JTTEE5 6:434-438

Properties of Plasma-Sprayed Freestanding Ceramic Parts

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(Submitted 27 December 1996; in revised form 7 April 1997)

Plasma spraying can be used for the production of freestanding parts, such as plates, pipes, and crucibles. However, published data on the properties of such freestanding bodies are scarce. White alumina, gray alumina, zircon, and their combinations were plasma sprayed on metallic mandrels using a water-stabilized plasma gun and then stripped off. The resulting tubes were tested for gas permeability, porosity, and elastic properties. Pipes also were made from a mixture of ceramic and aluminum metal powders, and from "sandwich" bodies consisting of ceramic/metal/ceramic layers. Comparison of as-sprayed samples and samples after various posttreatments showed that posttreatments (i.e., sealing with organic and inorganic compounds or with metals, sol-gel technique, calcination, etc.) generally decreases gas permeability and increases elastic properties.

Keywords freestanding parts, gas permeability, porosity, water-stabilized plasma, Young's modulus

1. Introduction

Two main procedures are used for the manufacture of freestanding parts (FSPs). One method uses a mandrel covered with a soluble layer, which is dissolved after ceramic deposition. The other method uses a mandrel with a thermal expansion coefficient different from that of the sprayed material; therefore, the sprayed ceramic part will release after cooling (Ref 1, 2). Various types of FSPs have been produced, such as simple plates, tubes, bowls, and crucibles as well as complex, specially shaped bodies. Near-net shapes with tolerances of approximately 0.1 mm or bodies with a large ratio of diameter to thickness (e.g., pipes with a diameter of 300 mm and a wall thickness of 1.5 mm) are produced, as well as sandwiches and functionally graded (FGM) structures.

For certain FSP applications, the decisive factor is porosity, which influences mechanical properties and protective capabilities. There are several mechanisms of pore formation (Ref 3), but quite often porosity is divided into two groups: (1) closed porosity, which occurs inside the deposited material and influences the physical properties of FSPs, and (2) open porosity, where all the surfaces are connected, which influences the physical as well as the protective properties. The porosity in plasma-sprayed FSPs is usually distributed unevenly, with a larger number of pores between each deposited layer and shorter transverse pores between the splats. These morphological features arise because all FSPs are sprayed by successive passes of the thermal spray torch to achieve the desired wall thickness.

Various postspray methods have been developed to reduce porosity. Calcination of the as-sprayed FSPs can change the phase content, and connected volume changes can alter the porosity or, at higher temperatures, the FSP can be fully sintered. Another method seals the pores with additional matter (e.g., organic or inorganic by using, for instance, the sol-gel process). On the other hand, porosity can be increased by leaching out the metal from the deposited metal/ceramic mixture. This paper presents results of porosity, gas permeability, and Young's modulus measurements on various as-sprayed and posttreated FSPs.

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2. Experimental Method

Freestanding parts were plasma sprayed in air using the PAL 160 water-stabilized gun (IPP, Prague, Czech Republic) with two feedstock injectors. The feeding rate was 26 to 29 kg/h. A preheated steel mandrel with no soluble layer was used to produce pipes with an internal diameter of 83 mm, a length of 500 mm, and a wall thickness from 1.6 to 4.0 mm. The materials listed in Table 1 were used either as single components or as blends.

2.1 *Gas Permeability Measurements*

A sample of the plasma-sprayed pipe was sealed on both ends, placed in an evacuated vessel, and overpressurized with 30 to 150 kPa of air. The increase of pressure in the evacuated vessel due to air penetrating from the pipe sample was then measured. The gas permeability (for an area of 100 mm^2, a wall

Table 1 Materials and sample codes

Sample code	Composition, wt%
J, L	99.9 white alumina
CH, I	Gray alumina (alumina with 4.6 TiO_2 and 1.3 Fe_2O_3)
Z	Zircon ($ZrSiO_4$)
D	90 gray alumina + 10 zircon
H	95 gray alumina + 5 zircon
E	(90 gray alumina + 10 zircon) + 7.6 Al (metal)
F	(90 gray alumina + 10 zircon) + 13.3 Al (metal)
M	White alumina + 6.9 Al (metal)
R, V	White alumina + two nickel (metal) intermediate layers

thickness of 1 mm, an outside temperature of 20 °C, and a pressure of 10^2 Pa) was then calculated.

2.2 *Young's Modulus*

Rings with a width of $(b) = 9$ to 11 mm were cut from the sample pipes. These rings were then loaded in tension (using two bars), and changes of the inside diameter with respect to load were recorded. Each sample was loaded and unloaded at least three times. The Young's modulus (E) was then calculated from (Ref 4):

$$E = 1.785\left(\frac{a^3 F}{b\, h^3\, \Delta a}\right) \quad \text{(Eq 1)}$$

where a is the pipe (ring) diameter and Δa its change, h is the wall thickness, and F is the loading force.

2.3 *Porosity Measurements*

The volume of the open porosity (i.e., the surface-connected pores) was measured by the Archimedean weighing method. Samples were weighed in air (G_0), in water after soaking for 60 min at 4 kPa pressure (G_1), and again in air with the penetrated water inside (G_2). Then the open porosity was found from:

$$p_z = \frac{G_2 - G_0}{G_2 - G_1} 100\,[\%] \quad \text{(Eq 2)}$$

and the sample density from:

$$y_z = \frac{G_0}{G_2 - G_1} y_{water} \quad \text{(Eq 3)}$$

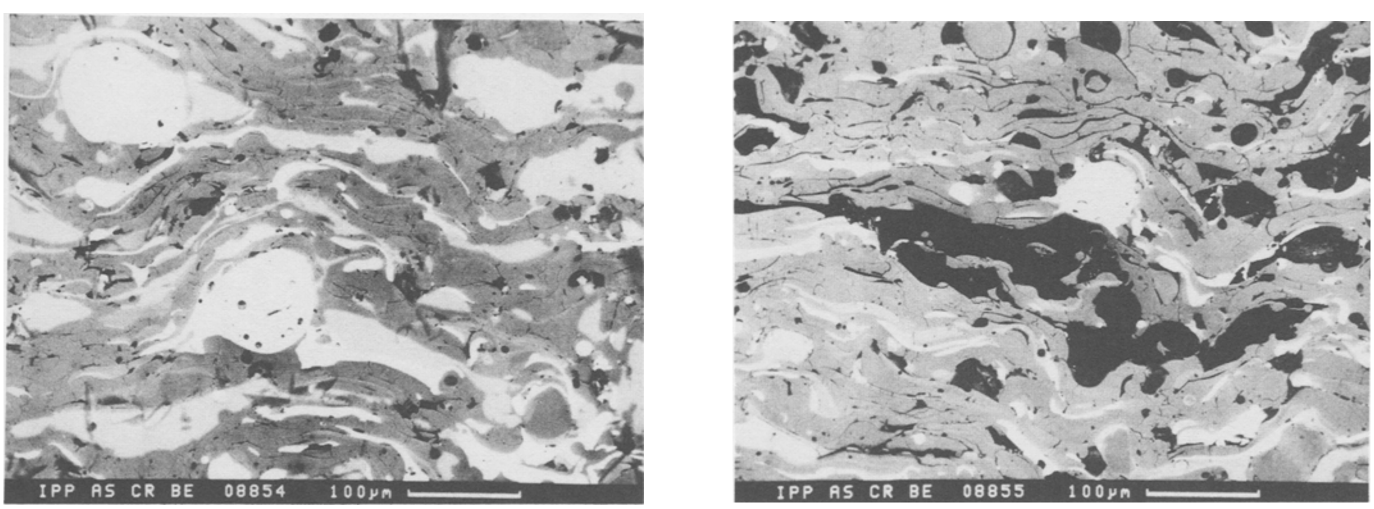
where y_{water} is water density at the measuring temperature.

Table 2 Properties of FSPs based on white alumina

Sample	Treatment	Gas permeability, cm^3/min	Porosity, %	Skeleton density, g/cm^3	Young's modulus, GPa
J	As sprayed	2.54	4.86	3.377	147.7
J	Resin	0	4.51	3.391	266.4
L	As sprayed	2.47	6.62	3.331	177.5
L	1300 °C	21.86	7.69	3.449	198.5
L	1520 °C	...	7.79	3.482	333.6
L	1730 °C	0.75	3.39	3.675	463.2

Table 3 Properties of FSPs based on gray alumina

Sample	Treatment	Gas permeability, cm^3/min	Porosity, %	Skeleton density, g/cm^3	Young's modulus, GPa
CH	As sprayed	2.18	4.9	3.406	121.8
CH	1300 °C	9.62	5.19	3.52	352.7
CH	1520 °C	0	0.48	3.607	425.3
I	As sprayed	1.59	3.92	3.418	132.4
I	Resin	0	3.96	3.426	258.9



(a) (b)

Fig. 1 Structures of gray alumina + zircon + aluminum. (a) As-sprayed. (b) After leaching for 340 h

The final result for a sample is the average of at least four measurements, and the precisions are ±0.06% for p_z and ±0.002 g/cm^3 for y_z. Scanning electron microscope images of selected cross sections of samples were used for comparison.

3. Results

Typical results for the as-sprayed and posttreated samples are summarized in Tables 2 to 8.

3.1 *Resin Impregnation*

As-sprayed samples were dipped three times into a resin (Epoxy ChS 371, EPRO, s.p., Plzen, Czech Republic) diluted by acetone and ethyl alcohol (in weight parts of 1 + 3 + 8, respectively) (Ref 5). The average weight increase of samples after hardening was around 1%, which was sufficient to suppress totally the gas permeability (see Tables 2, 3, and 5) in all materials. At the same time, the Young's modulus increased for all samples.

3.2 *Ceramics with Metal Components*

Aluminum powder was mixed into the ceramic feedstocks at varying proportions and sprayed. To achieve a porosity *decrease*, the as-sprayed pipes were annealed for 2 h at 850 °C, which is above the melting point of aluminum (660 °C) and lower than the main phase change temperatures of alumina. Partial redistribution of liquid aluminum in the ceramic matrix slightly decreased the gas permeability and markedly increased

Table 4 Properties of FSPs based on zircon

Sample	Treatment	Gas permeability, cm³/min	Porosity, %	Skeleton density, g/cm³	Young's modulus, GPa
Z	As sprayed	44.58	7.73	3.625	22.9
Z	As sprayed	23.33	5.73	3.739	44.3
Z	1300 °C	36.98	6.75	3.764	105.9

Table 5 Properties of FSPs based on gray alumina and zircon

Sample	Treatment	Gas permeability, cm³/min	Porosity, %	Skeleton density, g/cm³	Young's modulus, GPa
D	As sprayed	2.11	4.33	3.475	168.1
D	Resin	0	3.896	3.478	186
D	1300 °C	13.38	6.124	3.571	324.62
H	As sprayed	1.67	3.939	3.434	128.5
H	Resin	0	3.97	3.439	249.6
H	1300 °C	9.68	5.171	3.562	318.1

Table 6 Properties of FSPs based on white alumina and aluminum

Sample	Treatment	Gas permeability, cm³/min	Porosity, %	Skeleton density, g/cm³	Young's modulus, GPa
M	As sprayed	1.78	4.28	3.297	199.3
M	850 °C	1.16	4.21	3.317	244.2

Table 7 Properties of FSPs based on gray alumina, zircon, and aluminum

Sample	Treatment	Gas permeability, cm³/min	Porosity, %	Skeleton density, g/cm³	Young's modulus, GPa
E	As sprayed	1.99	4.1	3.308	165.7
E	Leached	75.02	13.77	3.094	98.6
F	As sprayed	2.89	5.04	3.196	150.9
F	Leached	360.7	23.84	2.742	81.1
F	850 °C	1.93	4.902	3.195	198.5

Table 8 Properties of FSPs made of alumina ceramics, and metal sandwich

Sample	Treatment	Gas permeability, cm³/min	Porosity, %	Skeleton density, g/cm³	Young's modulus, GPa
R	As sprayed	5.77	5.62	3.544	106.3
V	As sprayed	2.63	5.165	3.681	127.2

the Young's modulus (Tables 6 and 7). For porosity *increase* (e.g., for membranes), the ceramic/metal as-sprayed pipes were soaked in dilute HCl for up to 340 h. The aluminum metal was leached out and the porosity increased as shown in Fig. 1 and Table 7 (Ref 5).

Sandwich FSPs with nickel layers (Fig. 2) exhibit no special features indicating properties inferior to those of white alumina (compare Tables 2 and 8). This occurs because too many interfaces probably exist in the samples. It is not known whether annealing at a higher temperature would help.

3.3 *Sol-Gel Sealing*

Samples of white alumina were calcined (1300 °C for 2 h), dipped for 30 s in the sol of alumina (prepared from the aluminum isopropylalcoholate), and annealed again at 1300 °C for various times. The recorded changes were relatively small (not shown in the tables).

3.4 *Sintering*

Samples of gray and white alumina were sintered at 1520 or 1730 °C for 2 h. No gas permeability could be detected even at 500 kPa overpressure (Tables 2 and 3). Typical structures of gray alumina in the as-sprayed condition and after annealing are shown in Fig. 3(a) and (b), respectively.

4. Discussion and Concluding Remarks

Generally, the technology of FSP preparation based on exploitation of the differences in thermal expansions of mandrels and deposits has been improved and enhanced properties have been obtained for the as-sprayed samples. Also, development of the gas permeability measuring technique using the overpressure inside the sample halped to precisely define differences for individual materials and treatments. Several conclusions will be summarized here.

Generally, the best posttreatment for plasma-sprayed ceramics is annealing at or near the sintering temperature for a given material. The gas permeability is practically zero, probably due to pore closure by the plastic material. Also, the Young's modulus of such treated materials increases and reaches values close to the bulk ceramic (see sample L, 1730 °C, for white alumina; and sample CH, 1520 °C, for gray alumina). On the other hand, calcination at 1300 °C for alumina and alumina-base materials leads to a marked increase of gas permeability, probably caused by incomplete phase transformation (Ref 6). However, the structural and phase changes are sufficient to substantially increase the Young's modulus.

Aluminum co-sprayed with alumina does not have a large effect on sealing and Young's modulus. However, it can be used to prepare membranes with a high porosity by leaching out the aluminum.

A slight increase in all physical parameters is achieved for alumina + zircon blends compared to alumina only. Previous results (Ref 6, 7) have indicated decomposition of zircon on plasma spraying into fine crystalline ZrO_2 and glassy SiO_2. It is

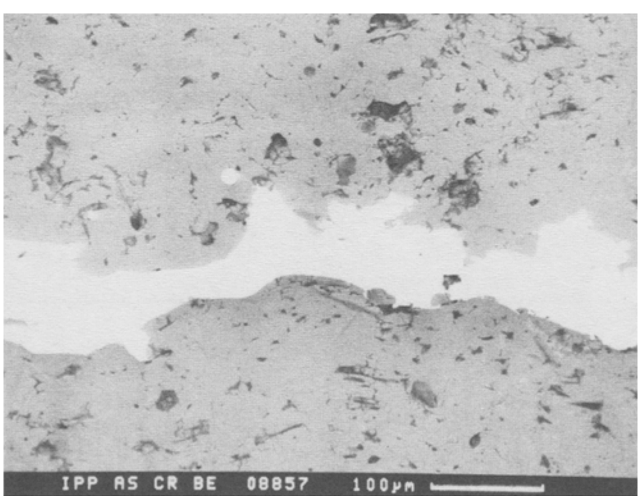


Fig. 2 Ceramic/metal sandwich (gray alumina + nickel).

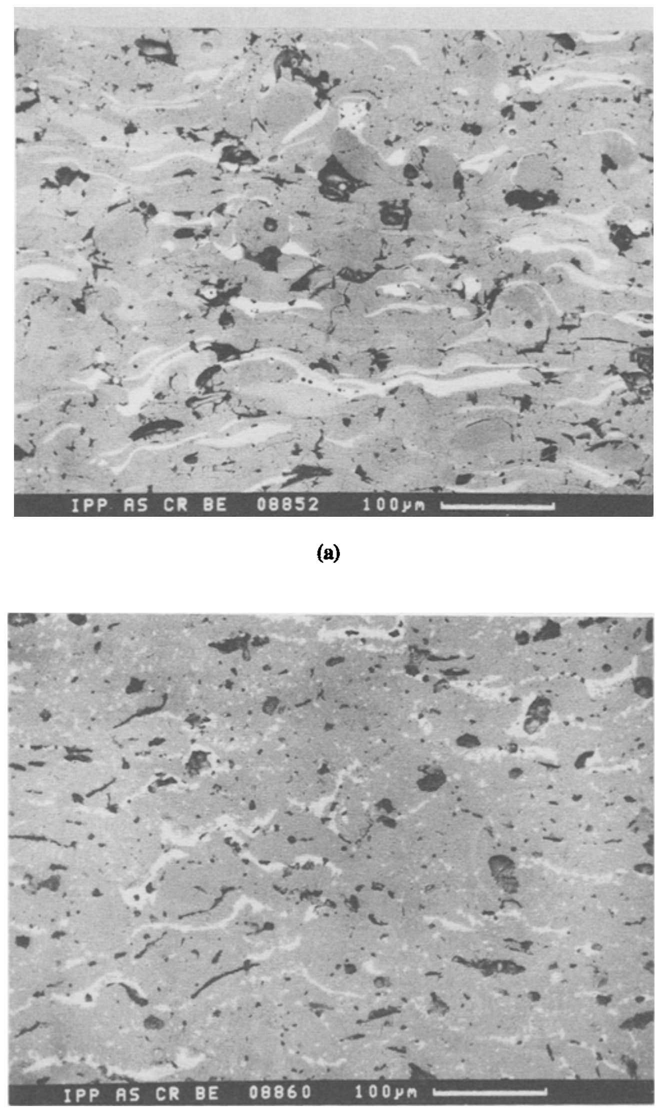


Fig. 3 Structure of gray alumina. (a) As-sprayed. (b) Annealed at 1520 °C

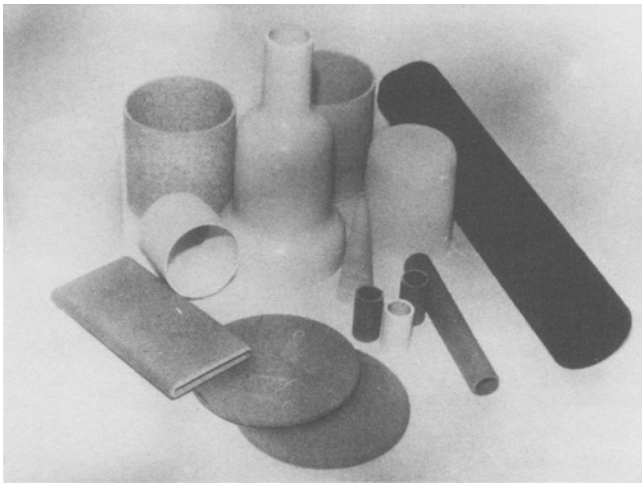


Fig. 4 Examples of plasma-sprayed FSPs. The large cylinder on the right is 300 mm long

well known that fine zirconia addition to alumina produces zirconia-toughened alumina. Zirconia-toughened ceramics also can be prepared on the basis of mullite ($3Al_2O_3 \cdot 2SiO_2$). It is therefore very likely that the slight increase in properties of blends compared to alumina can be ascribed to the zirconia toughening. At the same time, glassy silica phase can seal some pores.

Beneficial results were obtained for the resin-impregnated samples. Regardless of the as-sprayed material, impregnated parts exhibit zero gas permeability and a substantial increase of E (in most cases, by almost 100%). However, applications of these FSPs are limited to low temperatures because the organics used are unstable above 100 to 150 °C.

Plasma-sprayed FSPs can be manufactured in a variety of shapes (Fig. 4), and their properties can be enhanced to values comparable to the bulk ceramics by posttreatment. Thus, another area of technology has evolved for plasma spraying, especially for plasma systems with a high feedstock throughput rate.

Acknowledgments

This work was partially supported by the following grants: COST CZ 515.10, GACR 104/96/1353, GACR 202/95/0216, and NSF INT 9317415.

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