

# Thermal Spraying and Adhesion of Oxides onto Graphite

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Surface treatment of graphite (Cg), which is based on thermal spraying of oxides ( $Al_2O_3$ ,  $ZrO_2$ ), is proposed to reduce graphite reactivity and permeability toward oxygen.

The study of coating adhesion allows recognition of the parameters that favor mechanical and chemical bonds. It also indicates the pretreatment of graphite, which leads to  $Cr_3C_2$  or SiC bond coats. Different graphite-oxide systems were examined and showed that adhesion particularly depends on the thermal expansion coefficient mismatch between Cg, oxide, and the bond coat.

Therefore, a post-treatment based on an impregnation with enamel of the porous oxide is essential to obtain effective protection of the graphite against the external environment.

**Keywords** oxide-graphite adhesion, wettability, carbides, impregnation, oxidation

## 1. Introduction

It is necessary to reduce graphite (Cg) reactivity and particularly its oxidation in order to expand its performance and its application. It is, therefore, essential to protect it from the environment through metal or ceramic coatings. A previous paper showed that molybdenum coating adhere to graphite because molybdenum, a metal with a low stability carbide, wets the graphite, unlike coatings of alloys such as NiCr or 4%Ni, which adhere poorly. In these latter examples, a metallic coating can be obtained by using a  $Cr_3C_2$  or SiC bond coat.<sup>[1]</sup>

Particularly, the refractory characteristic of the oxide ceramics<sup>[2]</sup> can be exploited to compensate for the graphite inadequacies.

The manufacture of the various graphite-ceramic systems leads to the use of the thermal spray technique. Optimal behavior for the thermal spray method is attained by,<sup>[3]</sup> first, good wetting of the substrate, which favors both chemical and mechanical adhesion,<sup>[1]</sup> and, second, good adaptation of the thermal expansion coefficients of the deposits and substrate (Table 1).

In the present work, research is focused on the adhesion of two oxides ( $Al_2O_3$  and  $ZrO_2$ ) on graphite or graphite precoated by carbides ( $Cr_3C_2$ , SiC).

## 2. Materials and Methods

As a basic material, the graphite used was "Carbone Lorraine" (Groupe Carbone Lorraine, Paris Le Défense, France) containing 9.1 ppm of impurities and 9.97% open porosity (0.9 mm diameter pores). It was in disk form of 25 mm diameter and 5 mm thickness. Before use, samples were ultrasonically cleaned in alcohol and annealed at 1000 °C in vacuum for 2 h. In order to favor me-

chanical adhesion, the surface to be coated was sand blasted before the thermal spray process. Coatings were obtained by thermal spraying either with a Metco (Sulzer Metco AG, Wohlem, Switzerland) type 6P11 torch combined with an atmospheric powder distributor Metco (type 4MP) or with a plasma torch type PS 4GMA-SNMI (SNMI, Avignon, France) using a hydrogen-argon mixture.

The sprayed powders were zirconia (Metco 201NS), white alumina (Metco 105), and gray alumina (Metco 101). The principal spraying parameters are shown in Tables 2 and 3. In some cases, and in order to increase the adhesion of coatings, graphite was

**Table 1 Thermal expansion coefficients for different materials<sup>[4]</sup>**

Material	Thermal expansion coefficient ( $\times 10^{-6}$ degree <sup>-1</sup> )
Graphite	$\alpha = 4$
SiC	$\alpha = \alpha_{20} = 4.32 - \alpha_{1000} = 5.4$
$Cr_3C_2$	$\alpha_{20} = 9.9$
$Al_2O_3$	$\alpha_{20} = 8 - \alpha_{1000} = 14$
$ZrO_2$	$\alpha_{20} = 7.5 - \alpha_{1000} = 15.3$

**Table 2 Plasma spraying parameters for zirconia (Metco 201NS)**

Plasmagen gas rate	Ar: 30 L/min H <sub>2</sub> : 11 L/min
Powder carrier gas	Ar: 6.2 L/min
Powder output rate	12.5 g/min
Spraying distance	85 mm
Current intensity	500 A
Voltage	60–63 V
Plasmagen gas pressure	$0.13 \times 10^5$ Pa
Rotating speed of specimens	7 m/s

**Table 3 Flame spraying parameters for alumina (Metco 105, Metco 101)**

Gas output and pressure	O <sub>2</sub> : 37 L/min, $2.1 \times 10^5$ Pa C <sub>2</sub> H <sub>2</sub> : 22 L/min, $10^5$ Pa
Powder output rate	15 g/min
Spraying distance	75 mm

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thermochemically pretreated prior to spraying according to the slurry coating process.<sup>[5,6]</sup> In this process, metallic powders are deposited on the surface using a binder-based suspension (vinyl varnish). In a second step, a thermal treatment is performed in vacuum to produce interdiffusion.

Scanning electron microscopy, x-ray microanalysis, conventional x-ray diffraction, and grazing incidence x-ray diffraction (GIXRD) allowed analysis of the multilayers. The thermo-mechanical properties were characterized by thermal shock resistance and by oxidation tests.

### 3. Results

#### 3.1 Adhesion between the Oxides and Graphite

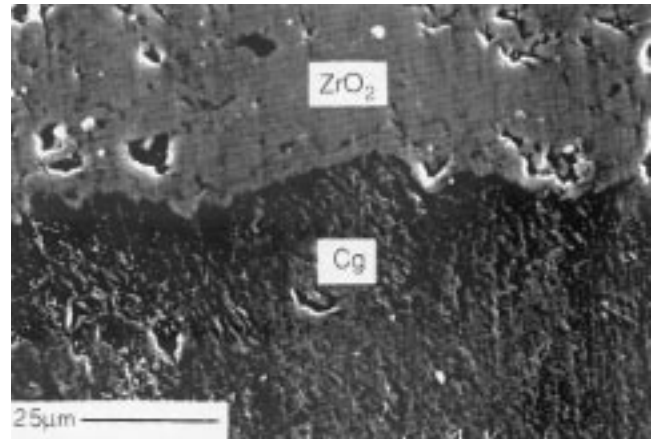
Alumina has a higher stability with respect to carbon (standard free enthalpy of the reaction:  $2\text{Al}_2\text{O}_3 + 9\text{C} \rightarrow \text{Al}_4\text{C}_3 + 6\text{CO}$  is  $66.1 \text{ kcal mole}^{-1}$  at 2000 K) compared to zirconia ( $\text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO}$  is  $5.6 \text{ kcal mole}^{-1}$  at 2000 K).<sup>[7,8]</sup> The direct spraying of alumina by flame or plasma gives very poor adhesion results, whereas plasma spraying of zirconia leads to a  $\text{ZrO}_2$ -graphite interface without decohesion (Fig. 1).

Nevertheless, after thermal shock (heating in vacuum at  $1000 \text{ }^\circ\text{C}$ , followed by air cooling), interfacial fracture appears. Also, as cracks related to inadequate adhesion between zirconia and graphite and to an inability to resist the mismatch in thermal expansion coefficients of the two materials. Consequently it is necessary to research intermediate layers to favor both adhesion and thermal stresses.

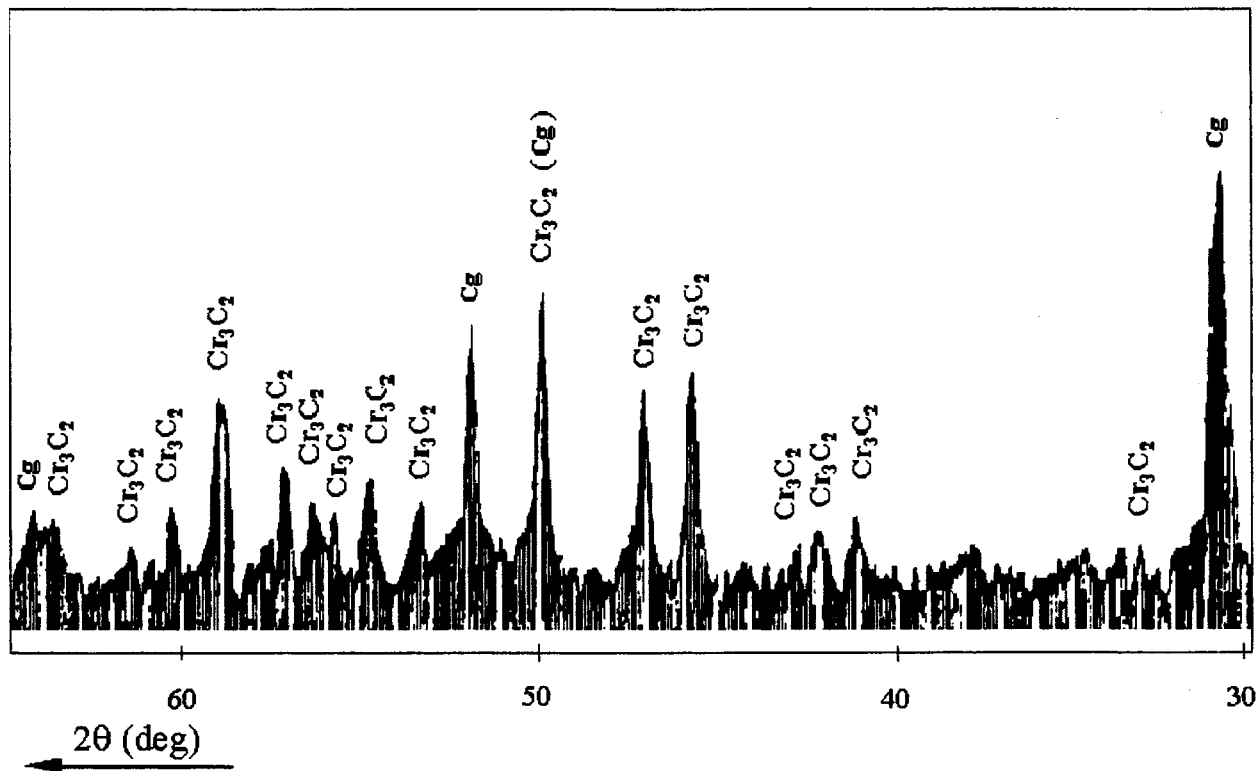
#### 3.2 Oxides-Carbides Adhesion

**Between the oxides and carbides.** To obtain a superficial layer of chromium carbide ( $\text{Cr}_3\text{C}_2$ ), a slurry, containing 98% of chromium and 2% of powdered  $\text{NH}_4\text{Cl}$  mixed with vinyl varnish (binder), was deposited on the graphite surface. Afterward, Cr-C interdiffusion was achieved at  $1000 \text{ }^\circ\text{C}$  in vacuum for 4 h. As shown in Fig. 2 and 3, a continuous layer of  $\text{Cr}_3\text{C}_2$  is obtained on the graphite surface.

Good adhesion of ceramics ( $\text{ZrO}_2$  or  $\text{Al}_2\text{O}_3$ ) onto precoated graphite was observed (Fig. 3). Following air cooling from



**Fig. 1** Scanning electron micrograph of the  $\text{ZrO}_2$ -Cg interface after direct spraying of zirconia into graphite.

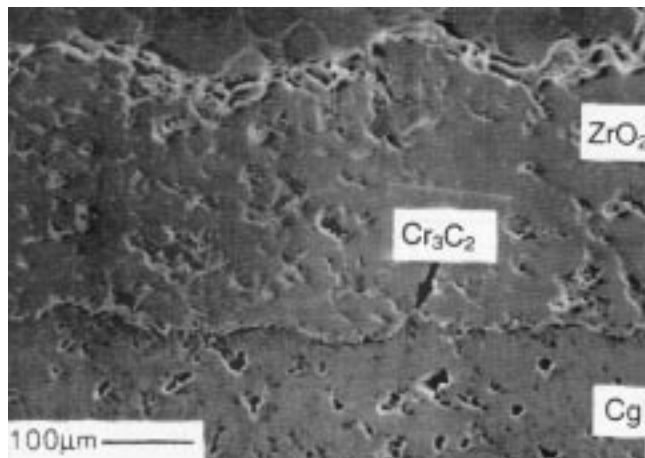


**Fig. 2** X-ray diffraction spectrum (Co  $K\alpha$ ) of the Cg pretreated by slurry coating, at  $1000 \text{ }^\circ\text{C}$  for 4 h, in vacuum. Obviously,  $\text{Cr}_3\text{C}_2$  carbide is observed.

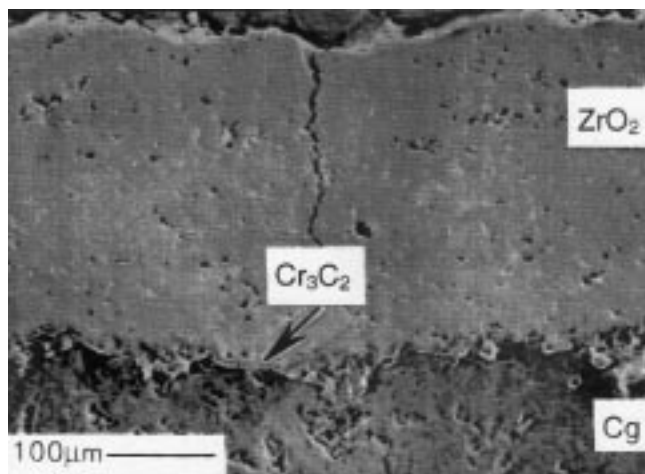
1000 °C, zirconia shows some cracks perpendicular to the Cg-oxide interface (Fig. 4), *i.e.*, with no interfacial propagation. Thus, adhesion between ZrO<sub>2</sub> and Cr<sub>3</sub>C<sub>2</sub> is excellent; certainly better than that between Al<sub>2</sub>O<sub>3</sub> and Cr<sub>3</sub>C<sub>2</sub>, where interfacial cracks appear following cooling (Fig. 5).

**Oxides-SiC-Cg Systems.** In the same way, Cg can be treated with a Si slurry using a suspension composed of pure silicon mixed with vinyl varnish. Optimal results were obtained after diffusion at 1450 °C for 30 min in vacuum.<sup>[9]</sup> The superficial layer consists of cubic SiC<sub>β</sub> crystals (Fig. 6 and 7) exhibiting a rough surface, which favors mechanical adhesion. SiC appears to penetrate into the graphite pores (Fig. 8). The advantage of SiC is that its expansion coefficient is better suited to graphite than that of Cr<sub>3</sub>C<sub>2</sub> (Table 1).

After ceramic spraying (Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>), the Cg-oxide adhesion was obvious even after thermal shock during cooling. Zirconia always reveals fissures perpendicular to the layers, whereas alumina perfectly resisted several thermal shock events (Fig. 9).



**Fig. 3** Scanning electron micrograph showing the ZrO<sub>2</sub> layer deposited on Cr<sub>3</sub>C<sub>2</sub> precoated graphite, as sprayed.

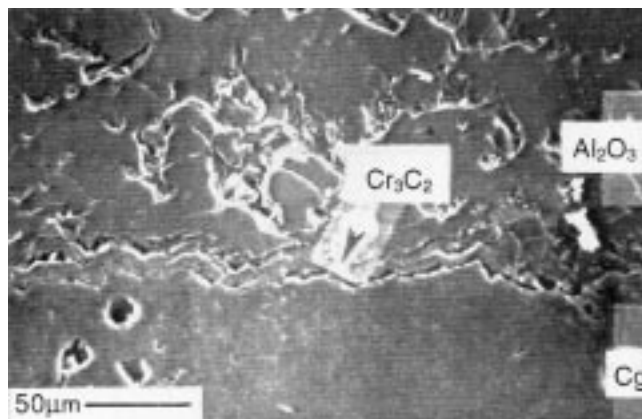


**Fig. 4** Scanning electron micrograph showing the ZrO<sub>2</sub> layer deposited on Cr<sub>3</sub>C<sub>2</sub> precoated graphite after thermal shock. Some cracks appear perpendicular to the surface.

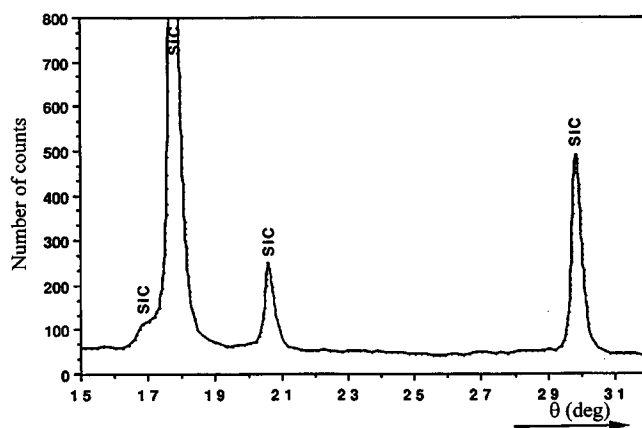
## 4. Resistance to Oxidation

Oxidation tests were conducted on cylindrical samples (70 mm long × 8 mm diameter), which were totally coated with carbide (SiC or Cr<sub>3</sub>C<sub>2</sub>) by a slurry coating process. The mass loss progress during thermal treatment in air at 1050 °C showed that precoated graphite is totally oxidized after 8 h (Fig. 10). Likewise, the resistance to oxidation of graphite remains very poor after the spraying of oxides (alumina or zirconia), even with a SiC or Cr<sub>3</sub>C<sub>2</sub> bond coat, because of the porosity of the plasma sprayed layers. Samples were post-treated using a slurry to fill this porosity, essentially composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and additional oxides, and impregnated under vacuum. The slurry composition is given in Table 4. An enameling treatment at 1250 °C in vacuum permitted obtaining of a dense superficial layer (150 μm thickness) (Fig. 11).

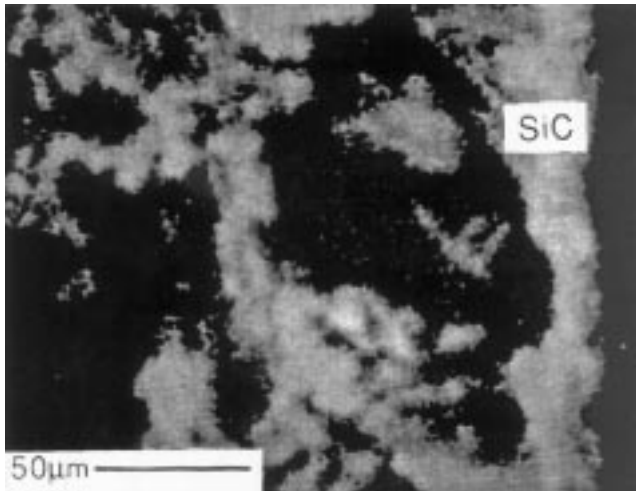
Significant protection of the so-treated graphite was observed after oxidation in air at 850 °C for 4 h. Optimal results were obtained using impregnated gray alumina (Metco 101), as shown in Fig. 12 (Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>/SiC/Cg system). This beneficial effect is found also during severe oxidation conditions at 1050 °C (Fig. 13).



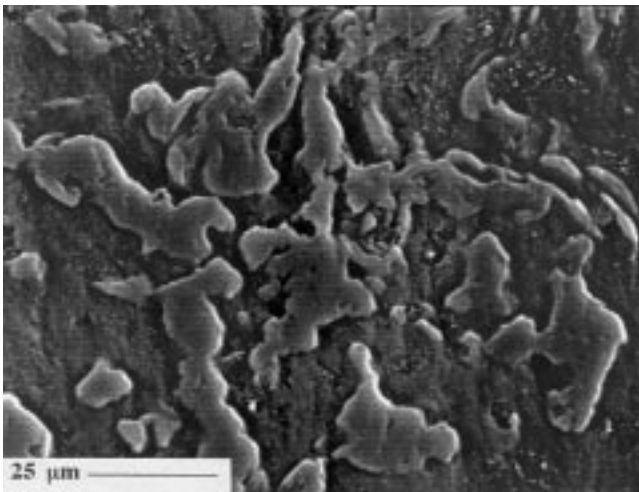
**Fig. 5** Scanning electron micrograph showing Al<sub>2</sub>O<sub>3</sub> deposited on Cr<sub>3</sub>C<sub>2</sub> precoated graphite. Interfacial crack appears after thermal shock.



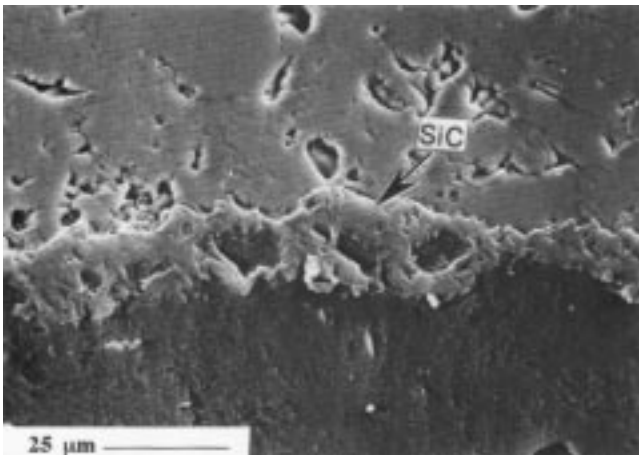
**Fig. 6** GIXRD spectrum (Cu K $\alpha$ ) of the SiC precoated graphite, treated at 1450 °C for 30 min, in vacuum. Obviously, only bSiC is observed.



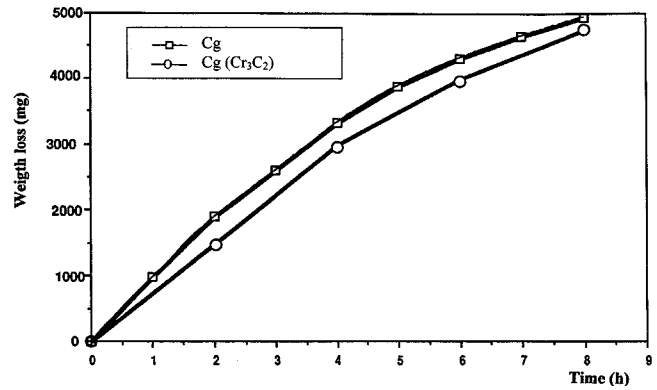
**Fig. 7** Microprobe analysis of silicon showing a continuous SiC layer on the surface and a SiC-Cg inlaid area.



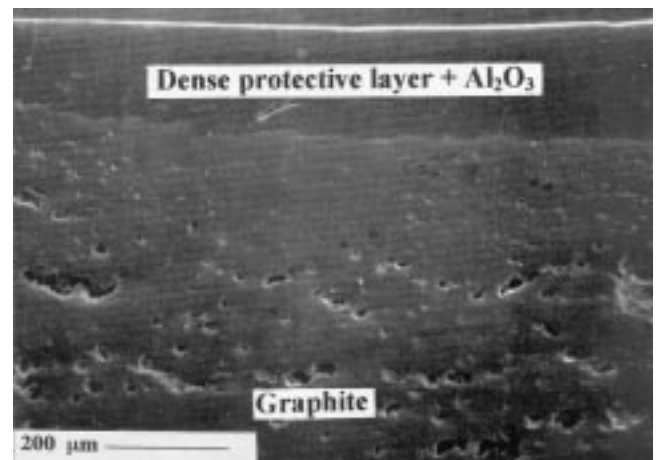
**Fig. 8** Scanning electron micrograph showing SiC agglomerates, inlaid in Cg treated by slurry coating at 1450 °C for 30 min, in vacuum.



**Fig. 9** Scanning electron micrograph showing Al<sub>2</sub>O<sub>3</sub> deposited on SiC precoated graphite. After thermal shock, no cracks appear in both the coating and interface.



**Fig. 10** Mass loss evolution vs oxidation time in air at 1050 °C of the graphite or the pretreated graphite (Cr<sub>3</sub>C<sub>2</sub>).



**Fig. 11** Scanning electron micrograph of an alumina deposit post-treated by enamel impregnation. A dense protective layer is obtained on the alumina surface.

**Table 4** Enamel composition for impregnation

Material	Wt%	Material	Wt%
SiO <sub>2</sub>	52.4	ZrO <sub>2</sub>	5.16
Al <sub>2</sub> O <sub>3</sub>	15.15	SnO <sub>2</sub>	4.9
K <sub>2</sub> O	9.9	B <sub>2</sub> O <sub>3</sub>	3.24
Na <sub>2</sub> O	6.58	TiO <sub>2</sub>	2.59

## 5. Conclusions

Adherent oxide coatings onto graphite were achieved by thermal spraying. Graphite wettability by a liquid oxide (during spraying) seems to be better for an oxide that exhibits a low stability with respect to carbon, but adhesion depends on the expansion coefficient disparity.

The oxide-graphite adhesion can be improved by using interlayers such as Cr<sub>3</sub>C<sub>2</sub> and SiC. These bond coats formed by thermochemical slurry coating processes permit both accommodation of stresses and thermodynamic adhesion. Silicon carbide proved to be better than chromium carbide because its expansion



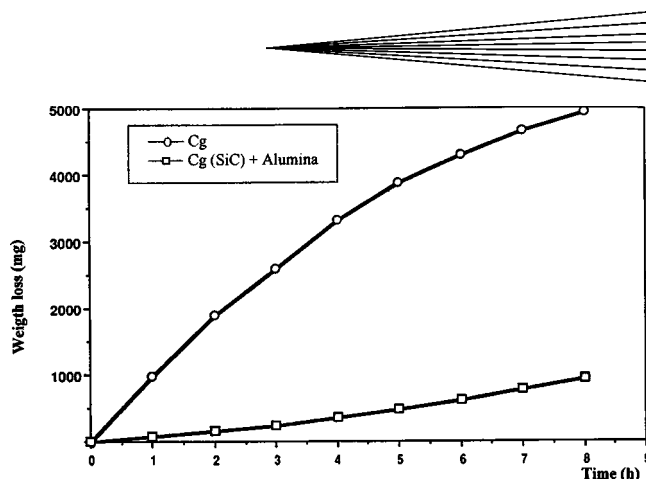
**Fig. 12** Mass loss of graphite after oxidation in air at 850 °C for 4 h for different surface treatments. 1: Cg, 2: Cg (SiC), 3: Cg (SiC) + Metco 105, 4: Cg (SiC) + Metco 101, 5: Cg (SiC) + (Metco 105) enameled, and 6: Cg (SiC) + (Metco 101) enameled.

coefficient is intermediate between those of graphite and of the tested oxides, such as  $ZrO_2$  and  $Al_2O_3$ .

Therefore, for significant protection of graphite from oxidation, postenameling using a  $SiO_2$ - $Al_2O_3$  slurry can fill the porosity of thermal sprayed oxides. Optimal results were observed for a multilayer system of SiC-gray alumina soaked by a vitrocement. The resistance to oxidation of the so-treated graphite is significantly improved above 1000 °C in air.

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**Fig. 13** Mass loss evolution of Cg and pre-coated (SiC) graphite protected by impregnated alumina vs oxidation time in air at 1050 °C.