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Laboratory Report—Thermal Spraying at the Shanghai Institute of Ceramics

D. Chuanxian and T. Zhaohe

Plasma spraying has received considerable attention as a process for obtaining protective coatings. In this article, experiments and results obtained at the Shanghai Institute of Ceramics pertaining to the developments and application of plasma-sprayed coating materials such as thermal barrier, wear resistance, infrared radiation, electrode materials, biomedical materials, and diamond films are presented. The physical, mechanical, and thermal properties of the coatings were measured. The microstructural features of the coatings were also examined. Examples of applications of plasma-sprayed coatings in various industries are illustrated. In addition, the manufacture of some oxide powders and their characteristics are discussed.

1. Introduction

In the later 1950s and early 1960s, plasma spraying equipment with a clean, stable, and long service life was set up at the Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS).[1] Extensive work on the research and development of plasma-sprayed coating materials has taken place. Several coating materials have also found broad use in various branches of industry. The coating materials concerned were oxides, metals, carbides, and mixtures of oxides and metals. Table 1 summarizes the materials that have been examined at SICCAS.

2. Manufacture of Oxide Powders

It is essential that the feedstock powder has chemical and structural uniformity and good flow behavior to ensure that reliable properties of coatings are obtained. A slurry spraying and drying process was developed for manufacturing powders of TiO_2, Al_2O_3, Al_2O_3-TiO_2 and Cr_2O_3.[9] With this method, silica sol was used as the blend for agglomerating fine particles. The slurry was sprayed in air, dried, and cured in an oven to obtain suitable powders for plasma spraying.

The properties of the oxide powders such as bulk density and morphology were measured. Particle size and distribution of the powders were ascertained by standard sieving methods. From Table 2 and Fig. 1, it can be seen that most of the particles were in the 38 to 76 μm size range. The deposition efficiencies for the Cr_3O_2 and Al_2O_3-TiO_2 powders under typical conditions were greater than 60 and 70%, respectively, and were therefore suitable for plasma spraying.

Key Words: applications, diamond coatings, laboratory report, thermal properties, yttria stabilized zirconia

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Table 1 Coatings Developed at SICCAS[2]

Coatings	Engineering environment	Engineering application
Al_2O_3, Cr_2O_3, Al_2O_3-TiO_2, WC-Co Cr_3O_2-NiCr	Wear	Mechanical parts in textile and oil machines[3,4]
TiO_2-ZrO_2-Nb_2O_5	Infrared radiation	Electric heating[5]
Ni-Al	Low polarization potential	Electrode materials for water electrolysis[6]
ZrO_2, bioglass	Biological compatibility	Bioceramics for artificial joints[7]
ZrO_2, Al_2O_3	Low thermal diffusivity	Thermal barrier coatings for diesel engines and aircraft[8]

Table 2 Physical Properties of Oxide Powders

Materials	Morphology	Bulk density, g/cm^3	Particle size, μm
Cr_2O_3	Spherical, porous	1.44	38-76
Al_2O_3-TiO_2	Irregular, porous	1.42	38-76

Table 3 Physical and Mechanical Properties of Various Coatings[10]

Coating materials	Porosity, vol%	Bulk density, g/cm^3	Bend strength, MPa
Al_2O_3 (type 1)	3.0	2.58	49.0
Al_2O_3 (type 2)	5.7	3.23	76.0
Cr_2O_3	4.7	4.52	81.3
ZrO_2-5wt.%CaO	8.7	5.52	49.0
ZrO_2-18wt.%Y_2O_3	9.7	5.40	67.6
80wt.%Al_2O_3-20wt.%TiO_2	6.0	3.48	89.2
75wt.%TiO_2-20wt.%ZrO_2-5wt.%Nb_2O_5	4.9	4.03	30.4
88wt.%WC-12wt.%Co	10.8	13.87	112.7
75wt.%Cr_3C_2-25wt.%NiCr	10.8	6.16	274.4
80wt.%Ni-20wt.%Al	5.7	6.42	343.0
W	12.0	15.19	117.6
Mo	13.5	7.85	127.4
53wt.%NiAl-47wt.%ZrO_2	7.1	6.27	169.5
50wt.%W-50wt.%ZrO_2	12.2	9.32	66.6
50wt.%Mo-50wt.%ZrO_2	9.8	6.80	112.7

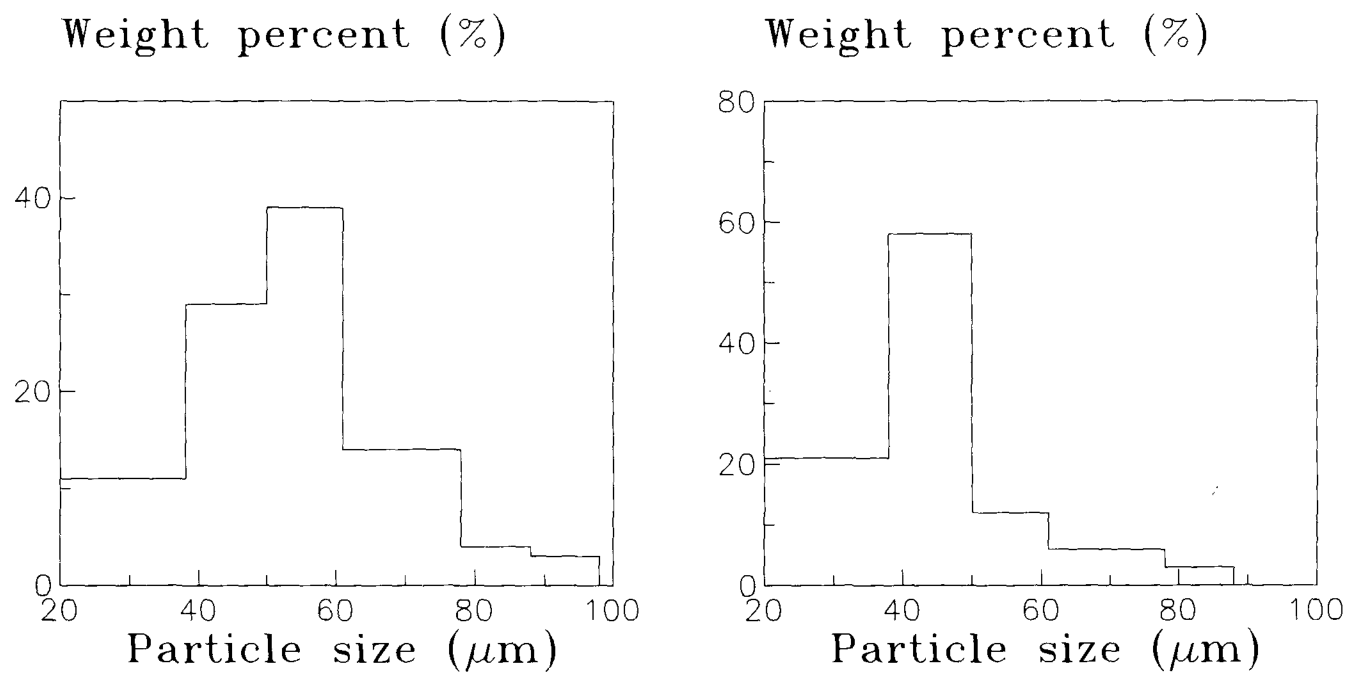

Figure 1 Particle size distribution of Cr_2O_3 (**a**) and Al_2O_3-TiO_2 (**b**) powders.

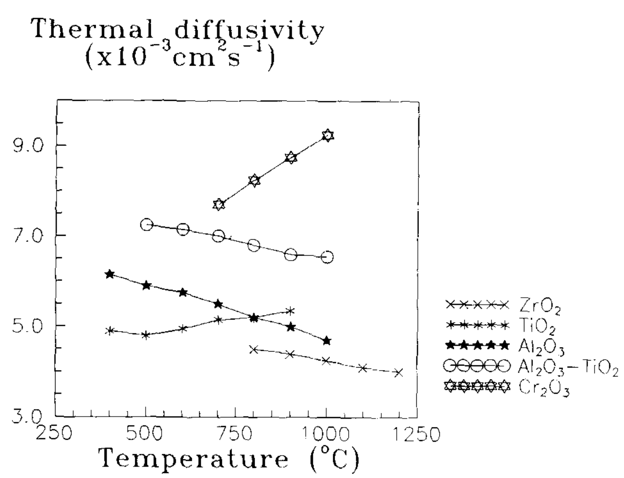

Figure 2 Thermal diffusivity of oxide coatings at different temperatures.

3. Characteristics and Properties of Coating Materials

Porosity and bulk density were measured by the water immersion method. Bend strength was determined from a three-point bend test. Table 3 lists the physical and mechanical properties of the coatings. The thermal diffusivity of some oxide coatings is shown in Fig. 2. The thermal diffusivity of most oxide coatings decreases with increasing temperature. However, the thermal diffusivity of Cr_2O_3 and TiO_2 coatings increase with an increase in temperature. This indicates advantages with respect to wear resistance when this coating is used at elevated temperatures. For example, addition of TiO_2 to Al_2O_3 improves the thermal diffusivity of the coating and thereby improves the wear resistance of such coating systems. The thermal diffusivity of a ZrO_2 coating is lower than that of other plasma-sprayed oxide coatings and therefore makes it useful as a thermal barrier on metals.

The bonding strength and thermal shock resistance of oxide coatings have been improved by manufacturing graded metal-oxide coatings of ZrO_2-W, ZrO_2-Mo, and ZrO_2-NiAl. The graded thermal barrier coating with the ZrO_2 content varied from 0 to 100%, and the thickness of the coating was 1 to 2 mm. The thermal expansion behavior of coatings has also been investigated, and the data are presented in Table 4.

Table 5 presents the results of thermal shock tests for different coatings. The results (an average of five specimens) indicate that this graded coating material is more thermal shock resistant than the single and duplex coating materials that were also tested. The reason for this phenomenon may be explained by the following two factors. The graded coating has a lower thermal expansion mismatch between the substrate and coating, and therefore, thermal stress is reduced. Also, the metallic particles may play a role in impeding initiation and propagation of cracks, thereby improving the toughness of the coating.

4. Applications

4.1 *Electrode Materials*

The spray process, the composition, and electrochemical properties of plasma-sprayed Ni-Al coatings were investigated.

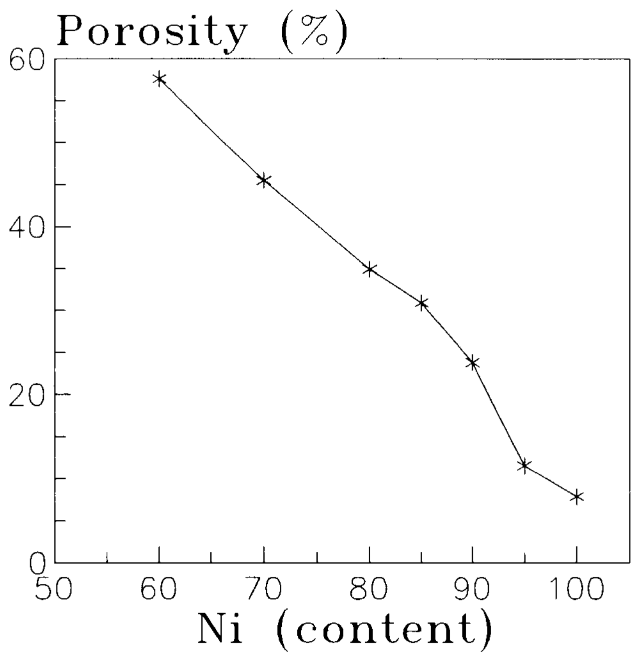

Figure 3 Relationship between the porosity of a Ni-Al coating and its composition.

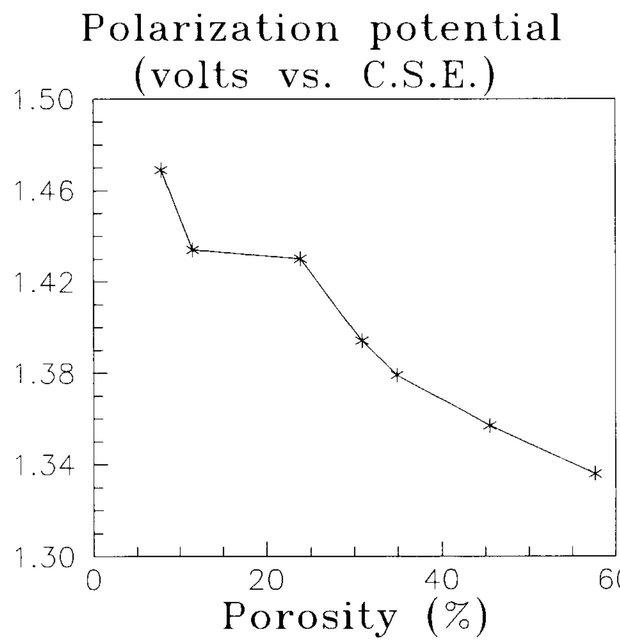

Figure 4 Effect of porosity of a Ni-Al coating on its polarization potential.

Table 4 Thermal Expansion Coefficients of Oxide Coatings

Coating materials	Thermal expansion coefficient ($\times 10^{-6}$/°C) at: 200 °C	400 °C	600 °C	800 °C	1000 °C
ZrO_2-5wt.%CaO	8.66	9.81	9.75	9.87	9.91
ZrO_2-18wt.%Y_2O_3	7.33	8.76	9.34	10.00	10.53
Cr_2O_3	6.00	6.50	6.45	5.88	...
80wt.%Al_2O_3-20wt.%TiO_2	5.57	6.59	6.47	5.56	...
ZrO_2-NiAl graded coating	9.00	10.70	10.80	11.80	...

The electrochemical properties of Ni-Al coatings were expected to depend on the porosity, microstructure, and state of the surface; this was confirmed by the data presented in Fig. 3 and 4. Typical data for the cell voltage of water electrolysis, in which plasma-sprayed Ni-Al was used as an electrode material, are plotted in Fig. 5. The efficiency of the electrodes was significantly improved by using plasma-sprayed Ni-Al coating due to low overvoltages for hydrogen and oxygen.[6]

Table 5 Results of Thermal Shock Tests

Coating system	Average thermal cycles
Pure stabilized ZrO_2 coating	8
Nickel-base alloy bond coating + stabilized ZrO_2 top coating	21
Nickel-base alloy + stabilized ZrO_2 composition graded coating	30

4.2 *Infrared Radiation Coating*

Plasma-sprayed infrared radiation coatings, which consist of TiO_2, ZrO_2, and Nb_2O_5, have higher emissivity at wave lengths ranging from 1 to 25 μm. The emissivity of a 75wt.%TiO_2-20wt.%ZrO_2-5wt.%Nb_2O_5 coating is about 0.9 (Table 6). This coating has been applied to the surface of electric heaters to improve energy transformation efficiency.[5]

4.3 *Thermal-Sprayed Bioceramics*

Plasma-sprayed zirconia and bioglass-ceramic coatings have good biological compatibility and chemical inertness. These coatings were implanted into bodies of rabbits and dogs. The results demonstrated that the bony tissues of the animals surround and adhere to the coating surface.[11]

4.4 *High Refractive Index Materials*

Conventional flame spraying (*i.e.*, $O_2 + C_2H_2$) has been used to deposit special coating materials at SICCAS. A high refractive index glass powder that consists of TiO_2 and BaO has been melted and quenched by O_2-C_2H_2 flame spray. These glass beads have a refractive index as high as 2.1.[12]

Table 6 Emissivity of 75wt.%TiO_2-20wt.%ZrO_2-5wt.%Nb_2O_5 Coating

Wave band, μm	1-25	1-14	1-8	1-4
Emissivity	0.90	0.89	0.90	0.90

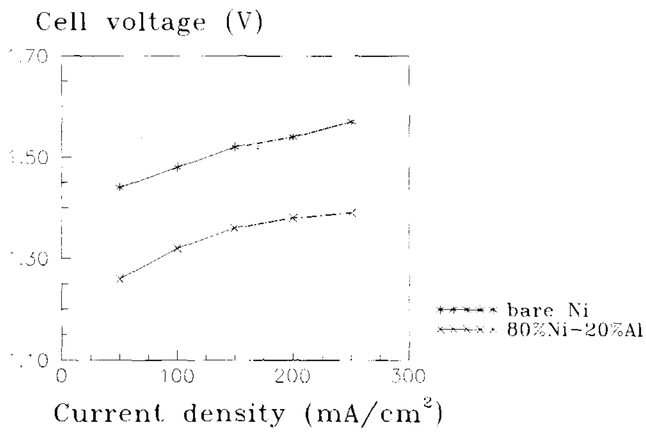

Figure 5 Cell voltage with different electrode materials.

4.5 *Diamond Coatings*

Diamond coatings have been synthesized by a flame spraying method. Figure 6 shows a SEM photograph and Raman spectrum results of the synthesized diamond. The growth rate of the diamond coating is about 60 to 80 μm/hr, and the thickness of the diamond coating is more than 0.3 mm. Diamond coating using a plasma spraying method is also currently being developed.[13]

5. Concluding Remarks

This article has focused on the research and development activities in the field of plasma-sprayed coating materials at SICCAS. Coating materials that are based on oxides, metals, carbides, and mixtures of these have been described. The physical, mechanical, thermal, and other properties of the coatings were measured. For example, some coatings have high microhardness and high thermal diffusivity and are suitable for wear resistance. Other oxide coatings have a low thermal diffusivity and are used as thermal protection materials. The thermal shock resistance of the thermal barrier coatings was improved by manufacturing graded metal-oxide coatings.

Plasma-sprayed zirconia and bioglass coatings have good biological compatibility and are acceptable for bony tissues. Other coatings have specimen properties such as high emissivity, low polarization potential, and high refractive index. In addition, diamond films were also deposited. These coatings have found wide application in various industrial sectors in China.

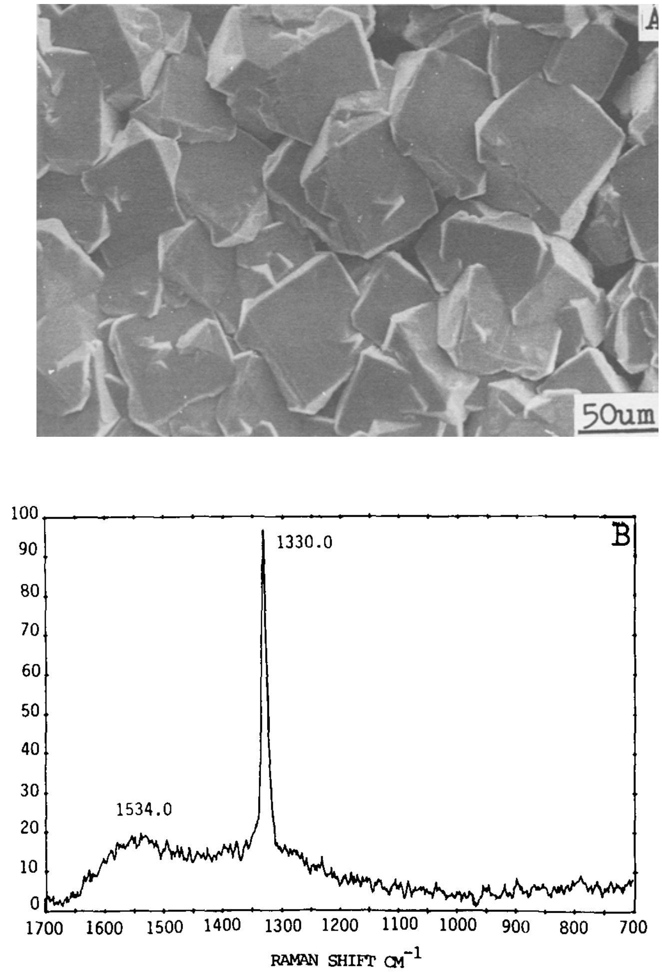

Figure 6 Scanning electron micrograph (**a**) and Raman spectrum (**b**) of diamond films using O_2-C_2H_2 flame spraying.

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