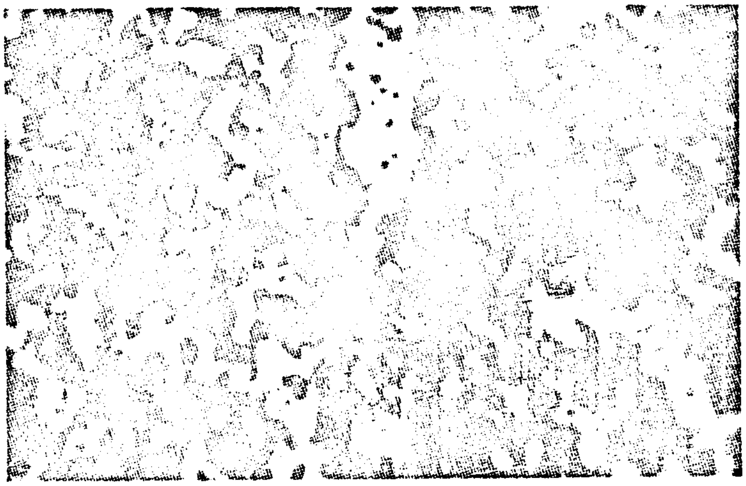


50(3.5 CaO-96.5 ZrO_2)-50 $TaSi_2$ 400x
Unetched

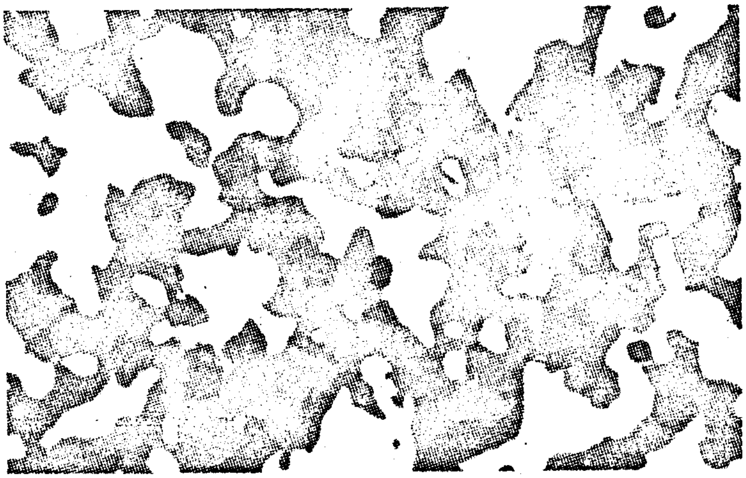
FIGURE 11

PHOTOMICROGRAPHS OF SINTERED
CaO-STABILIZED ZrO_2 COMPOSITES

(Sintered 3.5 hrs. at 1725°C in Argon)



$50(8Y_2O_3\text{-}92ZrO_2)\text{-}50MoSi_2$ 400x



$50(8Y_2O_3\text{-}92ZrO_2)\text{-}50(90ZrB_2\text{-}10MoSi_2)$ 400x

FIGURE 12

PHOTOMICROGRAPHS AT 400X MAGNIFICATION OF 8% Y_2O_3 STABILIZED ZrO_2 COMPOSITES

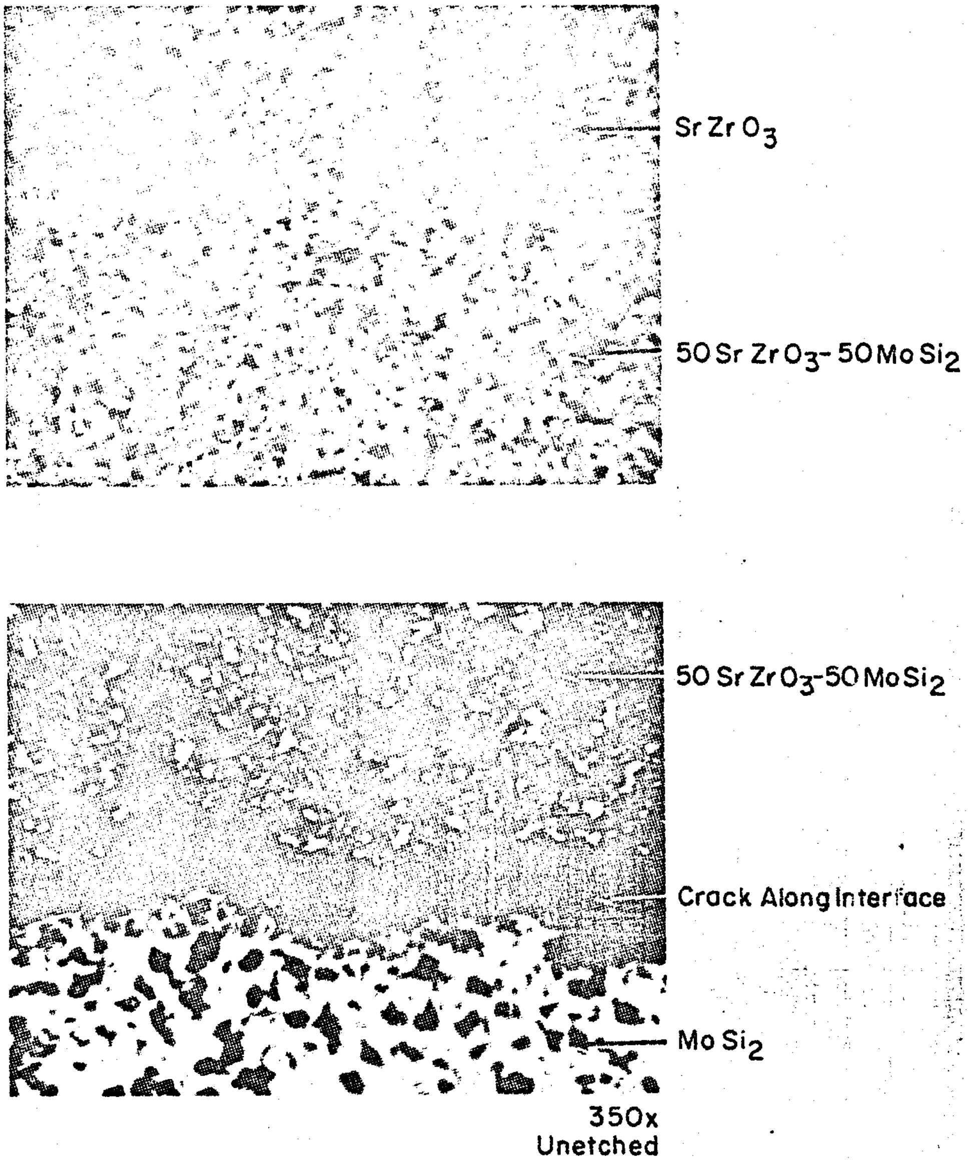


FIGURE 13

$SrZrO_3$-$MoSi_2$ THREE-LAYER COMPOSITE

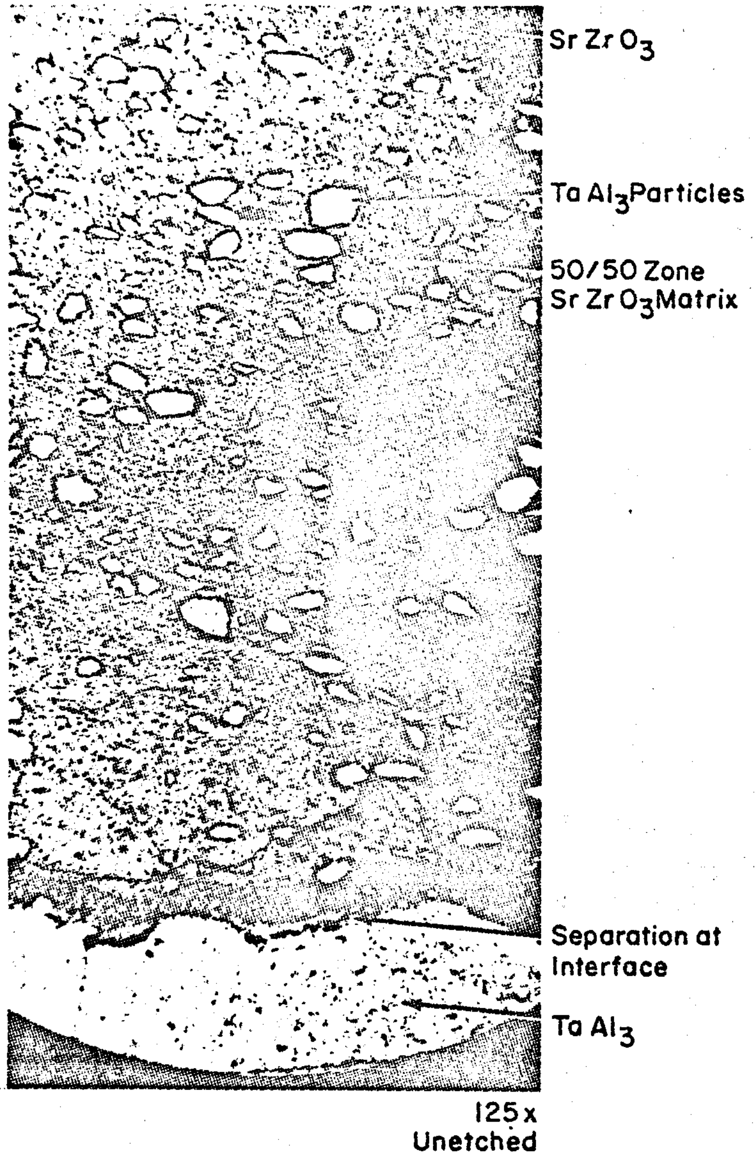
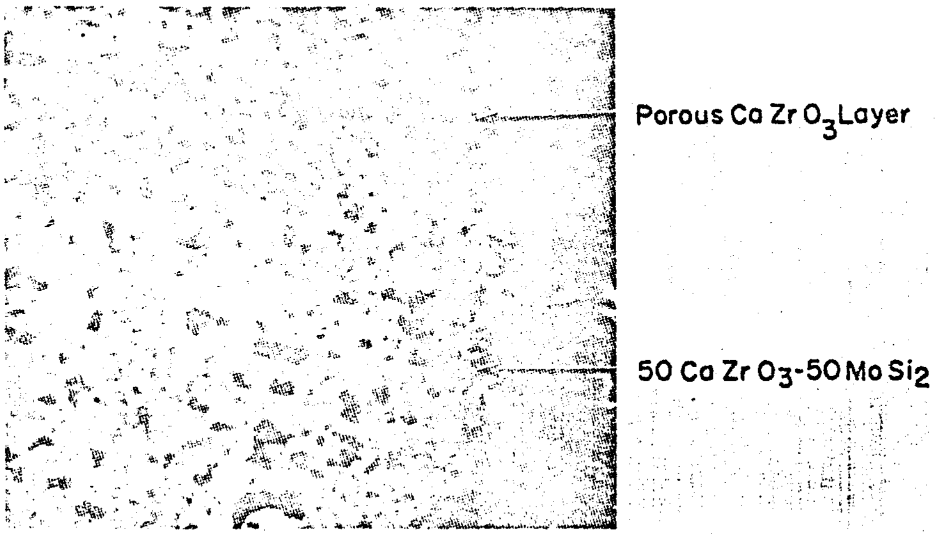
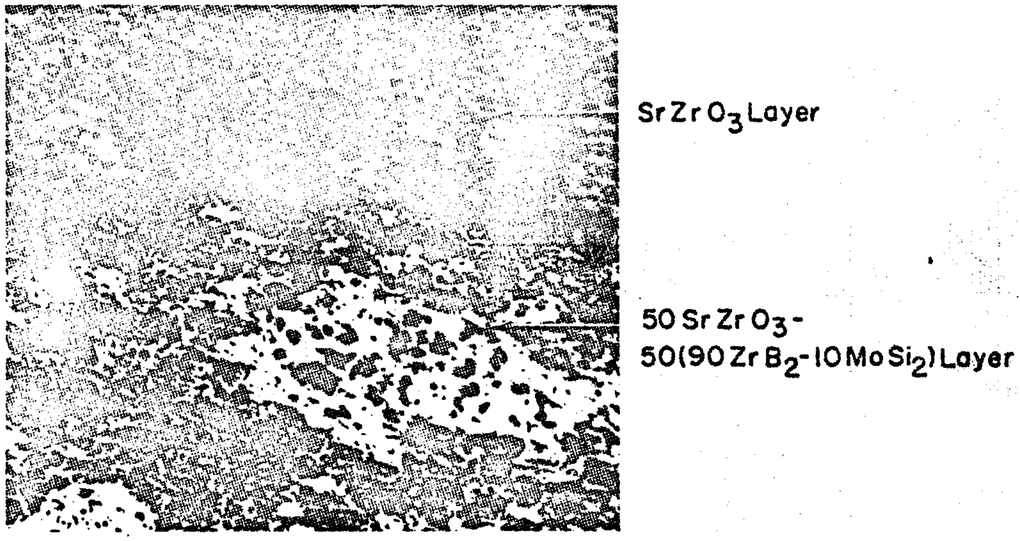


FIGURE 14

$SrZrO_3$-$TaAl_3$ THREE LAYER COMPOSITE (OVERALL VIEW)



350x Unetched



350x Unetched

FIGURE 15

INTERFACE BETWEEN PURE OXIDE AND
50/50 OXIDE-INTERMETALLIC IN THREE LAYER
COMPOSITES OF
$CaZrO_3$-$MoSi_2$ and $SrZrO_3$-($90ZrB_2$-$10MoSi_2$)

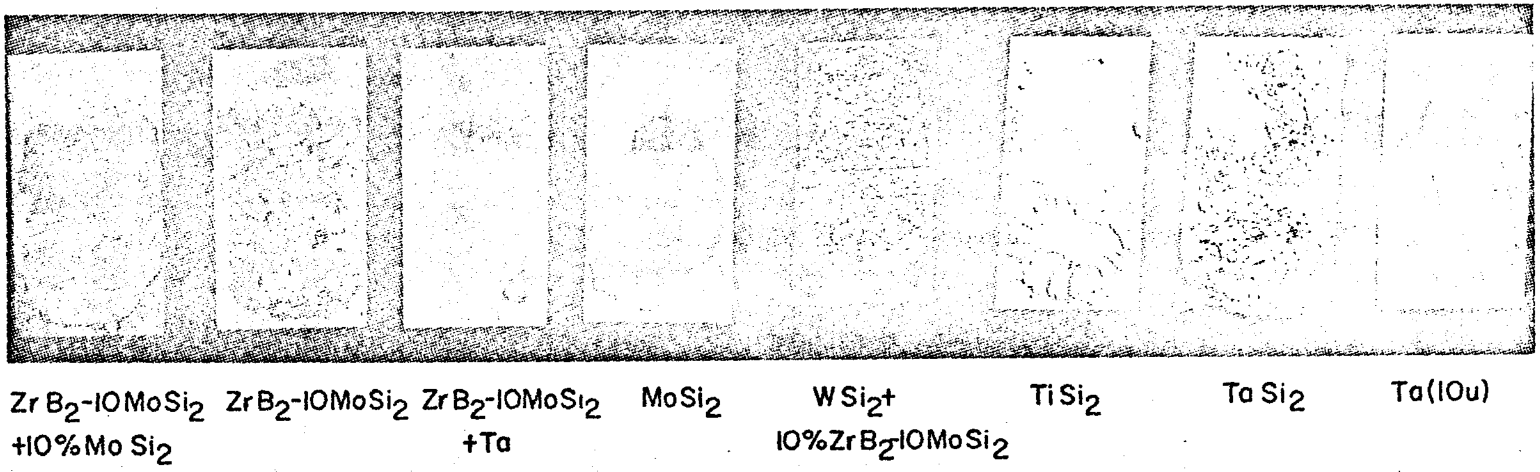
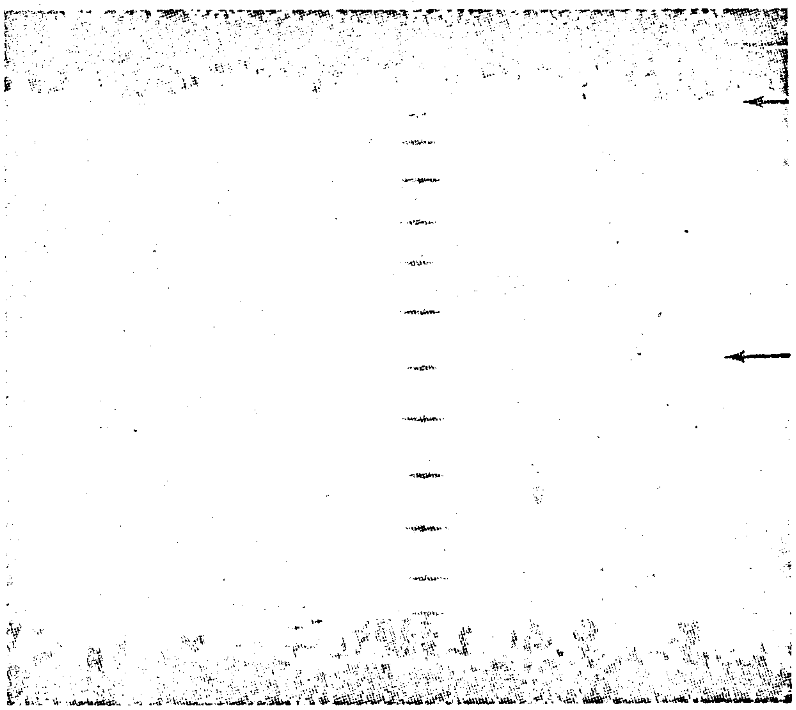


FIGURE 16

REACTION OF INTERMETALLIC COMPOUNDS WITH Ta-10W AT 1750°C - 1800°C IN ARGON

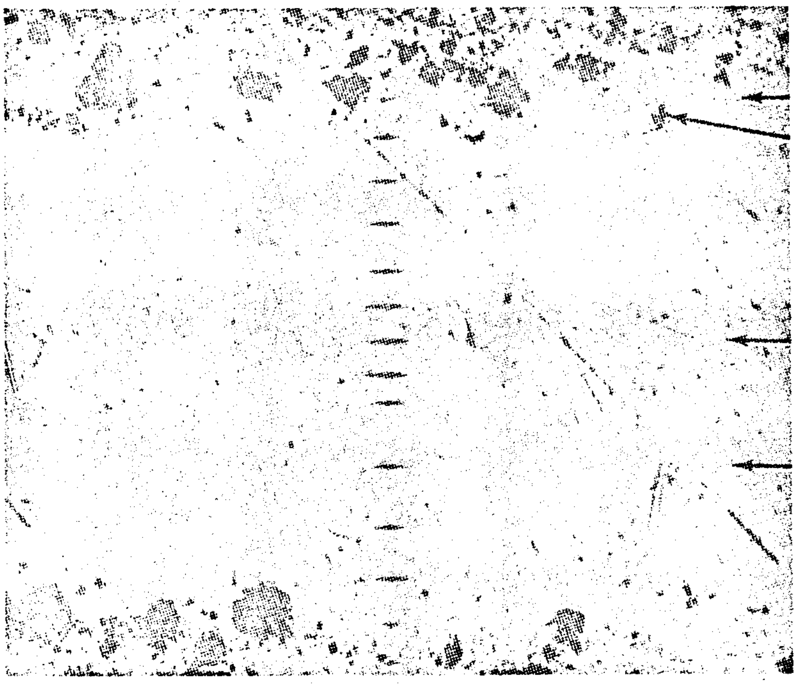


W Si_2 Coating Hardness 1970 kg/mm^2

Diffusion Zone Hardness 580 kg/mm^2

Ta-10 W Substrate Hardness 340 kg/mm^2

Pressed 25 tsi
1700°-1750°C, 1 hr, Argon



90 ZrB_2-10 Mo Si_2

Void

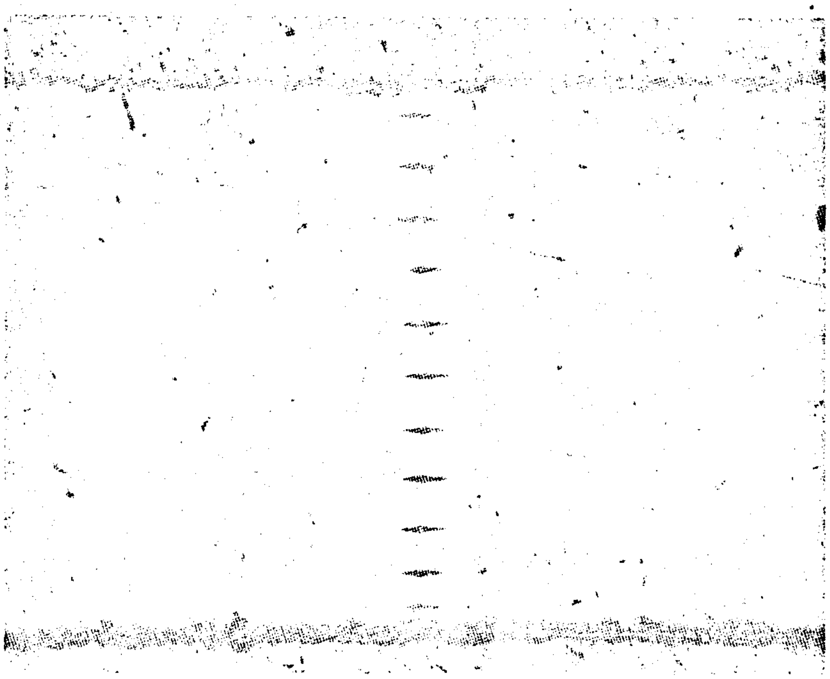
Ta-10W Substrate Hardness 460 kg/mm^2

Substrate Showing Grain Boundary Diffusion Of Coating

Pressed 25 tsi
1700°-1750°C, 2 hrs, Argon

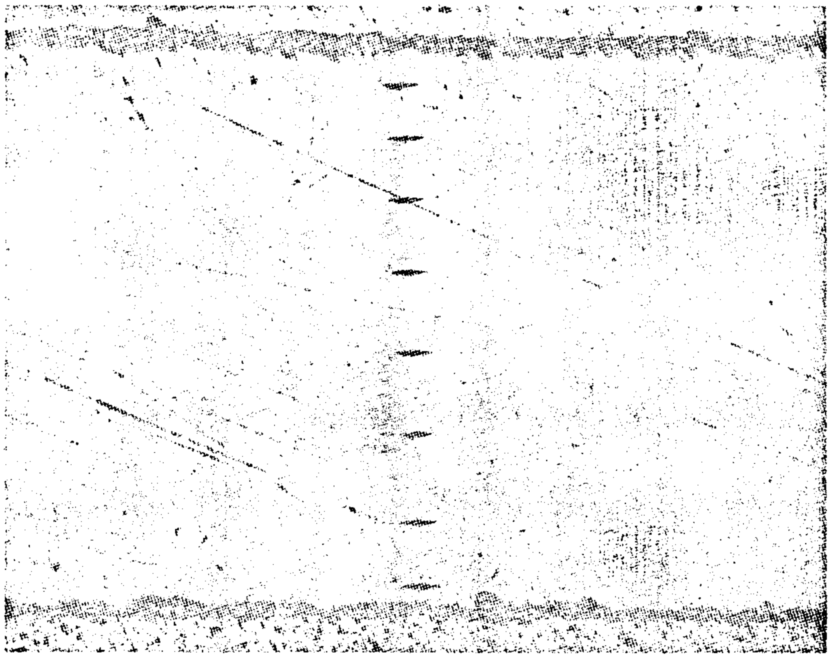
FIGURE 17

WSi_2 AND 90 ZrB_2 - 10 $MoSi_2$ COATINGS ON Ta-10W ALLOY
(Magnification 150X, Unetched)



Microhardness $340 kg/mm^2$

Ta-10 W As Received



Microhardness $470 kg/mm^2$

After Heating
1700°-1750°C, 1hr, Argon

FIGURE 18

EFFECT OF HEAT-TREATMENT ON MICROHARDNESS OF Ta-10W SUBSTRATE (Magnification 150X, Unetched)

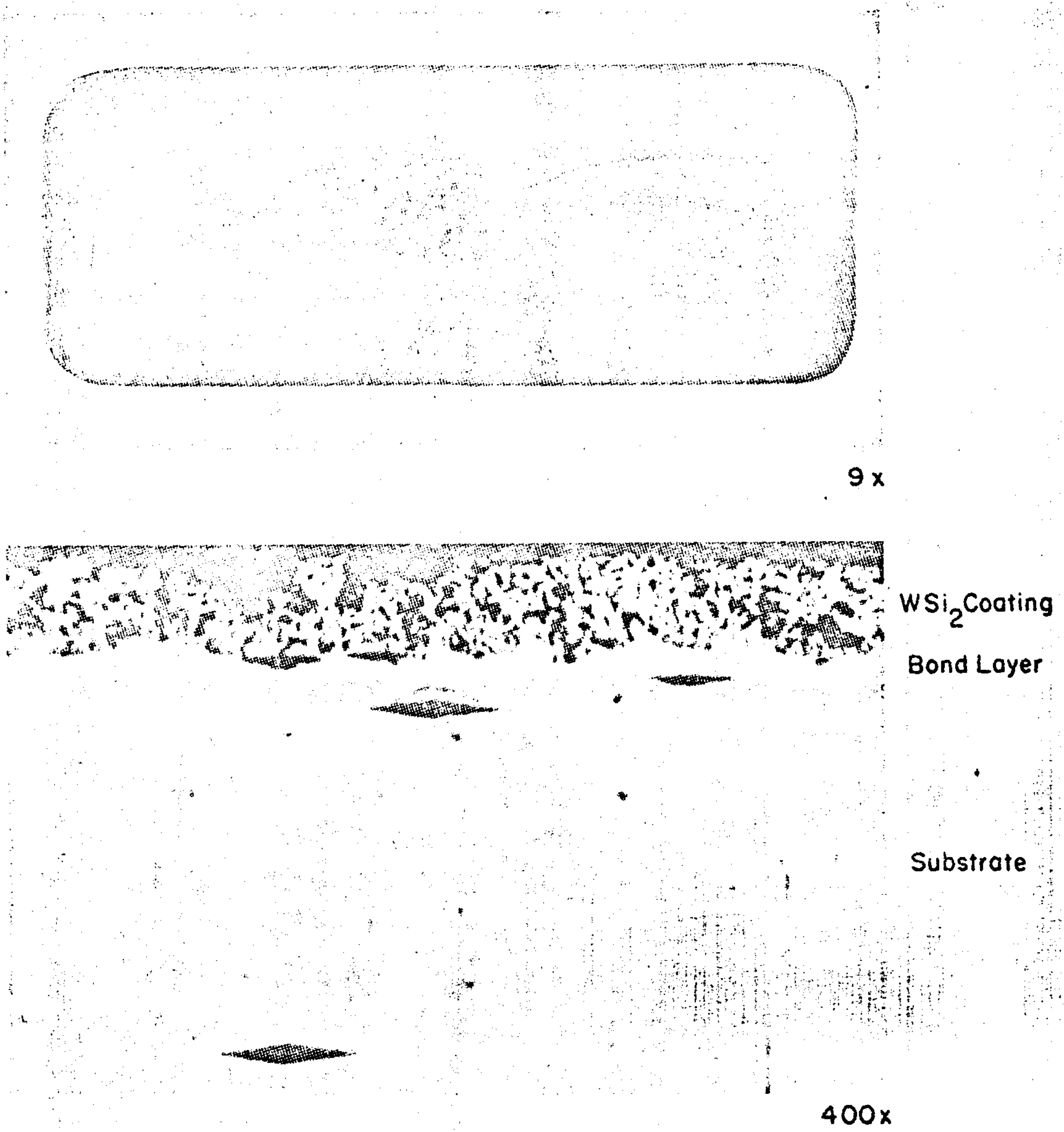


FIGURE 19

Ta-10W SPECIMEN, COATED WITH WSi_2, SINTERED AT 1400°C, AND SILICONIZED AT 1350°C

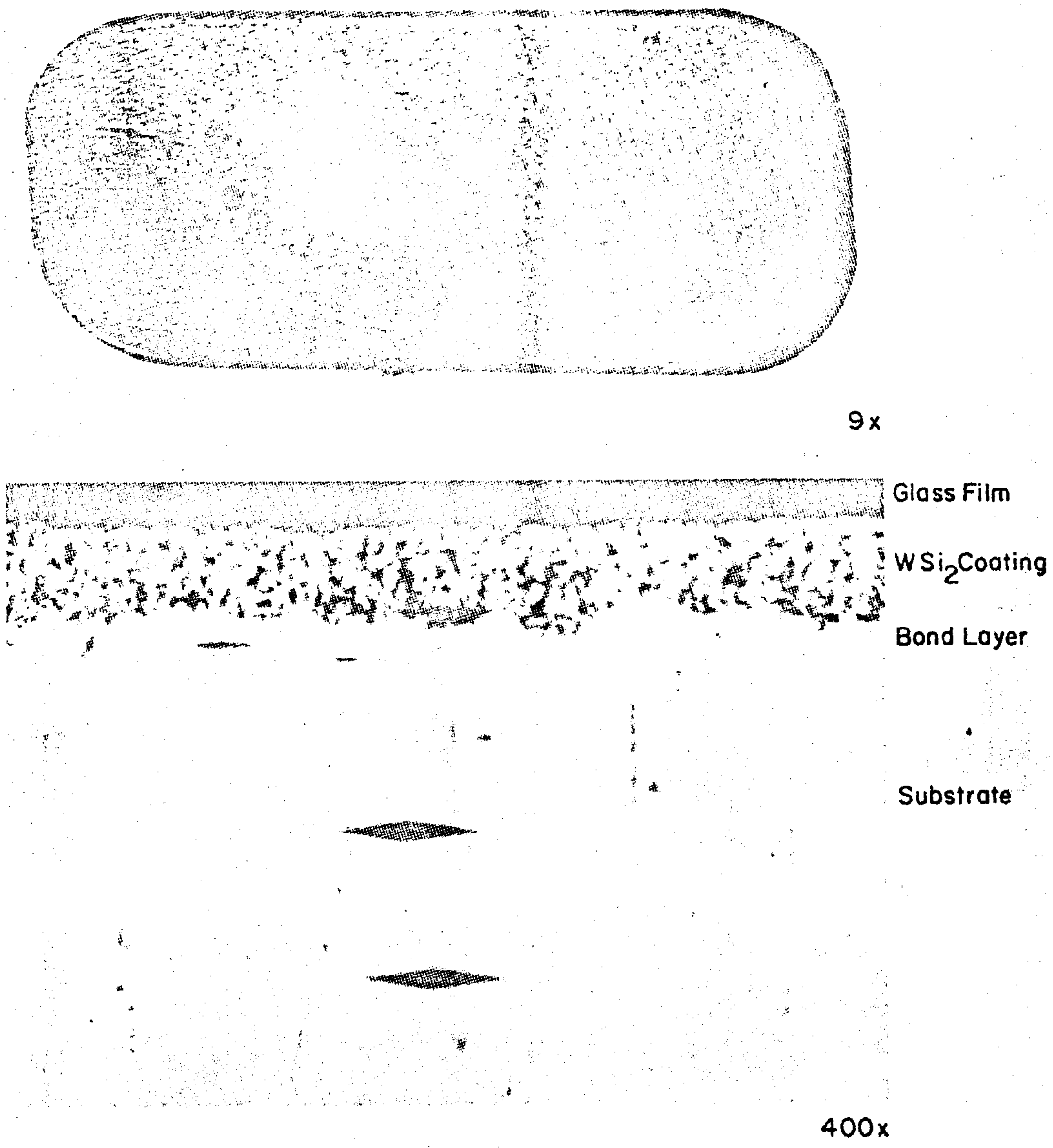


FIGURE 20

WSi_2-COATED Ta-10W SPECIMEN AFTER STATIC OXIDATION FOR 30 MINUTES AT 3000°F

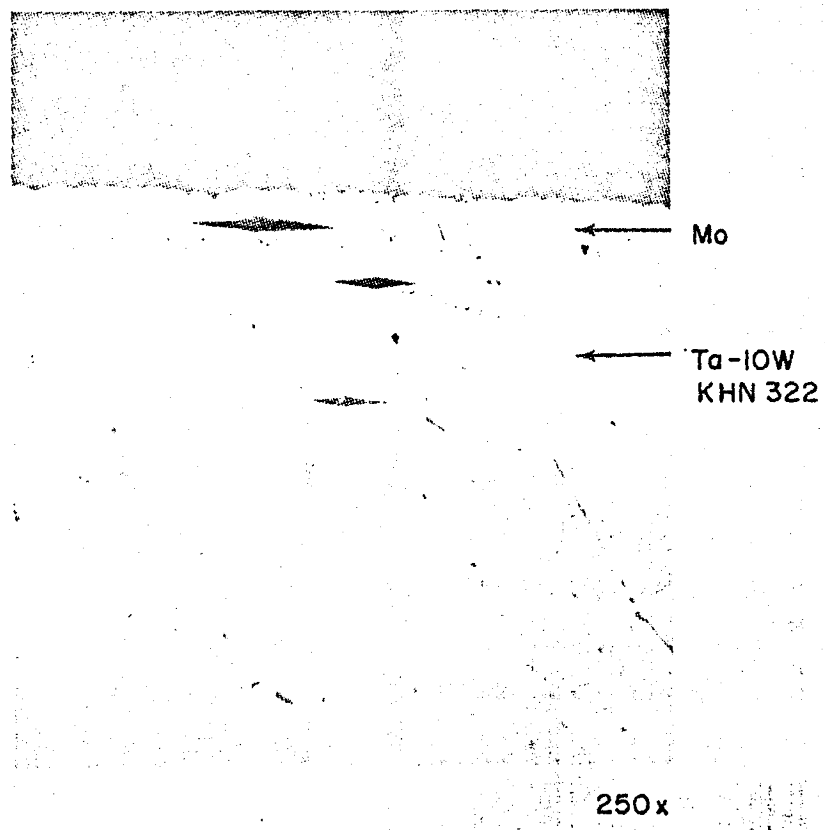


FIGURE 21

Mo COATING ON CHEMICALLY CLEANED Ta-10W
FIRED IN ARGON AT 1400°C FOR 2 HOURS

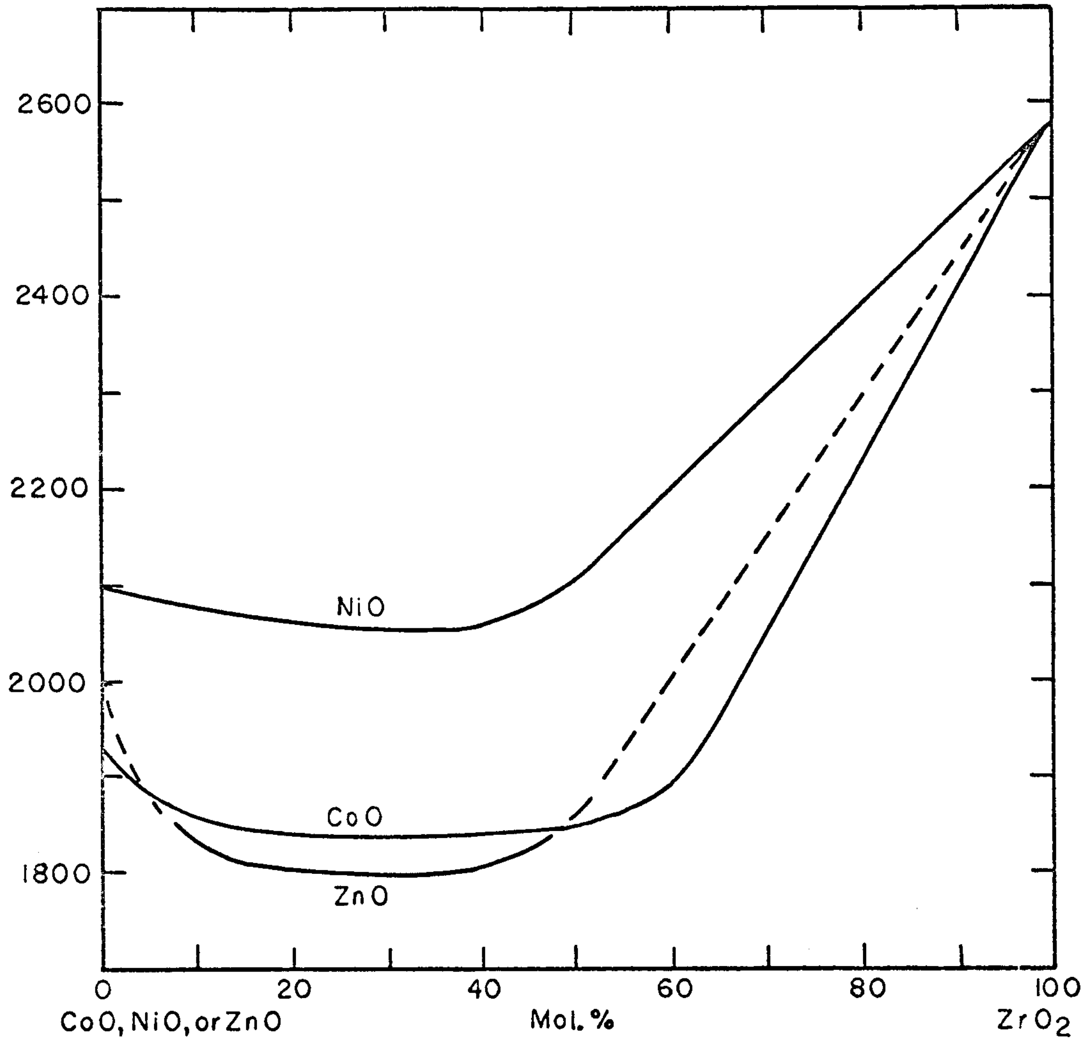


FIGURE 22

LIQUIDUS CURVES OF SYSTEMS
$CoO-ZrO_2$, $NiO-ZrO_2$, and $ZnO-ZrO_2$

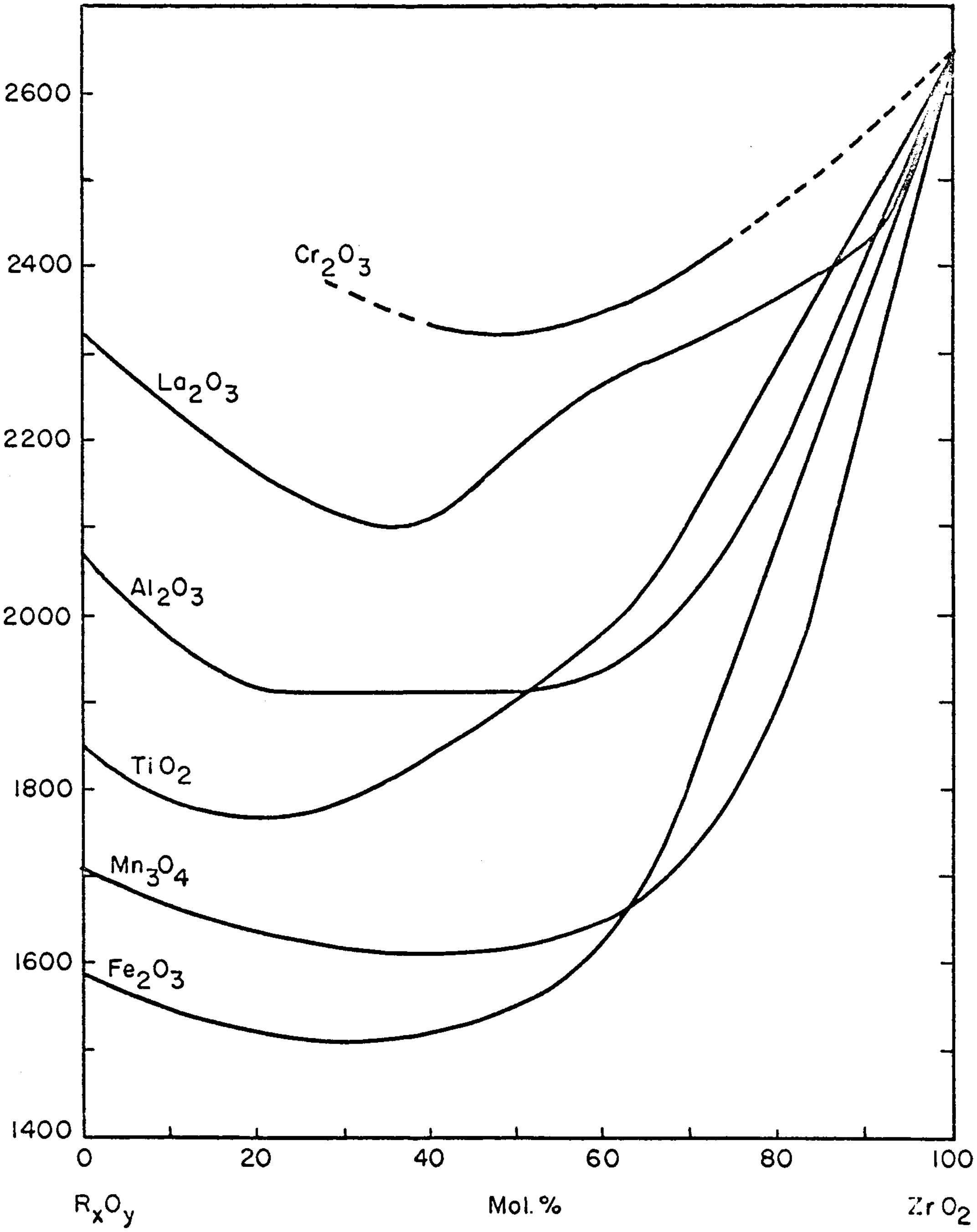
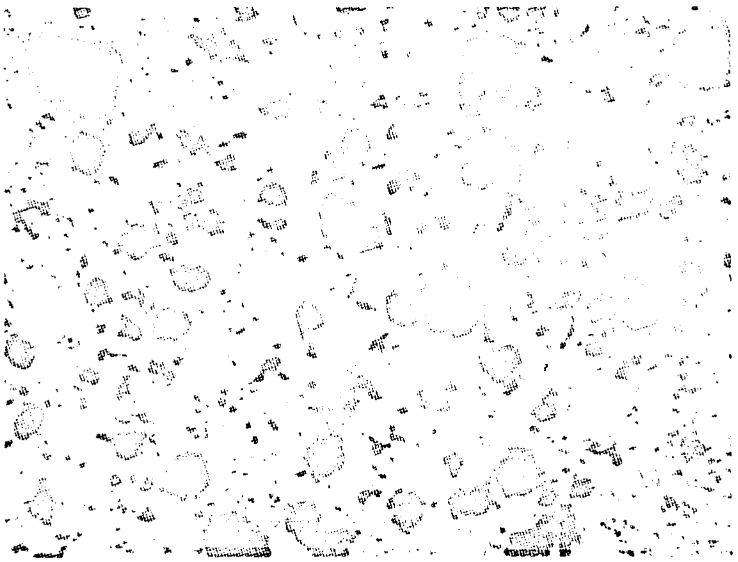
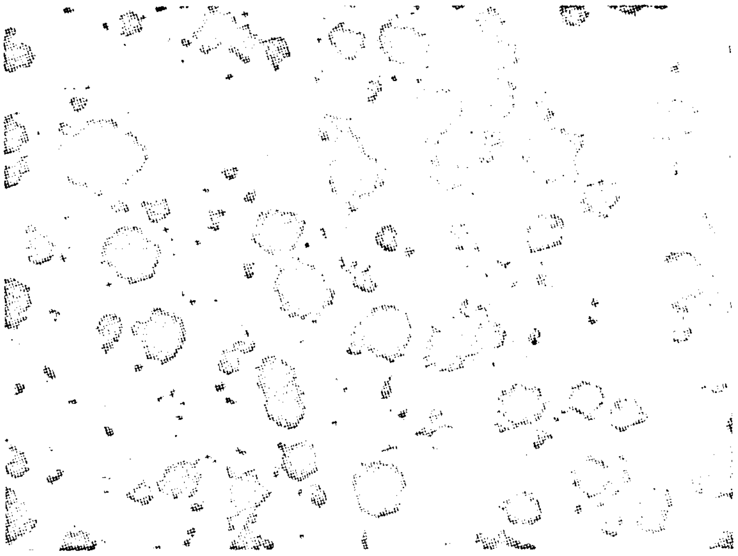


FIGURE 23

LIQUIDUS CURVES OF SYSTEMS Al_2O_3-ZrO_2, Cr_2O_3-ZrO_2 Fe_2O_3-ZrO_2, La_2O_3-ZrO_2, Mn_3O_4-ZrO_2, and TiO_2-ZrO_2



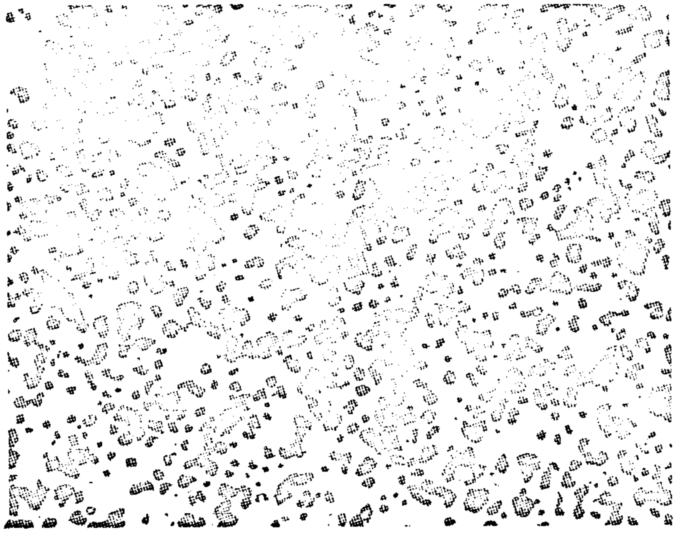
5W/O Al_2O_3 200X



10W/O Al_2O_3 200X

FIGURE 24

CROSS SECTIONS OF Al_2O_3 MODIFIED
CaO STABILIZED ZrO_2 SPECIMENS



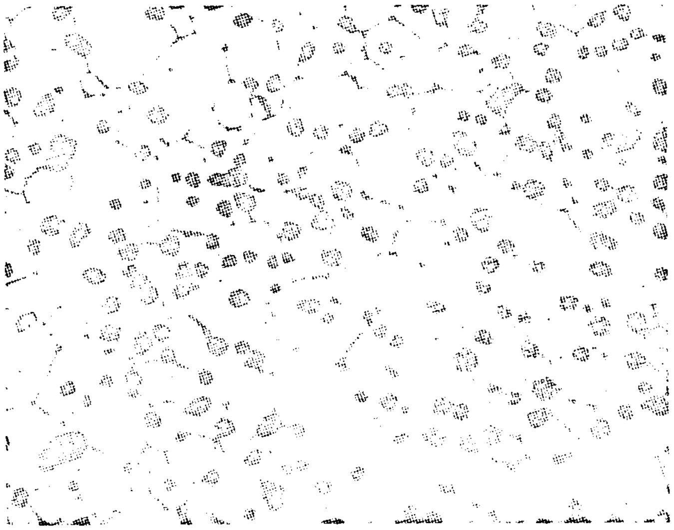
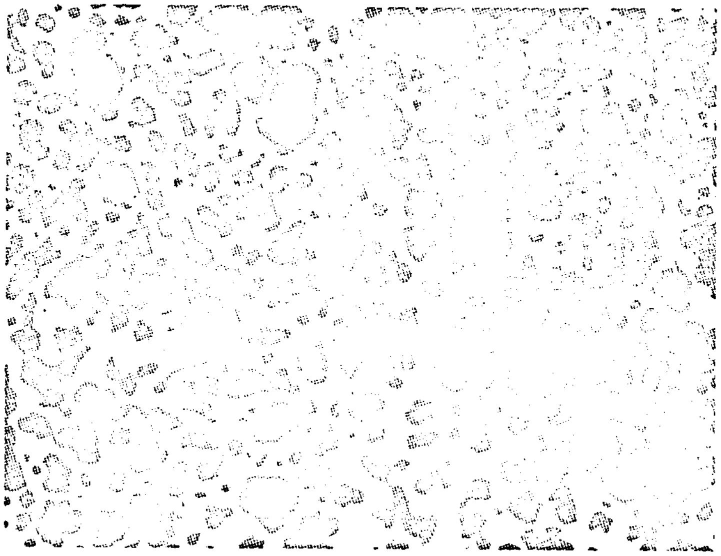
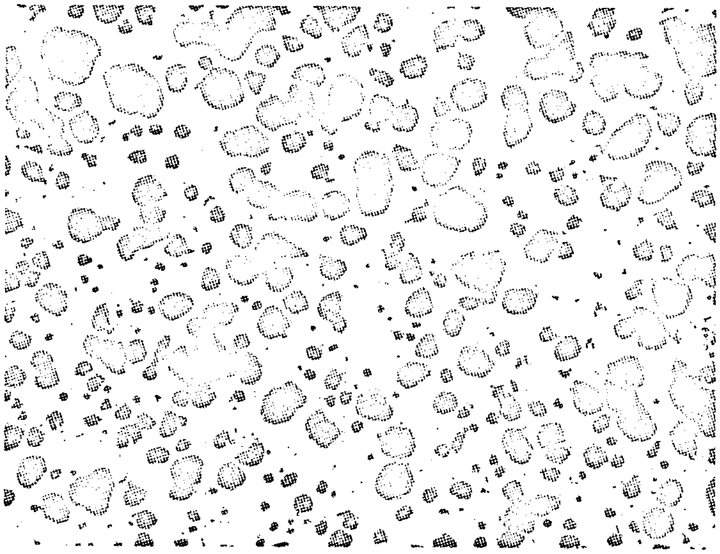


FIGURE 25

CROSS SECTIONS OF TiO_2 MODIFIED CaO STABILIZED ZrO_2 SPECIMENS



5 W/O Co_2O_3 200X



10 W O Co_2O_3 200X

FIGURE 26

CROSS SECTIONS OF Co_2O_3 MODIFIED CaO STABILIZED ZrO_2 SPECIMENS

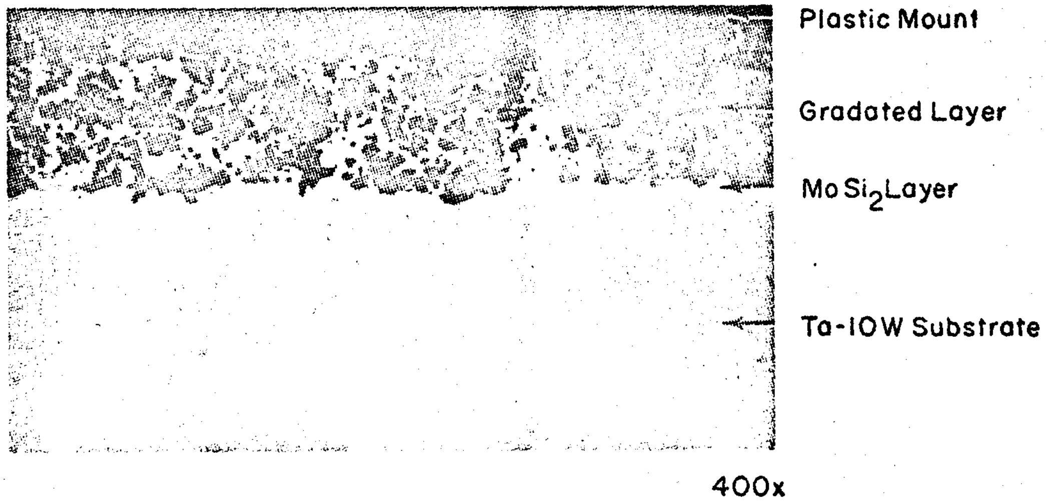


FIGURE 27

$MoSi_2$-ZrO_2 (3.5% CaO Stabilized)
GRADATED COATING OVER SINTERED $MoSi_2$
(Sintered 1400°C, 1 hour, Argon)

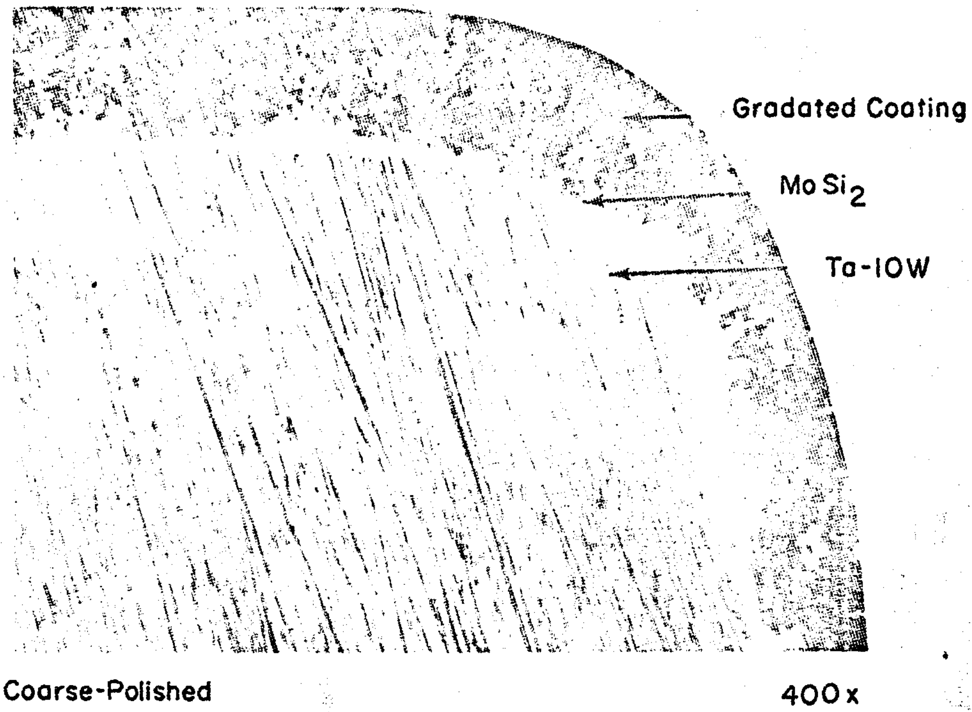


FIGURE 28

MoSi$_2$-ZrO$_2$ (3.5% CaO Stabilized)
GRADATED COATING OVER SINTERED MoSi$_2$
(Coating Sintered in Argon, 1400°C, 1 Hour
Resintered 1 Hour at 1700°C)

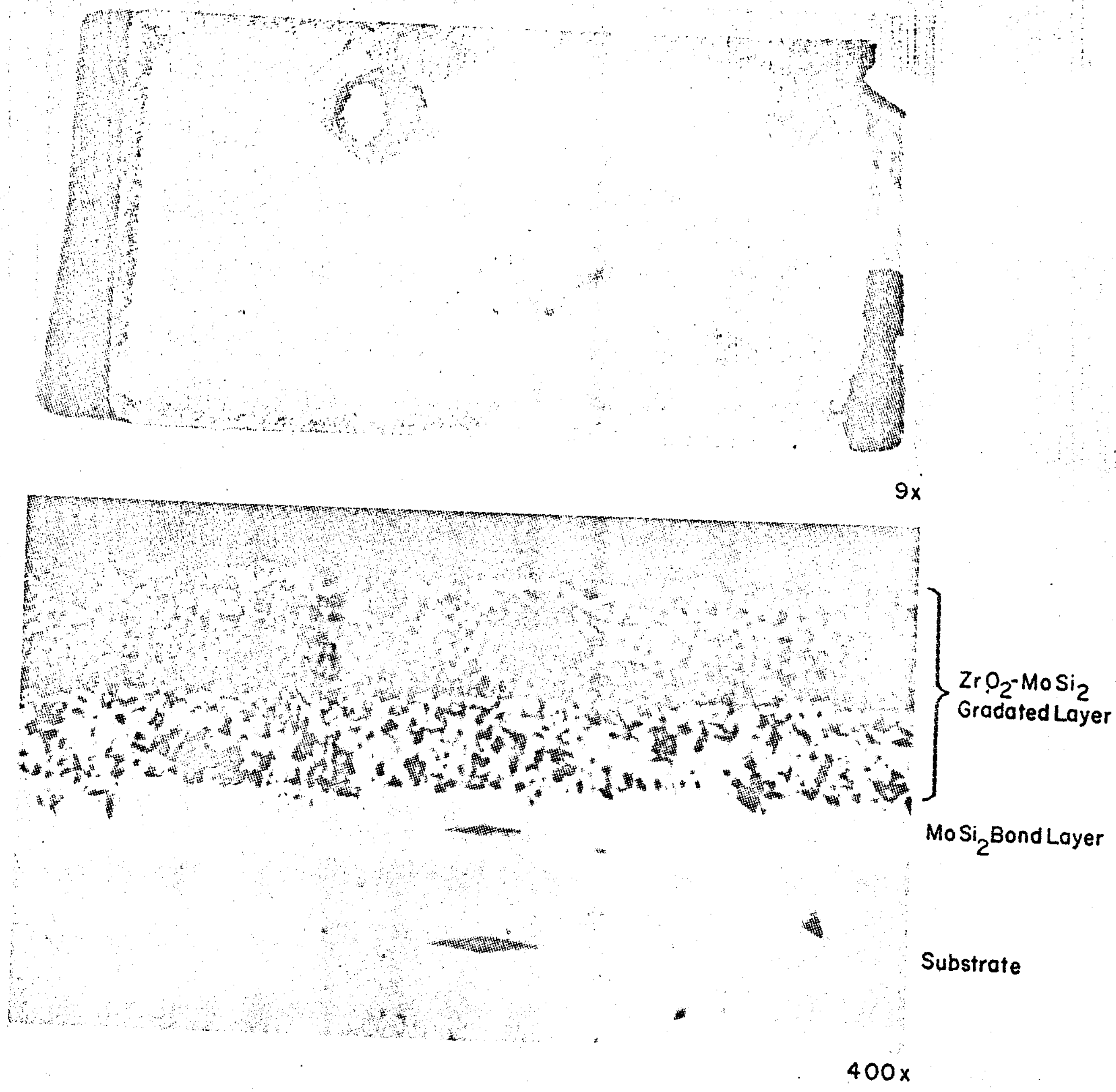


FIGURE 29

$MoSi_2$-ZrO_2 GRADATED COATING ON Ta-10W SPECIMEN AFTER OXIDATION AT 1600°C - 1650°C FOR 20 MINUTES

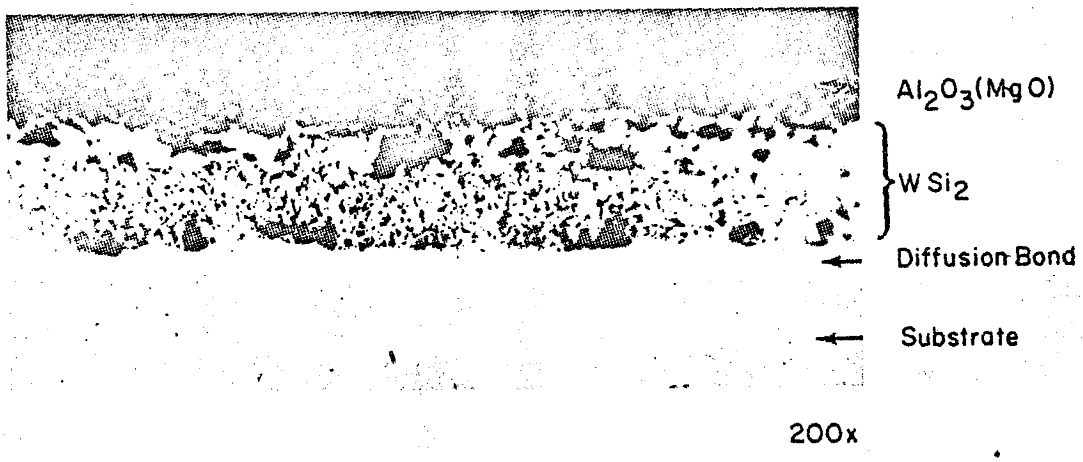


FIGURE 30

CROSS SECTION OF $Al_2O_3(MgO)$ - WSi_2 GRADATED COATING ON Ta-10W AFTER STATIC OXIDATION TEST AT 2912°F

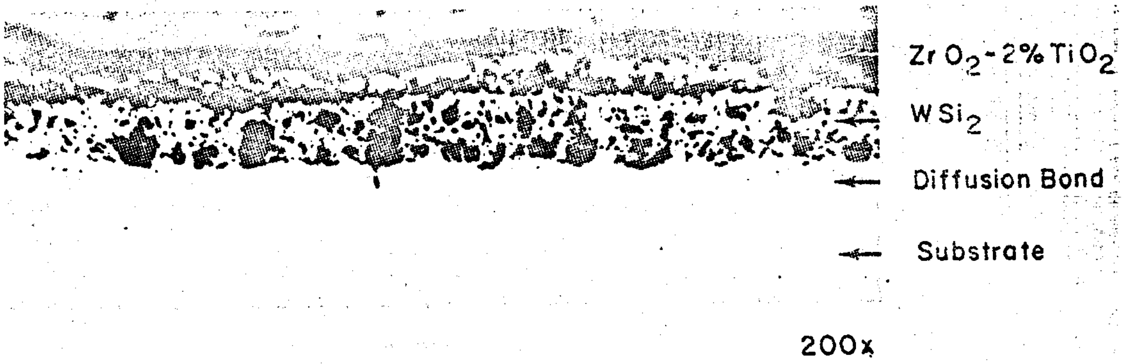
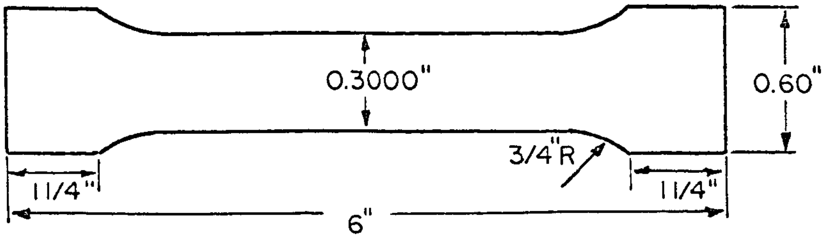
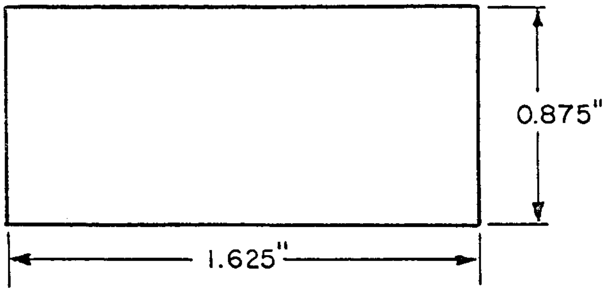


FIGURE 31

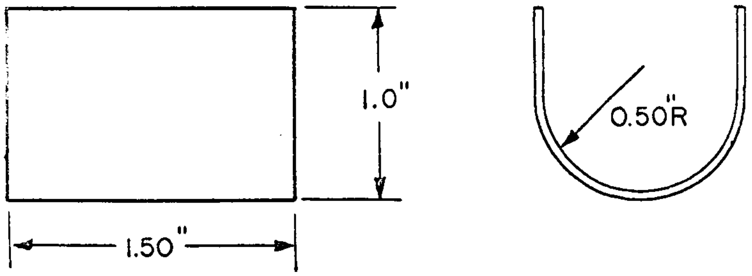
CROSS SECTION OF 3.5% CaO STABILIZED (ZrO_2-2%TiO_2)-WSi_2 ON Ta-10W AFTER STATIC AIR OXIDATION TEST AT 3000°F



SHEET TENSILE SPECIMEN



COUPON



SIMULATED LEADING EDGE

Material - Ta-10W Foil, 0.008 in. Thick

FIGURE 32

SPECIMENS COATED FOR NASA EVALUATION