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Plasma-Sprayed Tantalum/Alumina Cermets

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PLASMA-SPRAYED TANTALUM/ALUMINA CERMETS

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ABSTRACT

Cermets of tantalum and alumina were fabricated by plasma spraying, with the amount of alumina varied from 0 to 65 percent (by volume). Each of four compositions was then measured for tensile strength, elastic modulus, and coefficient of thermal expansion. In general, strength and strain to failure decreased with increasing alumina content: 62 MPa for 100 percent Ta to 19 MPa for 35 v% Ta. A maximum of 0.1 percent strain was observed for the sprayed 100 percent Ta specimens. The coefficient of thermal expansion measured for the pure Ta was 6.2 (10^{-6})/K.

EBB

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PLASMA-SPRAYED TANTALUM/ALUMINA CERMETS

Introduction

Ceramic/metal combinations (cermets) are of interest to materials engineers because a cermet may exhibit desirable properties of both the metal and the ceramic of which it is composed; for instance, increased hardness, wear resistance, and high temperature strength. The combination of these characteristics on a microscopic scale would be very valuable in an application such as a heat shield. Here the ceramic would absorb the heat from the thermally conductive metal because the relationship of the two materials would be intimate but distinct. Plasma spraying offers a unique opportunity to fabricate such an intimate, but distinct, mixture of materials which would react chemically if combined by means of the conventional powder material techniques of sintering and hot pressing.

This paper describes an experiment in which cermets of tantalum and alumina were fabricated by plasma spraying, removed from the substrate, and measured to determine tensile strength, elastic modulus, and coefficient of thermal expansion as a function of composition.

Plasma Spraying Technique

The principle of plasma spraying is to melt powder particles and accelerate them onto a substrate. An electric arc is used as the heat source

to generate a partially ionized gas stream. A cross section of a plasma spray gun (Figure 1) shows the anode and the cathode, which have different voltages. The arc gas ionizes in the cavity between the electrodes, and the flame quench device reduces the heat flux to the substrate by diverting the plasma flame with a stream of argon. The operating fluid (in this study He and Ar were used) transfers heat to the powders as the gaseous ions and electrons recombine. The temperature of the particles is a function of the thermal properties of the material, the powder particle mass and shape, the heat transfer characteristics of the plasma stream, and the dwell time in the stream.[1] In previous studies, experimenters have observed temperatures in excess of 20,000 K in the gas,[2,3] and the heat transfer of the plasma has been sufficient to melt even refractory materials.[4]

The character of the plasma-sprayed deposit may be widely varied, depending upon the powder and spray conditions used.[1] The porosity, strength, and phase distribution are sensitive to the plasma gun design, the spraying parameters, and the properties of the powder. In one study the spraying conditions were correlated with the coefficient of friction of the resulting deposit.[1] Other studies of plasma spraying have shown that the helium in the plasma arc gas increases the heat transfer characteristics with respect to the powder[5] and that a size fraction of 10 to 70 μm particles is appropriate.[6] Larger particles are not sufficiently molten, and smaller particles tend to vaporize. Although plasma spraying is a high-temperature process, materials with vastly different melting points can be mixed and co-sprayed with little interaction in the plasma stream.

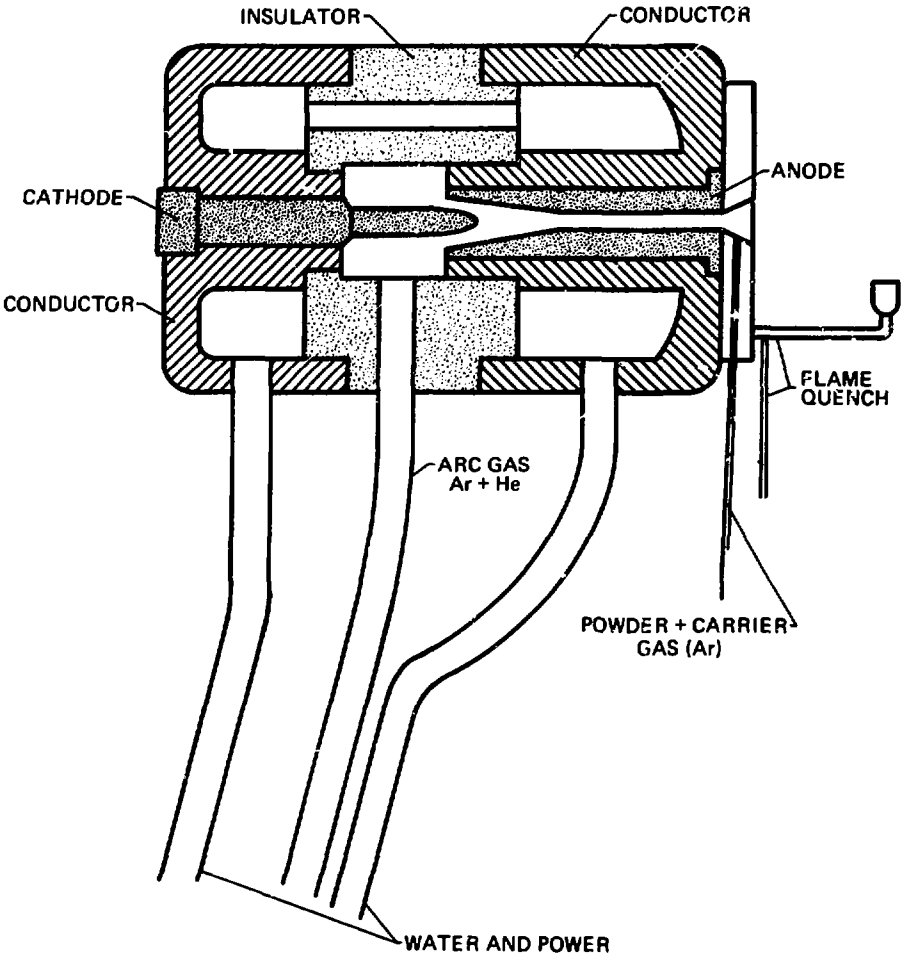


Figure 1. Plasma Spray Gun

Because the plasma can be an inert gas rather than the reactive gases of a flame, oxidizable and pyrophoric materials can be sprayed with minimum contamination.[7] When necessary, the whole operation can be enclosed in a chamber filled with an inert gas to further minimize contamination; such enclosures also permit the spraying of toxic materials.

The optimum parameters for this study were chosen from preliminary experiments on the basis of spraying efficiency, which refers to the amount of powder deposited compared to the amount fed through the plasma spray gun.

Experimental Procedure

Powder Character

Buehler 400 grit alumina and tantalum powder supplied by Union Carbide were used for the cermet fabrication. The alumina was a fine, closely sized powder, with 85 percent in the range of 10 to 37 μm, as determined by precision sieve analysis. The surface area of the alumina was 0.340 m^2/g or 4.4 μm equivalent spherical diameter. Figure 2a is a scanning electron photomicrograph illustrating the irregularly shaped grains and adherent fines of the alumina. X-ray analysis showed that the powder was mainly alpha-alumina; however, two other minor phases, the γ-Al_2O_3 phase and one containing silica and alumina, were present. The powder was 95 wt% alumina, did not flow well, and had an apparent density of 35 percent of theoretical.

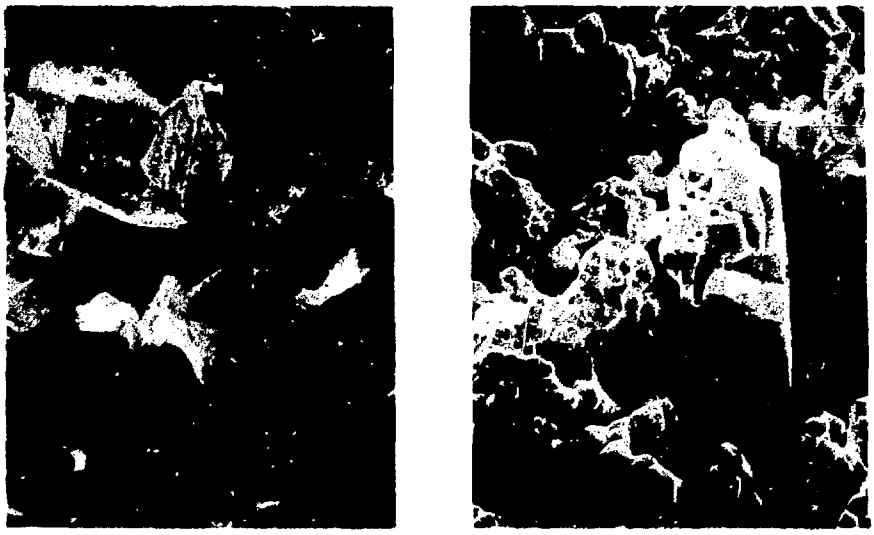


Figure 2. Starting Powders of (a) Alumina and (b) Tantalum for Plasma Spraying Cermets

The tantalum used was pure and flowed very easily, and 96 percent of the powder was 10 to 34 μm in size. As shown in Figure 2b, the tantalum was composed of branched and faceted chains. The apparent density of the powder was 19 percent of theoretical and much lower than that of the alumina. Surface area of the tantalum was 0.09 m^2/g or 4.0 μm equivalent spherical diameter.

The apparent particle sizes of the metal and ceramic powders were similar; however, their morphologies varied greatly.

Fabrication

Three different compositions of tantalum and alumina were mixed in a V-blender. The mixtures were denoted 51, 81, and 95, indicating the weight percentage of tantalum in each. A fourth powder was composed of 100 percent tantalum. Prior to spraying, the plasma spray powder feeder was calibrated for each mixture.

The plasma gun used for spraying the cermets was a modified Plasmadyne SG-1B, mounted for remote control in an argon atmosphere glove box. The powders were injected externally at an angle of 13 degrees. Specific spraying conditions are listed in Table I. The major difference between the spraying conditions for the pure tantalum and those for the cermets was the arc gas He/Ar ratio. Since the flame quench attachment diverted the low-density alumina, it was used only with the 100 percent tantalum. Samples of each composition were sprayed on rectangular

TABLE I

CONDITIONS USED FOR PLASMA SPRAYING CERMETS

Cermet Mixture (wt% Ta)	Arc Gas Mixture	Amperage (A)	Stand-Off (cm)	Powder Gas (ℓ/hr)	Feed Rate (g/min)	Flame Quench
100	50 He/50 Ar	400	9	200	20	yes
95	37 He/63 Ar	400	9	200	20	no
81	37 He/63 Ar	400	9	200	10	no
51	37 He/63 Ar	400	9	200	7	no

prisms (5 x 5 x 15 cm) of polished aluminum rotating at 100 rpm, with the gun traversing the length of the rotating substrate. Because of the great difference between thermal expansion of the aluminum and that of the deposit, the sprayed cermet could be easily removed without removing any substrate.

Testing

Samples of each composition were analyzed by wet chemistry, mounted for metallographic examination, tested for porosity and thermal expansion, scanned by X-rays, and fabricated into tensile bars. To measure the coefficient of thermal expansion with a low force dilatometer the samples were heated at 20 K/min to 1000°C in a gettered argon atmosphere.

Each combination of tantalum and alumina was very friable and had to be machined by electro-discharge machining or diamond grinding. The tensile bars were 0.8 to 1.8 mm thick and had a gauge section 1.25 cm wide by 2.5 cm long. The ends of the samples were cast in plastic with strips of aluminum to facilitate gripping the tensile bar in the Instron testing machine. A 1.25-cm extensometer monitored the strain as the samples were pulled at the rate of 0.13 mm/min. Specimens were repeatedly loaded and unloaded when possible, and the elastic modulus (E) and ultimate tensile strength (UTS) were computed for each specimen. The first loading curve was discarded in the computation of moduli, since it was consistently lower than successive measurements and included adjustment of the specimens in the grips. The measured elastic moduli for each composition are graphically illustrated in Figure 3 and the tensile strengths are illustrated in Figure 4.

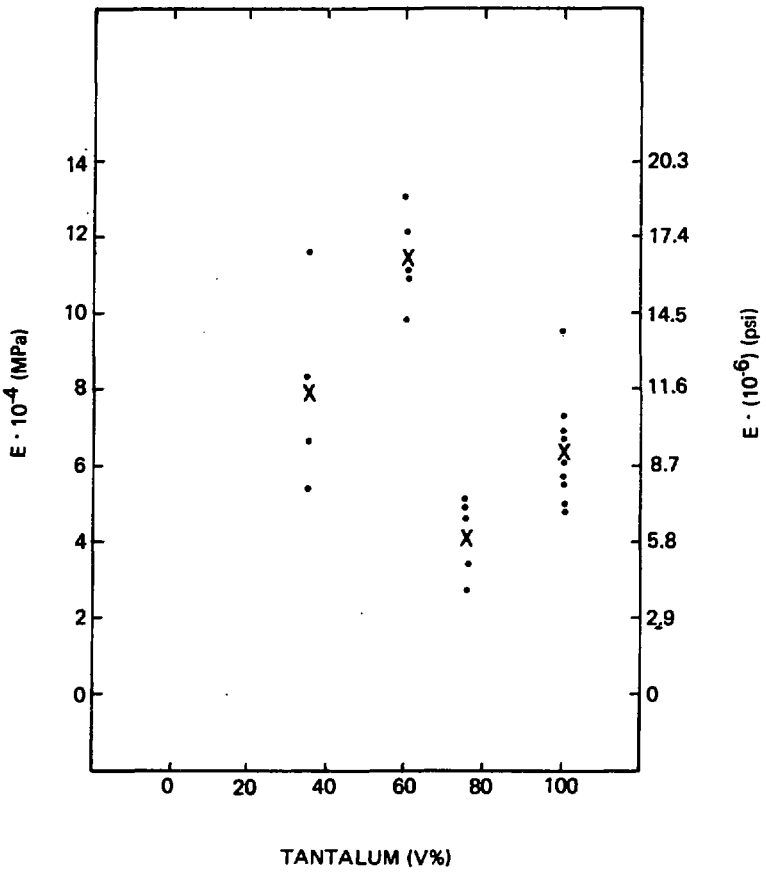


Figure 3. Elastic Modulus of Plasma-Sprayed Ta/Al_2O_3 Cermets

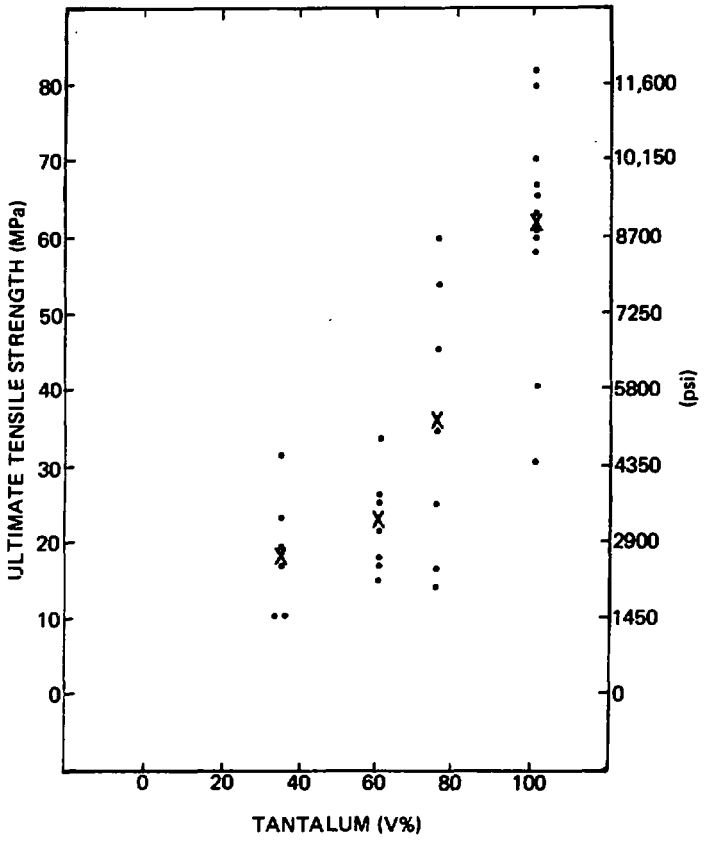


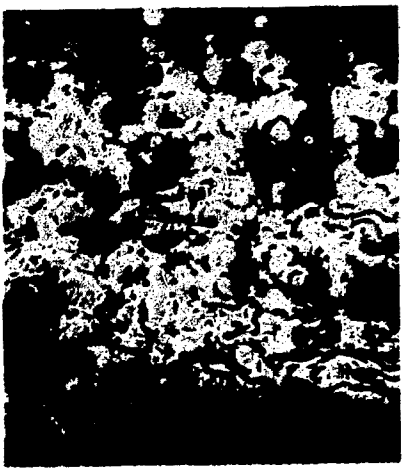
Figure 4. Ultimate Tensile Strength of Plasma-Sprayed Ta/Al_2O_3 Cermets

Results

Before the actual tests were run, some preliminary studies were conducted on a coarse grade of tantalum powder (70 to 100 μm) to determine the effect of various spray parameters. The most dramatic effect was seen when the percentage of helium in the arc gas was changed, as illustrated in Figures 5 and 6. The degree of melting, the density, and the deposition efficiency increased markedly as helium was added to the ionized gas stream. The sequence of micrographs in Figure 5 illustrates the transition of the coarse Ta to a laminar structure as more helium was added to the plasma. The deposition efficiency of the alumina was highest at a He/Ar ratio of 37/63, and the deposition of the finer Ta was not much decreased at spray conditions of 37 percent He. Therefore, during the experiment, the cermets were sprayed at an arc gas ratio of 37 He/63 Ar, while the pure Ta was sprayed at 50 He/50 Ar.

Results of the chemistry, X-ray, and density tests on the four samples are summarized in Table II. The volume percent of the metal, ceramic, and pore phases was substantiated by cross sections analyzed using the Quantimet, a computerized metallographic tool. Figure 7 shows cross-section photomicrographs for each composition. The mechanical properties, which were measured perpendicular to the spraying direction, are summarized in Table III.

The laminar microstructures illustrated in Figure 7 contrast with the starting powder morphology. Melting and spreading is evident for each

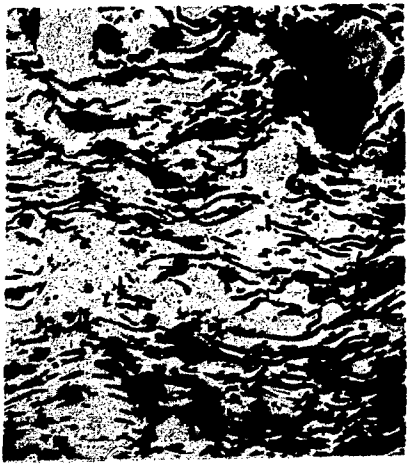


100% Ar/0% He
arc gas content

200μm

85% Ar/15% He

200μm



37% Ar/63% He

200μm

50% Ar/50% He

100μm

Figure 5. Effect of Increasing Helium in Arc Gas While Plasma Spraying Coarse Tantalum Powder

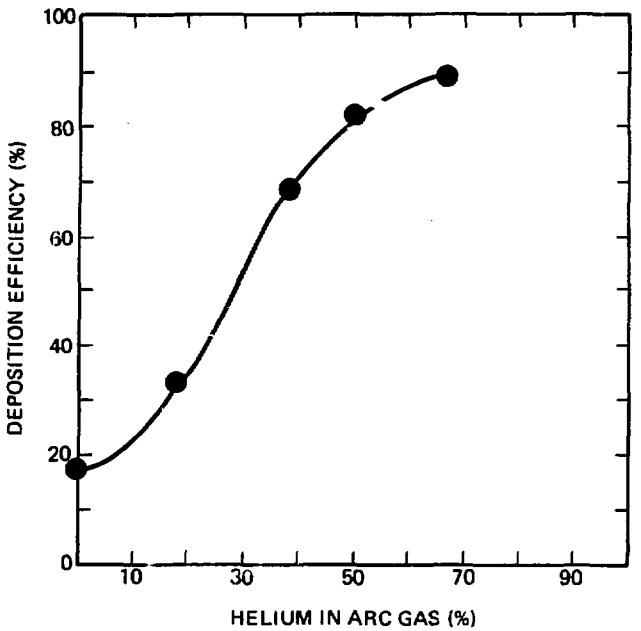


Figure 6. Increase in Deposition Efficiency as a Result of Increasing Helium in the Arc Gas During Plasma Spraying Coarse Tantalum Powder

TABLE II

TEST RESULTS

Mixture	Ta* (wt%)	Ta† (v%)	Phases Detected by X-Ray∞				P†† (%)
			Ta_2O_5**	αAl_2O_3	γAl_2O_3	Ta	
100	--	--	3-U	--	--	1	8
			7-T	--	--		
95	93	75	1-U	--	6-T	2	10
			--	4-T	5-U		
81	86	60	3-U	--	4-U	3	7
			6-T	2-T	3-T		
51	56	35	5-U	3-U	2-U	4	10
			2-T	1-T	1-T		

*By wet chemistry

†Calculated from chemistry and Quantimet areal analysis

**Minor phase compared to Ta

††Porosity from Hg porosimetry and Quantimet areal analysis

∞In decreasing order in any column (if detected), U = underside, T = top side

TABLE III

MECHANICAL PROPERTIES OF PLASMA-SPRAYED TANTALUM/ALUMINA CERMETS

Mixture (wt% Ta)	Ta (v%)	p* (%)	Ultimate Tensile Strength (MPa)	(psi)	(No.)**	Elastic Modulus (MPa)	(10^6 psi)	(No.)**	CTE† (10^{-6})/K	Total Strain (%)
100	100	8.0	62	8,900	11	65,000	9.4	11	6.2 ± 0.7	0.1
95	75	10.0	36	5,200	7	42,000	6.1	6	10.9 ± 1.2	0.09
81	60	7.3	23	3,300	7	115,000	17.	6	11.1∞	0.03
51	35	10.3	19	2,800	7	81,000	12.	7	9.3∞	0.03

*Open porosity

**Number of samples

†Coefficient of thermal expansion

∞One measurement only

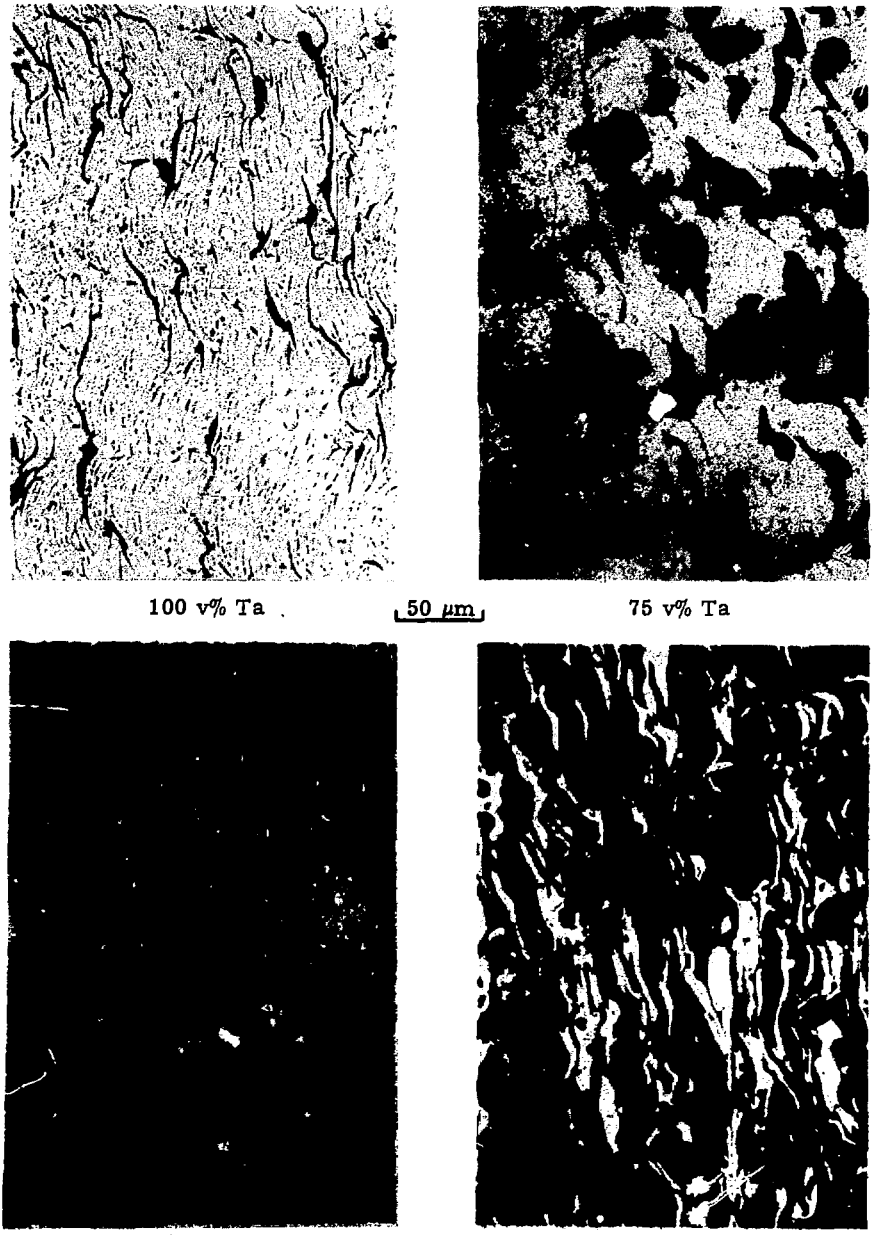


Figure 7. Cross-Section Photomicrographs of the Four Samples of Ta/Al_2O_3 Cermets

phase, but no reaction between the metal (white phase) and ceramic (grey phase) is apparent. Much of the alumina phase is globular, indicative of partial solidification at the time of impact, and some agglomeration of the alumina is evident as a result of the poor flow character of the powder. Aggregation and partial solidification probably caused the porosity in the vicinity of the ceramic phase. Larger pores were observed in the samples containing greater amounts of alumina.

The wet chemical analysis showed that the Ta/Al_2O_3 ratio could be reproduced within 2 wt% Ta. Tantalum oxide (Ta_2O_5) was detected by X rays. It was concluded that the tantalum powder gettered the residual oxygen in the argon atmosphere of the glove box since the relative amount of Ta_2O_5 was less for the last layers of the high tantalum samples. Presumably the Ta_2O_5 was a crust on each splat of tantalum. Gamma-alumina was detected in all cermets. The gamma phase, which is a weaker, metastable, less dense form than the alpha-alumina,[8] has also been observed in plasma-sprayed $Al-Al_2O_3$.[9] Alpha-alumina observed on the upper surfaces of the cermets indicates that slower cooling was occurring on the upper surface, away from the thermally conductive aluminum substrate. The thermal gradient and differential cooling rate probably caused the build-up of residual stresses[10] that were evidenced by the curvature of the samples.

Examination of the fracture surfaces of the tensile specimens revealed inter- and intra-particle separation. Both alumina and tantalum splats were fractured in Figure 8a. Figure 8b shows that fracture propagated

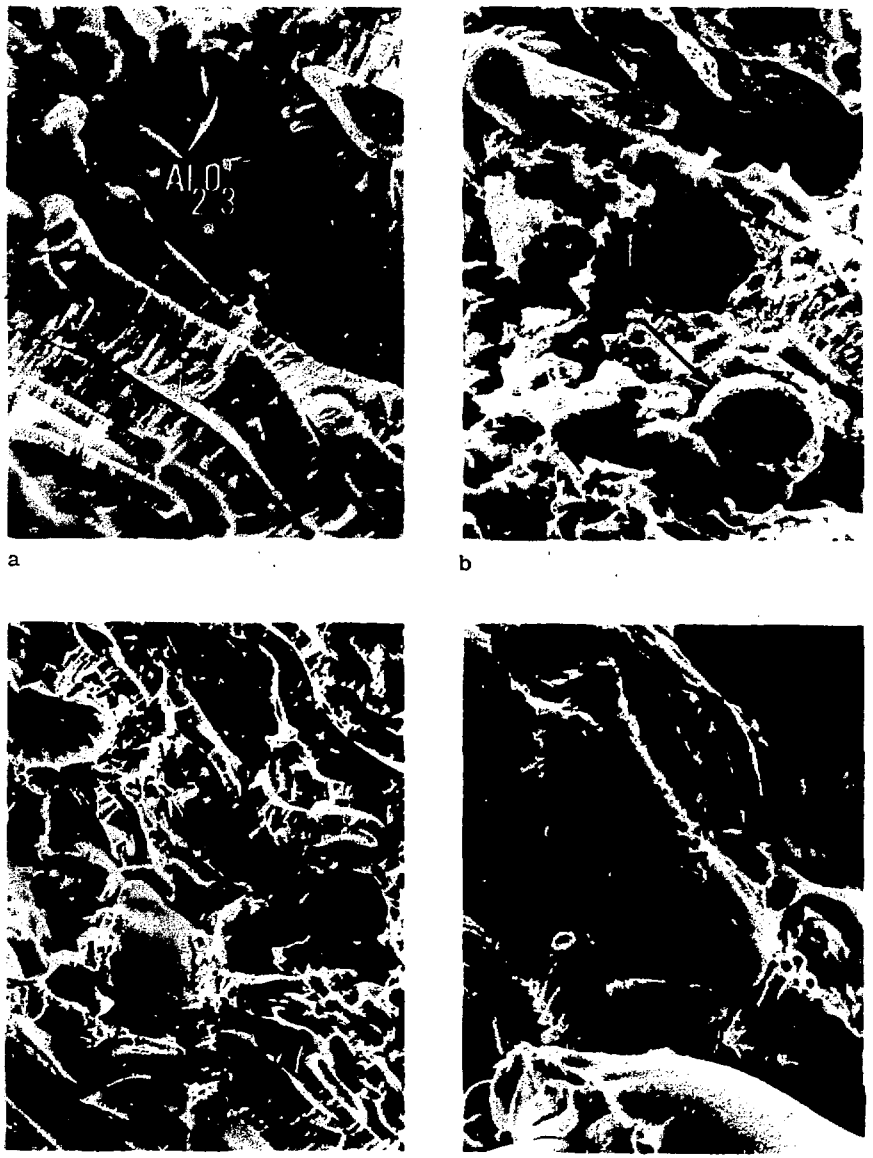


Figure 8. Fracture Surfaces of Cermets of Ta/Al_2O_3 Illustrating Intra- and Inter-particle Fracture in Both Phases

around some spherical particles, which are probably the harder alpha-alumina phase. Like other multiphase materials having a harder dispersed phase, the alpha-alumina will divert cracks, while the presence of the weaker gamma-alumina allows cracks to progress undiverted. Some separation occurred along the microcracks, which are a result of cooling stresses incurred during fabrication (Figure 8c). Figure 8d shows the tracks of the cooling front progression into the metal particles. These observations and those on the magnitudes of the mechanical properties may be notably different for material tested parallel to the spraying direction.

The ultimate tensile strength of the cermets decreased with increasing alumina content from 62 MPa for 100 percent Ta to 19 MPa for 35 percent Ta. The scatter in the data was large (see Figure 4). All the specimens broke in the gauge section; however, most broke at the extreme end of the reduced section, where stress concentrations are developed during machining. Those specimens that did break in the center of the tensile bar did not exhibit significantly different strengths.

In Table IV pertinent mechanical properties from the literature, including the results of this study, are summarized. Values for tensile strength are much higher for annealed tantalum sheet. The values obtained in Reference 5 compare most closely to those in the present study, since this author and Abbatiello used identical systems and powder. The relation

TABLE IV

MECHANICAL PROPERTIES OF SAMPLES FROM THE LITERATURE AND THIS STUDY

Source	Ultimate Tensile Strength (MPa)	(psi)	Elastic Modulus (MPa)	(psi)	Coefficient of Thermal Expansion[c]	Porosity (%)
TANTALUM						
Ref. 11[a]	344	50,000	186,000	$27(10^6)$		
Ref. 12[a]	193 (0.0 at.% oxygen)	28,000	193,000 (0.0 at.% oxygen)	$25.7(10^6)$	$7.7(10^{-6})$/K	
Ref. 12	882 (1.5 at.% oxygen)	128,000	192,000 (2.5 at.% oxygen)	$27.9(10^6)$		
Ref. 5[b]	48 (99.7% Ta)	7,040	32,000	$4.6(10^6)$	$7.0(10^{-6})$/K	12
This study[b]	62	8,900	65,000	$9.4(10^6)$	$6.2(10^{-6})$/K	8
ALUMINA						
Ref. 13[d], 14	37 (γ-Al_2O_3)	5,300	43,000 (0.3 to 2.8% porosity)	$6.3(10^6)$	$7.0(10^{-6})$/K	8.7
Ref. 15[e]	172 (α-Al_2O_3) (3.3% porosity)	25,000	414,000 (0.2% porosity)	$60.0(10^6)$	$4.7(10^{-6})$/K (2% porosity)	

[a] annealed sheet

[b] plasma-sprayed

[c] 0° to 1000°C

[d] flame sprayed (oxyacetylene) alumina rod

[e] sintered alumina

of Duckworth[16] and the data from this study and that of Abbatiello were used to compute the values of constants σ_0 and b_1 for plasma-sprayed tantalum to normalize the mechanical properties with respect to porosity.

$$\sigma_P = \sigma_0 \exp(-b_1 P) \quad (1)$$

$$\sigma_P = 103 \text{ MPa} \cdot \exp(-6.4P)$$

where

P = porosity

σ = tensile strength

Values for b_1 in the literature average about 10. At zero porosity plasma-sprayed tantalum has one-third to one-half the tensile strength of tantalum prepared by conventional methods. Oxide layers or dissolved oxygen in the tantalum reduce the strain to failure and embrittle the material;[11,12] both of these phenomena are probably occurring in this system. The plasma spray process produces microcracks in the metal structure that are not present in conventionally formed tantalum; this accounts for the low value of σ_0 compared to annealed sheet.

The stress-strain curves of the tantalum and tantalum/alumina did not exhibit perfect elastic behavior. A small deviation from linearity was seen. Young's moduli measured in the elastic region of cermet behavior did not reveal any one trend (probably due in part to residual stresses) as had the tensile strength with respect to composition before normalization with respect to porosity. The values measured in conventionally processed

tantalum or alumina were much higher; this may be accounted for by the highly defective structure of plasma-sprayed material. The average values of this study (illustrated in Figure 3) and those of Abbatiello for Ta were used in the relationship of Spriggs[16] [Equation (2)] for the elastic modulus of porous materials, which is analogous to Equation (1).

$$E_P = E_0 \cdot \exp(-b_2 P) \qquad (2)$$

where

E = Young's modulus

For plasma-sprayed tantalum this relationship is

$$E_P = 268{,}000 \text{ MPa} \cdot \exp(-17.7P)$$

This value of b_2 is three times that observed for other materials, and E_0 is relatively close to that measured for tantalum sheet.

If these values of b_1 and b_2 are used for the cermets, E_0 and σ_0 for each composition may be calculated as in Table V. Presence of alpha-alumina greatly raised the elastic moduli of the cermets to values similar to those for the sintered alumina. Normalized values for the metal-rich cermets and pure tantalum are higher than the values reported for annealed tantalum sheet, indicating the effect of the stiffer crust of oxide on the metal particles, and probable solution of oxygen in the tantalum.

Normalized values for the tensile strengths of the high alumina cermets compare well with those for flame-sprayed alumina. This illustrates how the alumina dominates the tensile strength for 60 volume percent metal or less. The total strain exhibited a downward trend as the volume percent of tantalum was reduced below 75 v%.

TABLE V

NORMALIZED MECHANICAL PROPERTIES OF Ta/Al_2O_3 CERMETS

Mixture	Ta (v%)	Open Porosity (%)	E_0 (MPa)	σ_0 (MPa)
100	100	8.0	268,000	103
95	75	10.0	247,000	68
81	60	7.3	419,000	37
51	35	10.3	501,000	37

The thermal expansion of plasma-sprayed tantalum in this study was similar to the values given in the literature for conventionally prepared tantalum. No definite trends were observed with compositions for the expansion coefficients of the cermets. Probably there were annealing processes occurring during the thermal expansion tests which altered the results. The anomalous rise and fall of the expansion coefficients with increasing alumina cannot be explained. It is believed that the most reliable expansion data is for the 100 percent plasma-sprayed tantalum sample.

Conclusions

This study showed that the properties of plasma-sprayed cermets can be tailored by powder and process parameter choice. The tensile strength of tantalum/alumina cermets increased from 19 MPa for 35 v% Ta to 62 MPa for 100 v% Ta. The metal increased the total strain to failure. Inter- and intra-particle fracture was observed for both phases. Normalization of the mechanical properties with respect to porosity is necessary to reveal significant trends with respect to composition.

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