Improving the water-wettability and oxidation resistance of graphite using Al_2O_3/SiO_2 sol-gel coatings

S. Zhang, W.E. Lee*

The University of Sheffield, Department of Engineering Materials, Mappin Street, Sheffield, S1 3JD, UK

Abstract

Transparent Al_2O_3, Al_2O_3–SiO_2 and SiO_2 sols were prepared via hydration of TEOS and $Al(OC_3H_7)_3$ in distilled water and used to coat natural flake graphite. Graphite coated with these sols was dried at 120 °C for 12 h and heat-treated at 500 °C for 2 h to gel the sols. Water-wettability and oxidation resistance of as-received (uncoated) and coated graphites were examined. Al_2O_3, Al_2O_3–SiO_2 and SiO_2 coatings improved graphites water-wettability and SiO_2-coated graphite showed the best water-wettability. All the coatings also improved the graphites oxidation resistance, especially at high temperatures (>1100 °C). Addition of Si greatly improved the oxidation resistance of as-received graphite whereas the oxidation resistance of the coated graphites was only slightly improved, suggesting that it is possible to decrease the level of antioxidant used in commercial castable systems.
© 2002 Published by Elsevier Science Ltd.

Keywords: Al_2O_3; Castables; Coatings; Graphite; Oxidation; SiO_2; Sol-gel processes; Wetting

1. Introduction

Monolithic, or unshaped, refractories such as castables have been applied extensively over the last two decades due to their quicker and cheaper installation and properties approaching those of shaped (brick) refractories.[1] However, because these castables mainly comprise oxides, they suffer the same drawbacks as oxide-based refractory bricks, for example, poor corrosion resistance and spalling resistance. These problems result in decreased lining lifetime and hinder the application of oxide-based castables in many areas including steel ladle slag-lines. The successful development of oxide-C bricks in the 1970s by adding C to oxide brick formulations, suggested that introducing carbon/graphite to current oxide-based castables would give improved properties. Carbon (graphite) has many advantages such as being non-wetted by molten metal/slag and having high thermal conductivity.[2] Unfortunately, however, trying to incorporate carbon/graphite in castables introduces many new problems arising from,

e.g. its poor water wettability and oxidation resistance, which have hindered the development and application of carbon-containing castables.[3]

Various methods have been investigated to improve graphites water wettability and its dispersion in water.[3] One of the most efficient is to coat the graphites surface with materials which have better water-wettability. Pitch, a bi-product of petroleum distillation, was initially used as it melts at a low temperature (100–200 °C), so coating is easy and cheap. However, because pitch has only a slightly better water wettability than graphite, it is still not possible to incorporate a large amount of graphite, and environmental concerns about carcinogenic fume on decomposing pitch remain. CVD–SiC coatings greatly improve graphites water-wettability.[4] Unfortunately, this method is too expensive and so not commercially viable. A cheaper method, "the high speed impact treatment"[4] has also been suggested. Although this method improves graphites water-wettability, it has some limitations. Firstly, activation of the graphite surface might reduce its oxidation resistance, and secondly, SiC is only physically adsorbed onto the graphite surface, so many uncovered areas remain. Furthermore, the SiC coating easily peels off on prolonged mixing.[3]

* Corresponding author.
E-mail address: w.e.lee@sheffield.ac.uk (W.E. Lee).

Apart from pitch and SiC, oxide coatings have also been tried. Yoshimatsu et al.[5] mixed graphite with $Al(OC_3H_7)_2(C_6H_9O_3)$ solution in a spinning mixer. The mixture was then dried 3 h at 100 °C and heated to 500 °C so that the $Al(OC_3H_7)_2(C_6H_9O_3)$ solution converted to an alumina coating. With increasing Al_2O_3, graphites water-wettability was improved. Recent studies revealed that Al_2O_3 coating could also improve the fluidity of graphite in water.[6,7] Using Al_2O_3-coated graphite, Kawabata et al.[8] made Al_2O_3-C castables and tested their properties. They found that castables using Al_2O_3-coated graphite showed better flowability, lower porosity and higher bend strength than those containing uncoated graphite. Yu et al.[9] TiO_2 coated graphite using a similar method and showed that graphites water wettability could be improved greatly when the coating level was above 0.5 wt.% TiO_2. ZrO_2 coatings have also been prepared by controlled hydrolysis of zirconium oxychloride $(ZrOCl_2.8H_2O)$ aqueous solution.[10] Although they improved graphites oxidation resistance, their effect on its water-wettability was not reported.

Besides single oxide coatings, binary oxide coatings such as Al_2O_3–SiO_2 have been prepared. Among the Al_2O_3-based binary oxide coatings, an Al_2O_3–SiO_2 coating with composition of 90 wt.% Al_2O_3 + 10 wt.% SiO_2 showed the best oxidation resistance.[11] A recent study by the same authors[12] revealed that the fluidity of graphite coated with Al_2O_3–SiO_2 was similar to that of graphite coated with Al_2O_3 if no dispersing agent was added, but better than the latter if a dispersing agent was added.

This paper aims to examine the effect of 50 wt.% Al_2O_3 + 50 wt.% SiO_2 sol-gel coatings on graphites water-wettability and oxidation resistance and compare the results to those from pure Al_2O_3 and SiO_2 coatings prepared by a novel sol-gel route. In addition the effect of deoxidising additives, such as Si metal powder, on these properties is described.

2. Experimental

2.1. Raw materials

Chinese natural flake graphite (purity > 98%, grain size < 200 μm), Aldrich tetraethyl orthosilicate TEOS $(Si(OC_2H_5)_4$, purity > 98%), ethyl alcohol (purity > 99%), hydrochloric acid, HCl (37 wt.% in water), and aluminium isopropoxide, $Al(OC_3H_7)_3$ (purity > 98%), were the main raw materials. Distilled water was used as solvent for the sol-gel processing, and Aldrich silicon powder (purity > 99%) was used as an antioxidant.

2.2. Coating preparation

A SiO_2 sol was prepared starting from TEOS, ethyl alcohol, and water with volume ratios of 1:1:2. After

this initial solution was agitated using a magnetic stirrer at room temperature for 30 min, HCl was added to adjust the solution pH to ~3. Finally, the solution was further stirred for 1 h to get a transparent sol.

An Al_2O_3 sol was prepared following the method of Yoldas.[13] 0.1mol $Al(OC_3H_7)_3$ was hydrated in 15mol distilled water which had been preheated to about 90 °C. After the solution had been stirred thoroughly for 1 h, HCl was added to adjust the solution pH to ~3. Then the solution was further stirred for 1 h and a nearly transparent sol obtained. The Al_2O_3–SiO_2 sol was prepared by mixing and stirring the Al_2O_3 and SiO_2 sols $(Al_2O_3:SiO_2$ weight ratio = 1:1) for 1 h.

Five hundred grams of as-received graphite was mixed with the Al_2O_3, SiO_2 and Al_2O_3–SiO_2 sols respectively in a Hobart-type mixer for 30 min. The amounts of sols used were equivalent to 1 wt.% Al_2O_3, 2 wt.% SiO_2, 0.5 wt.% Al_2O_3 + 0.5 wt.% SiO_2 respectively on the graphite surface. The coated graphite was left in air for 12 h and then dried in an oven at 120 °C for another 12 h. It was then heated to 500 °C at a heating rate of 2 °C/min and held at 500 °C for 2 h. The cooling rate of the furnace was also 2 °C/min. To assist in the understanding crystallisation behaviour of the gel coatings on graphite surfaces upon heating, bulk Al_2O_3, SiO_2 and Al_2O_3–SiO_2 gels were also prepared following the same drying and heating schedules.

2.3. Crystallisation behaviour of gels

The dried Al_2O_3, SiO_2 and Al_2O_3–SiO_2 gels and those heated at 500 °C for 2 h were crushed and sieved (< 200 μm), and then examined by XRD powder analysis (Model No. PW1050, Philips Electronic Instruments, Mahwah, NJ). The spectra were recorded at 30mA and 40kV, using Ni-filtered CuKα radiation. JCPDS cards used for identification were boehmite (21–1307) and γ-Al_2O_3 (29–63).

2.4. Graphite water-wettability

Relative water-wettabilities of as-received and coated graphites were compared using a similar method to that of Yoshimatsu et al.[5] Graphite (10 g) and 200 ml water were put in a graduated cylinder (45 mm in diameter and 300 mm in height). After agitating the graphite and water for 1 min, the slurry was set aside for 1 min. The height of the graphite sediment layer and the amount of floating graphite were measured, and sediment volume (SV), packing density of the sediment layer (PD) and floating ratio (FR) calculated according to,

$$SV(cm^3/g) = \text{Volume of Sediment Layer}/$$
$$\text{Weight of Sediment Layer}$$

$$PD(\%) = 1/(\text{Volume of Sediment Layer}$$
$$\times \text{ Graphite True Density}) \times 100\%$$

$$FR(\%) = (\text{Weight of Floating Graphite}/$$
$$\text{Total Weight of Graphite}) \times 100\%$$

SV and FR are ideally low and PD high for good graphite water-wettability.

2.5. Graphite oxidation resistance

As-received or coated graphite (5 g) was placed in an alumina crucible and heated in air at a heating rate of 10 °C/min to 800, 900, 1000 and 1100 °C respectively, held at temperature for 1 h and then naturally cooled. The weight loss of the graphite was measured and oxidation ratio calculated according to,

$$\text{Oxidation ratio}(\%) = (\text{Weight Loss}/$$
$$\text{Original Graphite Weight}) \times 100\%$$

To further understand the effect of antioxidant on oxidation resistance of coated graphite, 10% Si powder was mixed with as-received and coated graphites respectively, and the mixture oxidation resistance evaluated using a similar method.

2.6. Microstructural observation

Microstructures of as-received and coated graphites and relics of the coatings after oxidation testing were examined using an SEM (Camscan Electron Optics, Waterbeach, Cambridge, UK) equipped with an EDS analyzer (Model No. AN10000, Link Systems, High Wycombe, Buckinghamshire, UK).

3. Results

3.1. Crystallization behaviour of gels

Fig. 1 shows XRD of the Al_2O_3, Al_2O_3–SiO_2 and SiO_2 gels after drying at 120 °C for 12 h. No sharp crystal peaks were detected, although in Al_2O_3 and Al_2O_3–SiO_2 gels, broad peaks corresponding to boehmite appeared. XRD of the three gels after heating at 500 °C for 2 h are shown in Fig. 2. Instead of boehmite, γ-Al_2O_3 peaks were found in the Al_2O_3 gel, no crystal phases were detected in the Al_2O_3–SiO_2 gel, while SiO_2 gel remained predominantly amorphous.

3.2. Microstructural characterisation

Fig. 3 reveals the morphology of the as-received graphite, showing grains of various sizes with some < 20 μm

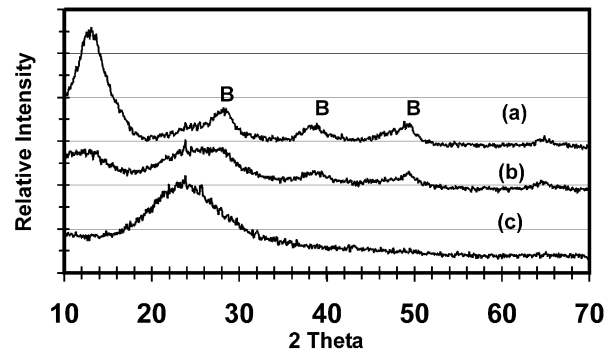Fig. 1. XRD of the dried gels (120 °C for 12 h). B = boehmite. (a) Al_2O_3 gel, (b) Al_2O_3–SiO_2 gel, (c) SiO_2 gel.
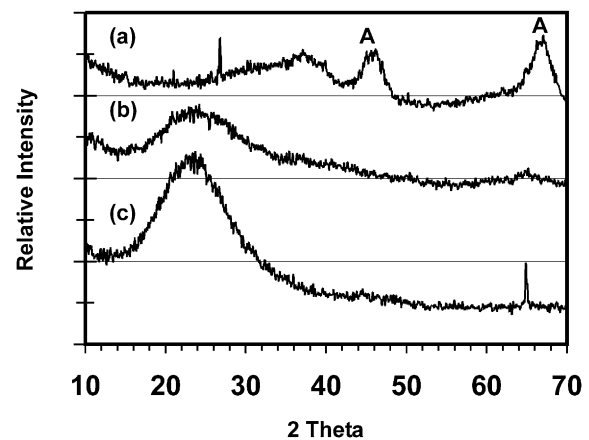
Fig. 2. XRD of the gels after heating at 500 °C for 2 h. A = γ-Al_2O_3, (a) Al_2O_3 gel, (b) Al_2O_3–SiO_2 gel, (c) SiO_2 gel.
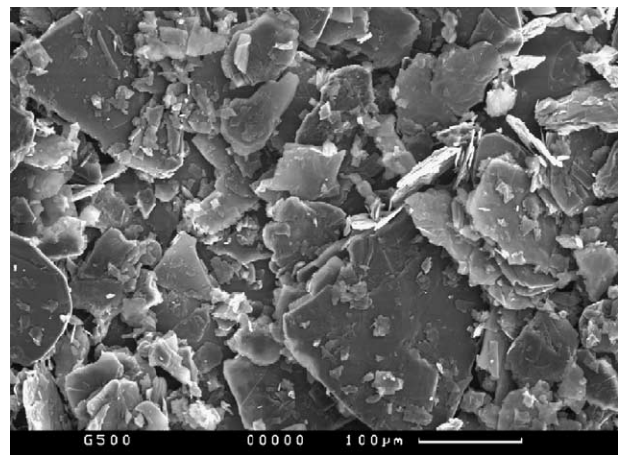

Fig. 3. Secondary electron image of as-received graphite.

but others > 100 μm. The morphologies of the graphites coated with Al_2O_3 (AS), SiO_2 (SG) and Al_2O_3–SiO_2(ASG) were similar to each other. Fig. 4, as an example, shows the SG. Smaller graphite grains had bonded to larger grains to form agglomerates and EDS analysis (not shown) verified the presence of Si and/or

Al containing species on the graphites surface. While the microscopes resolution meant the coatings on the graphite were not directly discernable, the relicts of the coatings after the coated graphite was completely oxidised confirms their presence. Fig. 5, shows the relicts of the SiO_2 coating after SG was oxidised in air at 1100 °C for 2.5 h. The relicts retain the original shape of the coated graphite grains (or agglomerates), and small pores (<1 μm) were present in them.

3.3. Water-wettability of graphite

Sediment volumes (SV) from as-received graphite are much higher than those of coated graphites (Fig. 6). For example, after 3 h, the SV of as-received graphite was 5.2 (cm^3/g), whereas that of AG was 3.0 cm^3/g. Fig. 6 also shows that the SV of AG was slightly higher than that of ASG, and both were higher than that of SG. After 3 h, SV of AG was 3.0 cm^3/g, and those of ASG and SG were 2.7 and 2.2 cm^3/g respectively. Fig. 7 shows the packing densities (PD) of as-received and coated graphites. The coated graphites showed higher PD than as-received graphite and SG had the highest PD. Fig. 8 illustrates floating ratio (FR) of as-received and coated graphites. FR of as-received graphite was about 12%, whereas those of AG, ASG, and SG were 0.5, 0.2 and ∼0%, respectively.
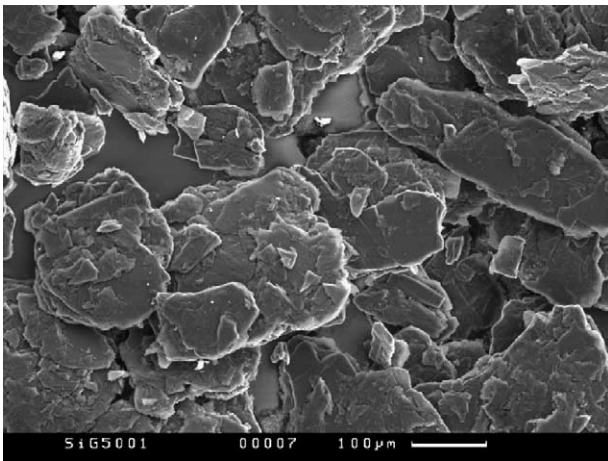

Fig. 6. Sediment volumes of as-received (G) and coated graphites.

Fig. 7. Packing densities of the sediment layer of as-received (G) and coated graphites.

Fig. 8. Floating ratios of as-received (G) and coated graphites.

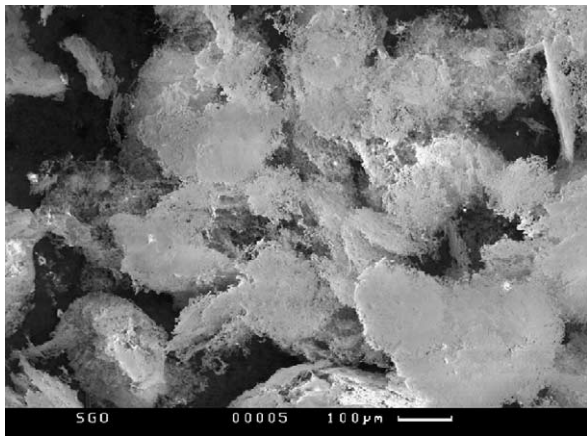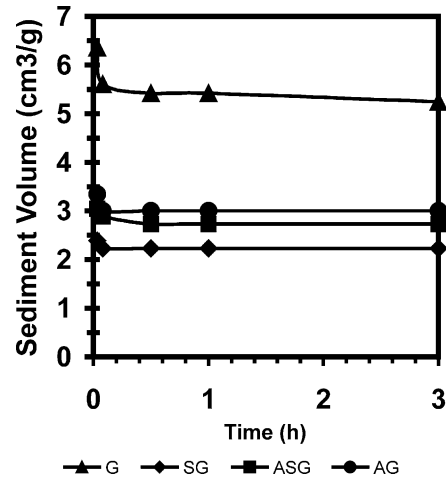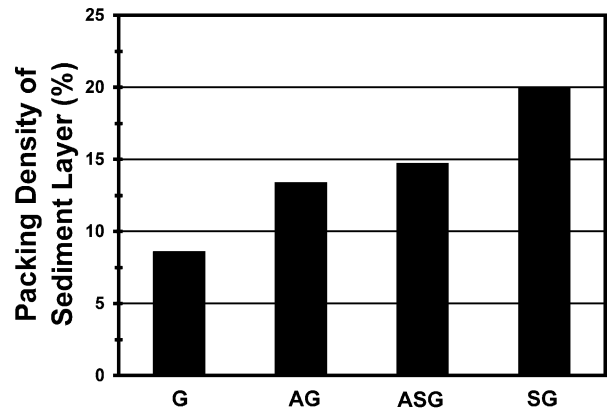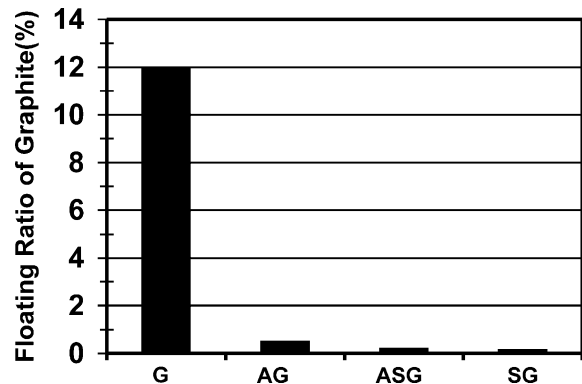Fig. 4. Secondary electron image of graphite coated with the SiO_2 gel.

Fig. 5. Secondary electron image of the relicts of the SiO_2 coating after SG was oxidised in air at 1100 °C for 2.5 h.
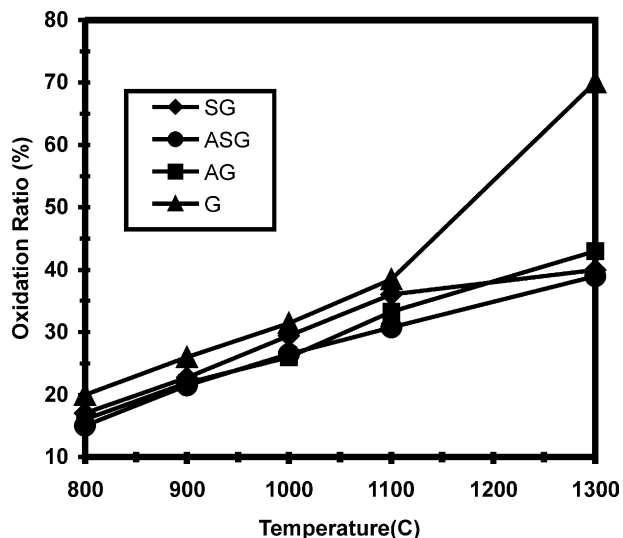
Fig. 9. Oxidation ratios of as-received (G) and coated graphites heated in air at different temperatures for 1 h.

3.4. Oxidation resistance of graphite

Fig. 9 shows the oxidation ratio of as-received and coated graphite (without Si) after oxidation in air at 800–1300 °C for 1 h. All coated graphites had better oxidation resistance than as-received graphite, although at temperatures higher than 1100 °C, the coatings were more effective. At 1000 °C, the Al_2O_3–SiO_2 coating decreased the graphite oxidation ratio from 38.5% (as-received graphite) to 30.8%, whereas at 1300 °C, it decreased the ratio from 70 to 39%.

The oxidation ratios of as-received and coated graphites with and without Si after oxidation at 1300 °C for 1 h are given in Fig. 10. Si addition greatly decreased the oxidation ratio of as-received graphite but only slightly decreased those of coated graphites. For as-received graphite, Si addition decreased the oxidation ratio from 70% (without Si) to 37% (with Si), whereas
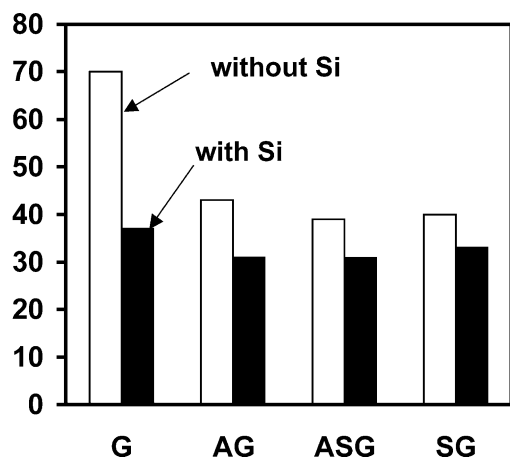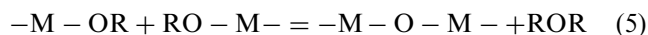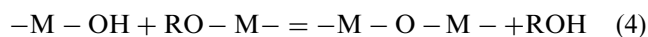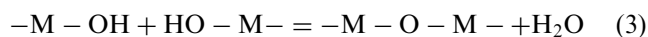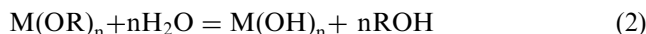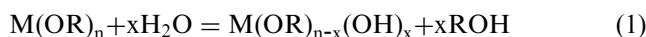

Fig. 10. Oxidation ratios of graphites (with and without Si) heated in air at 1300 °C for 1 h.

for the coated graphites, Si addition only decreased the oxidation ratios from 43% (AG), 39% (ASG), and 40% (SG) to 31, 30.9, and 33%, respectively.

4. Discussion

The mechanisms of sol-gel formation using metal alkoxides as precursors have been well documented.[14–16] A metal alkoxide, $M(OR)_n$ (M = metal, R = alkyl group, n = metal valency), is initially hydrolised in water to form partially hydrolysed molecules $M(OH)_x(OR)_{n-x}$ [Reaction (1) or completely hydrolysed molecules, $M(OH)_n$ and alcohol ROH (Reaction (2)]. Next, two hydrolysed molecules can link together and liberate a small molecule, such as water or alcohol a [Reactions (3)–(5)] These reactions can continue to build a larger and larger oxide network which eventually links up throughout the liquid volume (polymerization).[14–16]

$$M(OR)_n + xH_2O = M(OR)_{n-x}(OH)_x + xROH \quad (1)$$

$$M(OR)_n + nH_2O = M(OH)_n + nROH \quad (2)$$

$$-M-OH + HO-M- = -M-O-M- + H_2O \quad (3)$$

$$-M-OH + RO-M- = -M-O-M- + ROH \quad (4)$$

$$-M-OR + RO-M- = -M-O-M- + ROR \quad (5)$$

After drying at low temperatures, some free water and alcohol in the sol will evaporate and a gel with a very low crystallinity (or glassy structure) can be obtained. This was verified by XRD results of the dried gels (Fig. 1). All three dried gels showed limited crystallinity (Fig. 1), although peaks corresponding to boehmite were observed in Al_2O_3 and Al_2O_3–SiO_2 gels (Fig. 1a and b). On heating chemically-bound water is released from the hydrolysed molecules leading to oxide formation.[14,16] For example, Si–OH in the SiO_2 gel may decompose to form SiO_2, and boehmite in Al_2O_3 gels may decompose to form γ-Al_2O_3.[14,16] XRD analyses shown in Fig. 2 revealed that after heat-treatment at 500 °C for 2 h, boehmite peaks in dried Al_2O_3 and Al_2O_3–SiO_2 gels (Fig. 1a and b) disappeared, and at the same time γ-Al_2O_3 was detected. SiO_2 gel after heat-treatment still remained essentially amorphous, indicating that most of the SiO_2 [from decomposition of Si–OH and Reactions (3)–(5)] in the gel had not well crystallised. The above results indicated that the gel coatings on graphite surfaces after heat-treatment at 500 °C were essentially amorphous.

EDS analyses revealed the presence of Si and/or Al containing species on the graphite surfaces. This, along with the microstructure of the coating relicts (Fig. 5), verified the presence of the coatings which would affect graphites surface properties. Figs. 6–8 show the effects of the coatings on the water-wettability of graphites.

Compared with as-received graphite, coated graphites all showed much lower SV and higher PD (Figs. 6 and 7). Furthermore, due to the coatings, FR was decreased from 12% (as-received graphite) to a very low level (close to zero; Fig. 8). These facts indicated that coatings on graphite surface improved the water-wettability of graphite. The water-wettability test results (Figs. 6–8) also showed that SG showed slightly lower FR and SV and higher PD than AG or ASG, indicating that SG showed best water-wettability. As-received graphites showed poor water-wettability, attributable to limited hydrophilic functional groups such as –OH present on their surfaces.[3] Many more –OH functional groups are present in the Al_2O_3, Al_2O_3–SiO_2 or SiO_2 gels.[14–16] It was these functional groups in the gel coatings which led to the improvement in graphites water-wettability. The reasons why SG showed best water-wettability were that as well as more –OH groups, rehydration of the Si–O–Si bonds[17] in the active SiO_2 gel coating also improved the affinity between water and the graphite.

The coatings on the graphite surface not only improved its water-wettability, but also contributed to its oxidation inhibition. The oxidation test results shown in Fig. 9 revealed that all coated graphites showed lower oxidation ratios than as-received graphite, indicating that the presence of the coatings on graphite improved its oxidation resistance. The improvement in graphites oxidation resistance is easy to understand, since smaller graphite grains formed the agglomerates (Fig. 4), decreasing the surface area, and the coatings isolated the contact between graphite and oxygen. The results in Fig. 9 also revealed that the coatings showed greater oxidation inhibition at higher temperature ($>1100\ °C$) than at lower temperature ($<1100\ °C$). The reason might be that at higher temperature, the very active SiO_2 and Al_2O_3 in the coatings began to sinter, and thus the coatings became denser than at lower temperature.

Besides the coatings, additions of Si further affected the oxidation resistance of graphite. As shown in Fig. 10, addition of Si greatly decreased the oxidation ratio of uncoated as-received graphite, but only slightly decreased the ratios of coated graphites. The effect of Si on graphite oxidation resistance has been well documented.[18,19] According to Yamaguchi, Si can reduce CO formed from oxidation of graphite back to C and form SiO(g). SiO(g) diffuses to the graphite surface where it is further oxidised to SiO_2. Reduction of CO(g) back to C and deposition of SiO_2 on the graphite surface explains why additions of Si greatly decreased oxidation ratio of as-received graphite (Fig. 10). In the cases of coated graphites, most of the graphite surfaces had already been covered by the coatings, so further deposition of SiO_2 by oxidation of Si could only help to decrease the oxidation ratio by covering uncovered areas and/or filling micropores in the coatings. Therefore,

additions of Si only slightly decreased the oxidation ratios of coated graphite (Fig. 10). From Fig. 10, it can also be seen that the oxidation ratio of as-received graphite with Si was close to the values of coated graphite without Si. This fact might suggest that when the coated graphites are used in commercial castable systems, the level of antioxidants could be decreased.

5. Summary

Al_2O_3, Al_2O_3–SiO_2 and SiO_2 sols were prepared using TEOS and $Al(OC_3H_7)_3$ as precursors and used to coat natural flake graphite. The graphites coated with the sols were dried at 120 °C for 12 h and heat-treated at 500 °C for 2 h so that gel coatings form on the graphite surface. XRD analysis showed that the gel coatings on the graphite surfaces were essentially amorphous. Water-wettability and oxidation resistance of as-received and coated graphites were compared by examining SV, PD, FR in water and oxidation ratios in air, respectively. Al_2O_3, Al_2O_3–SiO_2 and SiO_2 coatings improved graphites water-wettability and SiO_2-coated graphite showed the best water-wettability. The coatings also improved graphites oxidation resistance, especially at high temperatures ($>1100\ °C$). Addition of Si greatly improved the oxidation resistance of as-received graphite but only slightly improved the oxidation resistance of coated graphite, suggesting that when the coated graphite could be used in castable systems the level of antioxidant needed is decreased.

References

1. Lee, W. E., Vieira, W., Zhang, S., Ahari, K. G., Sarpoolaky, H. and Parr, C., Castable refractory concretes. *Int. Mater. Rev.*, 2001, **46**(3), 145–167.

2. Cooper, C. F., Graphite: nature's unique raw material. *J. Can. Ceram. Soc.*, 1994, **63**(3), 197–208.

3. Zhang, S. and Lee, W. E., Carbon-containing castables:current status and future prospects. *Trans. Br. Ceram. Soc.*, 2001, **101**(1), 1–8.

4. Ono, Y., Matsumoto, T. and Amemiya, Y., Development of the Basic Monolithic Refractories Containing Hydrophilic Graphite. *Reports Res. Lab. Asahi Glass Co., Ltd*, 1993, **43**(1), 35–46.

5. Yoshimatsu, H., Fujiwara, S., Konishi, R., Miyawaki, M. and Miura, Y., Wettability by water and oxidation resistance of alumina-coated graphite powder. *J. Ceram. Soc. Jpn.*, 1995, **103**(9), 929–934.

6. Kawabata, K., Yoshimatsu, H., Fujii, E., Hiragushi, K., Osaka, A. and Miura, Y., Fluidity of Al_2O_3-coated graphite powder slurry. *J. Ceram. Soc. Jpn.*, 2000, **108**(8), 753–757.

7. Kawabata, K., Yoshimatsu, H., Fujii, E., Hiragushi, K., Osaka, A. and Miura, Y., Effect of Al_2O_3 raw materials on fluidity of Al_2O_3-coated graphite powder slurry. *J. Ceram. Soc. Jpn.*, 2000, **109**(5), 470–473.

8. Kawabata, K., Yoshimatsu, H., Fujii, E., Hiragushi, K., Osaka, A. and Miura, Y., Properties of Al_2O_3-C castable refractories with graphite powder coated with Al_2O_3. *J. Ceram. Soc. Jpn.*, 2001, **109**(3), 270–273.

9. Yu, J., Ueno, S. and Hiragushi, K., Improvement in flowability, oxidation resistance and water wettability of graphite powders by TiO_2 coating. *J. Ceram. Soc. Jpn.*, 1996, **104**(6), 481–485.

10. Sunwoo, S., Kim, J. H., Lee, K. G. and Kim, H., Preparation of ZrO_2 coated graphite powders. *J. Mater. Sci.*, 2000, **35**, 3677–3680.

11. Kawabata, K., Yoshimatsu, H., Fujiwra, K., Mihashi, H., Hiragushi, K., Osaka, A. and Miura, Y., Oxidation resistance of graphite powders coated with Al_2O_3-based oxides. *J. Ceram. Soc. Jpn.*, 1999, **107**(9), 832–837.

12. Kawabata, K., Yoshimatsu, H., Fujii, E., Hiragushi, K., Osaka, A. and Miura, Y., Fluidity of a slurry of the graphite powder coated with Al_2O_3-based metal oxides. *J. Mater. Sci. Lett*, 2001, **20**(9), 851–853.

13. Yoldas, B. E., Alumina sol preparation from alkoxides. *Am. Ceram. Soc. Bull.*, 1975, **54**, 289.

14. Brinker, C. J. and Scherer, G. W., *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, Inc. 1990.

15. Aegerter, M. A., Jafelicci, Jr M., Souza, D. F. and Zanotto, E. D., *Sol-Gel Science and Technology*. Wold Scientific Publishing Co. Pte. Ltd., 1989.

16. Hench, L. L., *Sol-Gel Silica: Properties, Processing and Technology Transfer*. Nyes Publications, New Jersey, USA, 1998.

17. Sjoberg, S., Silica in aqueous environments. *J. Non-Cryst. Sol.*, 1996, **196**, 51–57.

18. Yamaguchi, A., Behaviour of SiC and Al added to carbon-containing refractories. *Taikabutsu Overseas*, 1984, **4**(3), 14–18.

19. Yamaguchi, A., Affects of oxygen and nitrogen partial pressure on stability of metal, carbide, nitride, and oxide in carbon-containing refractories. *Taikabutsu Overseas*, 1987, **7**(1), 11–16.