

Improving the Wettability and Oxidation Resistance of Graphite by Coating

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Abstract: In this research, the graphite powders were coated with Al₂O₃ by hydrolysis of an Aluminum nitrate aqueous solution. The surface of the graphite particles coated with Al₂O₃ was investigated by XRD and the quality of Al₂O₃ coating on the surface of graphite was observed by SEM and investigated by EDS. For detail investigation on the surface of coated graphite TEM was used and then wettability and oxidation resistance were investigated. To compare the effect of coating and antioxidant on oxidation resistance of graphite, Al and SiC were used as antioxidant. The results showed that the surface of graphite flakes was successfully coated and modified so that wettability and oxidation resistance of graphite greatly improved and the amount of antioxidant needed for application of graphite in the refractory decreased.

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1. Introduction

About 65% of the refractories produced in the world are used in the steel making industry [1]. Considering the new steel making processes and the need for corrosion resistance refractories for elevated temperatures, use of pure oxide refractories is becoming more and more restricted [2]. The reason for this is the high wettability of oxides with molten metals and therefore the high rate of corrosion in these refractories, which in turn lowers thermal shock resistance. This problem, however, can be resolved by introducing graphite into the oxide systems, because graphite reduces wettability and thermal expansion coefficient, improves corrosion and thermal shock resistance resulting in increasing of the service life of the refractories [1,3].

Graphite, however, has some drawbacks. Firstly, its wettability is poor, a fact that limits its use in castables, because the amount of water required for the preparation of the castables containing graphite is far more than that of the other castables which deteriorate its physical and mechanical properties. Secondly, graphite is prone to oxidation at elevated temperatures [4].

To improve the oxidation resistance of carbon, metallic or none metallic additives such as Al, Si, Al/Mg alloy, SiC and B₄C have been used, but problems such as Al hydration, formation of undesirable phases or decomposition of suitable phase will be occurred [5-8]. Furthermore, the negative role of some additives and the fact that there is no accurate method for determining the best antioxidant should be considered [9-10]. On the other hand, the application of these additives is limited, because of the high cost

of milling them to micron and nano-sizes [11]. Thus for effective use of graphite in castables, its poor wettability and oxidation resistance should be overcome. Some researches have tried to resolve these problems by Coating graphite. Zhang and Lee [12] heated a mixture of graphite and silicon in a reducing atmosphere and deposited a SiC layer on the graphite surface and hereby improved surface properties of graphite such as wettability. But the practical drawbacks of this method are the need for high temperature and reducing atmosphere. Sakamoto et. al. [13] prepared a mixture of SiC and graphite by using a high energy mill to coat graphite with a SiC layer. The adherence between the two was, however, weak and easily broke during mixing with other ingredients. Zhang and lee [14-15] and Zhoufu et al [16] coated graphite with TiO₂ and Al₂O₃ and SiO₂ by sol-gel and solution method. The problem with this method is its high cost of raw materials. Sunwoo et. al. [17] coated graphite with ZrO₂ by the controlled hydrolysis of a zirconium oxychloride aqueous solution. By this method the graphite wettability and oxidation resistance were improved. This method is also relatively costly. Yu et. al. [18] coated graphite with TiO₂ by ethanol solutions containing various amounts of an organic titanate and improved the wettability, flowability and oxidation resistance of graphite. But the use of this method is restricted, because organic materials similar to surfactants often interfere with other additives such as deflocculants and also have very bad smell.

In this research, graphite powder was coated with Al₂O₃ by hydrolysis of an aluminum-nitrate aqueous solution. This method is cheaper and proved to be

effective in improving the wettability and oxidation resistance of graphite.

2. Experimental procedure

2.1. Raw Materials

The raw materials used in this experiment included natural flake graphite (purity <97%, grain size <200 μ m) supplied from Sinorth Minerals Group Ltd. (China), Aluminum-nitrate and NH₃ (Merck, Germany), Aluminum powder (Atomizer International Co. Iran), and SiC powder (grain size <10 μ m, purity <92%) purchased from Saint-Gobin, SIKA, China. Distilled water was used as solvent for the coating process.

2.2. Coating Process

Aluminum-nitrate was dissolved in distilled water to prepare a 500ml solution of 0.2M concentration. This solution was stirred and heated at 60°C. In order to maintain PH at a constant, a small amount of NH₃ was added to the suspension. 40g flake graphite was added and stirred for 3 hours. The coated graphite particles were separated by filtering and vacuum pumping and then washed with distilled water repeatedly until the filtered liquor showed the natural pH. The coated graphite was then dried at 110°C for 24 hours and calcined at 700°C for 1 hour.

2.3. Characterization

2.3.1. Investigating the Quality of Coatings

In this research, the coated graphite and the quality of the coatings in terms of adherence and uniformity of the coatings were examined by XRD, SEM and EDS. Finally, for detail investigations of the coating quality on the surface of graphite TEM images was taken.

2.3.2. Oxidation Resistance Investigation

To evaluate the oxidation Resistance of the coated graphite and effect of this coating, graphite pellets (as-received and coated) of 4cm diameter and 1cm thickness were prepared and fired at different temperatures (700, 850 and 1000°C) under oxidizing atmosphere and the weight loss was measured. In some of the pellets Al and SiC was used as antioxidant and the amount of antioxidant was 50 wt.% of the graphite.

2.3.3 Wettability of Graphite

Floating process was used to study the of wettability characteristics of graphite. In this process 10 grams as-received and coated graphite was added to 100ml distilled water and mixed for 2 h. Then the weight percent of the floated graphite over the suspension was measured as floating ratio (F.R) using the following equation [14,18].

$$(F.R)\% = \frac{\text{Weight of Floating Graphite}}{\text{Total Weight of Graphite}} \times 100$$

Lower F.R ratio shows a better wettability. The samples investigated for wettability and oxidation resistance are listed in Table 1.

Table 1. Coding of different graphites

Code	Composition of Graphite
G	as-received Graphite
GC	Coated Graphite
GS	as-received Graphite with SiC
GCS	Coated Graphite with SiC
GA	as-received Graphite with Al
GCA	Coated Graphite with Al

3. Results and discussion

3.1. Coating mechanism

During coating graphite by controlled hydrolysis of the aqueous aluminum nitrate solution, maximum amount of aluminum hydroxide should be formed without precipitation. Thus, in order to have a proper coating, the term of $[Al^{3+}].[OH]^{-3}$ should have its maximum before k_{sp} (solubility limit) [19].

There are two ways to this aim:

1. Increasing the solution concentration to a level that prevents precipitation. This means increasing $[Al^{3+}]$ so that $[Al^{3+}].[OH]^{-3}$ is less than k_{sp} .
2. Increasing pH to a level that prevents precipitation. This means increasing $[OH]^{-}$ so that $[Al^{3+}].[OH]^{-3}$ is less than k_{sp} . Therefore, to reduce the amount of the main raw materials, i.e. aluminum nitrate, and to prevent precipitation, the concentration of the solution used was low (0.2M). To encourage the hydrolysis reaction and formation of aluminum hydroxide pH was increased by adding ammonia. The reason for using ammonia is that it does not introduce detrimental species such as Na. To encourage the reaction and increase the k_{sp} the reaction was conducted at 60°C. Continuous monitoring of pH during the coating process showed that pH was in the range of 2.41-2.65 before adding ammonia. By adding ammonia it was increased and during hydrolysis decreased and in the last 30 minutes become constant (3.8-4), showing that the hydrolysis was complete.

3.2. Phase and microstructure investigation

Fig. 1 shows XRD analysis of the coated graphite. Presence of Al₂O₃ in sample was confirmed. To make sure that the coating is uniform and no segregation occurred, SEM was used.

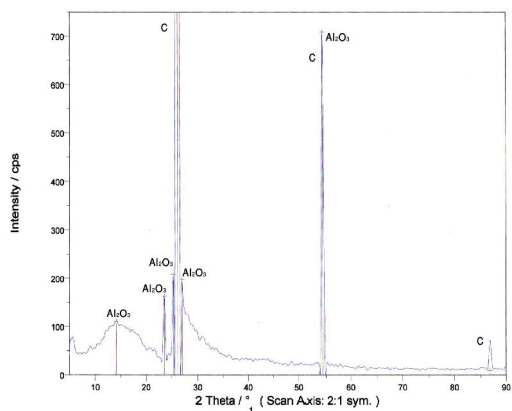


Figure 1. XRD pattern of the graphite particles with Al_2O_3 .

Fig. 2a shows the SEM micrograph of the coated graphite. It can be seen that the coating is almost uniform and no sign of segregation of alumina is observed. The EDS analysis of the sample (Fig. 2b) revealed the presence of Al_2O_3 on the graphite surface.

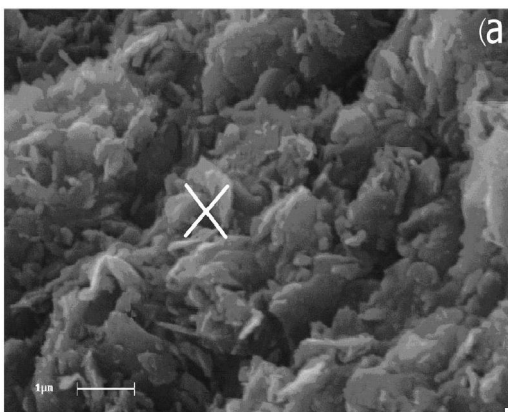


Figure 2a. SEM image of Al_2O_3 coated graphite

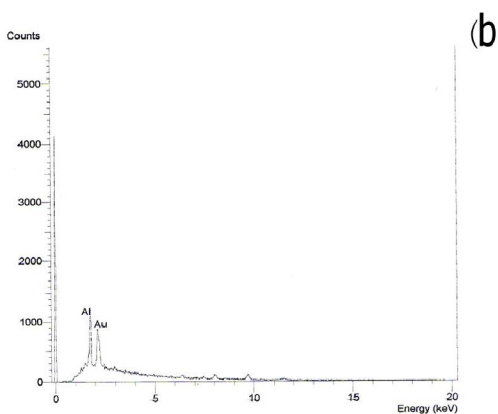


Figure 2b. EDS pattern of Al_2O_3 Coated Graphite.

Fig. 3 shows the coated graphite at a higher magnification and it is obvious that by coating operation, powders were not agglomerated.

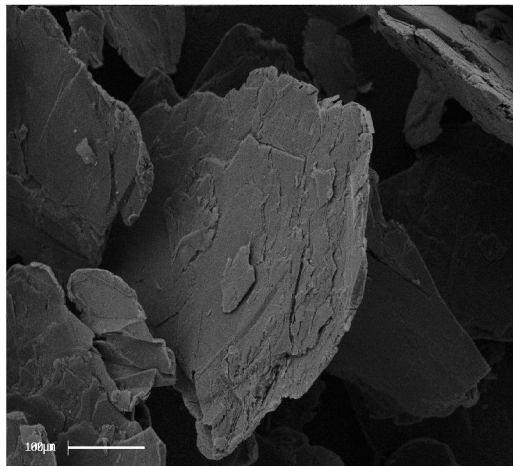


Figure 3. SEM image of Al_2O_3 coated graphite.

Fig. 4 shows the TEM image of the as-received and coated graphite showing the fluffy Al_2O_3 layer deposited on the surface of the graphite.

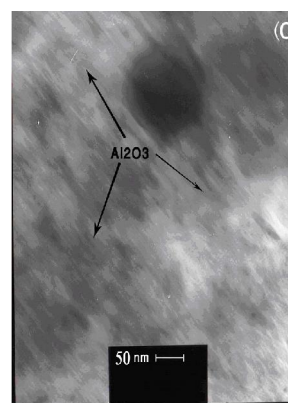
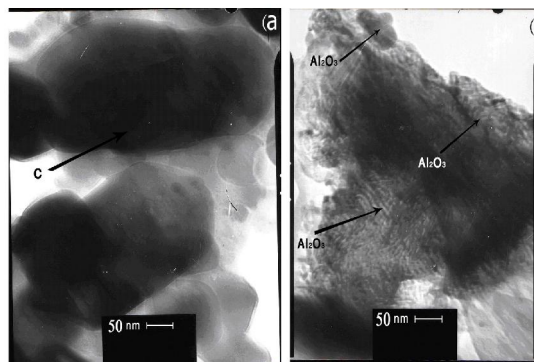


Figure 4. TEM images of (a) as-received and (b,c) Al_2O_3 Coated Graphite.

3.3. Wettability and oxidation resistance

The study of the wettability (Fig. 5 and 6) showed that the F.R ratio in the coated graphite was lower than that of the as-received graphite, therefore it can be concluded that the wettability of graphite was developed by coating. The reason for the development of wettability of graphite is attributed to the formation of active surface groups like $-OH$ and $Al-O$ on the surface of graphite [14,18].

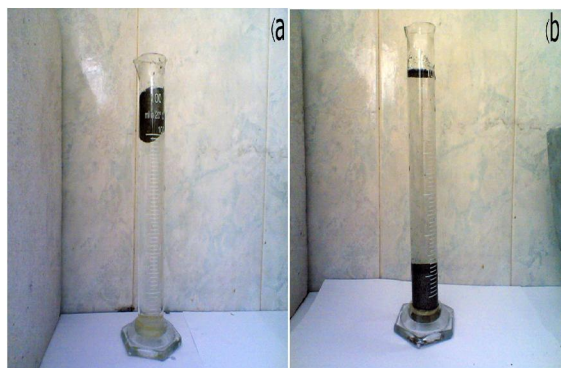


Figure 5. Photographs of the floating process for (a) as-received graphite and (b) coated Graphite.

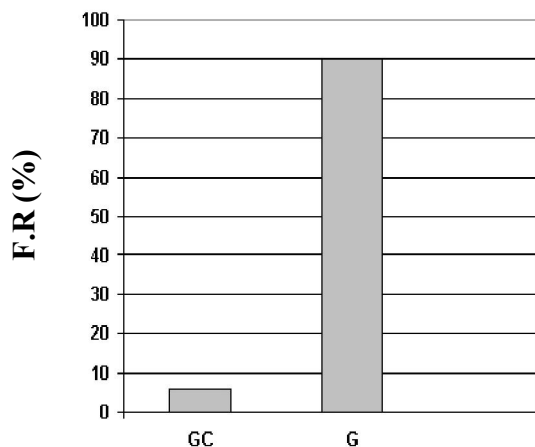


Figure 6. The Amount of F.R of as-received and Al_2O_3 Coated Graphite

The Al_2O_3 coating also increased the oxidation resistance of the graphite at all temperatures. The improvement in oxidation resistance of graphite powders was related to the change in the surface condition of the powders. On the surface of the graphite powders, there exist many effects such as cracks and edges which are usually occupied by hydrogen, oxygen and hydroxyl ions. Oxidation of the graphite powders occurs initially at these defects. During heating, the $Al(OH)_3$ on the surface of graphite powder reacts easily with these ions on

the surface of the graphite powders. The reaction products mainly form chemical bonds with the surface of graphite powders. Thus, defects such as edges are covered and the H, OH, and O ions desorbed. On the other hand, the coating prevents oxygen to contact with the graphite. Fig. 7 reveals that the coating reduces the oxidation rate even more effectively at higher temperatures, perhaps because of the decrease in permeability of the alumina layer due to sintering at higher temperatures.

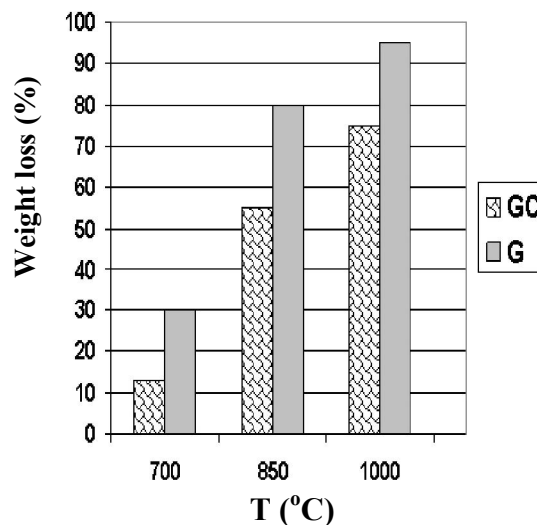


Figure 7. Loss of Weight of as-received and Al_2O_3 Coated Graphite.

Fig. 8 shows the effect of Al and SiC as antioxidant in as-received and coated graphite. It is obvious that introducing antioxidant in addition to coating improves the oxidation resistance. It seems that the reason for this behavior during heating is that, Al and SiC can be reduced by CO gas derived from oxidation of C and then changed to Al_2O_3 and SiO_2 .

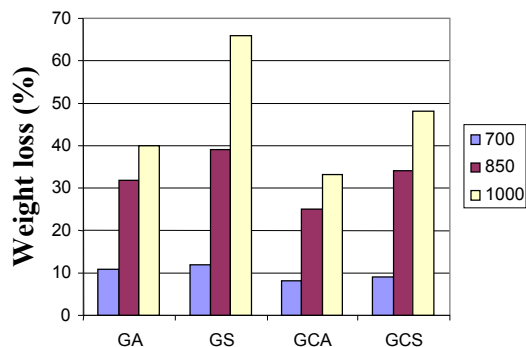


Figure 8. Effect of Al and SiC, as antioxidant in as-received and coated graphite.

These products (Al_2O_3 and SiO_2) fill the areas on graphite surface having no coating or in regions where coating layer is thin and also fill surface coating micropores and prevent from graphite oxidation and overall reduce oxidation rate and prohibit oxidation. But Al is more efficient than SiC, because Al oxidation caused the formation of Al_2O_3 and Al_2O_3 on the graphite surface bonded with coating easily and filled micropores of coating, therefore led to homogenous coating. The other important result of Fig.8 is that with coating, antioxidant amount decreased remarkably.

4. Conclusion

The effect of Al_2O_3 coating on wettability and oxidation resistance of graphite was studied. The coated graphite by solution process did not introduce agglomeration. The effect of coatings on oxidation resistance of graphite show that by Al_2O_3 formation on the surface of graphite the oxidation of graphite was limited in different temperature, under oxidizing atmosphere. Using Al and SiC as antioxidant could effectively enhance the oxidation resistance of graphite, but Al is more efficient than SiC. Applying coatings resulted in a decrease in the amount of the antioxidant needed.

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