THERMODYNAMIC CONSIDERATION ON OXIDATION OF CARBON/B_4C/SiC/ZrB_2 COMPOSITE IN MOIST AIR AT ELEVATED TEMPERATURE

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INTRODUCTION

Carbon and graphite materials are widely used for high temperature engineering materials, because of its excellent properties. However, the most serious failure of these materials is lacking in oxidation resistance at high temperature. Carbon/B_4C/SiC composite had an excellent property against high temperature air oxidation above about 1000°C and the oxidation resistant property was due to the surface oxide layer acting as a protective layer [1,2].

We have reported that in the presence of moisture at 800°-900°C, oxidation of carbon/B_4C/SiC composite proceeded extensively from surface to inside through the less protective layer [3,4]. It is considered that the degraded resistance to oxidation results from the oxidation-produced protective layer over B_2O_3 reacts with steam to produce HBO_2(g), $(HBO_2)_3$(g), and H_3BO_3(g) and the layer lose its protective functions [5].

In this study, the formation of oxide layer structure of the composite at 900°C in moist air was considered thermodynamically.

EXPERIMENTAL

The sample used for oxidation test was carbon/B_4C /SiC/ZrB_2 composite. The composite was fabricated from the mixed powder of coke of 47.6, B_4C of 4.8, SiC of 38.1 and ZrB_2 of 9.5 mass% and was sintered at 2150°C under atmospheric pressure of Ar. Oxidation tests were carried out in an electric furnace for the sample with 5x 5x60 mm in size at 900°C with reaction time 3.6-36ks in moist air. The moist air atmosphere contains 36vol% steam.

After oxidation, an influence of oxidation was investigated by measuring mass change, observing morphology of cross section of the sample by SEM, and analyzing depth profile of B and Si by Ion Micro Analyzer (IMA) and identifying the phase formed by X-ray diffractometry (XRD). The formation of oxide layer structure of the composite at high temperature was considered by means of thermodynamic calculations. The calculations were performed using JANAF data [6] and assuming activity of condensate phases equaled 1.

RESULTS AND DISCUSSION

Figure 1 shows SEM photograph for the cross section of the composite after oxidation at 900°C in moist air for 5 h. The temperature of 900°C was that at which oxidation occurred aggressively, and oxidation proceeded to the inside. Two different regions were clearly observed in Fig. 1. One was an outer porous region and the other was an inner dense region. From IMA and XRD results, carbon and boron element disappeared at the outer porous region, and Si element condensed in the outer porous region nearby surface. In the inner dense region, small quantity of ZrO_2 was formed. It indicated that oxidation proceeded to the inner dense region.

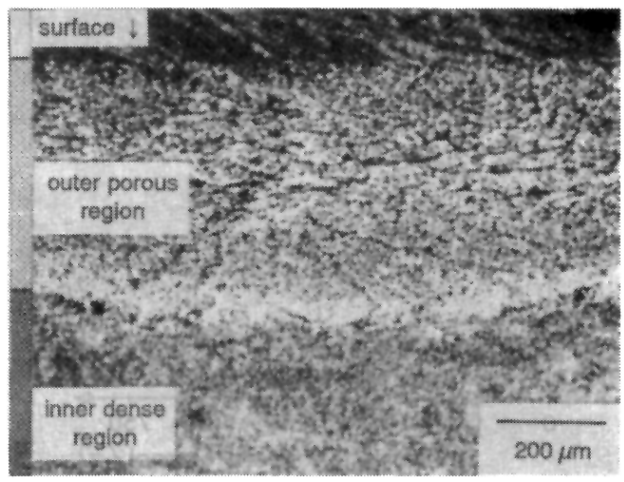

Fig. 1. SEM micrograph of the polished section of the composite after oxidation at 900°C in moist air for 5 h.

Figure 2 shows illustration of Fig.1 with its formation mechanism of oxide layers estimated from experimental results and thermodynamic considerations. We found that the oxidized sample has four regions by experimental results. At the beginning of oxidation, carbon, B_4C, ZrB_2 and SiC changed respectively to CO(g), B_2O_3(l), ZrO_2(s) and SiO_2(s). Here, as a reason for the reactivity of SiC [4], the reaction between SiC and O_2(g) or H_2O(g) was not so high at 900°C. B_2O_3(l) reacted with H_2O(g) immediately and formed HBO_2(g), $(HBO_2)_3$ (g) and H_3BO_3(g), therefore oxidation of carbon

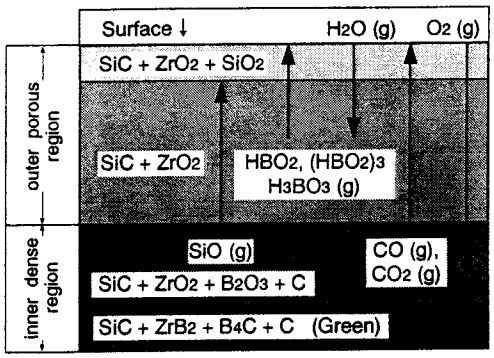

Fig. 2. Illustration of the composite after oxidation estimated from experimental results and thermodynamic considerations.

progressed simultaneously [5]. When the oxidation proceeded to the inside, the oxygen pressure at the inside oxidized region was lower than that at the nearby surface oxidized region. This phenomenon caused that four regions were built up into the composite in the following way.

Figure 3 shows Ellingham diagram that includes carbon, B_4C, SiC and ZrB_2. From this diagram, the equilibrium pressure of oxygen (PO_2) at oxidation/ reduction reactions for B_4C, SiC and ZrB_2 was lower ($PO_2=10^{-28}$) than that for carbon ($PO_2=10^{-19}$).

Oxidation of B_4C, SiC and ZrB_2 proceeded from surface to the inner dense region, but oxidation of carbon limited only in the outer porous region in the composite (Fig.2).

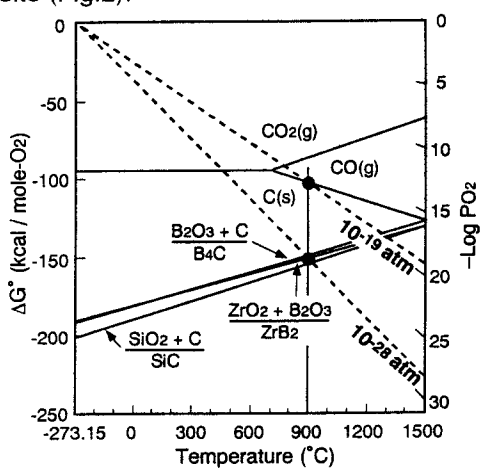

Fig. 3. Ellingham diagram for the C, B_4C, SiC and ZrB_2.

This distribution of oxygen also caused condensation of $SiO_2(s)$ in the outer porous region nearby surface. Figure 4 shows vapor pressure of SiC(g), SiO(g) and $SiO_2(g)$ with oxygen pressure (PO_2) at 900°C calculated thermodynamically. The vertical line indicating the equilibrium pressure ($PO_2 = 10^{-28.83}$atm) describes a

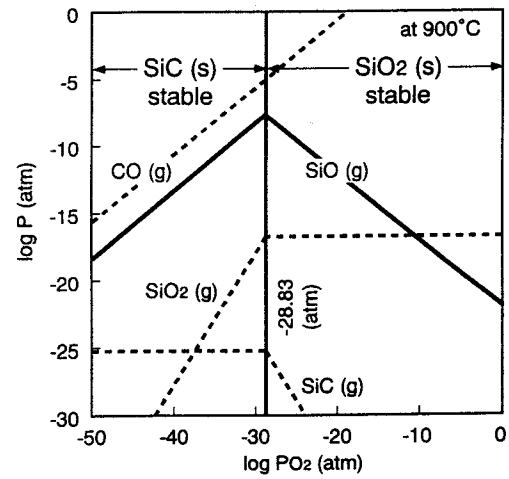

Fig. 4. Vapor pressure of gas phase for the SiC-O_2 system with oxygen pressure at 900°C calculated from thermodynamics.

boundary between the SiC(s) stable region and the $SiO_2(s)$ stable region calculated from following reaction ; $SiC(s) + 3/2O_2(g) = SiO_2(s) + CO(g)$. The vapor pressure of SiO(g) increased with the increase of PO_2 in the SiC(s) stable region because of oxidation of SiC(s) with following reaction ; $SiC(s) + O_2(g) = SiO(s) + CO(g)$, and decreased in the $SiO_2(s)$ stable region because of reaction between SiO(g) and $O_2(g)$; $SiO(s) + 1/2O_2(g) = SiO_2(s)$.

SiC changed to SiO(g) at the inside oxidized region, and SiO(g) reacted with $O_2(g)$ to produce $SiO_2(s)$ in the nearby surface region because of the oxygen pressure became high (Fig.2).

CONCLUSIONS

Formation of oxide layer structure was estimated at 900°C in moist air, and four layers with different components were considered by thermodynamic calculations.

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