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A STUDY OF Mo-V AND Mo-V-Fe ALLOYS FOR CONDUCTIVE CERMET APPLICATIONS

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Abstract

Molybdenum/alumina cermets are currently being used for small, simple geometry, electrical feed-throughs in insulating alumina ceramic bodies. However, with larger and more complex geometries, high residual stresses and cracking of the alumina ceramic occur due to differences in coefficient of thermal expansion (CTE) between cermet and the surrounding 94% alumina. The difference in CTE is caused by the Mo in the cermet, which lowers the CTE of the cermet relative to the 94% alumina ceramic. A study was conducted at Sandia National Laboratories to develop CTE-matched cermets based on binary Mo-V and ternary Mo-V-X alloy systems. It was found that the CTE of 94% alumina (over the range 1000°C to room temperature) could be precisely matched by a binary Mo-32.5V alloy. However, to address concerns regarding the selective oxidation of V. Mo-V-X alloys with CTE's similar to 94% alumina were made with Fe or Co additions. The ternary additions are limited to about 3 wt.% to maintain a single phase BCC alloy, and permit some reduction in the V addition. Powders were fabricated from both Mo-27V and Mo-22V-3Fe, and were evaluated in 3 hr./1625°C cermet sintering trials. The results of those trials suggest that extensive reaction occurs between the Vanadium component of the alloy and the alumina ceramic. In view of these results we have begun to evaluate the feasibility of fabricating Iridium/alumina cermets. Iridium is an attractive choice due to its close CTE match to 94% alumina ceramic. Preliminary results indicate there is no detrimental reaction between the Iridium and alumina phases.

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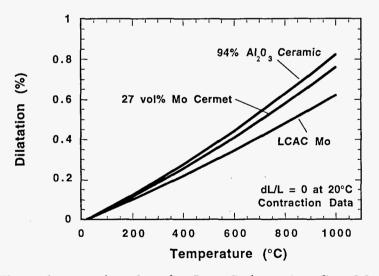
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Introduction

Conductive molybdenum/alumina cermets - with typically 50 wt. % molybdenum/50 wt.% alumina, corresponding to 27 vol.% molybdenum/73 vol.% alumina - were developed for high vacuum, high voltage applications in the early 1980's (1,2). The cermet material is either pressed and sintered as a monolithic powder mixture, or poured as a slurry into a green-machined 94% alumina body, followed by a 3 hr./1625°C sinter fire in wet hydrogen. For cermet/alumina piece parts, relatively simple cylindrical geometries such as conductive cermet feed-throughs were initially fabricated. No cracking was observed in these assemblies, because the tensile stresses in the alumina were minimized by the small cermet feature size relative to the surrounding alumina. This was despite the relatively large thermal expansion mismatch between the 94% alumina ceramic and unalloyed molybdenum, as shown in Figure 1. However, when more complicated piece parts were made with larger cermet features, the thermal expansion mismatch between the two materials led to higher tensile stresses in the alumina ceramic, resulting in cracks within the ceramic. For example, the unfired piece part shown schematically in Figure 2a was found to be cracked after firing, and Finite Element Analysis of the residual stresses developed in this piece part predicted peak tensile stresses as high as 150 MPa could be developed in the alumina ceramic. As shown in Figure 2b-c, the cracks in the sinter-fired parts appear to initiate in the alumina ceramic immediately adjacent to the edge of the cermet insert.



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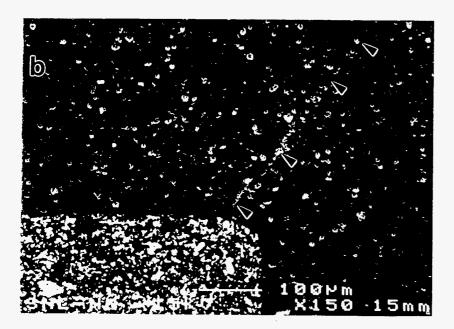
Figure 1. Thermal expansion data for Low-Carbon, Arc Cast Mo (LCAC Mo), 94% alumina ceramic, and the 27 vol.% Mo/73 vol.% alumina ceramic materials. Data obtained using the dilatometer run in contraction (during cooling from 1000 to 37°C). The dilatation is adjusted in this plot so that dL/L = 0 at 20°C.

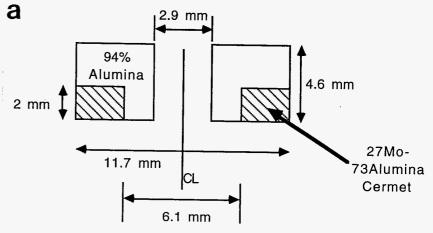
The present study was initiated as a response to the piece-part cracking problems described above. It was postulated that a binary addition to Mo could be found to increase the thermal coefficient of expansion (CTE) of the alloy so as to match that of the 94% alumina ceramic material. In addition to the CTE requirement, the new alloy must be compatible with current sintering and piece part vacuum bakeout processes. The approach taken was

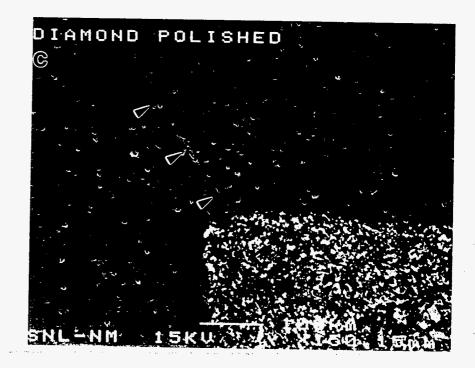
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Figure 2.

Example of a more complicated cermet/alumina piece part geometry which leads to cracking in the 94% alumina ceramic when it is co-sintered with the 27 vol.% Mo/73 vol.% alumina cermet material. (a) Schematic geometry of the part in the green or unfired condition. (b, c) SEM photos showing cracking in the alumina ceramic. In both photos, the cracks appear to start in the ceramic adjacent to the corner of the cermet insert.





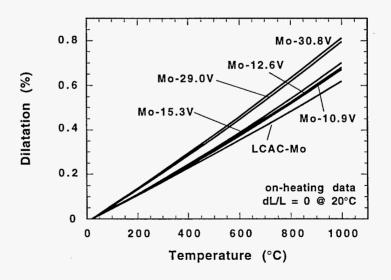


to develop a single phase BCC alloy, to ensure that no intermediate intermetallic compounds with low melting points are formed. The compatibility requirement dictates that the Mo-base alloy have little or no reaction with both the alumina ceramic and wet hydrogen atmosphere during the 3 hr. /1625°C cermet sintering treatment. Finally, the vacuum bakeout process requires that any alloying element have low vapor pressure at temperatures up to 1000°C.

A number of important results obtained during the initial alloy development phase of this study were previously (3, 4). In the present paper, we will refer to those reports where possible in order to present recent results in detail.

Results: Binary Mo-V Alloys to Permit CTE Matching with 94% Alumina Ceramic

A literature survey of binary phase diagrams and thermal expansion behavior of binary Mo-X alloy systems suggested that both Mo-V and Mo-Cr alloys would have the potential to match the CTE of the 94% alumina ceramic. However, due to the high vapor pressure of Cr, it was decided that Mo-Cr alloys would not be compatible with the vacuum bakeout process. As a result, a number of binary Mo-V alloys ranging from 10.9 up to 30.8 wt.% V were produced in laboratory batches to permit evaluation of CTE and micro-structure (3). Dilatation data for the various binary Mo-V alloys and Low-Carbon Arc Cast Mo (LCAC-Mo) are shown in Figure 3. Clearly, Vanadium additions to Molybdenum serve to increase thermal expansion. The average CTE for these alloys, over the interval 37-1000°C, are compared with the average CTE based on five separate lots of 94% alumina, are compared in Figure 4. The results shown in Figure 4 indicate that an alloy with composition of Mo-32.5wt.% V precisely matches the CTE of the 94% alumina ceramic over the temperature range 37-1000°C. Further details regarding these measurements, along with more detailed microstructural information, are available in reference 3.



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Figure 3. Dilatation data for LCAC-Mo and the various Mo-V alloys studied. The data shown were collected during heating, over the temperature range 20-1000°C. The individual data sets were fit to a polynomial equation and adjusted with a constant to impose dL/L = 0 at 20°C.

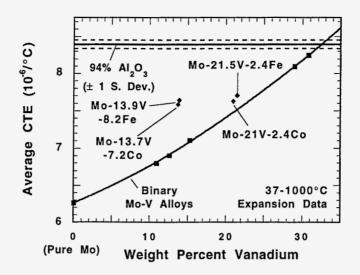
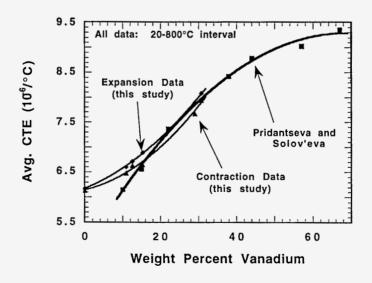


Figure 4. Effect of Vanadium addition to Mo on the average CTE, during heating from 37 to 1000°C. In addition to the binary Mo-V alloys, data are included for 5 different lots of the 94% alumina ceramic (±1 standard deviation shown), and the 4 ternary alloys.

The CTE data obtained for Mo-V alloys in this study are consistent with the data obtained by Pridantseva and Solov'eva (5) over a wider range of Vanadium additions. Figure 5 plots the on-heating and on-cooling data obtained in this study with the data from ref. 5 over the temperature range 20-800°C. Note that above 35 wt.% V, the trend curve based on the Prindantseva and Solov'eva data begins to asymptote, which is to be expected as the alloys begin to approach the CTE of pure Vanadium. Based on tabulated data (6), the average CTE for pure Vanadium over the temperature range 20-800°C is 10.5×10^{-6} /°C.



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Figure 5. Comparison of CTE data for Mo-V alloys studied by Pridantseva and Solov'eva (ref. 5) with the data generated in this study. All of the CTE data shown in this graph are for the temperature interval 20-800°C.

Ternary Mo-V-Fe and Mo-V-Co alloys With Reduced Vanadium Additions

The relatively large V addition needed to match the CTE of 94% alumina ceramic prompted an effort to identify ternary additions that would reduce the amount of V needed while simultaneously increasing CTE and producing a single phase alloy. Iron and Cobalt additions were first examined. The initial pair of alloys fabricated had actual compositions (3) of Mo-13.9V-8.2Fe and Mo-13.7V-7.2Co, as measured by electron microprobe analysis. While these alloys do have increased CTE relative to the binary Mo-V alloy trend line (see Figure 4), their microstructure was not single phase - containing a large amount of either Mo₆Fe₇ or Mo₆Co₇ intermetallic compound as a second phase. These second phases are considered undesirable because of their relatively low melting points (1550-1600°C), and presumed incompatibility with the 1625°C cermet sintering temperature.

A subsequent examination of the ternary phase stability of the Mo-V-Fe system (7) shows that at 897°C, the maximum amount of Fe that can be added to a 75 wt.% Mo alloy and still remain in the single phase BCC region is ~3.5 wt.% Fe. Thus, two additional alloy ingots were made, with nominal compositions of Mo-22V-3Co and Mo-22V-3Fe. Electron microprobe analysis of CTE samples cut from these ingots indicated actual compositions of Mo-21.0V-2.4Co and Mo-21.5V-2.4Fe (3). Optical microscopy of both alloys in the as-cast condition indicated that both alloys are single phase BCC. The on-heating dilatation behavior of these alloys is compared to that of the 94% alumina ceramic and LCAC-Mo in Figure 6. As in the case of the earlier alloys with Fe or Co additions, these ternary additions do serve to increase the CTE of the alloy relative to the binary Mo-V alloy, as shown in Figure 4.

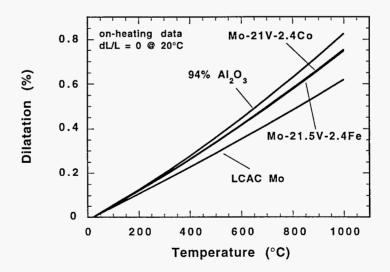


Figure 6. Comparison of dilatation data for LCAC-Mo, Mo-21.5V-2.4Fe, Mo-21V-2.4Co and 94% alumina ceramic materials. On-heating data, dL/L has been adjusted to 0 at 20°C.

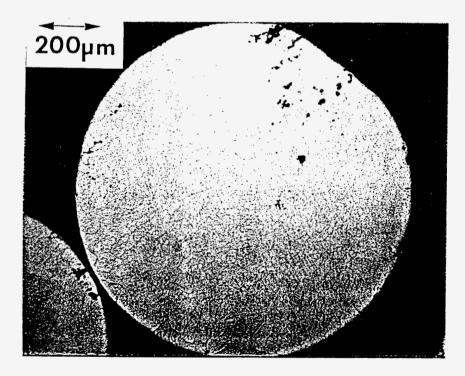
Fabrication of Powders from Binary Mo-V and Ternary Mo-V-Fe Alloys

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The promising CTE behavior of the Mo-V and ternary Mo-V-Fe alloys led to efforts to fabricate powders of these alloys that would permit evaluation of their use in new cermet

materials. Two distinct routes were pursued: (a) plasma arc melting of elemental bar stock material to produce a consolidated ingot which could then be processed into coarse powders using Plasma Rotating Electrode Process (PREP) and (b) Mechanical alloying from elemental powders. Complete details of these powder fabrication procedures will be contained in a forthcoming report (8).

For the case of the binary alloy, a Mo-27V alloy ingot was triply Vacuum Arc Remelted at Sandia/New Mexico. This ingot was final cast into a 12.7 cm (5 inch) water-cooled copper crucible, yielding an ingot measuring 12.4 cm diam. x 24.1 cm long, weighing 20.4 kg. Subsequent electron microprobe analysis indicated an average composition of Mo-24.02 V, with a standard deviation of ±1.93 wt.% V. Two electrodes for PREP powder processing were ground from this ingot, each weighing approximately 5.53 kg. The PREP melt spinning was performed at Nuclear Metals, Inc., Concord, MA. Problems were experienced with one of the electrodes being spun at too high a velocity, leading to fracture of this electrode with virtually no powder produced. The second electrode was spun at a speed of approximately 2500 rpm, and this ingot yielded about 2.3 kg. of relatively coarse (-14 mesh) powder ("particles"). An optical micrograph of a typical Mo-27V PREP particle is shown in Figure 7. To obtain finer powder sizes suitable for cermet fabrication, the Mo-27V PREP particles were milled in a Fritsch "Pulverisette 5" planetary mill for 11 hrs., in Methanol. For each 100 gm. of powder milled, eight Tungsten Carbide balls (20 mm. diam.) were used in a 250 ml. Tungsten Carbide lined cup. Final particle size parameters obtained for these conditions are shown in Table 1. Note that the 10, 50 and 90 percentile sizes of powder for the Mo-27V material following the 11 hr. planetary milling are comparable to the sizes obtained with the Mo powder normally used for moly/alumina cermets.



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Figure 7. Optical micrograph of a typical Mo-27V PREP particle. The sample was polished using a colloidal silica suspension to reveal fine structure. Note the dendritic structure apparent within the particle.

Table 1. Particle size parameters obtained for the materials used in the compatibility study. The 10, 50, and 90% columns are cumulative percentiles for particle diameter data, obtained on a volumetric basis with a Leeds and Northrop/Honeywell Microtrac SRA 150 Particle Size Analyzer.

Powder Lot	Nominal Composition (wt.%)	10 % (µm)	50 % (μm)	90 % (μm)
Mo for Cermets GE Mo matl.	unalloyed Mo	2.4	6.8	18.7
(Lot 1317-11)			<u></u>	
Mechanical Alloyed Powders			- <u> </u>	
88 hr. run	Mo-22V-3Fe	1.4	1.8	3.6
127 hr. run	Mo-22V-3Fe	1.7	8.6	21.5
PREP Powder (AR)		<u> </u>		
-14 mesh powder	Mo-27V	300	500	710
Milled PREP Powder				
11 hr., milled in methanol	Mo-27V	1.5	7.2	22.4

With respect to the ternary Mo-22V-3Fe alloy, initial alloy fabrication efforts for cermet evaluation focused on the use of mechanical alloying as an alternative to the ingot metallurgy process. The mechanically alloyed powders generated in this study were produced at University of California, Irvine. Elemental powders supplied by CERAC were used as follows: Mo (-325 mesh, 99.5% pure), V (-325 mesh, 99.5% pure) and Fe (-100, 200 mesh, 99.9% pure). Powder charges totaling 100 gm. were placed inside a stainless steel tank together with stainless steel balls using a ball to powder mass ratio of 20:1. Liquid methanol was introduced inside the tank to immerse the balls and powders. Prior to attritor milling, a positive pressure of Ar was imposed inside the tank to displace the air inside the sealed tank. The Ar cover gas was maintained over the entire milling period. Small amounts of powders were discharged from the tank at various intervals for X-ray diffraction measurements (8). By tracking the various individual elemental diffraction patterns, it was possible to determine the time needed for the Fe and V to dissolve into the Mo-rich phase. As suggested by Figure 8, the Fe and V patterns were found to dissolve

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completely following attritor milling for 25 and 65 hrs., respectively. Thus, to ensure complete formation of a solid solution alloy, the two powder lots (100 gm. total) were prepared by attritor milling for times of 88 and 127 hrs. Table 1 includes the particle size distributions for both of these powder runs. Based on the higher 90 percentile size for the 127 hr. run, it appears that clumping of particles becomes a problem if the powder is milled for excessive lengths of time.

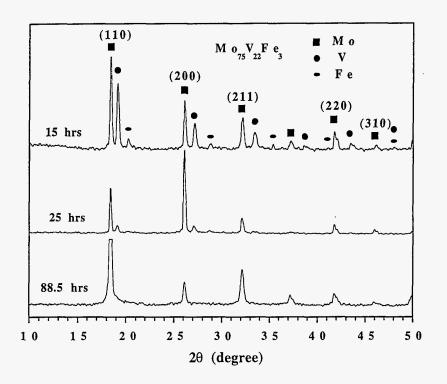


Figure 8. XRD patterns obtained for the Mo-22V-3Fe powder charge prepared by attritor milling in methanol for 15, 25 and 88.5 hrs. Note that the only XRD peaks remaining after 88.5 hrs. of attriting are the Mo lines.

Compatibility of alloyed Cermets with the Alumina Ceramic

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An initial cermet/alumina compatibility sample was made using the 11-hr. milled PREP powder of the Mo-27V alloy and 94% alumina ceramic. Based on a measured alloy density of 8.66 gm/cc and the measured 94% alumina ceramic density of 3.82 gm/cc, a nominal 73 vol% Al₂0₃/27 vol% Mo-27V cermet mixture was mixed by dry ball milling for 5 hrs. Using 30 gm. of powder, a 3.18 cm diameter cermet disk was uniaxially die pressed to 69. MPa (10 ksi). The pressing ram was then withdrawn from the die, an equal amount (30 gm) of 94% alumina ceramic powder was added, and the duplex assembly was again die pressed to 69. MPa. Subsequently, the duplex sample was placed in a latex bag and isopressed to 207. MPa (30 ksi). The assembly was then sintered using a standard cermet firing cycle of 3 hrs. at 1625°C in wet hydrogen. The cermet achieved a geometric density of 4.11 gm/cc, which is approximately 80% of the expected theoretical cermet density of 5.11 gm/cc.

A metallographic section of this duplex compatibility sample was cut, ground, diamond polished to 0.25 micron, then polished/etched using a colloidal suspension of silica. The metallographic results indicated that the grain size of the alumina ceramic adjacent to the

cermet/alumina interface had coarsened. In addition, little or no glass phase was apparent within the adjacent alumina (the 94% alumina body contains 6% glass). Both of these results indicated that the Vanadium in the Mo-27V alloy had reacted extensively with the alumina ceramic. This was later confirmed using electron microprobe analysis. Figure 9 is an electron microprobe line trace that starts from the cermet/alumina interface and proceeds into the bulk alumina ceramic. The dips in the Al₂O₃ trace are attributable to voids in the ceramic, since less than full density was achieved. These results indicate that extensive reaction of the alumina ceramic has occurred due to the reaction of the Vanadium with the alumina. It is apparent that the Vanadium is present as V_2O_3 at distances in excess of 100 μ m into the ceramic. These results suggested that the V addition to Mo required to match the CTE of 94% alumina is far too high from a reaction/compatibility point of view with the ceramic.

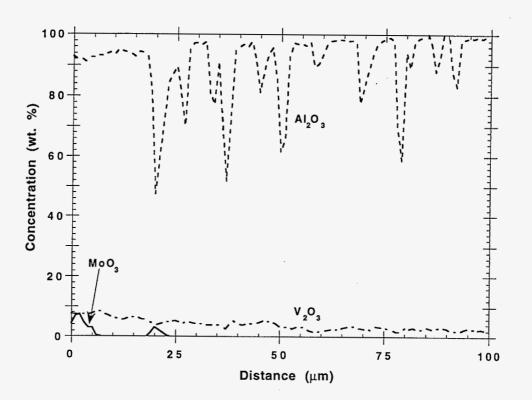


Figure 9. Quantitative electron microprobe line trace obtained from the alloyed cermet/ alumina duplex reaction couple. The left hand side of this plot is the cermet/alumina interface, and the trace proceeds perpendicular to that interface into the alumina ceramic. Note both the concentration gradient and extensive penetration of V_2O_3 into the bulk ceramic.

Evaluation of Alternative Materials for Cermets

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A more extensive evaluation of cermet/alumina ceramic compatibility (8) was completed using a variety of different metal phases for the cermet, including: (a) -250 mesh, 99.9% pure Mo powder from Alfa Asear (as a control sample); (b) planetary milled Mo-27V alloy derived from the PREP powder described previously; (c) mechanically alloyed Mo-22V- 3Fe alloy prepared by attritor milling; (d) -325 mesh, 99.8% pure Nb powder from Alfa Asear; and (e) -325 mesh, 99.9% Ir powder from Alfa Asear. Additionally, to assess the compatibility of the different metal/alumna cermets relative to the partial pressure of oxygen (P_{O2}) in the firing atmosphere, two different firing conditions were evaluated: (a) the standard 3 hr. at 1625°C in wet hydrogen (P_{O2} ~ 10⁻⁸ MPa), and (b) 3 hr. at 1625°C in UHP Argon gettered over Ti at 900°C (P_{O2} ~ 10⁻³⁰ MPa).

For the wet hydrogen firing experiments, coaxial samples comprised of a cermet cylindrical center surrounded by 94% alumina were prepared by dry pressing 0.63 cm tall alumina pellets at 173 MPa in a 1.27 cm diameter steel die, machining a 0.32 cm diameter hole through the concentric (radial) center of the green (unfired) alumina pellet, and filling that hole with the cermet. The cermet was added as a slurry, which was prepared by dispersing nominally 20 gm of the desired cermet powder in 10 ml of liquid Diethlyen Glycol Butyl Ether (DGBE) acetate (Aldrich Chemical). The cermet powders were themselves prepared by combining 20 gm. of nominally 27% (by volume) of the desired metal powder with 73% of spray-dried 94% alumina in an alumina jar and attritor milling for 5 min using a SPEX mixer/mill. In the first stage of the standard wet hydrogen firing cycle, the cellulose organic binders in the alumina were decomposed by heating in dry hydrogen to 700°C.

Coaxial cermet/alumina samples for Ar-firing were prepared in a similar manner to those for wet hydrogen firing, with some additional steps taken to completely remove the cellulose organic binder from the body prior to firing. Nominally 0.63 cm tall alumina pellets were die pressed at 173 MPa in a 1.27 cm diameter steel die, followed by machining a 0.32 cm diameter hole through the center of the green alumina pellet. The pellet was then bisque-fired at 1200°C for 12 min. to decompose the organics and lightly sinter the alumina body. The bisque-firing process produced a strong, nominally pure 94% alumina body of about 60% relative density (~1 % denser than the green, as-pressed alumina body) for subsequent processing. The cermet again, was added as a slurry to the hole within the alumina pellet, but the cermet powders were made with 94% alumina powder that had been calcined to 1000°C. This was high enough to remove the organics from the alumina powder (9, 10), but low enough to avoid sintering.

After sintering, all of the samples were mounted in epoxy, polished, and characterized using scanning electron microscropy (SEM). The SEM was operated in the backscattered electron imaging (BSE) mode to improve the contrast between the metal and the alumina phases.

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SEM analysis revealed gross cracking in the cermet and/or at the cermet/alumina interface in all of the samples, indicating differential sintering between the cermet and the alumina, Independent measurements of Mo cermet cylinders prepared by slurry filling a porous ceramic tube determined that the density of the cermet core of the coaxial cermet/alumina samples has a relative density of \sim 41% after drying. This value is considerably lower than the 59-60% relative density of the surrounding alumina body. This density gradient results in differential sintering in the cermet/alumina part during firing, in both wet hydrogen and in Ar. The lower relative density cermet core shrinks more than the surrounding alumina during sintering, resulting in the large cracks observed in the cermet and/or at the cermet/alumina interface.

Some minor microstructural differences were observed between the samples fired in wet

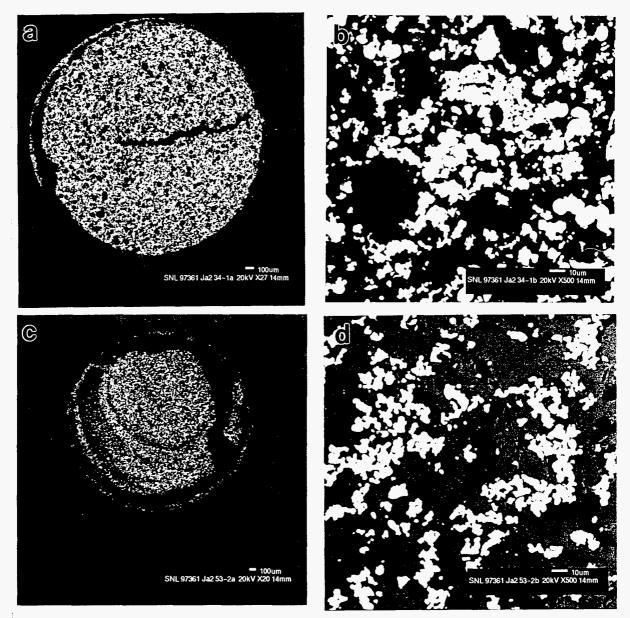


Figure 10.Backscattered electron images of compatibility samples - cermets in 94% alumina ceramic bodies wet fired in wet hydrogen for 3 hrs./1625°C. (a, b) control sample of the standard cermet, containing 27 vol.% Mo, 73 vol.% alumina ceramic. (c, d) cermet containing 27 vol.% Ir/73 vol.% alumina ceramic.

hydrogen versus those fired in Argon. In general, the wet hydrogen fired cermet/alumina samples appeared to sinter to higher densities and appeared to have more mature fired microstructures. The minor differences are likely attributed to minor differences in temperature and heating rates between the two different furnaces used to complete the firing studies; however, additional work would need to be conducted to completely rule out the possibility of firing atmosphere effects on densification.

From a reaction viewpoint, with the exception of the Nb cermets, little difference was observed between the wet hydrogen fired samples compared to the Argon fired samples. For this reason, we focused the following evaluation and discussion primarily on the wet hydrogen fired cermet/alumina samples.

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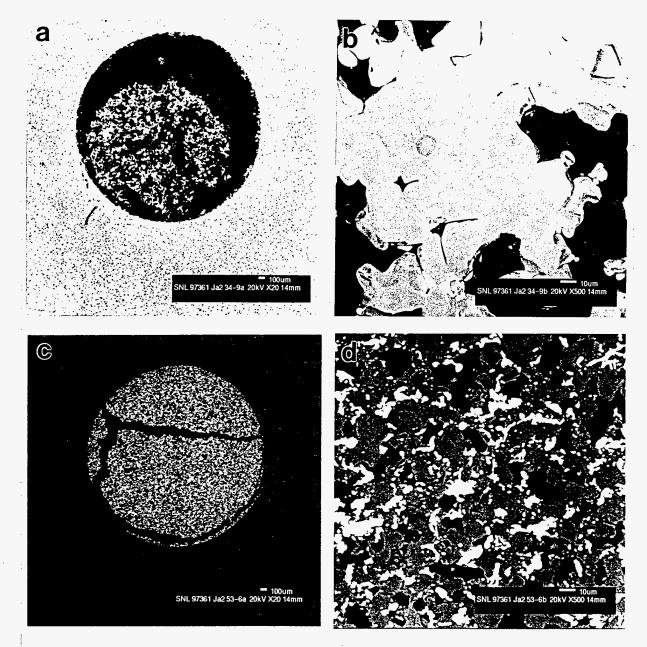


Figure 11.Backscattered electron images of compatibility samples - cermets in 94% alumina ceramic bodies wet fired in wet hydrogen for 3 hrs./1625°C. (a, b) cermet containing 27 vol.% Nb, 73 vol.% alumina ceramic. (c, d) cermet containing 27 vol.% Mo-27V/73 vol.% alumina ceramic.

Figures 10 and 11 are BSE micrographs that show the Mo cermet control sample, the Ir cermet sample, the Nb cermet sample and the Mo-27V cermet sample after wet hydrogen firing. The most encouraging results were observed with the Ir cermet sample (see Figure 10c-d). This sample exhibited good sintering behavior, and energy dispersive analysis of both nearby bulk and cermet-phase alumina ceramic did not show any evidence of undesirable reactions. In contrast, the Mo-27V cermet (see Figure 11a-b) underwent considerable reaction with the surrounding alumina ceramic body. There is also strong microstructural evidence that the metal phase is no longer a single phase alloy after sintering, and that it becomes depleted of Vanadium. Energy dispersive analysis revealed that the Vanadium migrates into and reacts with the 94% alumina to change its microstructure and presumable physical properties (based on the Vanadia-Alumina phase

diagram). Although not illustrated, the Mo-22V-3Fe cermet also exhibited unfavorable reactions and microstructural changes similar to the Mo-27V cermet. The Nb cermet sample sintered in wet hydrogen also showed that there was extensive migration of Nb into the surrounding alumina (see Figure 11c-d). While further characterization is needed for confirmation, it is believed that the Nb reacted with oxygen available in the relatively high PO_2 wet hydrogen atmosphere to produce Nb oxide(s) during firing. In contrast to wet hydrogen firing, the Nb appeared to remain in the core cermet region when the cermet/ alumina body was fired in the low PO_2 Ar atmosphere.

The results of these compatibility experiments indicate that Ir-containing cermet may have potential as a replacement for Mo cermets in electrical feedthrus. Data (6) showing the dilatation of Ir and 94% alumina ceramic as a function of temperature are shown in Figure 12. Comparison with the curve for LCAC-Mo in Figure 1 indicates that the Ir is a much closer match to the 94% alumina ceramic than pure Mo. There also are other considerations that make the Ir-based cermets an attractive option. For example, there is virtually no solubility for hydrogen in Ir (11), which is important for the vacuum bakeout requirement for cermets. In addition, the free energy of formation for IrO₂ is positive above approximately 1040°C (12). Of course, the cost of Iridium as a precious metal (~5./gm) may be somewhat of a disadvantage, but this must be weighed relative to the cost of fabricating reliable cermets with less ideal materials (i.e., regarding properties and chemical compatibility). Further developmental work is required to determine if Ir-based cermets can be economically produced for vacuum electronic applications.

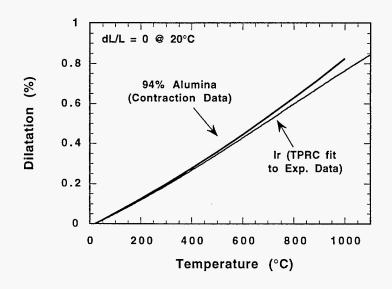


Figure 12. Thermal expansion data for Ir (ref. 6) compared to contraction data for 94% alumina ceramic. Both data sets have been adjusted so that dilatation (dL/L) is normalized to 0 at 20°C.

Summary

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This exploratory study originally aimed at developing an improved cermet material based on an alloy of Molybdenum that would more closely match the thermal expansion of the 94% alumina cermet material to make more reliable cermet/alumina structures. It was determined that the CTE of a binary Mo-32.5V alloy matches the CTE of the 94% alumina ceramic, and that limited amounts of Fe can reduce the amount of V needed to achieve this CTE match. However, the vanadium addition has proven too highly reactive with 94% alumina ceramic given the 1625°C/3 hr. process required for cermet sintering. Alternative materials such as Nb also appear to be too reactive in the standard wet hydrogen firing process. However, we have recently identified Ir as a promising candidate for use in metal/alumina cermets. Based on the initial promising compatibility results, we plan to further investigate cermet processing with this metallic element.

Acknowledgments

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References

- D. P. Kramer, K. White and M. D. Kelly, "Effect of Sintering Parameters and Composition on the Resistivity of a Cermet Used as an Electrical Feedthrough," Ceramic Engineering and Science Proceedings, September-October (#9-10), 1982, <u>3</u>, pp. 512-518.
- 2. Cermet Insert High Voltage Holdoff For Ceramic/Metal Vacuum Devices, U. S. Patent #4,704,557. Assigned: November 3, 1987.
- J. J. Stephens, B. K. Damkroger and S. L. Monroe, "Development of Mo Base Alloys for Conductive Metal-Alumina Cermet Applications," in G. Kneringer, P. Rodhammer and P. Wilhartitz (eds.), <u>Plansee Proceedings: 14th International Plansee Seminar '97</u>. Reutte, Tyrol, Austria: Plansee AG, 1997. vol. 1, pp. 87-100.
- 4. S. J. Glass, et. al., "Mo-Al₂O₃ Cermet Research and Development" (Report SAND97-1894). Sandia National Laboratories, Albuquerque, 1997.
- K. S. Pridantseva and N. A. Solov'eva. Metal Science and Heat treatment, <u>5-6</u> (May-June, 1966), 478-480.
- Y. S. Touloukian, R. K. Kirby, R. E. Taylor and P. D. Desai (eds.), <u>Thermophysical</u> <u>Properties of Matter, Volume 12: Thermal Expansion of Metallic Elements and</u> <u>Alloys</u>. New York: IFI/Plenum, 1976. p. 153, 373.

- 7. V. Raghavan (ed.) <u>Phase Diagrams of Ternary Iron Alloys, Part 6</u>. Calcutta: India Institute of Metals, 1993. pp. 997-1003.
- 8. J. J. Stephens, et. al. "Advanced Cermet Research and Development" (Report in preparation, Sandia National Laboratories, Albuquerque, 1998).
- K. G. Ewsuk, et. al., "Characterizing Organic Binder Burnout in Green Ceramic Powder Compacts," in <u>Proc. of the 27th International SAMPE Technical Conference.</u> <u>"Diversity Into the Next Century.</u> Society for the Advancement of Material and Process Engineering, 1995. pp. 914-26.
- B. F. Blackwell, et. al., "Experimental Characterization and Computer Modeling of Organic Binder Burnout from Green Al₂O₃ Ceramic Compacts," (report SAND96-2727). Sandia National Laboratories, Albuquerque, 1997.
- 11. W. M. Mueller, J. P. Blackledge and G. G. Libowitz, <u>Metal Hydrides</u>. New York: Academic Press, 1968. p. 633.
- 12. J. P. Coughlin, <u>Contributions to the Data on Theoretical Metallurgy</u>. Bulletin 542, Bureau of Mines. US Government Printing Office, 1954. p. 25.

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