NASA Technical Memorandum 88927

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(NASA-TM-88927) MORPHOLOGY OF ZIRCONIA PARTICLES EXPOSED TO D.C. ARC PLASMA JET (NASA) 17 p CSCL 11F

N87-16113

Unclas

G3/26 43316

Isidor Zaplatynsky
Lewis Research Center
Cleveland, Ohio

January 1987

NASA

E-3325

MORPHOLOGY OF ZIRCONIA PARTICLES EXPOSED TO D.C. ARC PLASMA JET

Isidor Zaplatynsky
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Zirconia particles were sprayed into water with an arc plasma gun in order to determine the effect of various gun operating parameters on their morphology. The collected particles were examined by XRD and SEM techniques. A correlation was established between the content of spherical (molten) particles and the operating parameters by visual inspection and regression analysis. It was determined that the composition of the arc gas and the power input were the predominant parameters that affected the melting of zirconia particles.

INTRODUCTION

An important application of the arc plasma spray technique has been the deposition of yttria-stabilized zirconia to form thermal barrier coatings (TBC) to be used in high heat flux applications such as the Space Shuttle main engine (SSME) thrust chamber and the hot components in the gas turbine and diesel engines. There is a considerable amount of literature on the subject of zirconia based TBC's (e.g., refs. 1 to 11). It deals mostly with formulating new zirconia and bond coat compositions and testing while the spraying technique remained an art arrived at by experience or some limited optimization procedure. It is probable that plasma spraying has reached the stage where empirical development is approaching its limit and any further improvement in coating performance will be the result of better scientific understanding of the fundamental processes that control the formation of the coating. Only recently some experimental and theoretical studies were reported (refs. 13 to 16). A model has been proposed (ref. 17) which calculates (from fundamental process variables such as power input, gas flow rate, particle size, etc.) velocity and temperature fields in plasma flame in the presence of a target. The model also calculates the particle histories and consequent build-up and solidification of coating on the target. Accuracy of this model is limited by the lack of data about the effective gas thermal conductivity and complications resulting from turbulent mixing of the plasma jet with the surrounding cold air. Also, evaporation may reduce the heat transfer and modify the plasma transport properties (ref. 18). As a result, the particle temperature calculated from gas temperature velocity and gas properties do not agree well with the experimental data. There is the possibility, that in the case of ceramic materials, one could have incompletely melted particles. R. McPherson (ref. 16) introduced the concept of "difficulty of the melting factor" DMF = $\Delta H_m \rho^{-1/2}$, where ΔH_m is the heat content per unit volume of a material just above its melting point and ρ is the density (ref. 17). Table I, taken from the above reference, indicates that oxides are more difficult to melt than the metals because of their high heats of melting and low densities. If some of the plasma-sprayed oxide particles are not molten or only partially molten, they will form solid inclusions in the coating and thus degrade its mechanical properties. In practice, very little attention has been paid to this question and precisely for this reason the present study was undertaken to determine the effect of various plasma gun-operating parameters on the morphology of zirconia particles sprayed into the water.

EXPERIMENTAL PROCEDURE

Material

The zirconia powder used in this study contained 6.89 wt % yttria, 1.79 percent hafnia and some very small amounts or traces of Al_2O_3, CaO, SiO_2, Fe_2O_3. Cr_2O_3, TiO_2, NiO, and MgO. The particle size of the zirconia powder was in the range between 200 and 325 mesh. SEM examination (fig. 1) shows the size and shape of the as-received zirconia particles. It reveals also that each particle was made up of small grains 3-10 μ in diameter. XRD analysis disclosed that about 1/3 of the zirconia was in monoclinic and 2/3 in cubic + tetragonal forms.

Experimental Design

In order to determine the effect of some arc plasma gun-operating parameters on morphology of thermal sprayed zirconia particles, the oxide powder was sprayed from a distance of about 18 cm into 4000 cc of distilled water contained in a 5000-cc glass beaker. The distance above indicated was large enough to insure that all the melted particles had solidified before impacting the water surface. Approximately 10 g of zirconia powder was collected in the beaker. The collected particles were washed in alcohol, dried, and analyzed by XRD, SEM techniques.

The following plasma gun-operating parameters were considered in this study: power input, powder feed rate, arc gas flow, feed gas flow, and gas composition. The design was an incomplete two-level factorial in which the feed gas flow parameter was used at one level in six instances. Table II lists the arc plasma gun-operating parameters and their values at the two levels used in the experiment. The compositions of the arc gas and feed gas were the same. Table III is a diagram of the experimental design. The last two columns of the table list the experimental results. Table III should be read as follows: for Sample No. 7, the spray parameters are (01001) which means that:

Power input	-	12.8 kW
Powder feed rate	-	35.6 g/min
Arc gas flow	-	24.9 SLPM
Gas composition	-	pure argon
Feed gas flow	-	5.5 SLPM

The total number of investigated samples was 25 including the as-received zirconia powder. A small amount of powder from each sample was prepared for SEM analysis, and photographs were taken at 100X and 500X. Also, some selected powders were mounted in epoxy resin, ground and polished to obtain cross sections of the grains which were examined by the SEM and photographed at 500X. XRD patterns of zirconia were taken using CuKα radiation.

RESULTS AND DISCUSSION

Visual examination of the photographs revealed the following features:

(1) Each sample contained melted particles, particles with different degrees of melting, and sometimes particles in their original shape. A particle with spherical shape and smooth surface is considered to have been melted, whereas a particle with elipsoidal shape and smooth surface is assumed to be partially melted. The relative amounts of each kind of particles varied with the change of gun operating parameters. Figure 2 shows photographs of zirconia particles representing Samples No. 2 and 16 which were sprayed under a different set of gun operating parameters (for details, see tables II and III). The difference between these two samples is obvious. In the case of Sample No. 2, the majority of particles was partially melted and only a few totally melted particles could be observed. Sample No. 16 presented an opposite picture; namely, nearly all the particles were molten with only some partially molten. The following figure 3 illustrates particles of the same Samples No. 2 and 16 but under higher magnification. It brings out in more detail the morphological differences between the particles of these two samples. Random cross-sections of the particles are shown in figure 4. One can see that the particles contain porosity, regardless of whether they were completely or partially melted. It appears that the particles which were completely melted formed hollow spheres.

(2) It can be seen from figure 5 that the particles representing Sample No. 7 are in general smaller than the particles of Sample No. 8. They may appear to be smaller as a result of spherodization. However, there is no real change in volume (porosity is retained (fig. 4)). Therefore, the reduction of the particle size can be explained to be the result of evaporation. Chen and Pfender (ref. 18) considered evaporation as an important factor where gaseous products, evolved from the particles during spraying, could affect plasma transport properties and its temperature. It may be of interest to indicate the gun operating parameters for both samples.

	Sample 7 (01010)	Sample 8 (01100)
Power, kW	12.8	12.8
Powder feed rate, g/min	35.6	35.6
Arc gas flow, SLPM	27.5	40.0
Gas composition. vol % He	20.0	0
Feed gas flow, SLPM	3.6	3.3

As one can see, the only differences between these two sets of parameters (the difference in feed gas flow is insignificant and can be disregarded) were arc gas flow and gas composition. From the examination of both photographs and the reference to table III, one can conclude that the presence of helium in the gas (arc and feed gas) promoted melting of the zirconia particles and that increased arc gas flow inhibited the melting. It is possible to discern in a very qualitative way the effect of different parameters by inspecting all the sprayed particle photographs associated with table III. However, it is more convenient to assign some numerical value to the observed effect (degree of melting). This was done by counting the number of spherical particles within an area (about 25 to 30 cm^2) of the photographs and expressing their content as percentage of total number of particles contained in this area. The values obtained are listed in the last column of table III. By applying regression analysis to these data, it was found that the correlation was not satisfactory. However, during the spraying process of certain samples, it was noted that the gun was not working properly; namely, the deposition of molten

zirconia occurred on the anode on the opposite side of the particle injection orifice. Apparently, high feed gas flow in combination with other parameters caused the gun to malfunction. This malfunction was observed while spraying Samples 2, 7, 22, and 24. By eliminating from the analysis the data pertaining to high feed gas flow, i.e., 2, 7, 11, 13, 17, 19, 22, and 24, we obtain an equation which quite accurately expresses the content (percent) of melted particles (MP) as a function of plasma gun operating parameters
MP = 2.72 * power - 0.634 * total gas flow + 2.280 * vol % He -0.0708 * (feed rate - average feed rate) * (total gas flow - average total gas flow).

The standard deviation of the predicted value about regression line is 4.369 and R^2 is 99.44 percent. Consequently, in order to secure the melting of zirconia one should increase the power input and increase the temperature and heat conductivity of the gas by adding more helium to argon. Arc gas flow and powder feed rate have a negative but considerably less significant effect. Considering the thermal conductivity values (at room temperature and 5000 K) for hydrogen, helium, nitrogen, and argon (ref. 19) one can see that by substituting nitrogen for argon, and perhaps enriching it with helium or hydrogen, the melting of the plasma sprayed particles would be enhanced.

Thermal conductivities at room temperature and 5000 K
(g • cal/(cm) • (sec) • (K))

	$\lambda_{300\ K}$	$\lambda_{5000\ K}$
Ar	42.7	277.7
H	553.4	3419.9
H2	455.8	3702.8
He	379.6	2330.4
N	88.6	625.9
N2	63.9	515.6

Besides morphological changes that zirconia particles undergo during plasma spraying, there are also crystallographic changes which took place. Namely, the content of monoclinic zirconia in the plasma sprayed particles was reduced from 29 to much lower values, depending upon the spray parameters. This was calculated using an equation

$$\frac{M_m}{M_{F,T'}} = 0.82 \cdot \frac{I_m(11\bar{1}) + I_m(111)}{I_{F,T'(111)}}$$

which expresses the ratio of the moles of the monoclinic phase (M) to moles of the cubic (F) plus tetragonal (T') phases (ref. 19). The calculated values are listed in table III. The inspection of this column revealed that the high values for $ZrO_{2(mon)}$ corresponded to low values of the content of spherical particles and low values for $ZrO_{2(mon)}$ corresponded to high values of the content of molten particles. Regression analysis yielded an equation:
% $ZrO_{2(mon)}$ = 6.35 - 0.0490 x percent melted particles, with R^2 = 50.5 percent and standard deviation about regression line of 1.351. While the correlation is only fair, the trend is obvious. The particles which were melted as a result of exposure to high temperature plasma contained less monoclinic form than the particles which were partially or not molten because of being entrained in the colder zones of plasma.

An additional experiment was performed to determine the effect of particle size upon their behavior in the plasma jet. The original zirconia powder was comminuted in a ball mill and the -325 +400 mesh fraction extracted by screening. This powder was sprayed into water under the same conditions (11110) as Sample No. 23. The results of the experiment are illustrated in figure 6. In the case of larger particles, a significant portion was only partially melted or not melted at all, whereas, nearly all of the small particles were melted. In addition, the small particles apparently formed hollow spheres some of which disintegrated upon impacting the water as evidenced by the debris seen in figure 6(b). This gives additional evidence to the assumption that nearly all zirconia particles can be melted in the plasma jet if they are small enough. Therefore, the particle size distribution should be considered as an important parameter in the fabrication of thermal barrier coatings.

SUMMARY

1. Power input and helium content in the arc gas were the most significant parameters that affected the melting of zirconia particles. Increase in power input and in helium content promoted the melting.
2. Arc gas flow and powder feed rate were less important parameters. Their effect was negative for the set of parameter values used in this study.
3. The reduction in size of the molten particles indicated that the evaporation process of zirconia took place during the short residence time of the particles in the plasma jet.
4. The obtained results confirmed that particle temperatures exhibit wide distribution due to temperature and velocity gradients in the plasma jet and consequently some of them were only partially melted or not melted at all.
5. An additional experiment revealed that particle size is an important parameter that affected the morphology of the plasma sprayed zirconia powder. Smaller particles melted easier than the large ones when sprayed in the same operating conditions.

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TABLE III. - DIAGRAM OF EXPERIMENTAL DESIGN AND RESULTS

Power	Feed rate	Arc gas flow	Gas composition	Feed gas flow	Specimen number	Monoclinic ZrO_2 content mol %	Content of spherical particles, percent
0	0	0	0	0	1	8.9	13
0	0	0	0	1	2	5.6	34
0	0	0	1	0	3	3.0	50
0	0	0	1	-	--	---	--
0	0	1	0	0	4	5.6	7
0	0	1	0	1	--	---	--
0	0	1	1	0	5	4.5	58
0	0	1	1	1	--	---	--
0	1	0	0	0	6	6.8	4
0	1	0	0	1	7	---	19
0	1	0	1	0	8	2.9	60
0	1	0	1	-	--	---	--
0	1	1	0	0	9	6.2	10
0	1	1	0	-	--	---	--
0	1	1	1	0	10	3.4	19
0	1	1	1	1	11	4.4	17
1	0	0	0	0	12	5.1	22
1	0	0	0	1	13	---	22
1	0	0	1	0	14	4.1	76
1	0	0	1	-	--	---	--
1	0	1	0	0	15	5.0	28
1	0	1	0	-	--	---	--
1	0	1	1	0	16	2.9	72
1	0	1	1	1	17	---	39
1	1	0	0	0	18	5.4	28
1	1	0	0	1	19	---	16
1	1	0	1	0	20	1.9	82
1	1	0	1	-	--	---	--
1	1	1	0	0	21	3.7	14
1	1	1	0	1	22	5.3	32
1	1	1	1	0	23	2.2	60
1	1	1	1	1	24	3.5	47

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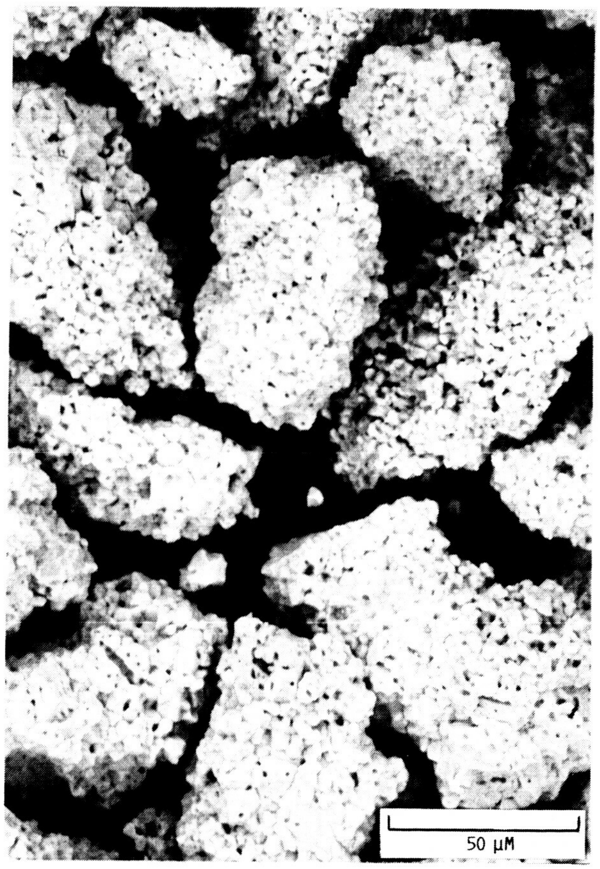
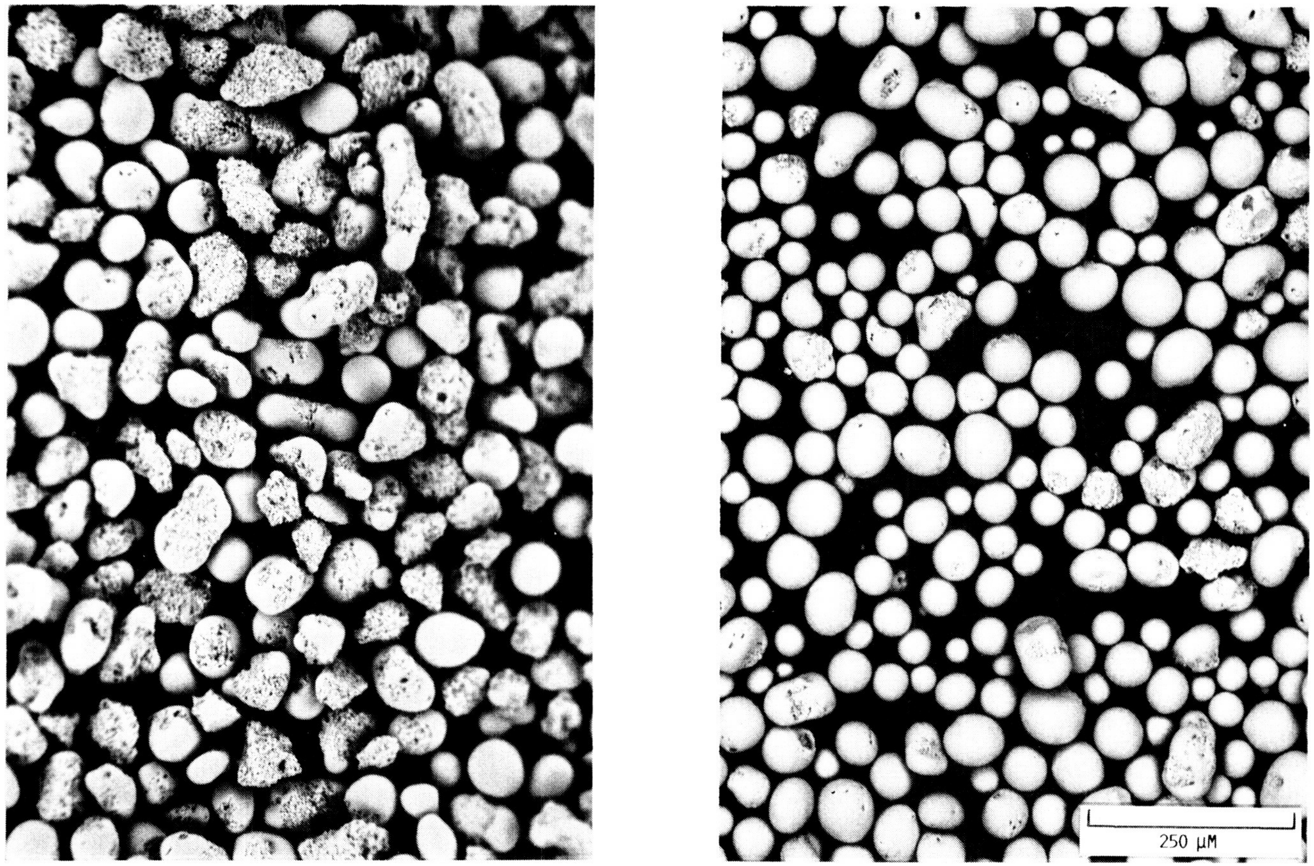


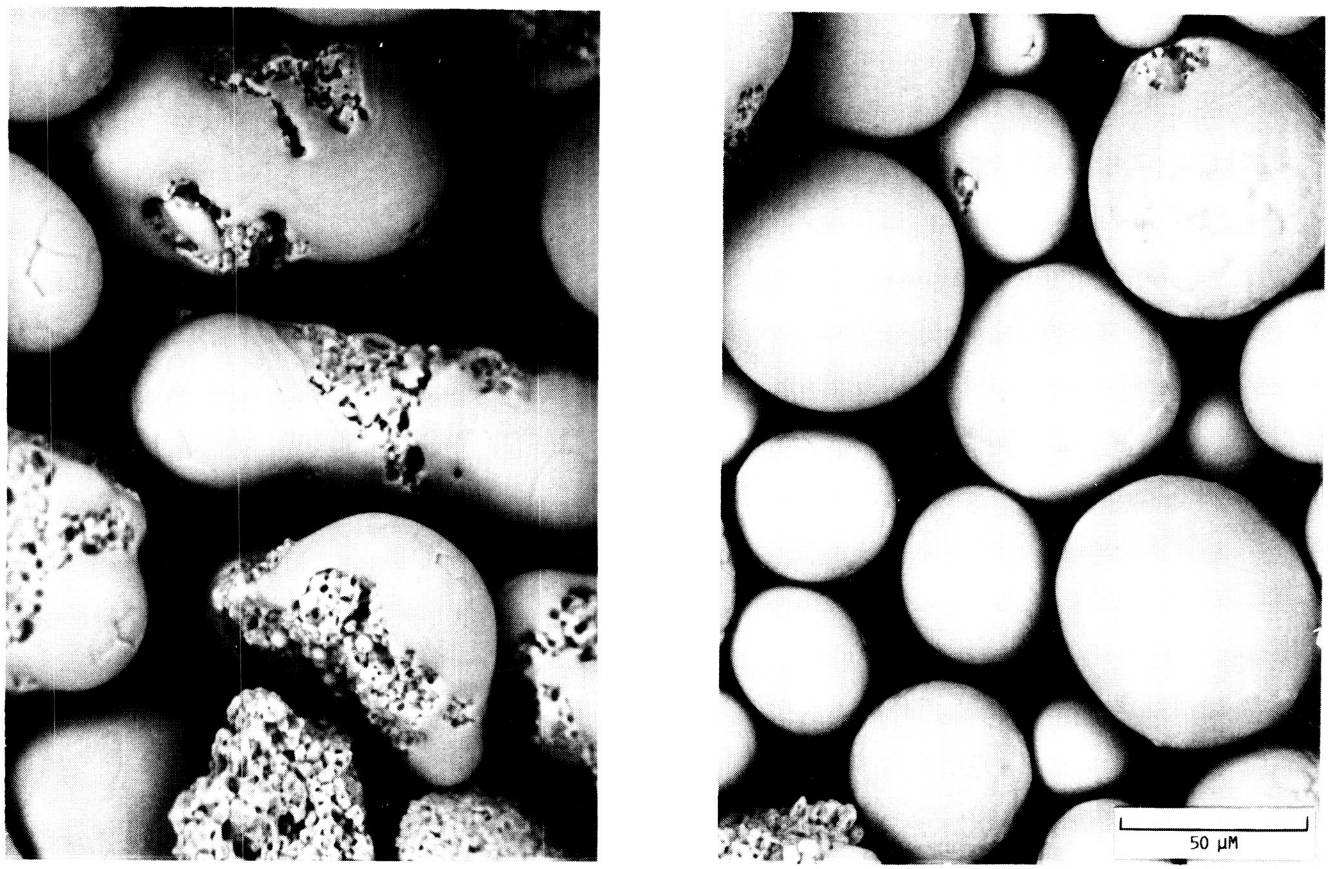
FIGURE 1. - SEM PHOTOGRAPH OF ZIRCONIA GRAINS IN AS RECEIVED CONDITION.



A. SAMPLE NO. 1.

B. SAMPLE NO. 16.

FIGURE 2. - SEM PHOTOGRAPHS OF PARTICLES REPRESENTING SAMPLES NO. 1 AND NO. 16 PLASMA SPRAYED IN WATER UNSING DIFFERENT SETS OF PARAMETERS.



A. SAMPLE NO. 1.

B. SAMPLE NO. 16.

FIGURE 3. - SEM PHOGRAPHS OF PARTICLES REPRESENTING SAMPLES NO. 1 AND NO. 16 BUT SHOWN AT HIGHER MAGNIFICATION.

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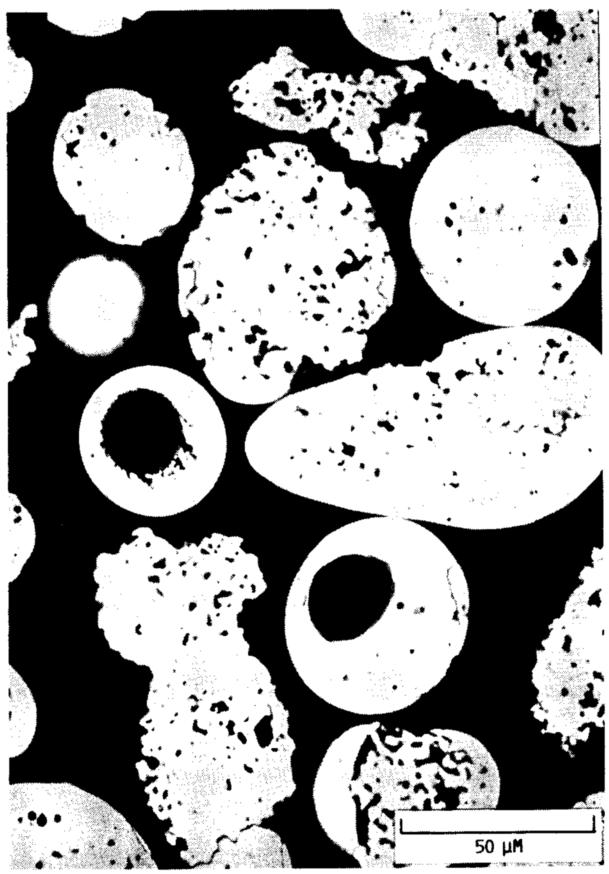
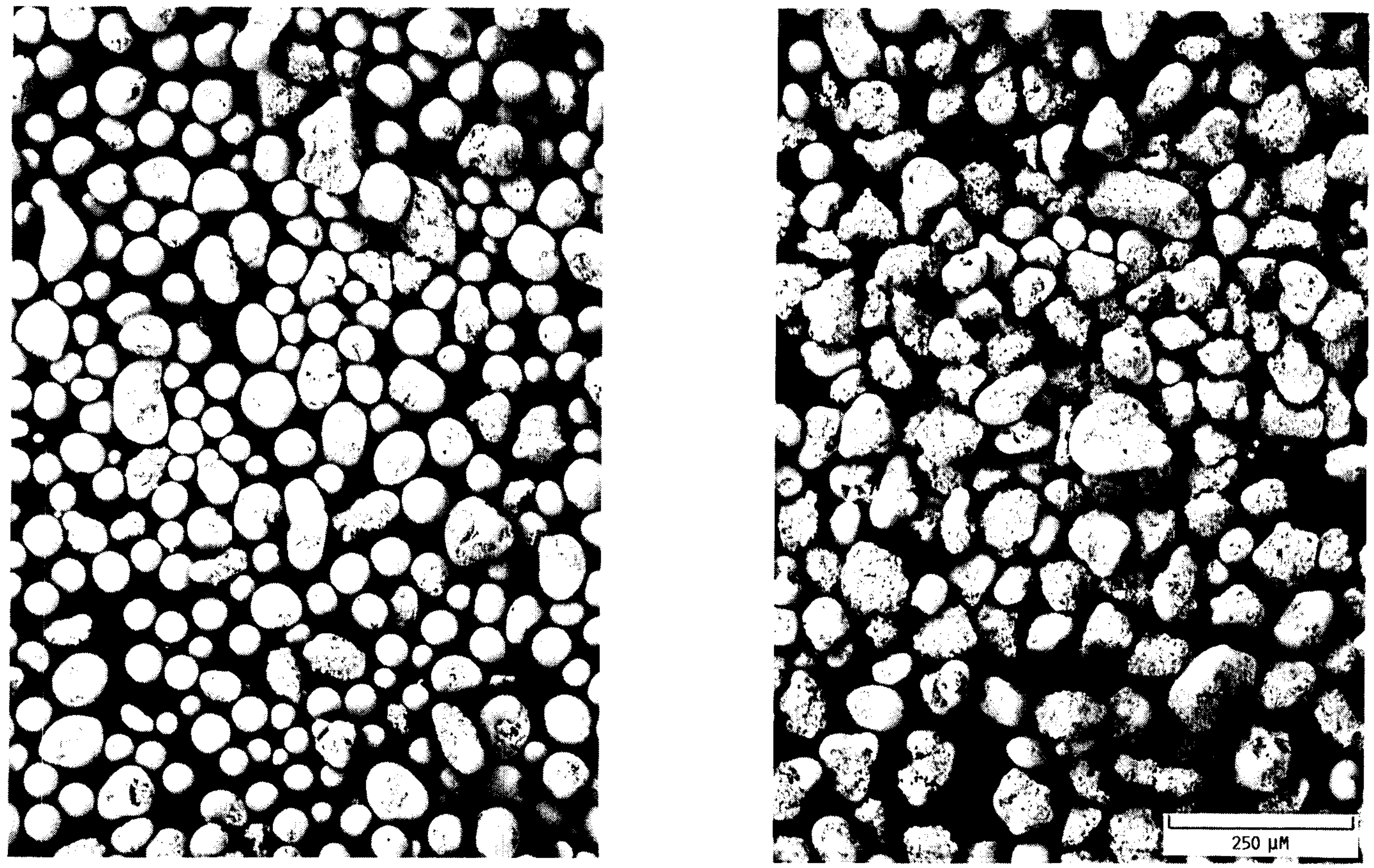


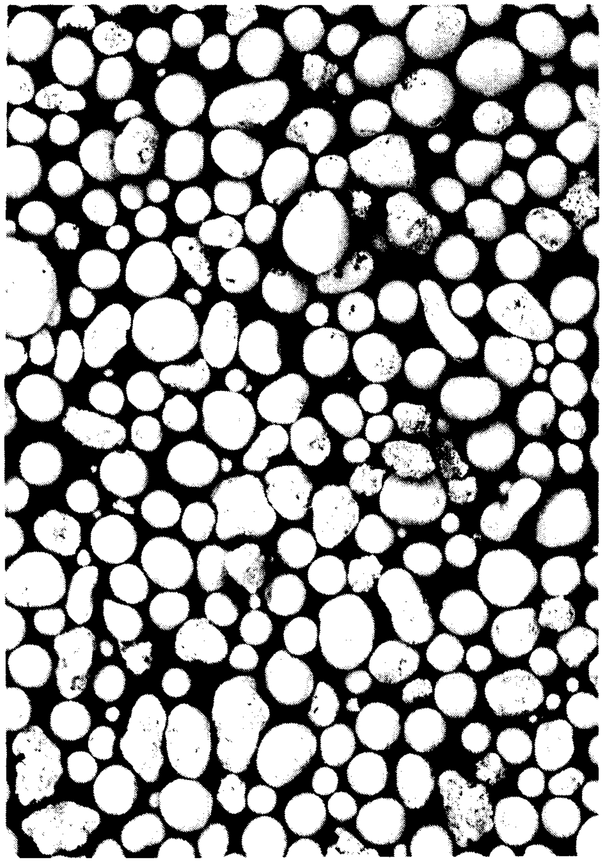
FIGURE 4. - SEM PHOTOGRAPH OF RANDOM CROSS SECTIONS OF ZIRCONIA PARTICLES PLASMA SPRAYED IN WATER SAMPLE NO. 18.



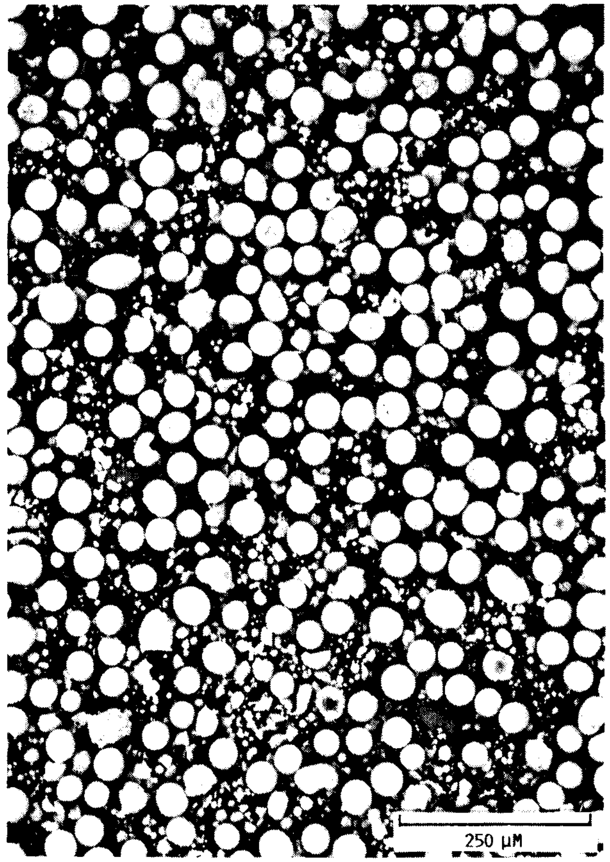
A. SAMPLE NO. 7.

B. SAMPLE NO. 8.

FIGURE 5. - SEM PHOTOGRAPHS OF PARTICLES REPRESENTING SAMPLES NO. 7 AND NO. 8 PLASMA SPRAYED IN WATER USING DIFFERENT SETS OF PARAMETERS.



A. PARTICLE SIZE -200 + 325 MESH.



B. PARTICLE SIZE -325 + 400 MESH.

FIGURE 6. - SEM PHOTOGRAPHS OF PARTICLES WITH DIFFERENT SIZE PLASMA SPRAYED IN WATER UNDER THE SAME SET OF PARAMETERS.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-88927		

4. Title and Subtitle Morphology of Zirconia Particles Exposed to D.C. Arc Plasma Jet	5. Report Date January 1987
	6. Performing Organization Code 505-63-01
7. Author(s) Isidor Zaplatynsky	8. Performing Organization Report No. E-3325
	10. Work Unit No.
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words (Suggested by Author(s))	18. Distribution Statement
Plasma spraying; Thermal barrier coating; Zirconia	Unclassified - unlimited STAR Category 26

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified		

*For sale by the National Technical Information Service, Springfield, Virginia 22161