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Oxidation Protection of Graphite by BN Coatings

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Increasing the service life of different graphite parts at high temperatures is very important in many industrial applications. One way to achieve this objective is to produce oxidation protection coatings of boron nitride on graphite substrates. The chemical inertness and oxidation resistance of boron nitride has led researchers to consider this material as one of the best coatings to protect graphite against oxidation. Many aspects of obtaining nitride coatings on graphite substrates by forming a boron nitride layer in a heterophase process have been investigated. Oxidation tests performed on the coated graphite have revealed a high efficiency of boron nitride coating for graphite protection. As compared with that of uncoated specimens the oxidation resistance of BN-coated graphite substrates was 8 times higher at 750°C and 12 times higher at 1200°C. The studies have shown that boron nitride coatings can effectively protect carbon materials against oxidation and increase the service life of these materials at high temperatures. © 2000 Academic Press

INTRODUCTION

Various graphite products are widely used in ferrous and nonferrous metallurgy and glass production. However, at elevated temperatures in air, graphite is prone to react with air to form carbon oxide.

The graphite product is deteriorated and loses its shape and mechanical strength. Therefore, the problem of increasing graphite resistance at higher temperatures in air (i.e., in an oxidizing atmosphere) is most important.

One way to solve this problem, that is to increase the resistance of graphite to burning at high temperatures (above 500°C), is to coat the graphite product with a protective layer which prevents interaction between graphite (carbon) and oxygen.

Such a coating can be obtained by depositing a film of a material which is supposed to be highly resistant to oxidation at temperatures up to 1000°C. Boron nitride is one of the options. Along with having a high oxidation resistance (T of oxidation onset is 900°C) boron nitride is not wetted by many molten nonferrous metals and glasses. This property makes boron nitride a good choice for graphite protection against high-temperature corrosion.

EXPERIMENTAL PROCEDURE

To obtain a boron nitride coating on graphite substrates, the chemical method of forming BN directly on the graphite surface was chosen.

It is well known that one way to obtain boron nitride is to reduce boron–oxygen compounds with carbon in a nitrogen stream (1).

In our case, we used graphite carbon as a reducing agent for boric acid.

However, temperatures above 1900°C are needed for carbon reduction of boric acid in a nitrogen atmosphere. Therefore, in order to lower the process temperature, an N-bearing organic (N–R) compound which would give ammonia on decomposition was used as a nitrogen-bearing precursor.

Graphites of GE and MPG-6 grades were used as substrates for the coating. Graphite specimens of the mentioned grades were prepared as $2 \times 10 \times 20$ mm plates and 40×10 mm rings.

The boron nitride coating on the graphite specimens was obtained by heat-treating the specimens in a sinter made by mixing boric acid with the N–R compound. In other cases the coating was obtained by heat-treating the specimens in a gas stream produced by decomposition of the sinter. The sinter was made by mixing boric acid with an N–R compound in a ratio of 1/2.5 followed by a heat-treatment inside a desiccator at 300–700°C. The sinter obtained was put, together with the graphite specimens, into a graphite cup. The cup was repeatedly (1–4 times) passed though a CTH-1,25-type furnace while the temperature inside the furnace working zone was increased from 1600°C to 1900°C.

In other experiments the graphite specimens were passed through the furnace without the sinter; i.e., the specimen was in the gas stream formed by decomposition of the sinter, in front of the retort. After each pass through the furnace, measurements of the specimen size, weight, and coating thickness were taken by cutting the graphite rings.

The heat-treated graphite specimens coated with boron nitride were submitted to high-temperature corrosion tests at 700°C in air.

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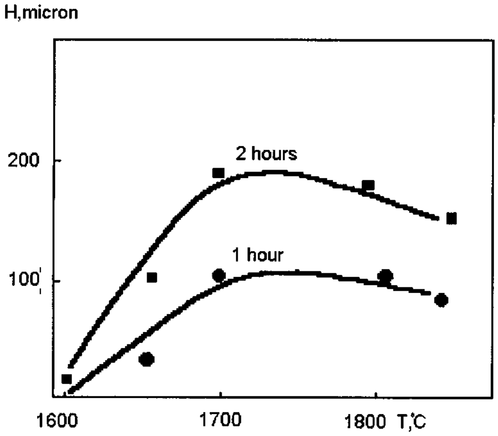

FIG. 1. BN coating growth (*H*) as a function of temperature and time.

The kinetics of graphite burning-out (change of specimen weight with time) at a constant temperature was studied using a dilatometer.

RESULTS AND DISCUSSION

Observation of the heat-treated graphite specimens shows the formation of a white layer of 50–100 μm thick boron nitride which appears after the first pass (dwell time inside the furnace working zone of about 1 hour). A soft BN layer was deposited both on the specimens in the sinter and on the specimens treated within the gas stream. The best results (a sounder coating) were obtained by using the sinter synthesized at 400–450°C. This can be explained by the fact that this sinter did not contain crystallization water, but had a high content of the boron–nitrogen compound (B–N–R).

The very first experiments showed that at 1700–1800°C a soft 200–500 μm thick boron-nitride coating is formed after two to three passes through the furnace.

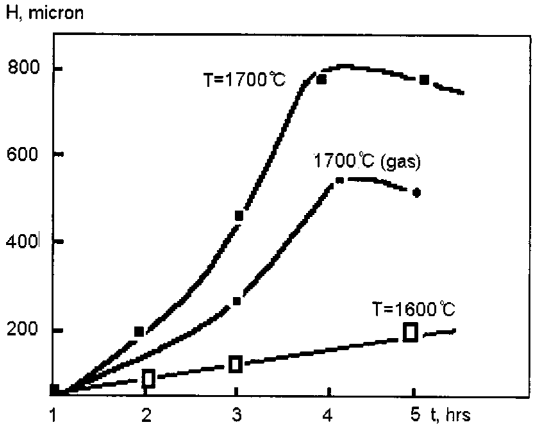

FIG. 2. BN layer growth as a function of temperature.

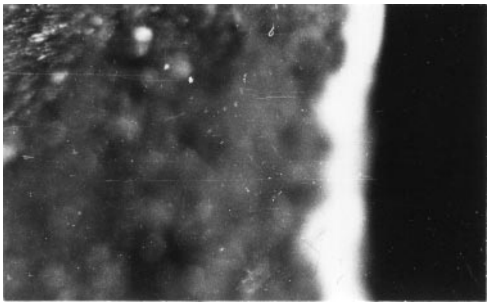

FIG. 3. Cross-section structure of BN coating on graphite. × 80. Treatment (1 hour) in gas.

Figures 1 and 2 show the results of the growth rate for boron nitride layers on graphite specimens at different temperatures. Figures 3 and 4 show the structure of the boron–nitrogen layer formed on the graphite surface in the gas over 1 hour and in the sinter over 3 hours, respectively.

The investigation of the BN coating process shows that the nitride layer formation proceeds through the carbothermic reduction of boron anhydride vapor in the presence of ammonia. Boron nitride is formed at the consumed carbon site by reduction in the graphite lattice, which means that the BN layer growth is directed inward in the graphite specimen.

The limiting step for BN layer formation is the diffusion of boron oxide and ammonia vapors toward the graphite carbon through the boron nitride layer formed. The size of graphite specimens does not change, as part of the graphite is replaced by boron nitride.

X-ray structural analysis of the layer formed has shown that boron nitride had an ordered hexagonal lattice. It has also been found that the rate of boron nitride coating deposition during the heat treatment in the sinter is 2.8–3.2 μm/min, while it is 2–2.5 μm/min during the heat treatment in the gas phase. The difference can be explained by the fact that the necessary precursors in the decomposed sinter are

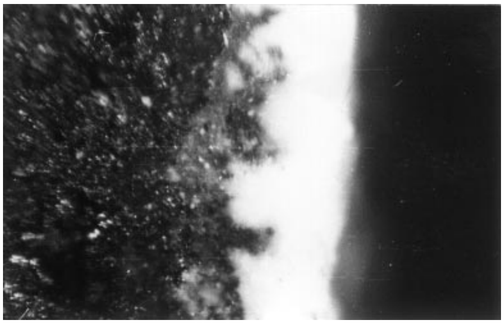

FIG. 4. Cross-section structure of BN coating on graphite. × 80. Treatment (3 hours) in sinter.

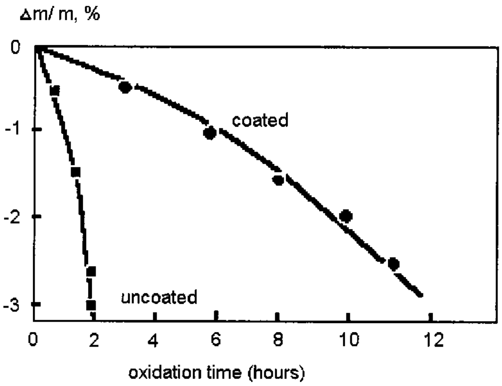

FIG. 5. Isothermal oxidation weight loss of uncoated and coated graphite at 700°C.

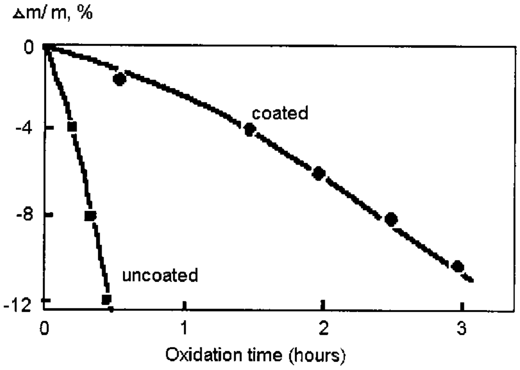

FIG. 6. Isothermal oxidation weight loss of uncoated and coated graphite at 1200°C.

closer to the graphite carbon, which is especially so for boron oxide vapors.

Figure 1 shows that the formation of a boron nitride layer on graphite starts at temperatures above 1600°C. The greatest rate of boron nitride formation occurs during heat-treatment in the temperature range of 1700–1750°C. Increasing the temperature above 1800°C reduces the boron nitride formation rate due to the onset of coating delamination.

The coating delamination may be caused by the precipitation of excessive boron oxide which penetrated into the coating at lower temperatures. This conclusion is confirmed by the fact that during BN synthesis in similar processes a drastic drop of boron oxide in BN (down to 0.04%) is possible only at temperatures above 1800°C under conditions favorable for withdrawal of boron anhydride vapors.

The graphite specimens with a 350–500 μm thick boron nitride coating were submitted to air hardening at 700–1200°C. The kinetic results were obtained by weight change measurements of graphite specimens with and without a coating respectively at 700 and 1200°C as shown in Figs. 5 and 6.

As can be seen from Fig. 5, a weight loss of up to 2% for an uncoated specimen is achieved after 30–40 min, while for a coated specimen it takes 250–300 min. Therefore, a boron nitride layer of about 400 μm increases the service life of graphite products at 700°C by 8–10 times. At 1200°C, the effectiveness of the protective coating is even higher (by 12 times); unprotected graphite is burned very quickly at this temperature.

This study shows that boron nitride coatings make possible the use of protected graphite products at temperatures over 1000°C for a short time (several hours). The results widen significantly the range of graphite application in nonferrous metallurgy and in glass production. The structure of the boron nitride coating is similar to the graphite one and, therefore, it adheres well to the substrate after fast heating or fast cooling.

SUMMARY

1. The formation of a boron nitride coating on graphite substrates is obtained by using graphite carbon as a reducing agent for boron oxide vapors in an ammonia atmosphere.
2. BN coatings are formed both on specimens heat-treated in a sinter and on specimens heat-treated in a flow of boron oxide–ammonia gas phase.
3. The highest rate of BN layer formation (2.8–3.2 μm/min) on graphite occurs when the graphite is heat-treated inside the sinter at 1700–1750°C.
4. Boron nitride coatings (350–500 μm thick) improve oxidation resistance of graphite in air at a temperature of 700°C by a factor of 8, and at 1200°C by a factor of 12.

REFERENCES

1. T. Kosolapova, "Non-metallic Refractory Compounds," p. 88, Metallurgiua, Moscow, 1985.