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ScienceDirect
Ceramics International 35 (2009) 2029–2034
CERAMICS INTERNATIONAL
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Synthesis and characterization of boehmitic alumina coated graphite by sol–gel method

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Received 8 July 2008; received in revised form 17 September 2008; accepted 9 November 2008
Available online 3 December 2008

Abstract

Non-wettability property makes graphite a good protecting material against the molten metal and/or slag. Properties like high oxidation potential between 600 and 1200 °C and non-wettability with water at room temperatures limits the usage of graphite in castable refractory applications. In this study, sol–gel method, which is a relatively cheaper process, was used. Boehmitic sol was obtained by hydrolyzing and peptiziting the alkoxide AIP (aluminum isopropoxide) used as alumina source. Then natural flake graphite was mixed with the boehmitic solution for coating of graphite. At 120 °C boehmitic sol coated graphite was dried and gelled. Then heat threaded at 550 °C for γ-Al_2O_3 transformation of boehmite. Products that obtained from the studies were characterized with FTIR and XRD tests. Alumina coated graphite samples were made by repeating the same steps and TG analysis were made to investigate the oxidation behaviour of the samples. Finally, SEM–EDS analyses were carried out to investigate the microscopic properties of the alumina coated graphite powders.

Keywords: Sol–gel coating; Alumina; Graphite; TG analysis

1. Introduction

The graphite is considered amongst the materials with special importance due to its versatile superior features. One of its major features includes non-wettability. For instance, this feature of graphite is mostly used in the metallurgy in the theme of liquid metal or liquid slag [1–5]. Various methods are tried to solve the problems related to oxidation of the graphite under the increasing temperature and non-wettability of the graphite with water under the room temperature [6–14]. The method sol–gel is a relatively cost-effective method used especially for production of various thin granular ceramic powders such as alumina and ceramic powders coating works. The sol–gel method is composed of various stages such as hydrolysis, peptization and heat treatment and alkoxide are used as the initiating materials [15]. The hydrolysis stage of the alumina production is carried out by the addition of aluminum alkoxide (aluminum isopropoxide, aluminum secondary butoxide etc.) to the water above 75 °C and by mixing the ingredients rapidly. The working temperature is an important parameter. Reason for that is the fact that, when working at lower temperatures, bayerite, an undesired product comes into being and peptization does not come into being with the addition of acid at a later stage. By adding acid to the system during peptization, precipitation of the colloid granules in the water is prevented. Thus, a transparent solution is generated. However, the type of acid matters more than the quantity of acid. For example, regardless of pH value of H_2SO_4 or HF addition, no positive effect has been observed. The boehmitic sol generated in this way is dried at 100–120 °C to remove water and alcohol, then, as a result of heat treatment carried out at 500–550 °C under low heating speeds, γ-alumina, polymorph structured amorphous of alumina, is generated [6,15–19].

By mixing ceramic powders with boehmitic sol generated in this manner, it is possible to produce ceramic powders coated

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doi:10.1016/j.ceramint.2008.11.006

with alumina. Zhang and Lee [6] prepared transparent Al_2O_3, Al_2O_3–SiO_2 and SiO_2 solutions by the way of hydration of aluminum isopropoxide (AIP) and tetra ethyl ortho silicate (TEOS) in the distilled water and used for the coating with natural layer structured graphite. In order to turn the graphite solutions coated with boehmitic sol into gel, it is dried at 120 °C for 12 h and heat treatment was applied for 2 h at 500 °C. The water-wettability and oxidation resistance of the coated and uncoated graphite were studied. Al_2O_3, Al_2O_3–SiO_2 and SiO_2 coatings improved the water-wettability of graphite and graphite coated with SiO_2 showed the best water-wettability. It was reported that all coatings improved the oxidation resistance of the graphite especially at high temperatures (>1100 °C). Sunwoo et al. [7] produced layered graphite powder coated with ZrO_2 by the way of controlled hydrolysis of the zirconium oxychlorure. It was possible to produce homogenous ZrO_2 layers by mixing. During the hydrolysis process, it was observed that homogenous layers turned into ZrO_2 particles. It was observed that these were the primary particles no larger than a few nanometer and the secondary particles larger than 0.1 mm. Saberi et al. [8] were studied to improve the water-wettability and oxidation resistance of the flaky graphite by coating $MgAl_2O_4$-spinel by using sol–gel method.

The aim of this study was the coating of the natural graphite with alumina by sol–gel method and characterization through FTIR, XRD, TG and SEM–EDS analyses.

2. Experimental procedure

2.1. Synthesis of alumina coated graphite by sol–gel

As initiating alkoxide material in the form of alumina source, AIP (aluminum isopropoxide ($Al(OC_3H_7)_3$) Aldrich, ≥98%) in the form of powder was used. Distilled water was heated up to 90 °C according to AIP, 15:0.1 mol ratio, at a reactor with four necks and a volume of 1000 ml, with heater and magnetic mixer equipped and 20.4 g AIP was mixed in 270 ml pure water for 30 min. At this stage, the system started to be mixed after adding HCl diluted up to 10% (Merck, 37%). After mixing it for 1 h, the dissolution was observed by adding HCl acid to sol. When measuring pH of the solution as 2.3, it was observed that a transparent solution was generated and the treatment was completed [17].

A sample is taken from generated boehmitic sol, and kept in the drying oven at 120 °C for 8 h. Then, the sample was heated for 20 min at a heat controlled SFL (UK) branded oven at 2 °C/min, heating speed up to 550 °C and was kept at this temperature for 3 h. Then, by performing FTIR and XRD analyses, alumina production process characterization studies were performed with sol–gel [17]. The same sample was heated in the heating controlled SFL (UK) branded HTCF 940A model laboratory type oven at a heating speed of 10 °C/min up to 1300 °C and was kept in the oven for 1 h and then it was allowed to cool down and the last form of sample so generated was subjected to XRD. The XRD analyses were performed by using Cu Kα radiation ($\lambda = 0.154$ nm) at Rigaku (Japan) D/Max–2200/PC branded device.

After seeing that α-Al_2O_3 could be produced, 150 g layered graphite powder was added to boehmitic sol and by mechanically mixing for 15 min, it is tried to wet the graphite surfaces. The natural graphite raw material originating from China contains ~94.5 wt% carbon, ~5 wt% ash and 0.05 wt% S with a grain size of <200 μm. Fig. 1 shows the diffraction pattern of the natural graphite sample. The positions of the diffraction lines according to the powder diffraction database (PDF) with $(h\,k\,l) = (0\,0\,2)$ and $(0\,0\,4)$ are indicated for

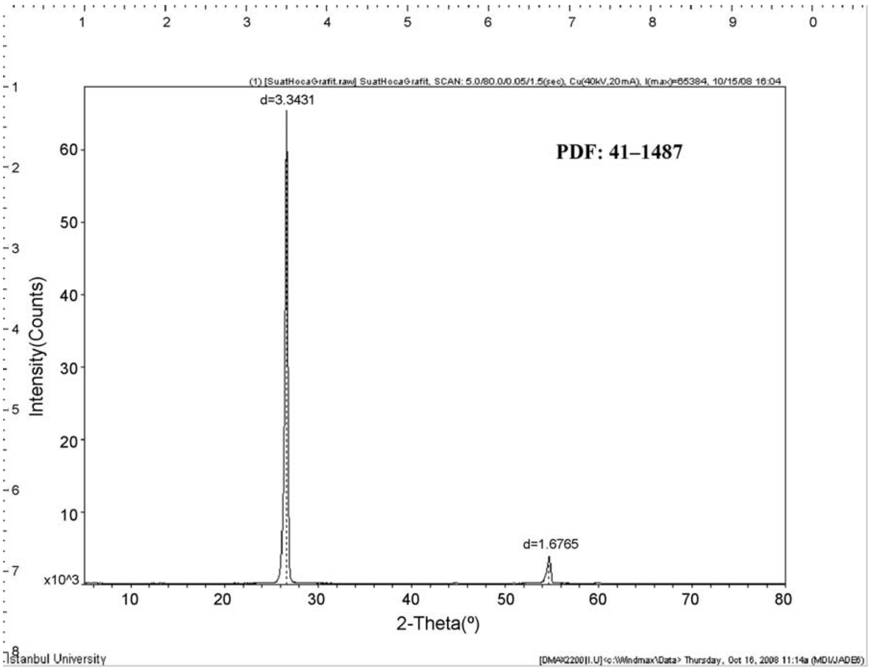


Fig. 1. XRD analysis of natural (uncoated) graphite.

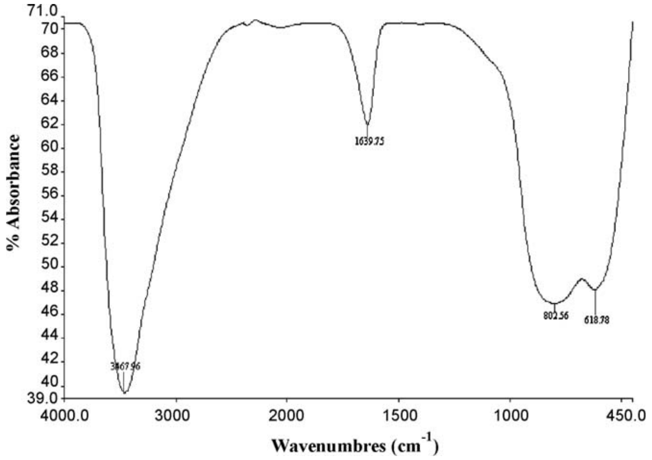


Fig. 2. FTIR analysis of the gel heat treated at 550 °C for 3 h.

graphite. After subjecting the samples coated with boehmitic sol to heat treatment at 550 °C, graphite powder samples coated with γ-Al_2O_3 were generated.

2.2. *TG-analysis*

The boehmite powder generated as a result of drying the boehmitic sol was subjected to thermo-gravimetric analyses under atmospheric conditions by using Shimadzu branded TG–60WS model (Japan) TG analysis device in order to describe the oxidation features of uncoated graphite and γ-Al_2O_3 coated graphite samples generated following the heat treatment at 550 °C.

2.3. *SEM–EDS analysis*

γ-Al_2O_3 generated following heat treatment at 550 °C as well as coated graphite powders and natural (uncoated) graphite powders were subjected to SEM and EDS analysis using JEOL JSM 5600 and IXRF 550i (integrated with JEOL SEM) brand scanning electron microscopy.

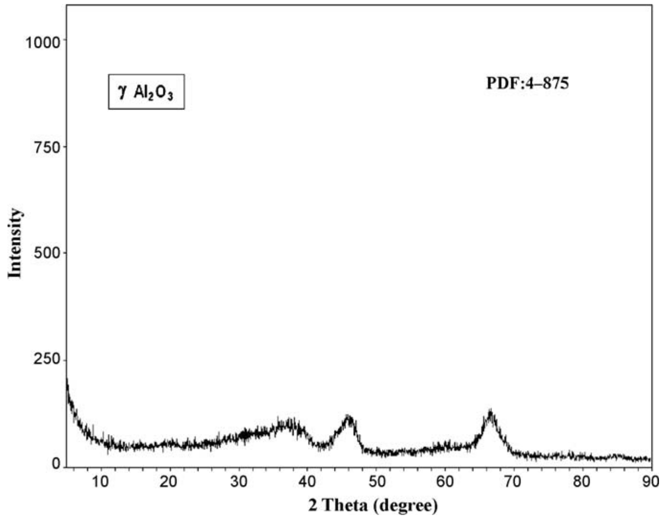


Fig. 3. XRD analysis of the gel heat treated at 550 °C for 3 h.

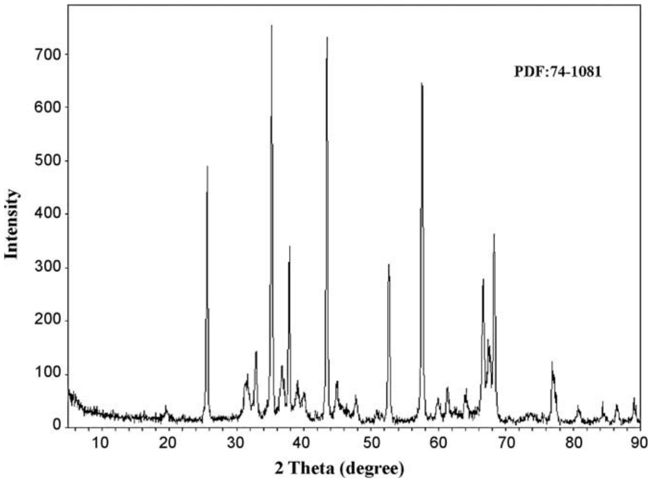


Fig. 4. XRD analysis of the gel heat treated at 1300 °C for 1 h.

3. Results and discussion

As a result of FTIR analysis seen in Fig. 2, it was found out that the peaks found at 3468 and 1640 cm^{-1} wave numbers pertain to O–H bonds, the peak found at 803 cm^{-1} wave number pertains to Al–O–Al bonds and the peak found at 619 cm^{-1} wave number pertains to Al–O bonds.

As expected, in the XRD results shown in Fig. 3, the structure is amorphous, and the clear peaks indicate the γ-Al_2O_3. Then, the result of the thermal treatment carried out at 1300 °C in order to convert to α-Al_2O_3, which was the main goal, is indicated in Fig. 4. As seen here, by starting from the alkoxide with the sol–gel technique, it was seen that α-Al_2O_3, the stable crystal structure of the alumina, could be produced.

Fig. 5 shows the weight loss at boehmite powder, uncoated graphite and γ-Al_2O_3 as well as coated graphite samples at the heating speed of 10 °C/min up to 1100 °C. As seen in Fig. 5, it is indicated that the oxidation speed of the graphite increases after 650 °C. The weight loss of the uncoated graphite sample was 94.3% between 650 and 1050 °C. Apart from the inorganic impurities contained in the graphite raw material, it

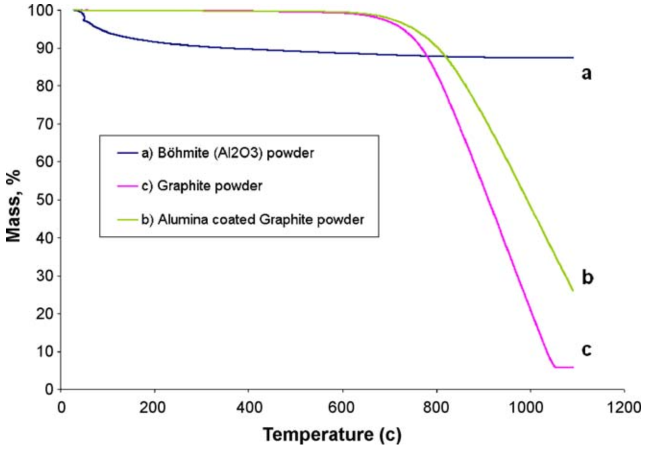


Fig. 5. TG results of boehmite, graphite and alumina coated graphite powders.

was found out that the entire carbon oxidized and evaporated. The weight of the coated graphite sample, however, dropped to 25.2% between 650 and 1095 °C and the loss turned out to be 74.8%. As a result of the experiments carried out under the same conditions, it is understood that the resistance of the coated graphite sample against the oxidation increased, to an unsatisfactory extent though. TG analysis applied to boehmite powder is seen in Fig. 5. Looking into this figure, it is seen that, as a result of keeping away the water, the weight rapidly decreases till 200 °C and, then, slowly to ∼600 °C and becomes stabilized up to 1095 °C. At 1095 °C, it was recorded that the weight goes back to 88% and the weight loss of the alumina is ∼12%. In the coated graphite samples, when the effect of such loss is taken into consideration, it is concluded that the graphite gets oxidized more. According to the study conducted, it was determined that its effect would be ∼2%. Thus, the portion caused by the burning of the carbon of the weight loss that takes place in the coated graphite sample at the rate of 74.8% should be expected to go over 75%. However, it may not be ignored that a better result than weight loss of the uncoated graphite at the rate of 94.3% was gained.

SEM image results are given in Fig. 6a–c and EDS analysis results are given in Fig. 7a–d. Figs. 6a and 7a are the results of uncoated graphite. The reason for oxidation of the graphite at a high level against the expectations is clearly seen in SEM photos in Fig. 6b and c. Due to the problem of failure of the boehmitic sol to wet the surfaces of the graphite, the fact that alumina grains precipitating as a result of the subsequent heat treatments to hang on the alumina surfaces gives rise to this result. It is observed that alumina grains which have not hung on the smooth surfaces of the graphite parallel to the layers hung on the rough areas on the surface of the layers and in the grain borders between the vertical layers very well. In Fig. 7b, as a result of EDS analysis derived from the grain borders close to vertical graphite layers, 100% alumina presence was detected. It is seen that, when proceeding from the grain border toward the graphite surface, the ratios of alumina and carbon are both approximately 50 wt% (Fig. 7c). It has been determined that the alumina quantity is extremely low at the surface centers of the graphite layers that could be considered smooth (Fig. 7d). It is understood that the graphite powder that can be partially coated with alumina give rise to loss due to easy oxidation at their open surfaces parallel to the layers that could not be coated.

In order to study the effect of heating speed on the oxidation feature at high temperatures, the graphite coated with γ-Al_2O_3 generated the following thermal treatment at 550 °C: TG analysis was conducted at 5, 10 and 15 °C/min heating speed up to 1100 °C and the results of such analysis are seen in Fig. 8. As seen in this figure, the higher the heating speed increases, the more weight loss decreases. Amongst the samples that were observed to oxidize as from 650 °C, it was found out that the coated graphite heated at the lowest heating speed of 5 °C/min completely oxidized at 1000 °C, and at the heating speed of 10 °C/min at 1095 °C, 75% of the graphite oxidized and underwent a weight loss, and at the heating speed of 15 °C/min and at 1095 °C, 52% of the graphite oxidized and a weight loss took place. Based on this point, it is found out that the more heating speed increases, the more oxidation quantity of the coated graphite decreases. The best protected sample was the one that was generated by protecting half of the graphite from oxidation at 15 °C/min heating speed.

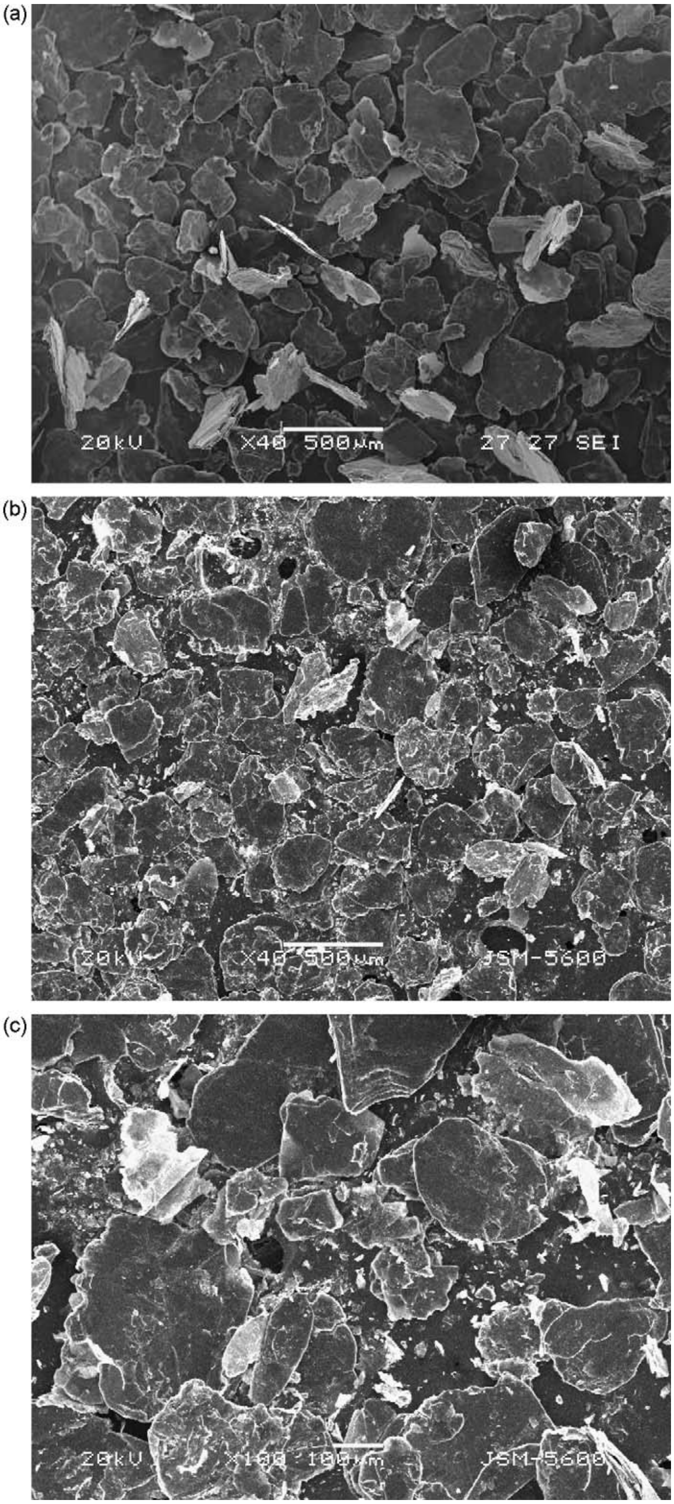
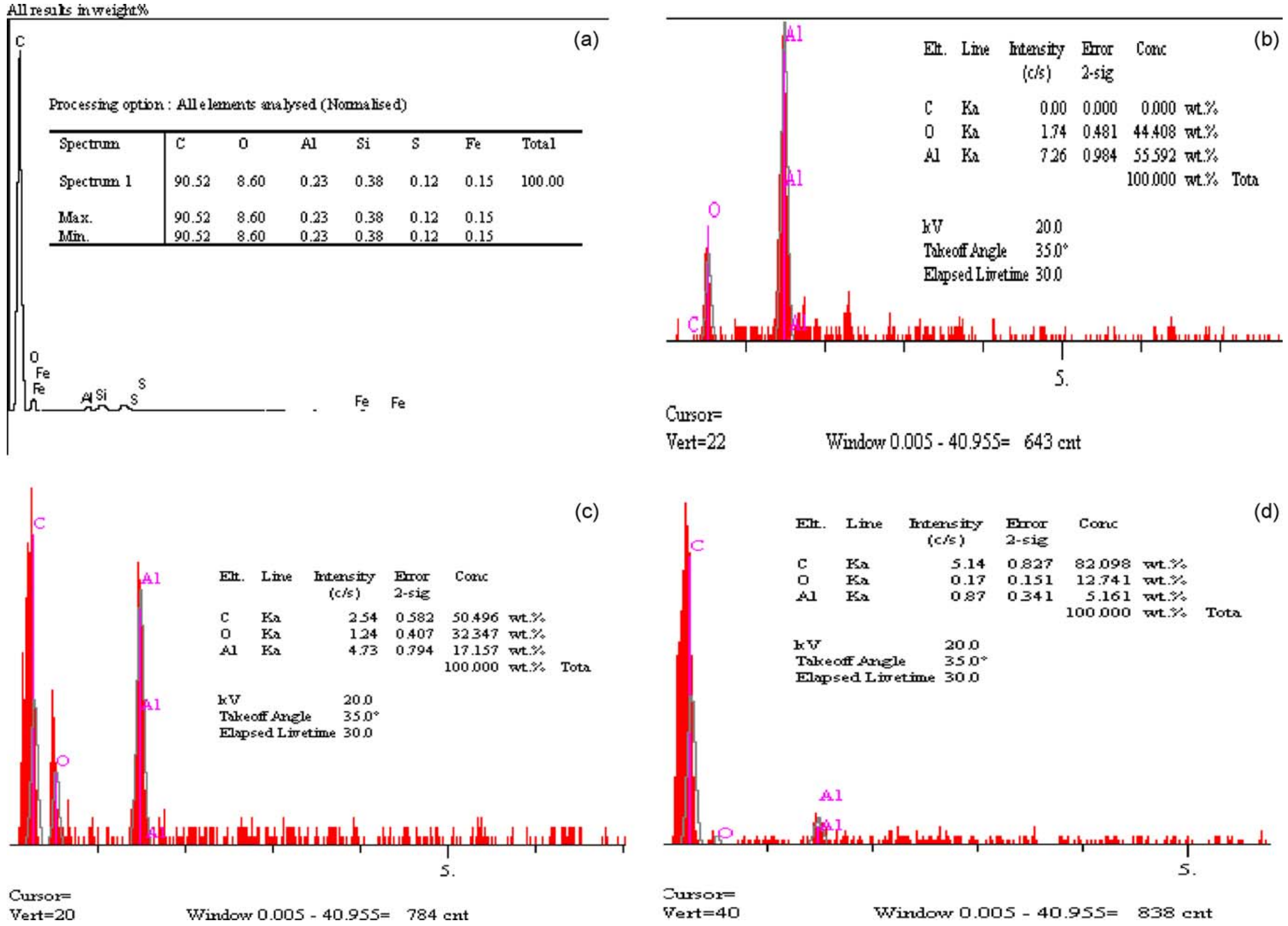


Fig. 6. SEM micrograph of (a) natural (uncoated) graphite (40×), (b) alumina coated graphite (40×) and (c) alumina coated graphite (100×).



All results in weight%

Processing option : All elements analysed (Normalised)

Spectrum	C	O	Al	Si	S	Fe	Total
Spectrum 1	90.52	8.60	0.23	0.38	0.12	0.15	100.00
Max.	90.52	8.60	0.23	0.38	0.12	0.15	
Min.	90.52	8.60	0.23	0.38	0.12	0.15	

(b)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc		
C	Ka	0.00	0.000	0.000	wt.%	
O	Ka	1.74	0.481	44.408	wt.%	
Al	Ka	7.26	0.984	55.592	wt.%	
				100.000	wt.%	Tota

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 30.0

Cursor=
Vert=22 Window 0.005 - 40.955= 643 cnt

(c)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc		
C	Ka	2.54	0.582	50.496	wt.%	
O	Ka	1.24	0.407	32.347	wt.%	
Al	Ka	4.73	0.794	17.157	wt.%	
				100.000	wt.%	Tota

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 30.0

Cursor=
Vert=20 Window 0.005 - 40.955= 784 cnt

(d)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc		
C	Ka	5.14	0.827	82.098	wt.%	
O	Ka	0.17	0.151	12.741	wt.%	
Al	Ka	0.87	0.341	5.161	wt.%	
				100.000	wt.%	Tota

kV 20.0
Takeoff Angle 35.0°
Elapsed Livetime 30.0

Cursor=
Vert=40 Window 0.005 - 40.955= 838 cnt

Fig. 7. (b) EDS analysis at grain borders vertical to the graphite layers. (c) EDS analysis of the area proximate to the grain borders of the graphite layers. (d) EDS analysis derived from the smooth surface of graphite layers.

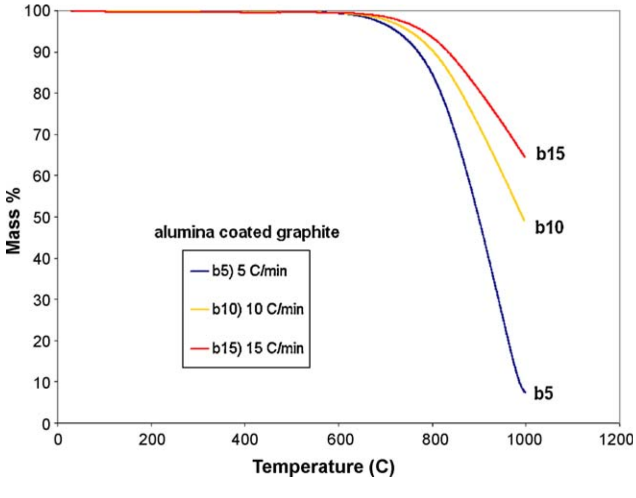


Fig. 8. TG results of alumina coated graphite powders at the heating rates of 5, 10 and 15 °C/min.

4. Conclusion

It was understood that, as a result of coating the graphite with natural layer and a grain size of <200 μm using the sol–gel method, a relatively cost-effective method, the oxidation resistance could be increased to a certain extent. The alumina sediments that could not be observed on smooth surfaces of the layered graphite parallel to the layer were found to be existing adjacent to the grain border of the graphite, in the areas perpendicular to the layers and smooth surface areas. As a result of non-wettability, it is understood that the graphite cannot be coated completely, particularly the smooth surfaces. The fact that average grain size of the graphite used is a lot larger than the alumina particles that precipitated gives rise to a disadvantage. It is thought that trying to coat the alumina by sol–gel at the graphite with a size smaller than micron and/or nanosize may be useful.

Increase in the heating speed decreases the oxidation speed of the coated graphite at elevated temperature and becomes useful. It has been found out that, at the heating speed of 15 °C/min, about half of the graphite can be protected from oxidation.

Acknowledgements

This work was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) with Project Nr.: 106M318, by Research Fund of Istanbul University with Project Nr.: UDP 2391 and by METAMIN Inc. in Istanbul.

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