REACTIVE HOT PRESSING OF CARBONIZED RICE HULLS TO SiC CERAMICS WITH THE ADDITION OF VARIOUS METAL OXIDES

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Introduction

Because of the intimate contact of so reactive carbon and SiO_2 when the rice hulls are carbonized (1), it had been thought that the formation and sintering of β SiC had proceeded at the same time with a hot-press if carbon to SiO_2 molar ratio could be properly adjusted. We successfully developed these procedures for the porous β SiC ceramics with the addition of iron compound(2.3). The porous β SiC ceramics have potential uses for thermoelectrics (4,5), catalyst support (6), high temperature heat storage(7) and so on. Some of these studies have shown that microstructures of β SiC ceramics , as well as stacking fault in β SiC are important for these purposes. Also β SiC ceramics have a potential use as composites with metal silicides(8). So far, there have been some papers which deal with carbothermal reduction of carbonized rice hulls to SiC with the addition of Fe(9,10,11) ,Co(10,11), and Ni(10,11). These were for the reaction under one atmosphere, that is , in a flow of inert gas. Also it has been found that the addition of Fe compound leads to the β SiC ceramics which have smaller stacking faults(3).

Here we investigated the effect of various metal oxides on the formation of SiC by reactive hot pressing of the carbonized rice hulls, and also grain growth and stacking faults of the resultant SiC.

Experimental

The rice hulls had been chopped into 17x50 mesh in size (Sumitomo Bussan, Japan) and carbonized at 773 K in a flow of nitrogen. Because the carbon content in the carbonized rice hulls used (molar ratio of C to SiO_2=7.5) was in a large excess compared to the stoichiometric molar ratio of 3.0 for synthesis of SiC, a part of carbon was burned-off in a range of 36～40 wt% at an oven temperature of around 623 K. The each oxidized samples were joined altogether. The molar ratio of carbon to SiO_2 in the rice hulls char, which had been previously heat-treated at 1273 K for 1 hr in Ar, was 2.2. This value shows a large deficient in carbon for 3.0. 0.01 M metal oxide and 18.0g of the oxidized rice hulls char were mixed by slurring in CH_3OH. Sixteen metal oxides from the IVa to the Ib group in the Periodic Table of the elements were used. The temperature of the hot-press was raised manually up to at around 1523 K and then programmed at a rate of 20 K/min up to 2173 K and 15 K /min from 2173 K to 2323 K. The hot-pressing pressure was, if unless otherwise stated, 14.7 Mpa. in Ar atmosphere.

Results and Discussion

In the carbothermal reduction of SiO_2 to β SiC, CO generates(1). Under the hot-pressing conditions, there occurred a large shrinkage with an increase in temperature, particularly during SiC formation(2). The total shrinkage is thought to be due to the decrease of voids between the particles, volatile matters at higher temperatures than 773 K, the decomposition of oxygen complexes on the oxidized rice hulls char, carbothermal reduction of SiO_2 to SiC and the reaction to their carbides or silicides, if metal oxide other than SiO_2 exists. In this study, the total shrinkage difference between with and without metal oxide was evaluated. As the formation of SiC without metal oxide was only a trace amount, then the shrinkage difference between them is thought to show the extent of the reaction to SiC. It is plotted on the group of the Periodic Table of the elements in Fig. 1.

It is found from Fig. 1 that the shrinkage of the oxides of the first row elements are essentially larger than those of the second and the third row elements and particularly the oxides of the VIII group are largest among the first row elements. As many researchers pointed out that the transition metal oxides such as Fe, Co and Ni were changed to their silicides after the carbothermal reduction of SiO_2(9,10,11), in this study Cr, Mn, Pd, Pt and Ru silicides were also identified in addition to FeSi, CoSi, $CoSi_2$ and Ni_2Si for all the metal oxide which have some catalytic effect at 1973 K. Because the reaction to SiC was found to proceed from the surface to the center of the compact, the completion of the reaction could be found by cutting the center of 3x3 mm SiC compact and seeing the unreacted carbon. The completion was seen for the SiC compacts which were formed with the addition of Fe(III), Co(II), Cr(III) and Mn(II) oxides. And because of the small shrinkage difference between the second, the third row elements and no metal oxide at 1973 K, the shrinkage measurements were carried out to see the effects of those oxides at 2073 K. The results are given in Fig. 2. The shrinkage of V(V), Mo(VI), W(VI), Pd(II) and Ru(IV) oxides are larger than that of no metal oxide. This means that these metal oxides also have catalytic effects. Ti(IV), Nb(V) and Ta(V) oxides, which have almost same shrinkage with no metal oxide, were changed to their carbides at 1973 K. It required higher temperatures than 2173 K to detect their silicides. The stacking faults of the resultant β SiC with the addition of the first row elements' oxides of the VIII group were smallest. Also the effect of C/SiO_2 molar ratio on the formation of SiC without metal oxide and the ratio of slicide to carbide in the SiC which was obtained with the addition of Nb_2O_5, will be shown in the conference.

Conclusions

The oxides of the first row elements of the VIII group in the of the periodic table are most active catalysts for the formation of SiC under the hot-pressing conditions. In all of the groups, the catalytic effects are decreased with the first row > the second row > the third row elements. Silicide formation is necessary to obtain small stacking faults of β SiC. It was ascertained that some metal oxides were changed from carbide to slicides with an increase in temperature. This procedure gives a convenient way to porous β SiC with small stacking faults.

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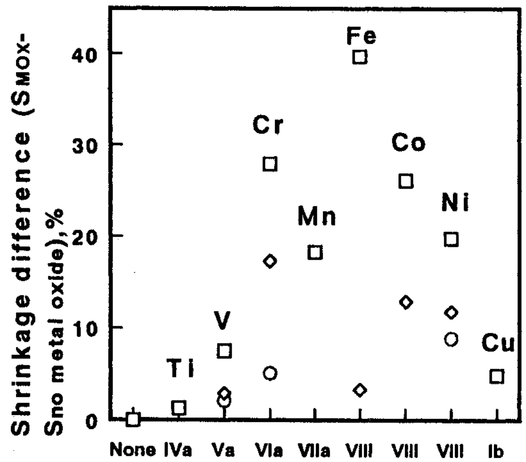

Figure1. Shrinkage difference between with and without metal oxides at 1973 K.
□,1st row; ◇,2nd row; ○,3rd row elements.

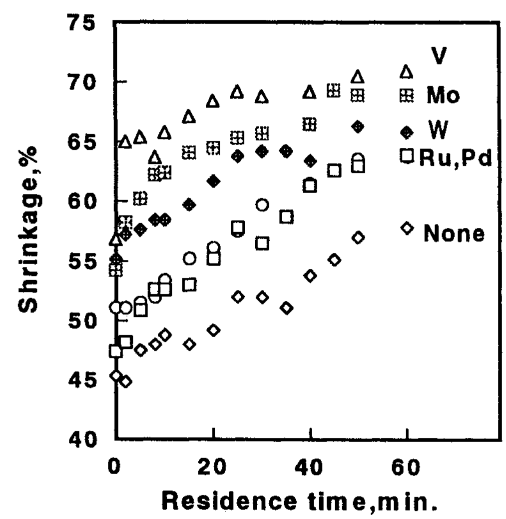

Figure 2. Shrinkage curves during hot-pressing at 2073 K.