JTTEE5 6:445-448

Plasma Spraying of Zircon

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(Submitted 15 June 1996; in revised form 7 April 1997)

Zircon, $ZrSiO_4$, is a natural mineral used for various applications as a refractory bulk material. It is an excellent feedstock for the plasma spraying of protective coatings and free-standing bodies. Zircon decomposes on spraying into t-ZrO_2 and glassy SiO_2, which can be preserved in deposits by fast cooling. This combination of zirconia and silica exhibits properties such as a high thermal shock resistance, good corrosion resistance, low wettability, etc. The final properties of deposits can be further enhanced by the addition of other materials such as alumina. For instance, alumina-zircon plasma-sprayed free-standing pipes have a low gas permeability. Several technical applications are discussed.

Keywords free-standing bodies, plasma spraying, protective coatings, zircon-base materials, zirconium silicide

1. Introduction

Zircon—zirconium silicide, $ZrSiO_4$—is found in nature associated with acidic igneous rocks, from which zircon sand forms through weathering. After an additional treatment, in which small amounts of rutile, quartz, and other minerals are separated, zircon sand is used as a refractory material for glazes, enamels, and as a raw material for electrotechnical ceramics, etc. The nominal chemical composition of zircon is 67.1 wt% ZrO_2 and 32.9 wt% SiO_2, but usually there are small amounts of Fe_2O_3, cerium, thorium, or hafnium. The lattice structure is tetragonal with each silicon atom surrounded by four oxygen atoms. Table 1 gives selected properties of zircon. Zircon is the only compound in the $ZrO_2 + SiO_2$ system that decomposes at temperatures above 1676 °C into the basic components, that is, zirconia and silica with silica in a glassy form. Zircon is generally highly resistant to most chemicals with the exception of hydrofluoric acid.

2. Materials and Methods

2.1 *General Comments on Plasma-Sprayed Zircon*

Zircon is not commonly used for plasma spraying with commercially available gas-stabilized plasma systems. Partially stabilized zirconia (PSZ) is commonly plasma sprayed. Conversely, zircon is one of the most commonly used feedstocks for plasma spraying with water-stabilized plasma (WSP) systems. Water-stabilized plasma systems have a high throughput rate (several tens of kilograms of powder per hour), and therefore, they are used mainly for large area coatings and the production of sprayed free-standing ceramic bodies. Zircon is an ideal material for these types of spraying because of low price and generally suitable technical properties of the plasma deposits produced at a relatively wide range of technological spraying parameters. One problem exists with using zircon for plasma spraying: the often varying chemical composition of the raw zircon sands. Varying concentrations of Fe_2O_3, TiO_2, cyanite ($Al_2O_3 \cdot SiO_2$), monazite ((Ce,La)PO_4), and other chemicals can complicate feedstock preparation, especially for materials that need the same particle size distribution.

It has been established that zircon, when plasma sprayed, decomposes into zirconia and silica (Ref 1-6), and it does not recombine if cooled quickly enough. The sprayed zircon deposits were observed with all three modifications of zirconia. Ault (Ref 1) reported zirconia in the cubic form. Okubo et al. (Ref 2) reported the tetragonal phase, and Krauth and Meyer (Ref 3) reported a mixture of monoclinic and tetragonal phases. Some authors suggested that the lattice type depended on the size of zircon particles (Ref 4, 7), and eventually, Wang and Wang (Ref 9) discussed the formation of phase modifications using concepts of irreversible thermodynamics. They concluded that although SiO_2 has the lowest critical undercooling parameter, the large difference in melting points between silica and zirconia results in metastable zirconia appearing from the melt first instead of from the silica. The cooling rate determines if t-zirconia or c-zirconia will form in the sprayed material.

2.2 *Experimental Techniques*

The water-stabilized plasma gun PAL 160 (IPP, 182 00 Prague, Czech Republic), working in air, was used for spray deposition of zircon powder. Coated steel substrates were sprayed, consisting of several layers of splats with a total thickness from 0.28 mm or larger, and the free-standing bodies were made with a wall thickness of several millimeters. Details on the WSP gun

Table 1 Selected properties of zircon

Properties	Value
Generally quoted density, gcm^{-3}	4.6
Range of found densities, gcm^{-3}	3.9 to 4.8
Softening point, °C	2015
Coefficient of linear expansion α, between 20 and 1550 °C	35 to 42 × 10^{-7}
Thermal conductivity, $Wm^{-1}K^{-1}$	4.0 to 5.86
Decomposition temperature, °C	1676
Lattice parameters, nm	a = 0.659, c = 0.594

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and the spraying parameters (especially for the spraying distance [SD] and feeding distance [FD] where the powder is injected into the plasma jet) and experimental techniques are given in Ref 6, 7, 10, and 11.

3. Results and Discussion

3.1 *Structure and Phases*

Using ion bombardment, a thin foil was prepared from the cross section of the first several splats perpendicular to the steel substrate (Ref 6). Transmission electron microscopy (TEM) and selected area diffraction (SAD) techniques, complemented by x-ray diffraction (XRD) studies, enabled distinction of several structural types and phases in the foil (Fig. 1). Directly adjacent to the deposit/substrate interface was a zirconia region with very small grains (25 to 50 nm) followed by a region with larger grains (50 to 100 nm), both with traces of an amorphous phase. Then there were grains of ZrO_2 arranged in bands separated by a glassy SiO_2 phase. Finally, there were larger crystalline remains from the first splat. Similar structural regions can be found in splats further away from the interface. However, they contain less of the fine structure and amorphous phase and a transient structure of zirconia, resembling that of an annealed metallic glass. All three modifications of zirconia were detected. Closer to the interface, the high temperature modifications, the cubic and tetragonal (prevailing), were found as a consequence of the faster heat transfer to the substrate and, thus, a faster local cooling rate. A certain amount of the low-temperature monoclinic phase was detected further away from the interface where the relative local cooling rate was lower in larger regions of splats. Generally, the dominant zirconia phase was the tetragonal phase with traces of the other phases.

Table 2 Adhesion data

Feeding distance/ spraying distance, mm	Adhesion, MPa	Deposits thickness, mm
23/100	5.91	0.75
23/245	5.62	0.80
23/290	5.64	0.54
28/200	6.40	0.67
28/245	6.21	0.55
28/290	10.44	0.57

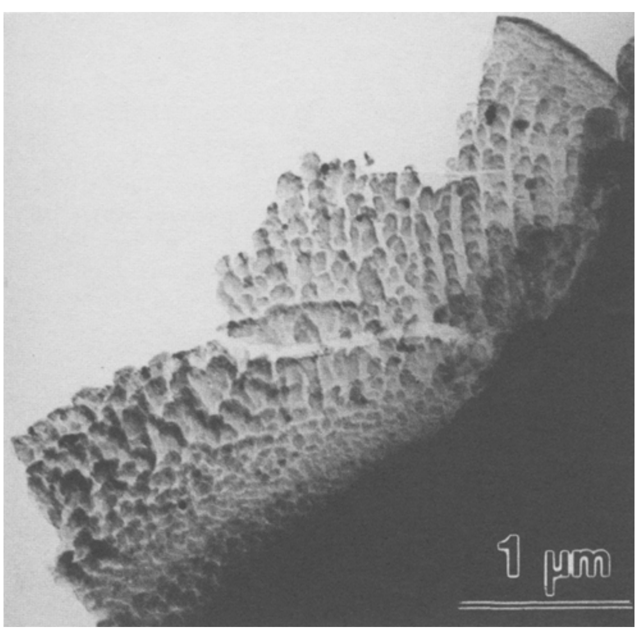


Fig. 1 Cross section TEM image of zircon

3.2 *Density*

The high-temperature dissociation of zircon during plasma spraying is accompanied by changes of the specific density from an initial value 4.6 gcm^{-3} for the feedstock zircon to, on average, 4.05 gcm^{-3} for the plasma-sprayed zircon deposits. However, the volume density is naturally lower because of porosity; it depends on the spray parameters and is usually between 3.20 and 3.75 gcm^{-3} for porosity between 3.6 and 28 vol%. Figure 2 illustrates the effect of the spraying distance (SD) on volume porosity at a constant position of the external powder injector in the plasma jet. The optimum SD for routine WSP spraying of zircon is approximately 300 to 400 mm, leading to a volume density of ~3.65 gcm^{-3} and an open porosity of ~6 to 7 vol%. The following data are given for these conditions unless otherwise stated.

3.3 *Thermal Expansion*

The thermal expansion behavior of the plasma-sprayed zircon deposits was different during and after calcination at temperatures of 1300 °C. The thermal expansion coefficient is different during the first heating cycle from values in the following cycles. A change of the initial value of $6.8 \times 10^{-6} K^{-1}$ to $5.2 \times 10^{-6} K^{-1}$ was reported (Ref 12). These changes are caused by changes in the deposited structure. Figure 3 shows a comparison of morphologies of the as-sprayed and calcinated deposits. The silica-base region of the structure was partly sintered, and there were some phase changes in zirconia above 1150 °C. Both proc-

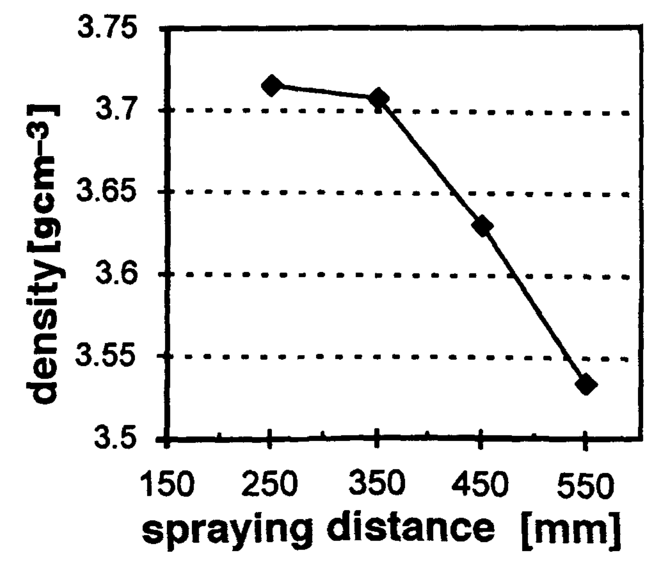


Fig. 2 Dependence of density on spraying distance

esses, as well as the thermal expansion coefficient, affect the porosity. Mercury intrusion porosimetry revealed a redistribution of pore sizes indicating larger pores. Generally, it appears that glassy silica is the controlling factor of physical properties of plasma-sprayed zircon coating at temperatures above 800 °C.

3.4 *Adhesion*

Table 2 presents the values of adhesion ("glue test," 30 mm diam sample, average of six samples) depending on spraying parameters SD and FD. The best adhesion was obtained for a combination of a longer dwell time at a lower temperature. The glassy silica in the plastic state represents the largest contribution to the adhesion values.

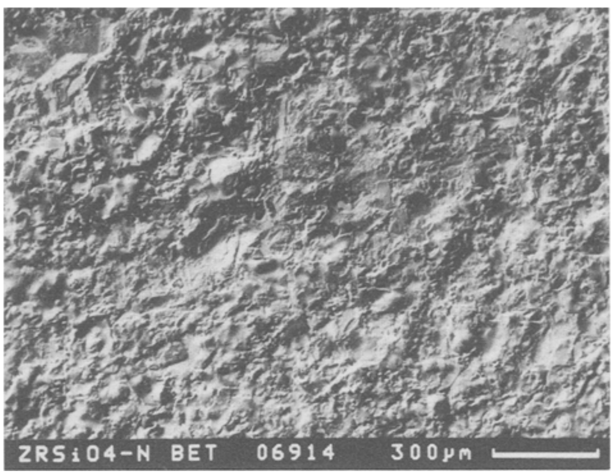
3.5 *Elastic Young's Modulus and Other Properties*

Table 3 presents the Young's modulus data measured from the tensile elongation of rings from the plasma-sprayed ceramic pipes (Ref 13, 14). The dimensions of the samples, however, do not entirely meet the requirements for the plane state of stress, and therefore, values of E in Table 3 do not represent the exact Young's modulus for the given structure (Ref 14).

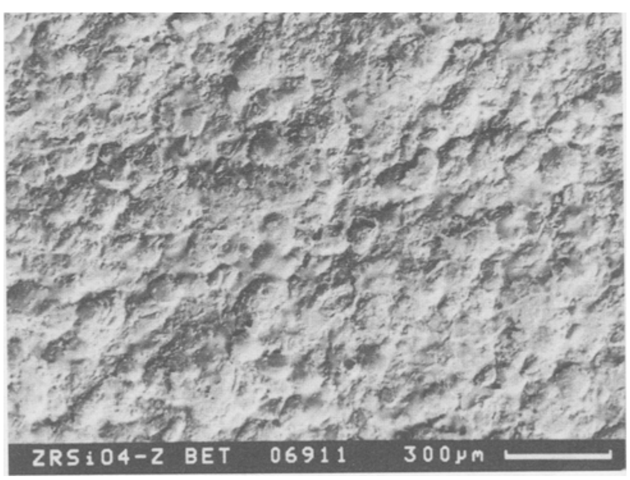
The porosity in plasma-sprayed pipes and the decomposed structure explain the good endurance to thermal shock (20, 1300, and 20 °C) in comparison to other sprayed and/or the same bulk ceramics. Conversely, the same microstructural features cause increased gas permeability of zircon pipes (Ref 11) compared to, for instance, alumina. Zircon deposits, actually a mixture of zirconia and silica, also exhibit good corrosion resistance to various chemicals, except for hafnium-base corrodents.

3.6 *Alumina-Zircon Materials*

Mixtures of zircon and gray alumina powder at various ratios were also used to spray ceramic pipes. The resulting as-sprayed structure (Fig. 4) consisted of t-zirconia, silica, and γ-alumina. There was an increase in E values (Table 3), especially after annealing. At the same time, the addition of zircon to alumina de-



(a)



(b)

Fig. 3 Different morgologies of zircon (a) as-sprayed and (b) annealed

Table 3 Young's modulus

Sample	Annealing temperature, °C	Young's modulus of elasticity, (E), GPa	Remarks
ZR	As-sprayed	17.6 to 51.6	1
	1300	70 to 110	1
25 ZR + 75 AH	As-sprayed	46.2	
10 ZR + 90 AH	As-sprayed	159.2	
	1300	307.5	
5 ZR + 95 AH	As-sprayed	130.7	
	1300	301.2	
AB	As-sprayed	147.7 to 168.1	1, 2
	1300	187.9 to 198.5	1, 2
AH	As-sprayed	115.3 to 132.4	1, 2
	1300	334.0 to 352.7	1, 2

ZR, zircon; AH, gray alumina; AB, white alumina; 1, value depends on the plasma-spray technology used; 2, for comparison

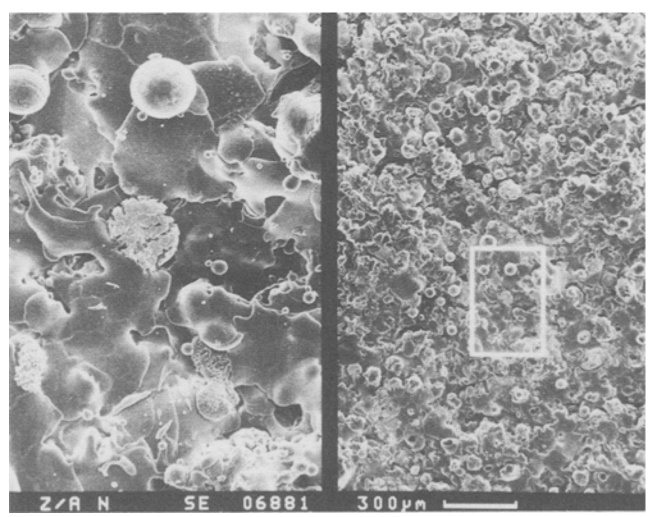


Fig. 4 Structure of as-sprayed alumina-zircon (90 wt% zircon)

creases the gas permeability to values less than that for alumina (Ref 11). Image analysis and porosity measurements also revealed that the open porosity of alumina-zircon materials was very low. Some pores in alumina are sealed by silica from the decomposed zircon. High-temperature calcination of the as-sprayed deposited silica also chemically reacts with alumina, and a certain amount of mullite ($Al_6Si_2O_{13}$) forms. The resulting structure represents a mixture of various modifications of alumina and zirconia with silica and mullite.

4. Examples of Applications

- The good adhesion and thermal cycling performance of zircon coatings have been used for metal feeders in the glass industry where plungers work at temperatures of approximately 1160 °C. The incorporation of zircon coatings increased lifetime from 2 to 4 months. The glass industry is an opportunity for zircon plasma coating because, in addition to several advantageous properties previously mentioned, zircon exhibits relatively low wettability.
- Zircon coatings are regularly made on metal plates used in high-temperature Drewer-type furnaces. The lifetime increases from 2 to 6 months if the operating temperature does not decrease below 450 °C. The same condition applies to the glass-coated metal feeders mentioned previously.
- The low thermal conductivity of plasma-deposited zircon coatings (1.1 to 1.3 $Wm^{-1}K^{-1}$ [Ref 12]) is used on metal parts, which are internally water cooled. An example of this application is glass stirrers, usually working at temperatures between 980 and 1420 °C. Zircon coatings in this case reduce the high-temperature corrosion of metal rods and the consequent plunging of the corrosion products into melt, which would result in coloring of the glass.
- Zircon is also used for manufacturing of plasma-sprayed porous ceramic membranes. Steel, molybdenum, or solid graphite are used as substrates, and two types of zircon (nonspheroidized and spheroidized powders) are used (Ref 15).
- Plasma-sprayed free-standing zircon pipes (inside diam 83 mm, wall thickness 1.5 to 2 mm, lengths up to 2000 mm) are used in furnaces as shields for heating elements.
- Relatively thick coatings (5 mm) of zircon are deposited on large rectangular aluminum alloy plates as parts of nuclear reactor probes.

5. Summary and Conclusions

Zircon is a feedstock material not yet fully appreciated for plasma-spraying applications. In many cases, especially for large area coatings and for manufacturing of free-standing ceramic bodies, zircon can be substituted for more expensive materials such as PSZ. Special properties of plasma-spayed zircon are induced by the thermal decomposition of zircon in spraying. The plasma deposits contain glassy silica and various modifications of zirconia in addition to a small amount of the amorphous phase. This "composite" material partially exhibits properties of its constituents. Zircon can be generally recommended for applications at higher temperatures (thermal barriers, thermal shock) and for protective coatings in chemically corrosive environments. In the as-sprayed condition, zircon does not have a larger Young's modulus and is not a hard facing material.

Acknowledgments

This work was partially supported by NSF, US-CR Inter. Program INT 9317415, and P. Chráska and K. Neufuss also acknowledge support from grant GA CR 104/96/1353. The authors also thank colleagues from IPP Prague (J. Dubsky, B. Kolman, Z. Travnicek) for their valuable help and comments.

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