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Chemical interactions between B_4C and stainless steel at high temperatures

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Abstract

With a view to investigating the chemical interactions between B_4C and type 304 stainless steel, the reaction couples of these two materials were isothermally annealed in the temperature range between 1073 and 1623 K. As a result of the chemical interactions, complicated reaction layers were formed at the interface of the reaction couple. To evaluate the reaction kinetics, the decrease in the thickness of stainless steel and the reaction layer growth were measured as a function of temperature and time. The overall reaction generally obeyed the parabolic rate law. Both a parabolic rate law constant and an apparent activation energy were determined. A discontinuity in the temperature dependence of the parabolic rate constants was found in the temperature range between 1473 and 1498 K. This corresponds to the formation of the liquid phase at the reaction interface.

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1. Introduction

Neutron absorber materials and structural materials such as Inconel and stainless steel are minor components of the reactor core of an LWR. They are thermodynamically not stable with each other at a temperature level assumed in a severe accident, thus chemical interactions may occur to form liquid phases prior to the melting of the fuel rod components during the accident.

A 1000 MW_e class BWR contains about 1200 kg B_4C and about 17000 kg stainless steel as a control rod component in the reactor core. The weights of these materials are equivalent to about 0.6% and 8% of the total core materials inventory, respectively. B_4C has a very high melting temperature of about 2620 K and it keeps compatibility with other components during normal operation. However, a couple of the bundle degradation experiments using BWR type fuel assemblies showed that the liquid phase formed in the control rod region significantly influences the damage of the surrounding fuel rods [1,2].

Parallel to the bundle experiments, so-called separate effect tests [3,4] in a laboratory scale have been performed. The tests aimed to obtain basic information to evaluate the initial stage progression of fuel assembly degradation in severe accidents, namely to obtain a quantitative data set of core materials interactions as a function of temperature and time. The chemical interactions between B_4C and stainless steel were extensively investigated up to 1473 K by Hofmann and Veshchunov [5,6]. They made in their study microstructural observations, chemical analysis of the reaction layers, evaluation of the reaction rate and modelling. However, they could not obtain the isothermal annealing data above 1473 K, since the sample became completely liquefied within a short time as a result of the formation of a eutectic. For the severe accident analysis purposes, it is very important to obtain the reaction rate at temperatures where significant liquefaction occurs in a short time. Therefore, we performed the experiment in a wider temperature range up to 1623 K. The investigation was rather focused on the high temperatures above that of the formation of the eutectic.

2. Experimental procedure

B_4C and type 304 stainless steel were used in the interaction tests. Stainless steel is hereinafter abbreviated

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as SS. A reaction couple consisting of an SS crucible and a B_4C pellet, schematically illustrated in Fig. 1, was used for isothermal annealing tests. The size of the crucible was 16 mm in outer diameter, 10 mm in inner diameter, 12 mm in height and 7 mm in depth. The B_4C pellet having a slightly smaller diameter than the inner diameter of the crucible was used to get a good contact in coupling. To investigate the influence of the physical form of B_4C, reaction couples consisted of B_4C powder and SS crucible were also tested. The weight of the B_4C powder, about 470 mg, used in a test was the same as that of the pellet. The density of the B_4C powder was 1.44 g/cm^3, while that of the pellet was 1.55 g/cm^3. The particle size was less than about 100 μm. The purity of B_4C pellet and powder was 99 wt% which contained 0.02 Si, 0.02 Fe, 0.01 Ca, 0.005 wt% Al, etc. as impurities.

Reaction couples were isothermally heated in a resistance furnace or an infrared furnace at predetermined temperatures between 1073 and 1623 K in argon at atmospheric pressure. The resistance furnace was used for rather long time annealing up to 2.5×10^6 s (696 h) at relatively low temperatures. The infrared furnace was used for the test at relatively high temperatures above 1473 K because of its excellent capability of both the rapid heating and cooling rates, which allowed short-time isothermal annealing of specimen. The heating rate was 10 K/s. After each annealing test, the reaction couple was mounted in epoxy and was vertically cut at its center line to polish the specific surface for metallurgical examination including elemental analysis with an EPMA and a SEM/EDX, WDS.

3. Results and discussion

3.1. Reactions between B_4C pellet and SS

3.1.1. Reactions below the eutectic formation temperature

In the temperature range below 1473 K, the experimental results obtained in the present study were mostly agreeable to those by Hofmann et al. [5]. Two reaction layers were formed mainly in the stainless steel region by the chemical interaction below 1373 K as shown in Fig. 2. The thin first layer adjacent to B_4C had a rather homogeneous appearance and the second layer was the SS matrix containing a considerable amount of precipitates inside grains and/or on grain boundaries. The detailed chemical analysis [6] showed that the first layer consisted of two layers of MeB (Me = Fe, Cr, Ni) and Me_2B, and the precipitates in the second layer consisted of Me_2B. Generally, diffusion of carbon was observed neither in the reaction layer nor in the SS matrix. This is explained by the observation that the formation of the compact (Fe, Cr, Ni) boride layer at the interface interrupts the diffusion of carbon into the SS [5]. On the other hand, in the latter paper [6], the authors showed diffusion and precipitation of a small amount of carbon deeper in the SS region than boron, and this was explained by the carbon diffusion in the early stage of the interaction process where the (Fe, Cr, Ni) boride layer was not formed homogeneously. Carbon-rich precipitates were found in the first layer of some samples in the present study. However, the precipitation was quite localized and did not affect the formation of the reaction layer. Therefore, diffusion of carbon and precipitation of a carbon-rich phase can be neglected fundamentally in the consideration of the reaction mechanism. The present results on the behavior of Cr and Ni in the reaction layers where boron diffused and the boride phases precipitated agreed with that observed by Hofmann et al. [5], namely the Cr concentration increased and the Ni concentration decreased in the reaction layer.

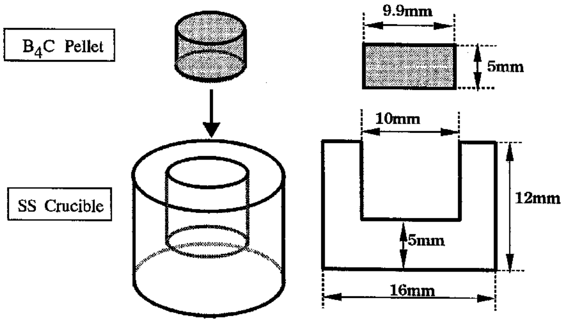

Fig. 1. Schematic illustration and geometry of the reaction couple.

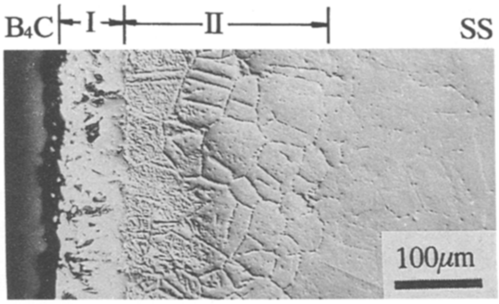

Fig. 2. Microstructure of the reaction layers in the B_4C pellet/SS reaction couples annealed at 1173 K for 1.2×10^6 s.

3.1.2. Reactions above the eutectic formation temperature

The cross-sections of the reaction couple heated at 1473 K for 9×10^4 s (25 h), 1498 K for 1.8×10^3 s (0.5 h), 1523 K for 3×10^2 s, and 1623 K for 90 s are shown in Fig. 3. The shape of the reaction layers clearly indicates the liquid phase formation at these annealing temperatures. The thickness of the reaction layer formed after the annealing at 1473 K for 25 h was about 1.2 mm. On the other hand, at the temperature of 1498 K which is higher by only 25 K, a thicker reaction layer was formed in 0.5 h. The reaction rate became very high with the increase of the annealing temperature. The decrease in the SS thickness at the bottom side was about 2.1 mm in average in the sample annealed at 1623 K for 90 s. The relocation of the B_4C pellet and the non-uniform dissolution of the SS crucible were often observed in the samples annealed above 1498 K.

The microstructure of the reaction layers formed in the temperature range 1473 to 1623 K are shown in Fig. 4. The structure of the reaction layer formed at 1473 K agreed with the observation by Hofmann et al. [5,6]. Three layers are observed at the interface. The chemical analysis in the reference [6] showed that the thin layer I on the side of B_4C consists mainly of Me_2B (Me = Fe, Ni) containing locally MeB. In the SS area, the region containing precipitates inside the grains and/or on the grain boundaries is seen (layer II). An apparent resolidified layer is observed between these two layers. The morphology of the reaction layer formed above 1498 K is quite different from that at 1473 K. The thin intermetallic compound layer is generally observed adjacent to the B_4C region as it is seen in the microstructure of the sample annealed at 1498 K. It was sometimes broken off by mechanical polishing. The second layer which exhibits the resolidified microstructure accounts for most of the reaction layer thickness. The morphology of the precipitates changes depending on the distance from the interface, which might indicate the concentration gradient of the components in the reaction layer. The layer II was formed in the SS region, although the thickness was much thinner than that of the resolidified reaction layer.

The result of EPMA on the reaction layer formed at 1523 K is shown in Fig. 5. The dark region on the left side is B_4C and the bright region on the right side is SS in the BE image. The reaction layer between them is mostly the resolidified layer. The observation with a microscope on a vertical cut surface of the specimen revealed that the initial interface was located nearly at the boundary between B_4C and the reaction layer. Therefore, it is considered that the reaction layer was considered to be mainly formed in the SS region. The characteristic X-ray image of boron indicates that the distance of the boron penetration into SS is nearly equal to the thickness of the reaction layer. On the other hand, no difference is seen in the distribution of carbon in the reaction layer and the SS region. Diffusion of carbon could be interrupted by the formation of the thin first layer at the interface as explained by Hofmann et al. for the reaction at relatively low temperatures [5]. The Cr concentration seems to be comparatively high in the reaction layer and the Ni concentration seems to be low. The distributions of these elements in the layers are common for the temperature range from 1498 to 1623 K and the distribution of each element in the resolidified layer is similar to that observed in the samples annealed below 1473 K. Therefore, the diffusion or movement of four elements, B, Fe, Cr, and Ni can be considered to play the dominant role on the formation of the reaction layer. Thus, the reaction could be analyzed by the quasi-ternary (Fe + Ni)–Cr–B system as proposed by Veshchunov [6].

For the temperature range above 1523 K, Veshchunov expected that the concentration gradient of Cr in the

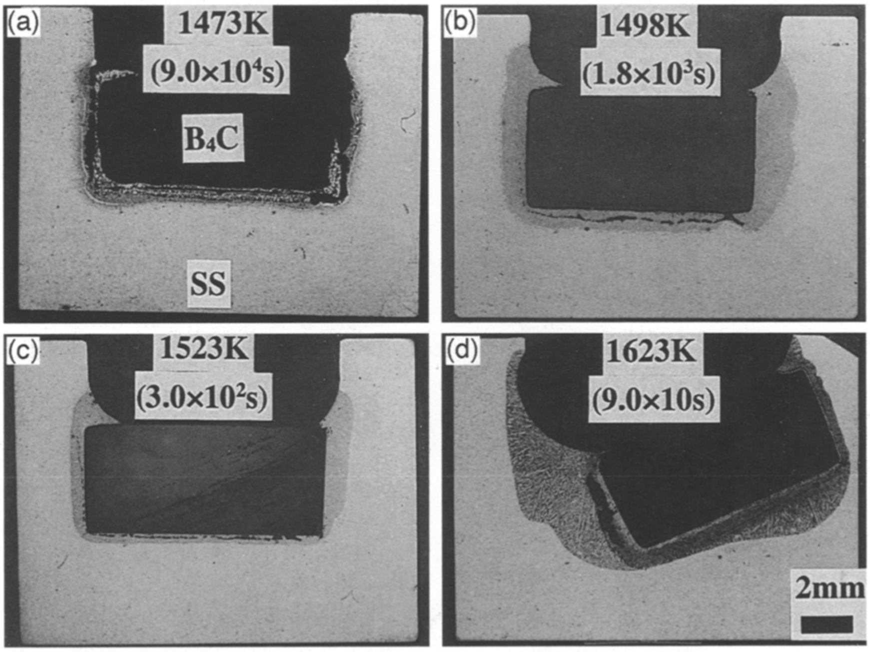

Fig. 3. Cross-sections of the B_4C pellet/SS reaction couples annealed at 1473 K for 9.0×10^4 s, 1498 K for 1.8×10^3 s, 1523 K for 3.0×10^2 s, and 1623 K for 9.0×10 s.

reaction layer is large due to the larger liquid phase area in the phase diagram of the (Fe + Ni)–Cr–B system and the reaction layer growth is accelerated. The apparent tendency of the morphology of dendritic precipitates is seen in Fig. 4, namely the precipitation of dendrites is considered to initiate at the interface between SS and the molten phase. A significant temperature gradient in the molten phase is hardly expected during the cooling down period in the present test. Therefore, such morphology of the precipitates might suggest the concentration gradient of some elements in the molten phase. We analyzed the chemical composition of the resolidified layer formed at 1523 K using a SEM/EDX, WDS. The analyses on both the matrix and the precipitate were performed for two positions in the vicinities of the molten phase/B_4C pellet and the molten phase/SS interfaces, respectively, and the results are summarized in Table 1. Although the number of the analyses is limited and the analysis results especially on the boron concentration contain considerable errors, no obvious difference in the concentration of each element can be found at the two positions.

Table 1
Result of chemical analysis on the reaction layer formed by the B_4C pellet/SS reaction at 1523 K for 6×10^2 s

Position		SEM/EDX [a] (weight fraction)			SEM/WDS (weight ratio)
		Cr	Fe	Ni	B/Fe
B_4C side	matrix	12	77	10	0
	precipitate	34	62	3	0.278
SS side	matrix	13	76	10	0.004
	precipitate	38	58	3	0.233

[a] The SEM/EDX analysis results contain the measurement errors less than 1 wt%.

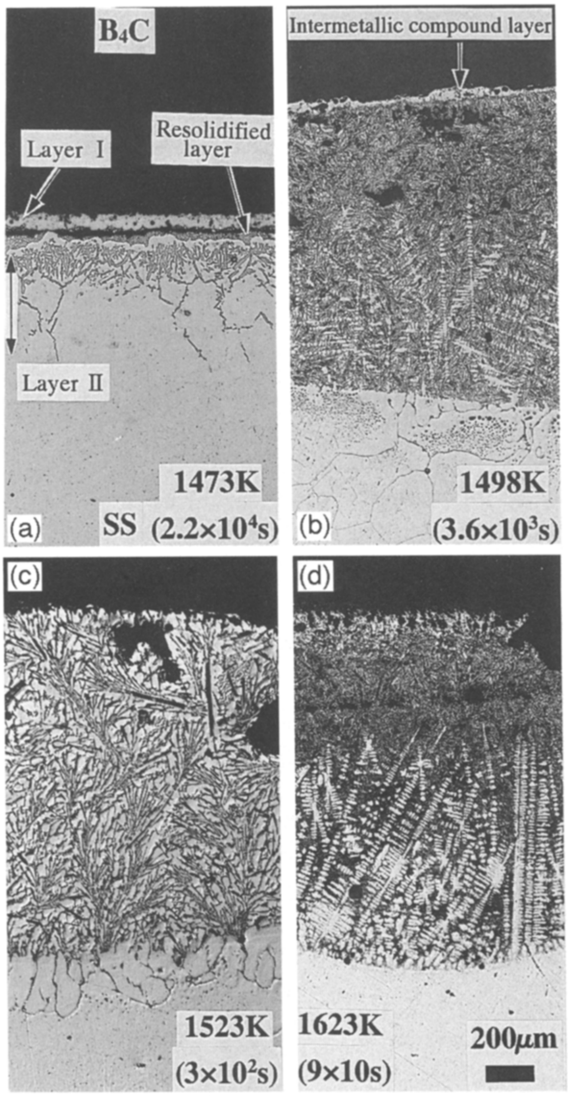

Fig. 4. Microstructure of the reaction layers in the B_4C pellet/SS reaction couples annealed at 1473 K for 2.2×10^4 s, 1498 K for 3.6×10^3 s, 1523 K for 3.0×10^2 s, and 1623 K for 9.0×10 s.

3.2. Reactions between B_4C powder and SS

Macrophotographs of the cross-sections of the B_4C powder/SS reaction couples heated at 1523 K and 1623 K are shown in Fig. 6. Not only the dissolution of the SS crucible, but also the penetration of the molten material into the B_4C powder region occurs, which is considerably different from the reaction behavior observed in the B_4C pellet/SS reaction. A microphotograph of the reaction layer of the sample heated at 1523 K is shown in Fig. 7. The about 200 μm thick layer adjacent to SS is quite similar to the resolidified reaction layer formed at the B_4C pellet/SS interface at 1523 K. This could be formed by the penetration of boron into SS. The microphotograph indicates that the melt formed at the initial interface invaded into the B_4C powder region through the space between particles and interacted with the B_4C particles. EPMA showed that the bright phase, i.e., the resolidified melt, consists mainly of Fe, Cr, and B. The analysis also indicated the relatively high C and Ni concentrations and the lower Cr concentration in the dark ring region surrounding the residual B_4C particles.

3.3. Reaction kinetics

The reaction layer thickness was measured in the samples annealed at temperatures below 1473 K for the evaluation of the reaction kinetics. In the measurement, the EPMA result was referred to confirm the distance of the boron penetration into the SS region which corresponded well to the reaction layer thickness. On the other hand, it was not possible to evaluate the reaction kinetics based on the thickness of the reaction layer for the temperature range above 1498 K, since the B_4C pellet often relocated from its original location in the B_4C pellet/SS test and the liquid phase formed at the interface invaded into the B_4C powder region in the B_4C powder/SS test. Therefore, the decrease in the SS crucible thickness at its bottom side was measured to evaluate the reaction kinetics for the higher temperature range. In the measurement, the cross-section area of the residual SS crucible was measured with an image analyzer on the macrophotograph, thereby the average decrease in the thickness was successfully determined.

Fig. 8 shows the correlation between the growth of the reaction layer and square root of the annealing time in the B_4C pellet/SS reaction for the temperatures below 1473 K. Fig. 9 shows the correlation between the decrease in the

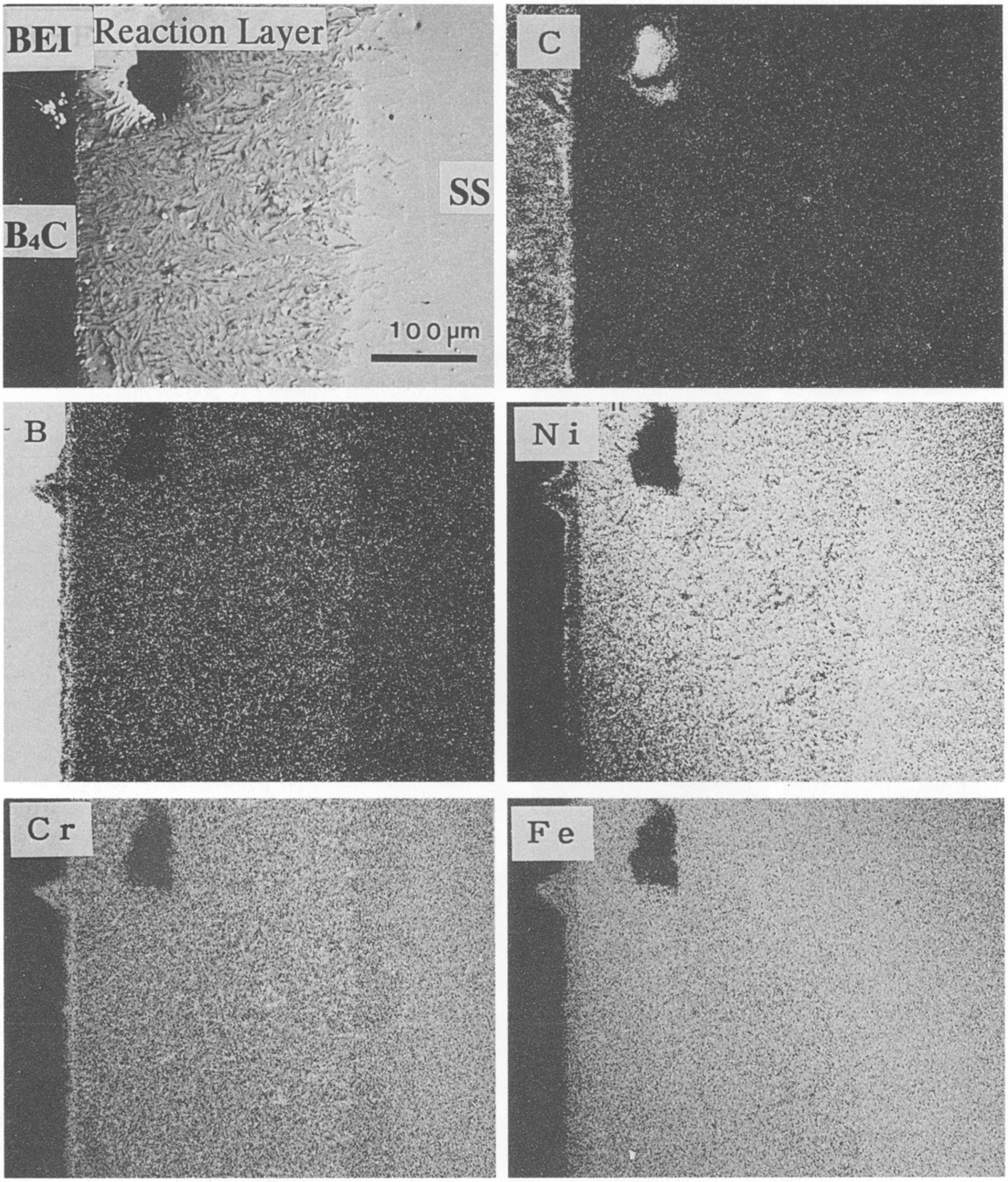

Fig. 5. BEI and characteristic X-ray images at the reaction interface of the B_4C pellet/SS reaction couple annealed at 1523 K for 1.2×10^2 s.

SS thickness and square root of the annealing time for the high temperature range. A linear relationship is generally found at every test temperature for the examined reaction time. Therefore, the progress of the reaction can be described by the parabolic rate law. The rate constant obtained in the present study is not 'the parabolic rate law constant' in a strict sense, since very complicated reaction processes including the formation of the liquid phase are involved in the reaction. However, such reaction rate constants are very useful to predict the possible reaction of core materials in a severe accident. Therefore, the parabolic rate law constant for the reaction, which corresponded to the slope of the lines in the figure, was determined for each test temperature.

The microstructural observation including the EPMA indicates that the thickness of the reaction layer is almost equivalent to the decrease in the SS thickness for the reaction temperatures below 1473 K. Then, all the obtained reaction rate constants are summarized in the same Arrhenius plot as the reaction rates for the decrease in the SS thickness as shown in Fig. 10. Although a slight difference is found in the rate constants between the B_4C(pellet)/SS and the B_4C(powder)/SS reactions in the higher temperature range examined, they agree very well with each other at temperatures below 1473 K. This difference might be caused mainly by the difference in the initial contact condition of the reaction couple and the invasion of the liquid phase formed at the reaction interface into the B_4C powder region. An obvious discontinuity in the temperature dependence of the parabolic rate law constant is seen between 1473 and 1498 K for the both reactions. There are two orders of magnitude of the difference in the reaction rate in the narrow temperature range. Significant growth of liquid phase at the interface as seen in Fig. 4 corresponds to this drastic change of the reaction rate constants. Therefore, the following temperature dependence of the parabolic rate law constant k was estimated separately for the two temperature ranges:

(1) B_4C pellet/SS reaction:

k (m^2/s) $= 1.49 \times 10^{-2} \exp(-250000/RT)$, 1073 to 1473 K.

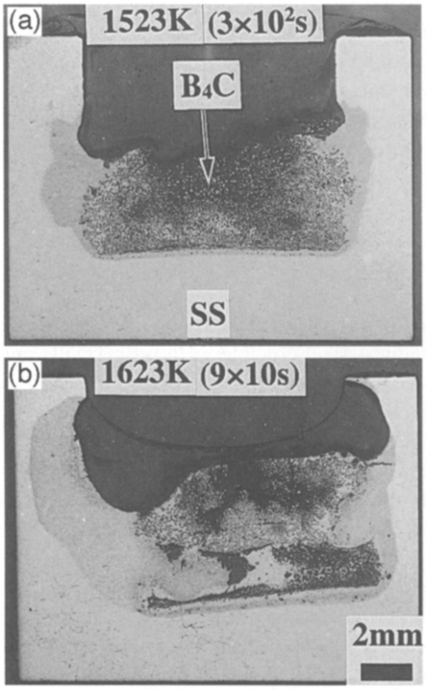

Fig. 6. Cross-sections of the B_4C powder/SS reaction couples annealed at 1523 K for 3.0×10^2 s and at 1623 K for 9.0×10 s.

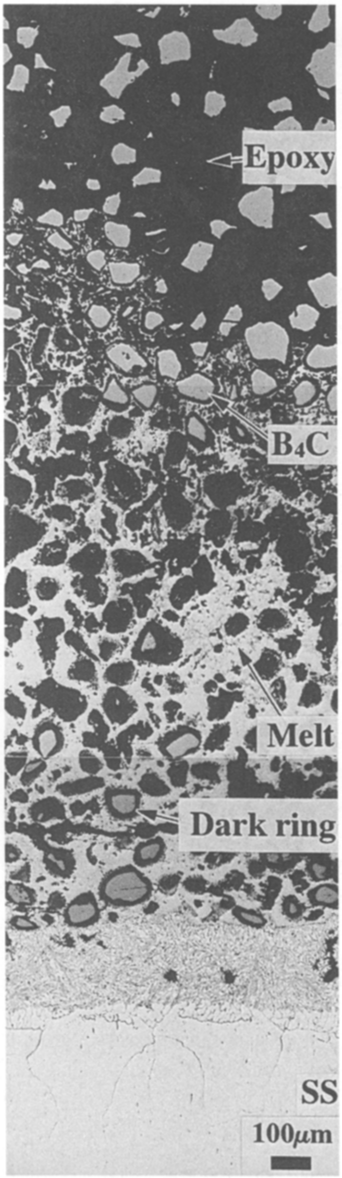

Fig. 7. Microstructure of the reaction layers of the B_4C powder/SS reaction couples annealed at 1523 K for 3.0×10^2 s.

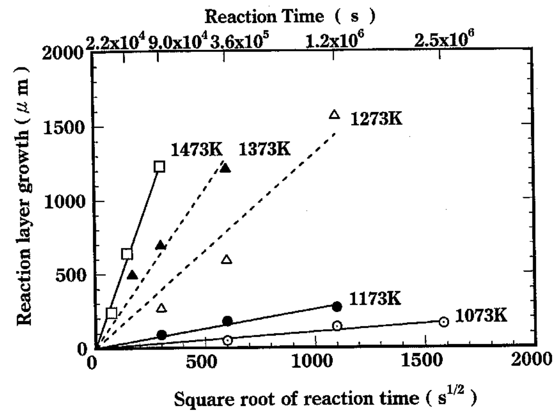

Fig. 8. Correlation between reaction layer growth and square root of reaction time in the B_4C pellet/SS reaction for the lower temperature range.

k (m^2/s) $= 1.40 \times 10^{10} \exp(-549\,000/RT)$, 1498 to 1623 K.

(2) B_4C powder/SS reaction:

k (m^2/s) $= 3.04 \times 10^{-1} \exp(-283\,000/RT)$, 1073 to 1473 K.

k (m^2/s) $= 3.15 \times 10^{7} \exp(-453\,000/RT)$, 1498 to 1623 Kwhere k is the parabolic rate law constant for the decrease in the thickness of SS, R is 8.314 J/K · mol and the activation energy is in J/mol.

The temperature dependence of the parabolic rate law constants in the relatively low temperature range below 1473 K obtained by Hofmann et al. in the B_4C powder/SS reaction experiment [5] are also plotted in the figure for comparison. Although they determined the reaction rates for the reaction layer growth, comparison is possible since the reaction layer is formed mainly in the SS region in the temperature range. The reaction rate constants obtained in both studies are equivalent to each other at 1373 K and 1473 K. However, the reference data show lower values below 1273 K. The reaction layer formed below 1273 K is not uniform in the microscopic scale and the progress of the reaction depends on the initial contact condition. Therefore, the differences might be caused by the different experimental procedures and estimation methods of the reaction amount employed in both experiments. The reaction layer thickness in the sample annealed at 1073 K for 696 h was about 160 μm, so that the difference in the reaction rates at lower temperatures is not so important in the overall severe accident analysis.

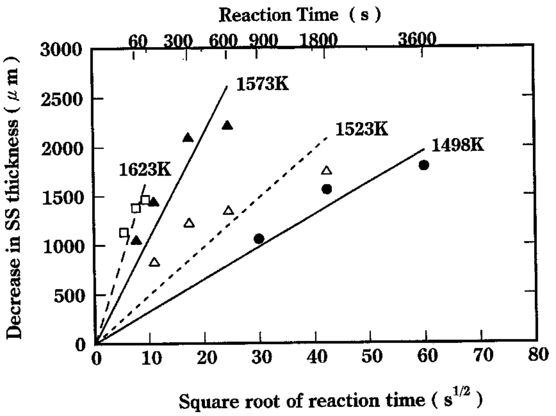

Fig. 9. Correlation between the decrease in the SS thickness and square root of reaction time in the B_4C pellet/SS reaction for the higher temperature range.

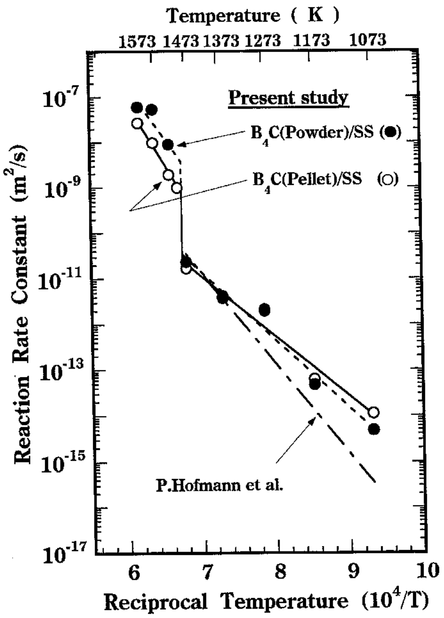

Fig. 10. Arrhenius plot of the reaction rate constants for decrease in the SS thickness of the B_4C/SS reaction.

4. Conclusions

Reaction couples consisting of a B_4C pellet or powder and a stainless steel crucible were isothermally annealed in the temperature range 1073 to 1623 K in argon to investigate the chemical interactions between them.

A significant growth of the liquid phase at the reaction interface was observed in the sample annealed above 1498 K, while the progress of the reactions were limited below 1473 K. To evaluate the reaction kinetics, the decrease in thickness of the stainless steel or the growth of the reaction layer was measured as a function of temperature and time. The overall reaction between B_4C and stainless steel generally obeyed a parabolic rate law, and a parabolic rate law constant for each temperature and an apparent activation energy were obtained. An obvious discontinuity in the temperature dependence of the parabolic rate law constants was seen at the temperature level between 1473 and 1498 K. This could be attributed to the formation of the liquid phase at the reaction interface. The temperature dependence of the parabolic rate law constant k was estimated separately for the two temperature ranges as follows:

(1) B_4C pellet/SS reaction:

k (m^2/s) $= 1.49 \times 10^{-2} \exp(-250\,000/RT)$, 1073 to 1473 K.

k (m^2/s) $= 1.40 \times 10^{10} \exp(-549\,000/RT)$, 1498 to 1623 K.

(2) B_4C powder/SS reaction:

k (m^2/s) $= 3.04 \times 10^{-1} \exp(-283\,000/RT)$, 1073 to 1473 K.

k (m^2/s) $= 3.15 \times 10^{7} \exp(-453\,000/RT)$, 1498 to 1623 K.

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