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COMPATIBILITY OF HEAT RESISTANT ALLOYS WITH BORON CARBIDE

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The solid state compatibility of Hastelloy X and Incoloy 800 with boron carbide (B_4C) were investigated at 850 - 1050°C for periods of 20 - 2000 hrs for potential control rod application for Very High Temperature Gas-cooled Reactor (VHTR). These studies have shown both the alloys were incompatible with nearly stoichiometric B_4C or B_4C+C (70 wt% carbon) and they were less compatible with nearly stoichiometric B_4C than with B_4C+C over the temperature range 850 to 1000°C. At 1050°C for 100 hrs both of the alloys reacted with nearly stoichiometric B_4C or B_4C+C were melt by producing eutectic alloys. It was observed that boron and carbon penetration in the alloy is dominated by the grain boundary penetration. And some had a uniform reaction layer near the surface as a result of volume penetration. In general Incoloy 800 was more compatible than Hastelloy X and it was clearly seen by comparing the volume penetration depth reacted with nearly stoichiometric B_4C at 950°C for 100 hrs. In Hastelloy X the depth was 225μm but in Incoloy 800 it was 117μm. The phases formed on alloys were identified to be Fe_2B, Cr_2B and Ni_2B by X-ray diffraction. By the tensile test of reacted Hastelloy X material, it was found that the ultimate tensile strength was reduced due to the reaction of alloy with boron carbide but there was no change on the yield strength.

Keywords; Compatibility, Heat Resistant Alloy, Boron Carbide, Hastelloy X, Incoloy 800, VHTR, Volume Penetration, Grain Boundary, Tensile Test

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耐熱合金と炭化ホウ素との両立性

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多目的高温ガス炉用制御材である炭化ホウ素とその被覆材候補である耐熱合金のハステロイ－X，インコロイ８００との両立性試験を行った。試験温度・時間は８５０℃～１０５０℃で２０～２０００時間である。試験の結果，１０００℃以下では，合金と黒鉛入り炭化ホウ素（炭素量で７０w／o）との両立性は合金と化学量論組成に近い炭化ホウ素の両立性に比べいく分良いが，両者共反応性に富んでいることが判明した。１０５０℃の試験では反応が著しく，１００時間では共晶合金を生成して，耐熱合金は共に溶融した。インコロイ８００の方がハステロイ－Xより両立性が良く，それは化学量論組成に近い炭化ホウ素との反応層厚さを比べると顕著である。例えば，９５０℃，１００時間で反応層厚さはハステロイ－Xで２２５μ，インコロイ８００で１１７μであった。反応の形態は合金中への炭素，ホウ素の粒界侵入が先行して起こり，続いて，層状の反応生成物の見られるものがあった。合金表面近傍の反応層においては，Fe_2B，Cr_2B，Ni_2Bの生成が認められた。反応前後におけるハステロイ－Xの機械的強度を，引張り試験法により調べた所，炭化ホウ素との反応により強度が減少することがわかった。

＋　大洗研究所材料試験炉部

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1. Introduction

Boron Carbide (B_4C) has been selected as a control rod material in a conceptional design of VHTR (Very High Temperature Gas-cooled Reactor) at JAERI [1]. Since B_4C is used in a form of hot pressed or sintered pellets in contact with metallic alloy as cladding material at high temperatures, a detailed knowledge is required on the compatibility of B_4C pellet with possible metallic alloys. Studies of compatibility of AISI type stainless steel and refractory material with B_4C have been reported in the past by several authors. [2],[3],[4]. No data are obtained of the compatibility between resistant alloys and B_4C. In this light, the study of compatibility of B_4C pellets with Hastelloy X and Incoloy 800 was performed.

2. Experimental

2.1 Materials

2.1.1 Boron carbide

Boron carbide powders were obtained from Denka Boron Co.. Two types of boron carbide were used for comparative purpose. One has stoichiometric composition and another has composition of B_4C+C as shown in table 1. The preparation of the B_4C pellet specimen was made by Mitsubishi Metal Research Institute with hot pressing method.
The condition of pressing is under a pressure of 200 - 250 Kg/cm^2 for 45 hrs at 2000°C in vacuum.
The size of pellets was 10 mm in diameter by 10 mm long.

2.1.2 Cladding materials

The chemical analysis of the alloys are given in table 2. All the specimens were solid solution treated at a temperature above 1100°C and then quenched in water. Both alloy in a form of rod was cut into discs of 5 mm thick and 10-11 mm in diameter. Plain surfaces of the discs were polished electrolytically after polishing them on silicon carbide paper up to 1200 grit.

2.2 Procedure and analysis

Before the test all the specimens were weighed, each metal specimen was sandwiched between B_4C pellets to form the reaction couples which were then stacked within a cylindrical holder made of 304 SS, as shown in fig.1. Additional pressure ($2.0 \times 10^4 N/m^2$) was applied to the specimens by a spring made of Inconel in order to keep the tight contacts among the specimens. The holder was horizontally loaded into a resistance heating furnace and heated in the range of 850 - 1050°C for 20 - 2000 hrs under a dynamic vacuum of better than 1 mPa (10^{-5}Torr) or in a stagnant helium atmosphere. The experimental conditions are shown in table 3. The temperature were measured with a Pt-13 Rh/Pt thermocouple. After the heat treatment, all the specimens were reweighed and metals were sectioned and polished for examinations. Prior to this metallographic treatment all the metals were nickel plated in order to avoid edge-wear of the specimen cross sections during polishing. Penetration depth was measured by metallographic examinations, by means of which measurable depth is limited down to about 1 μm. The reaction products were identified by electron micro-probe analysis and X-ray diffraction analysis. The direct solid-state reaction in a powder form of iron, nickel and chromium with boron carbide, boron and carbon were studied at 1000°C for 100 hrs under a dynamic vacuum of 0.1 - 1 mPa. The reaction products were identified by X-ray diffraction analysis. By the usual tensile test method it was determined the change of tensile properties by reaction.

3. Results and discussion

3.1 Compatibility tests

The amount of the reaction products of alloys with B_4C pellets increased with temperature. The reaction couples heated at temperatures less than about 1000°C were loosely adhered and the each specimen was easily seperated from another specimen of the couple. In the case of tests between alloys with B type B_4C pellets a gray coloured substance covered the whole surface of the B_4C pellets, while in the case of A type B_4C pellets no change was observed in the appearances of the pellets. In the couples heated at 1050°C for 100 hrs Hastelloy X was melt down completely and Incoloy 800 reacted over all the specimen volume. This temperature is below the melting points of the alloy and B_4C. This phenomenon shows that in the results of reaction it was produced an eutectic alloy of a low melting point. This is very important phenomenon to design the control rod system under a condition that the clad and B_4C touches directly.

3.1.1 Weight change measurement

After separating the couples into the B_4C and the alloys, they were weighed with a balance. Most of the alloy specimens reacted with B type B_4C showed weight loss which increased with temperature. On the contrary some alloy reacted with A type B_4C shows the increase of weight. It is mainly due to adhesion of a part of B_4C on the alloy. A type B_4C shows the loss of weight, while B type B_4C shows a weight gain more than a weight loss by the contacted alloy specimen. Such extra weight gain of the B type B_4C pellets may be due to the reaction of B_4C with the evaporated metal from the specimen alloys and stainless steel holder. According to [5] [6], chromium evapolates from the alloy substrate selectively above 800°C.

3.1.2 Attacked depth measurements

In some case the reaction product grew into a layer of nearly uniform thickness under the surface of each alloy. The reaction regions formed at 850 - 1000°C for 100 hrs are shown in fig.2. It is apparent from these figures, preferential growth of the reaction product along the grain boundary was dominant and the uniform reaction layer was also formed under the surface. The attacked depth, respectively in the layer and on the grain boundary, was measured metallographically. Each value listed in table 4 is an average of depth measured. As seen from fig.3 the grain boundary penetration rate in Hastelloy X is as high as that in Incoloy 800. But the volume penetration rate in Hastelloy X is higher than that in Incoloy 800. At 1050°C for 100 hrs the alloys were almost melt by producing eutectic alloys with the element of boron and carbon as shown in fig.4.

3.1.3 Hardness measurements

Micro Vickers Hardness was measured on the cross section of alloys reacted. As shown in fig.5 and fig.6, the surface layer is very hard and the hardness value reaches over H_k=2460 in the case of both alloys with A type B_4C. These hardness value correspond to that of boride. Comparing the combinations of alloys with B_4C pellets, the increasing of hardness of Hastelloy X with A type B_4C is greater than that of others.

3.1.4 Composition change in alloy specimens

Fig.7 shows the distributions of respective elements across the cross section of the alloy specimens measured by line scans with electron microprobe. It is known from the figure boron and carbon penetrate into the substrate from the surface. The penetration rate of boron is higher than that of carbon. Behavior of iron in the substrate is similar to that of nickel. On the other hand the behavior of chromium is similar to that of molybdenum. Where iron and nickel are rich, chromium and molybdenum are depleted. Reaction products in the uniform layer consist of chromium, molybdenum, boron and carbon. Fig.8 is the composition image of the reaction zone by electron microprobe and indicates that the reaction products consist of mainly nickel and iron in the subscale and chromium and molybdenum on the grain boundary. Molybdenum in Hastelloy X distributes on the grain boundary as same as chromium. In the case of Incoloy 800 molybdenum distributes not so clearly as in Hastelloy X.

3.2 Identification of reaction products

The presence of metal borides such as Cr_2B, Fe_2B, Ni_2B was confirmed by X-ray diffraction analysis on the surface of the alloy specimen as shown in table 5. By another experiment using powder material such as iron, chromium and nickel with B_4C, boron and carbon, the reaction products are identified to be Cr_2B, Ni_2B and Fe_2B.
On the surface of B type B_4C pellets of the diffusion couple annealed at 950°C for 500 hrs, it was observed a gray colored thin substance. This substance was identified to be composed of Cr_2B, Fe_2B and a little amount of carbon. The former two reaction products were formed by the reaction of evaporated chromium and iron from the alloys with B_4C.
Fig.9 is the cross section of both alloys reacted with boron and carbon at 1000°C for 100 hrs. It is clear that in the case of alloys-boron interaction the reaction zone appears in the form of layer under the metal surface. On the other hand alloys-carbon interaction shows only grain boundary penetration. By X-ray microprobe analysis, the main metal element in the reaction layer is chromium.

3.3 Evaluation of the compatibility test

Fig.10 is the metal cross section reacted at 850°C for 2000 hrs. In the case of reaction of Incoloy 800 with B type B_4C a little reaction zone is observed after a long period at 850°C, while no reaction is observed at 950°C for 20 hrs. As seen in the figure, in all the range of experimental conditions alloys are more compatible with B type B_4C than with A type B_4C. The volume reaction rate of Hastelloy X is higher than that of Incoloy 800. Hastelloy X is a nickel based alloy while Incoloy 800 is an iron based one as shown in table 2.
This corresponds the difference of compatibility of the alloys.
Comparing with the phase diagrams of nickel-boron and iron-boron, it can be understood the eutectic point of the former combinations is lower than the latter ones. [7] In this point it can be thought that the nickel based alloys are not more compatible than the iron based alloys. From this study it is not clear why only the B type B_4C forms the reaction products such as Fe_2B and Cr_2B on its surface. These products reduce the rate of reaction between the alloys and B_4C as shown in fig.11. In other words, Fe_2B and Cr_2B formed on the B_4C roles the reaction barrier between the alloys and B_4C.
The change of the ultimate tensile strength and the yield strength are shown in fig.12 as a function of temperature in the case of Hastelloy X where the solid line and broken line correspond to the tensile strength of reacted specimen and controlled specimen. While the broken dotted line is the calculated value assuming that volume penetration area dose not contribute to the strength of base metal. By the reaction the ultimate tensile strength was reduced but to ignore the strength of volume penetration area is too coservative to evaluate the effect of reaction.

Summary

1. Hastelloy X and Incoloy 800 were found to be incompatible with stoichiometric B_4C for 100 hrs at temperatures from 850 to 1050°C.
2. Alloys with stoichiometric B_4C are less compatible than those with B_4C+C (70 wt% carbon).
3. The reaction rate of Hastelloy X with B_4C is higher than that of Incoloy 800 with B_4C.
4. Boron and carbon penetration in the alloy is dominated by the grain boundary penetration.
5. The reaction products on the alloy surface are identified to be Fe_2B, Cr_2B and Ni_2B by X-ray diffraction analysis.
6. The ultimate tensile strength of the alloys were reduced by the reaction. But the reaction did not affect on the yield strength of the alloys.

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Table 1 Chemical compositions of boron carbide

Boron Carbide	Tatal B	Total C	Soluble B	B/C
A type (B_4C)	77.95	20.88	0.51	4.15
B type (B_4C+C)	31.51	68.0	0.11	

Table 2 Chemical compositions of alloys

(wt%)

Metals	C	Mn	Si	Ti	S	Cr	Cu	Mo	W	Fe	Ni	Al
Hastelloy X	0.08	0.65	0.03	0.02	0.005	21.98		8.81	0.54	18.38	Bal	<0.02
Incoloy 800	0.03	0.90	0.33	0.36	0.005	20.70	0.21			Bal	33.23	0.44

Table 3 Experimental conditions of compatibility test

Temp (°C) \ Time (hrs)	20	50	100	500	2000
1050	○	○	○△	○△	
1000	○	○	○△	○△	
950	○	○	○△	○△	
900			○△		
850			○△		○△

Note; ○ with B type B_4C

△ with A type B_4C

Table 4 Summary of penetration depth data in alloys reacted for 100 hrs (μm) (*)

Temp. (°C)	Type of B_4C	Hastelloy X		Incoloy 800	
		volume	grain boundary	volume	grain boundary
850	A type (B_4C)	92.2 ± 0.8	230.2 ± 6.3	56.0 ± 0.9	217.2 ± 5.3
	B type (B_4C+C)	—	71.0 ± 4.2	∿10	71.4 ± 7.8
900	A type (B_4C)	140.0 ± 2.5	300.6 ± 8.0	81.0 ± 1.3	361.0 ± 11.7
	B type (B_4C+C)	—	101.6 ± 5.2	—	146.4 ± 11.7
950	A type (B_4C)	225.0 ± 2.4	448.0 ± 8.6	116.6 ± 1.3	328.0 ± 5.8
	B type (B_4C+C)	—	303.0 ± 14.6	—	430.0 ± 10.7
1000	A type (B_4C)	330.4 ± 4.9	668.0 ± 8.9	322.6 ± 2.9	838.6 ± 10.4
	B type (B_4C+C)	—	509.8 ± 27.7	∿20	∿900

(*) All the alloy specimens were melt down at 1050°C for 100 hr.

Table 5 Results of X-ray diffraction from the reaction products formed on alloys

[1] Hastelloy X (reacted with A type B_4C powder, 1000°C, 100 hrs)

dÅ	I/I_o	Fe_2B	Cr_2B	Ni_2B	matrix	B_4C	unknown
2.786	20		○			○(110)	
2.513	12	○ (220)	○	○		○(104)	
2.342	27		○			○(021)	
2.066	100		○		○ (111)		
2.021	27	○ (121)					
1.992	29						
1.963	26		○				
1.823	13	○ {(112) (220)}	○				
1.789	51			○	○ (200)		
1.262	31	○ {(132) (440)}	○	○	○ (220)		
1.078	23	○ (402)					
1.032	13	○ (332)					
0.820	13				○ (331)		
0.819	13						○

[2] Incoloy 800 (reacted with A type B_4C powder, 1000°C, 100 hrs)

dÅ	I/I_o	Fe_2B	Cr_2B	Ni_2B	matrix	B_4C	unknown
2.154	21						
2.079	100	○ (002)	○		○ (111)		
1.799	78		○		○ (200)		
1.270	22	○ {(132) (440)}	○		○ (220)		
1.083	25	○ (402)					
1.036	14	○ (332)					
0.897	13				○ (004)		
0.822	19				○ (331)		
0.820	11						○

Note Fe_2B; ASTM3-1053, Cr_2B; ASTM 18-380, Ni_2B; ASTM 3-883, B_4C; ASTM 6-555

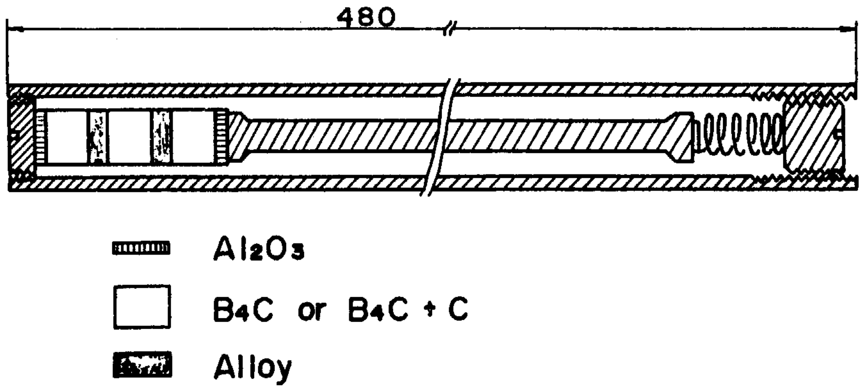


Fig. 1 Schematic diagram of specimen holder and arrangement

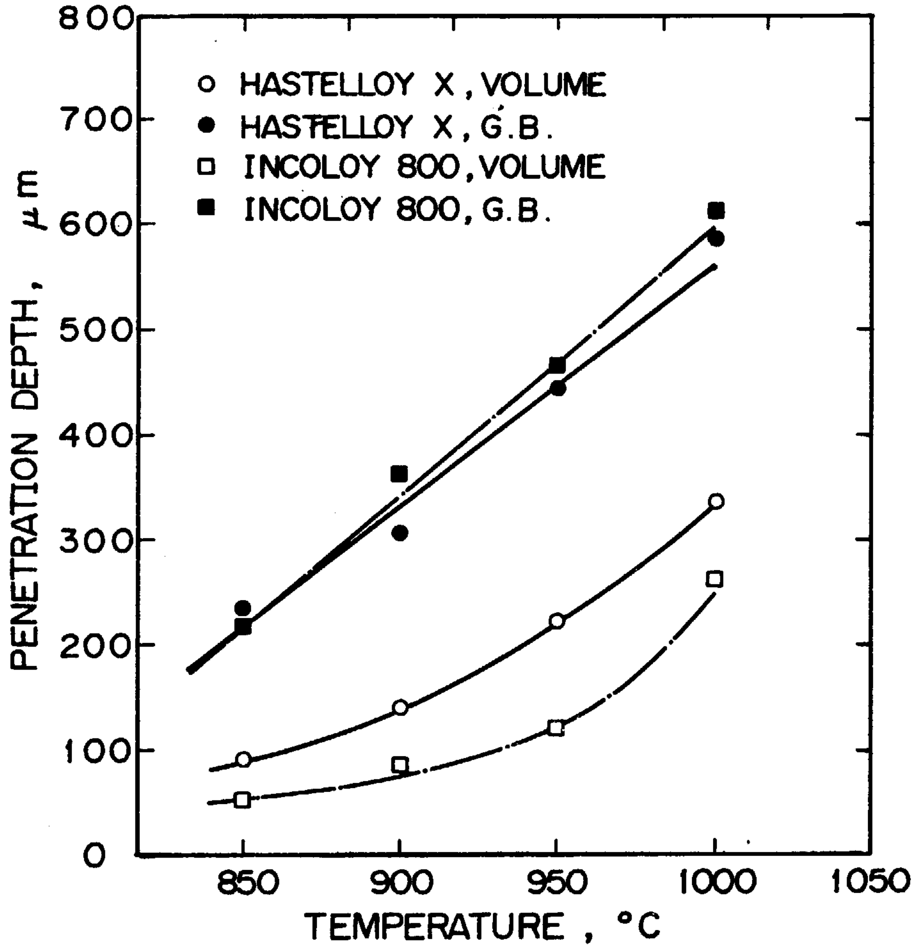


Fig. 3 Relationship between attacked depth and temperature for a reaction period of 100 hrs (Alloys-A type B_4C)

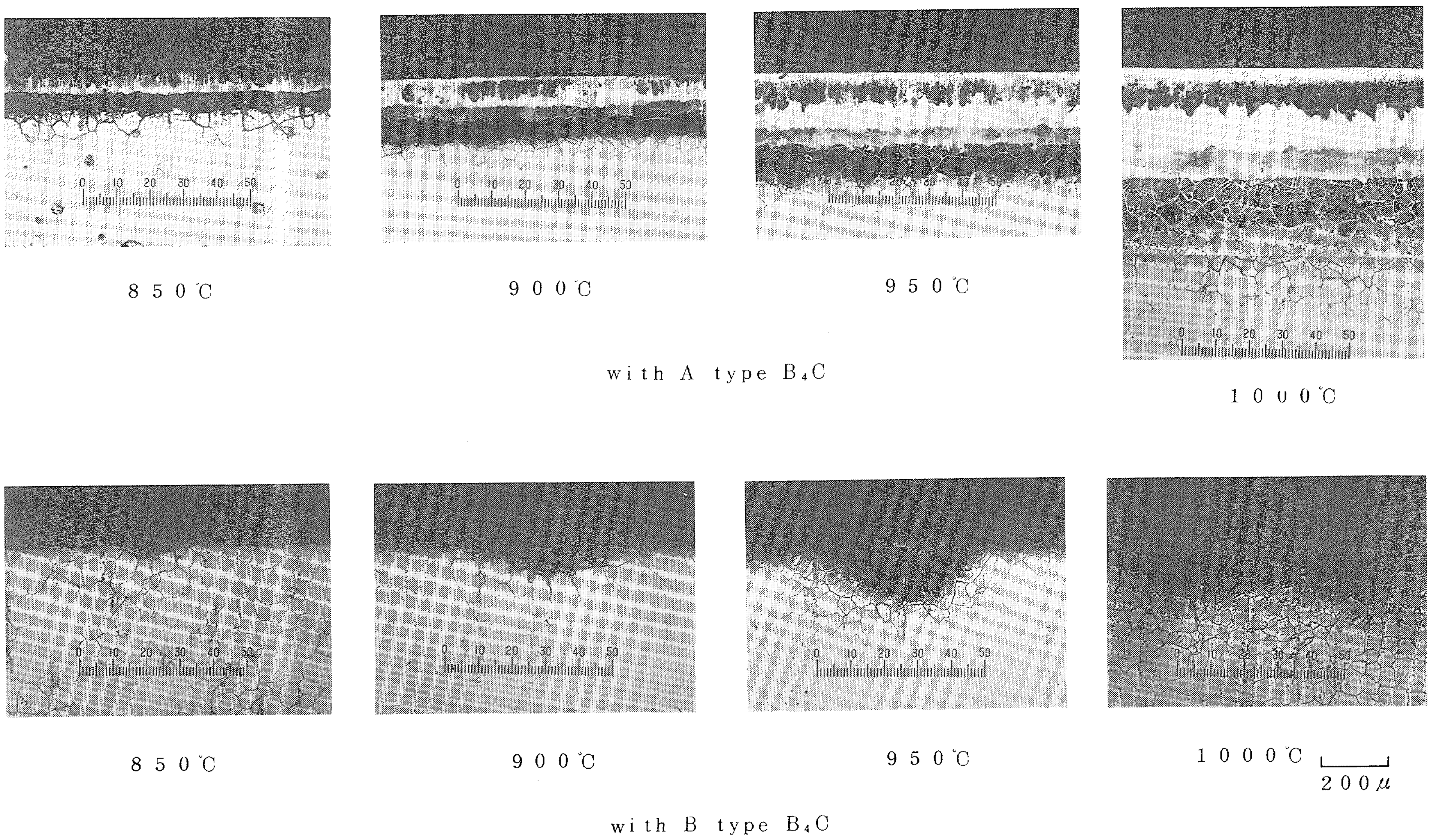


Fig. 2.1 Microstructures of Hastelloy X reacted with B_4C pellets at 850-1000℃ for 100 hrs

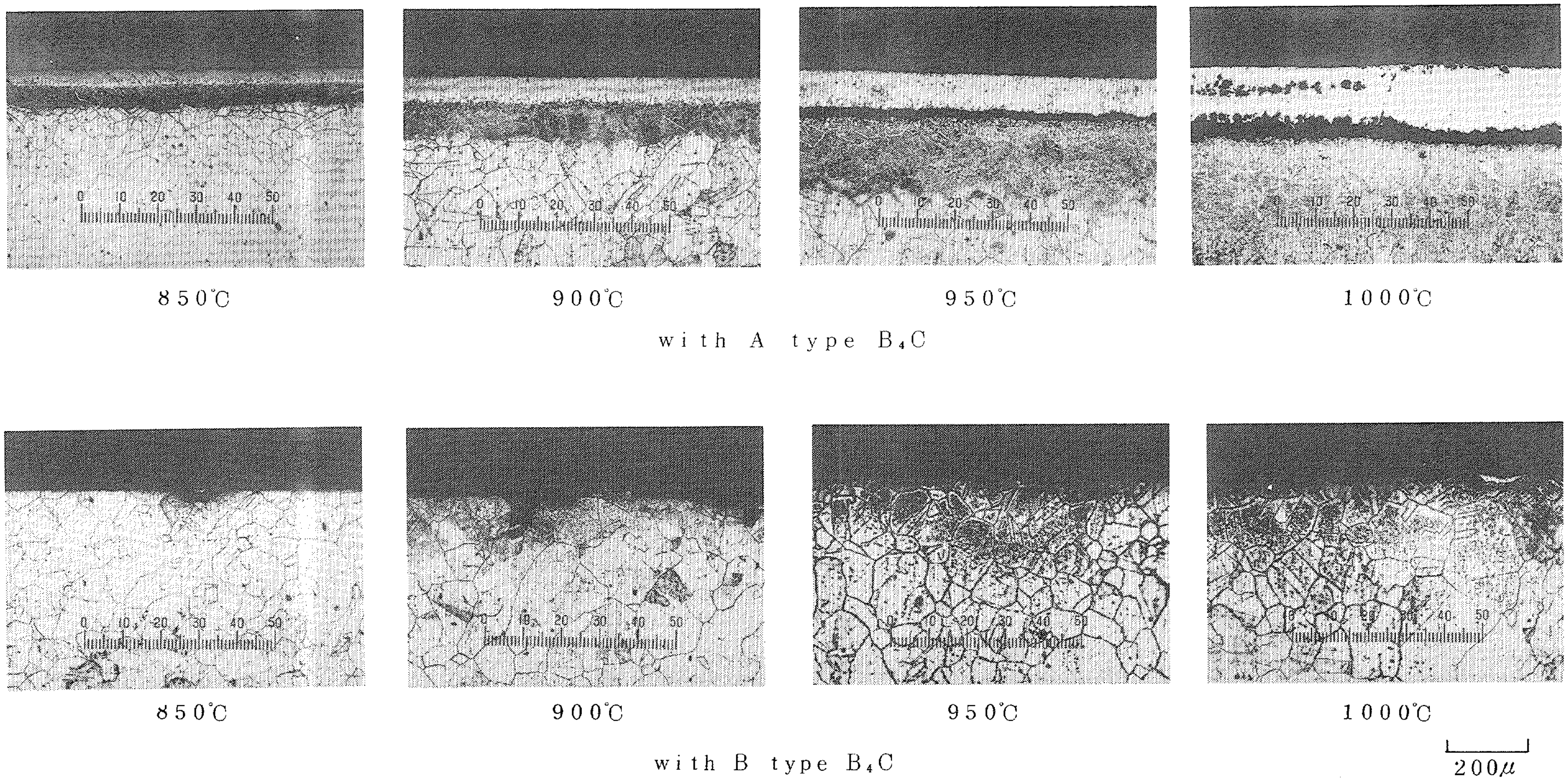


Fig. 2.2 Microstructures of Incoloy 800 reacted with B_4C pellets at 850-1000℃ for 100 hrs

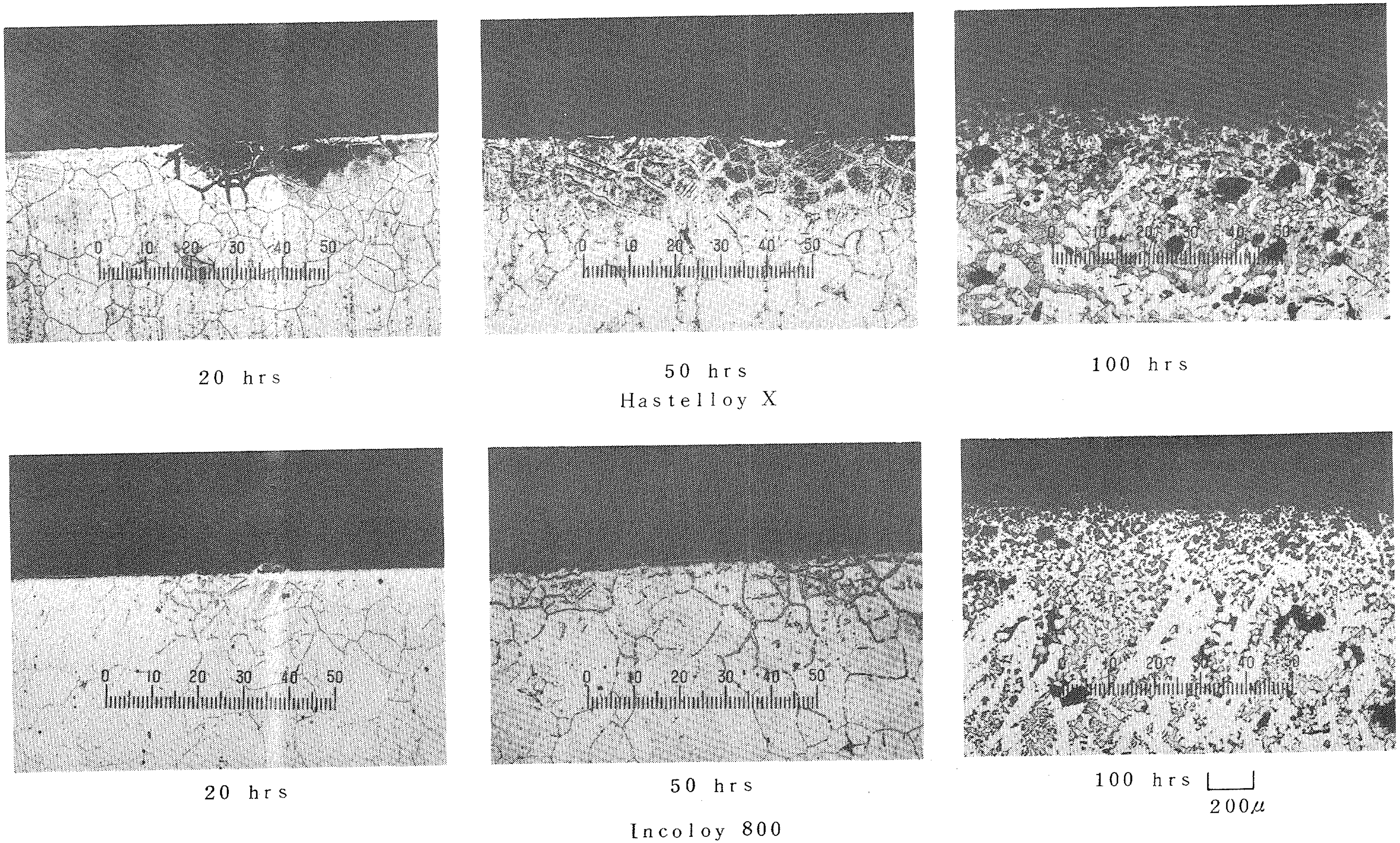


Fig. 4 Microstructures of alloys reacted with B type B_4C at 1050℃

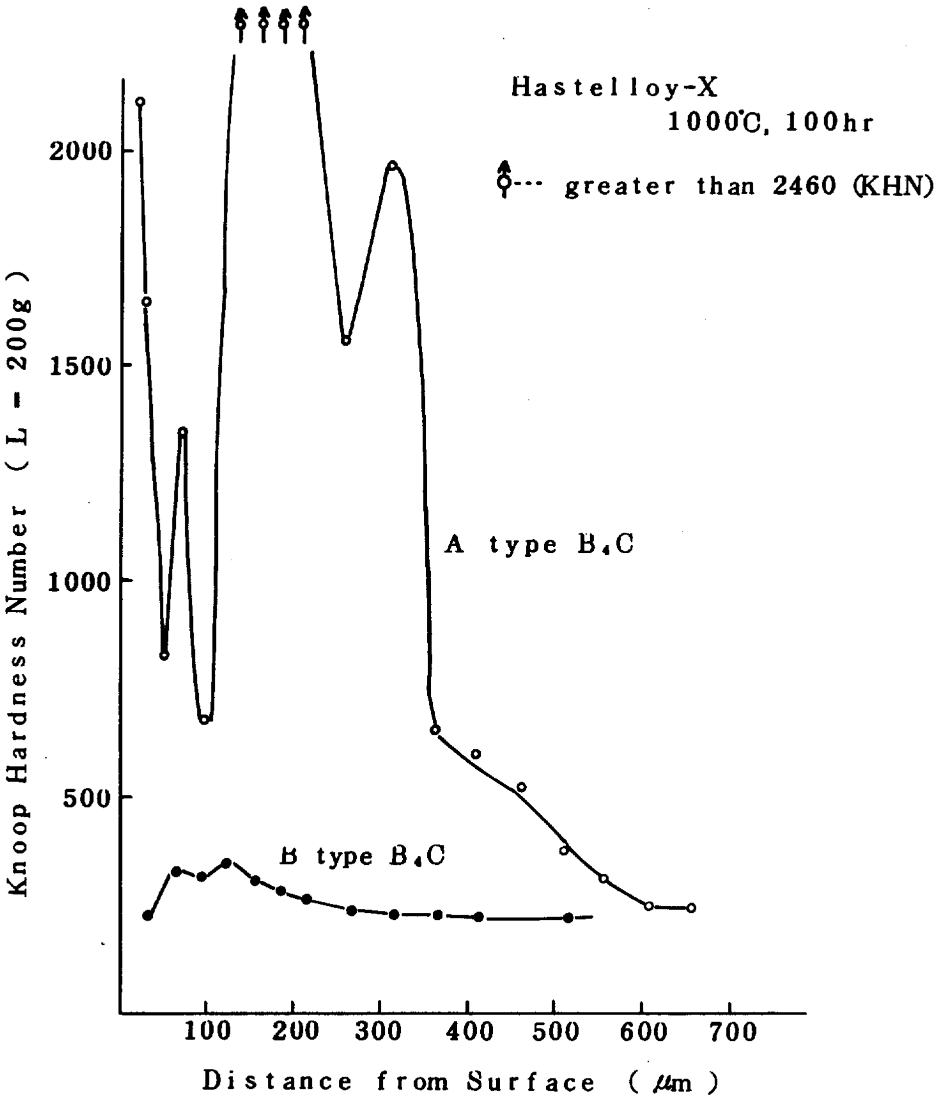


Fig. 5 Micro hardness of Hastelloy X reacted with A and B type B_4C

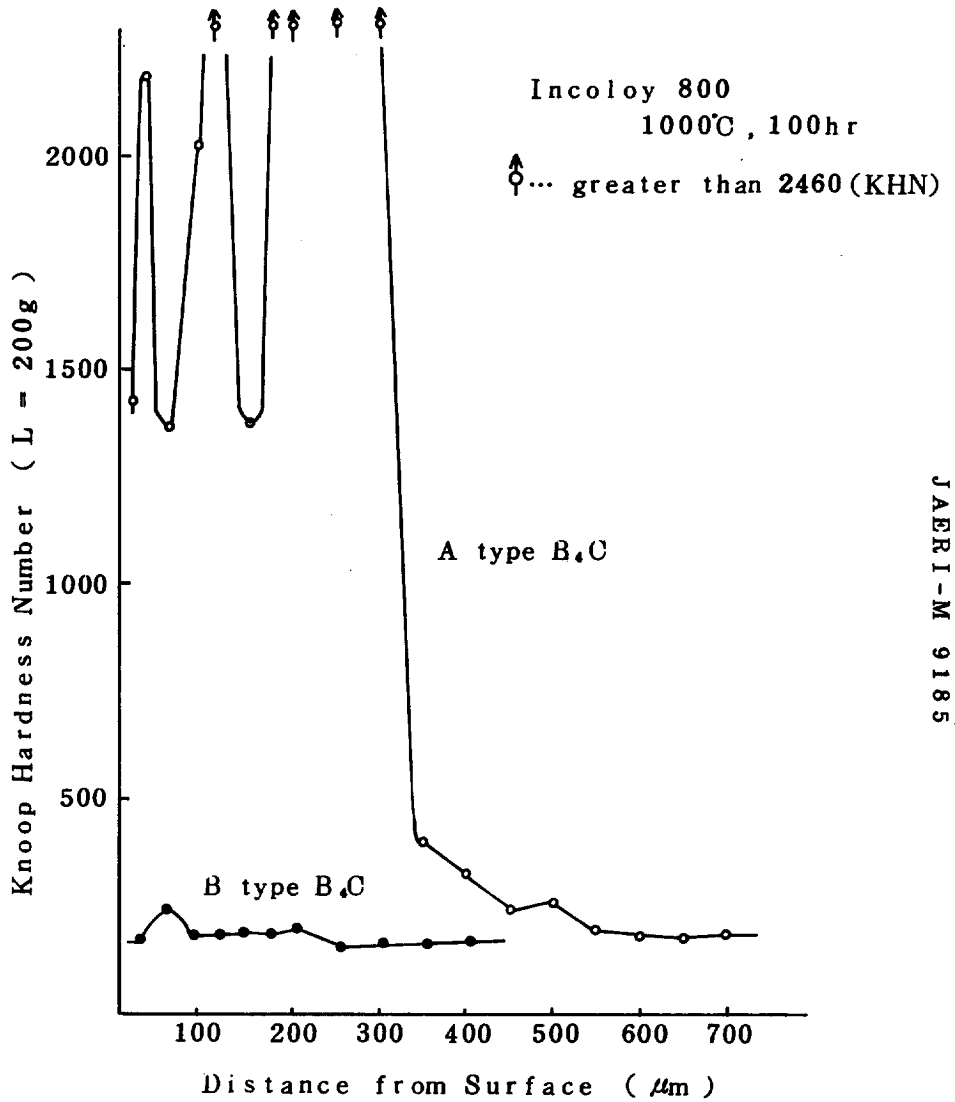


Fig. 6 Micro hardness of Incoloy 800 reacted with A and B type B_4C

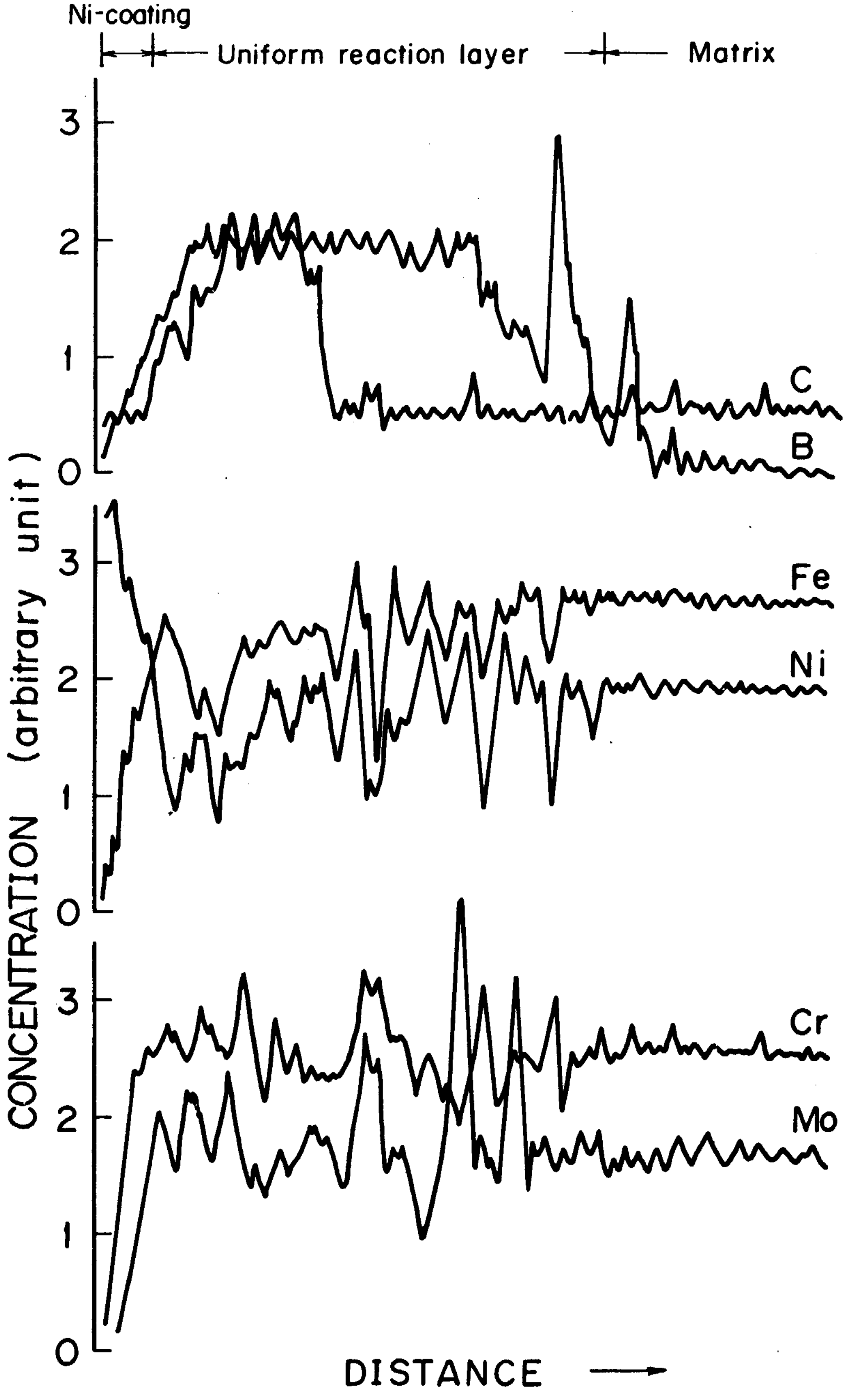


Fig. 7 Compositional changes of each element across the cross section of Hastelloy X reacted with A type B_4C at 950℃ for 100hrs

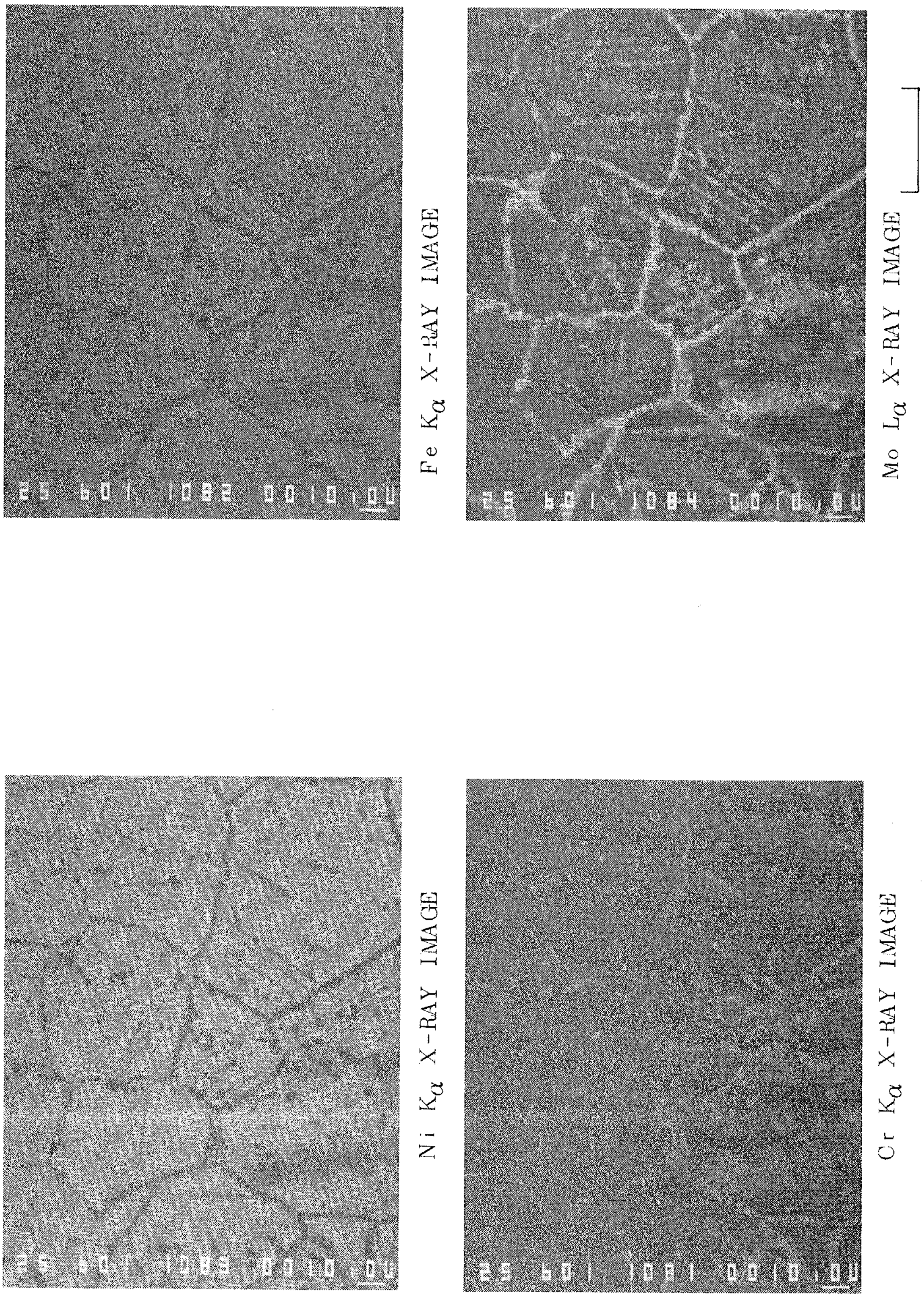
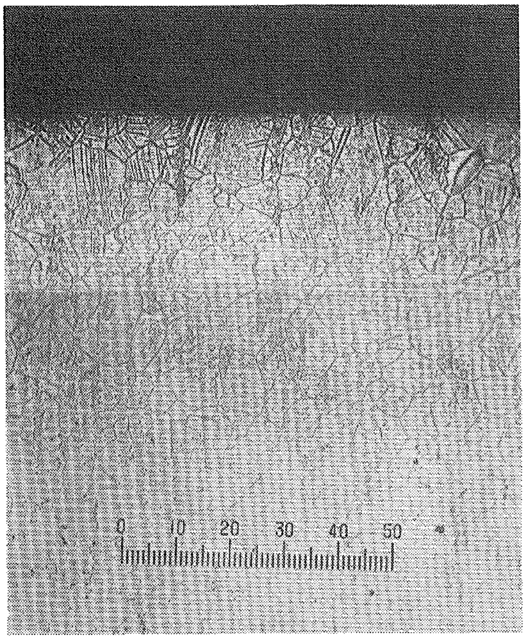
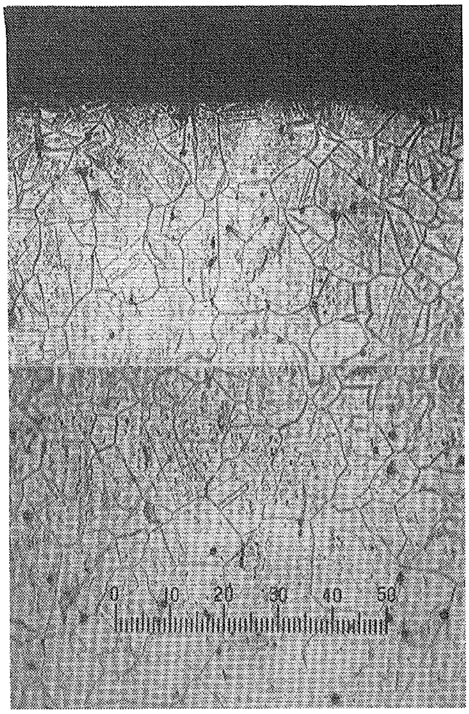


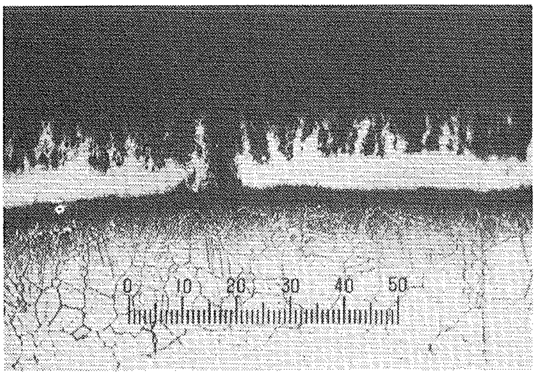
Fig. 8 Electron microprobe composition image of the cross section of Hastelloy X reacted with A type B_4C at 950℃ for 100 hrs

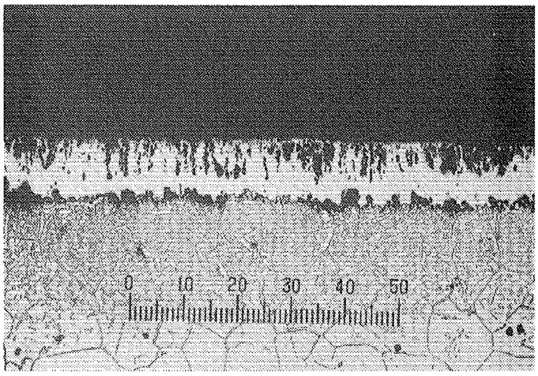


Hastelloy X-C



Incoloy 800-C



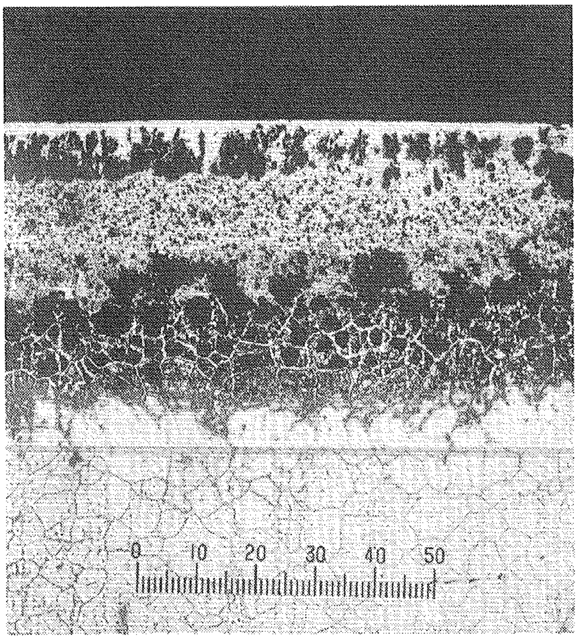


200μ

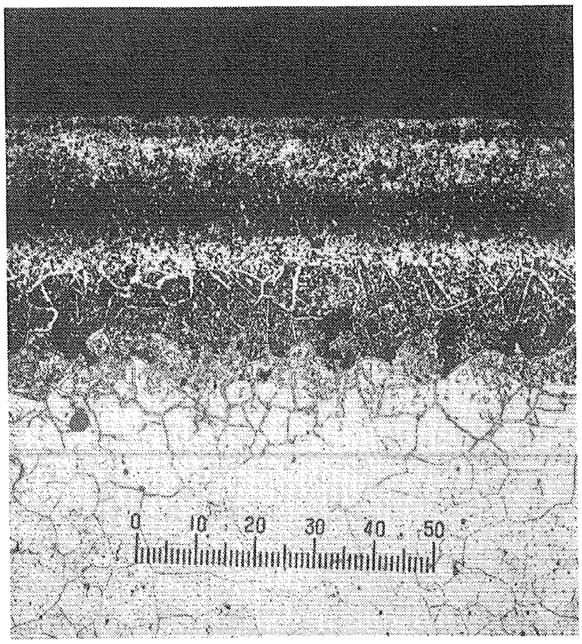
Hastelloy X-B

Incoloy 800-B

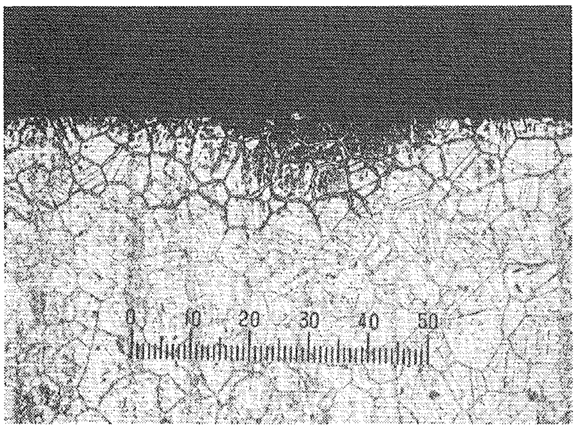
Fig. 9 Microstructures of alloys reacted with boron and carbon at 1000°C for 100 hrs



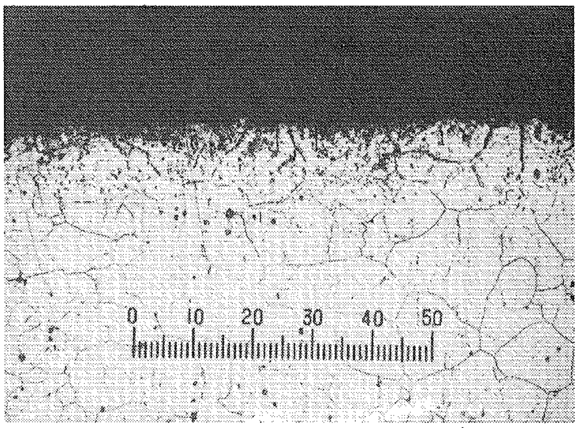
Hastelloy X-A type B_4C



Incoloy 800-A type B_4C



Hastelloy X-B type B_4C



200μ

Incoloy 800-B type B_4C

Fig. 10 Microstructures of alloys reacted with B_4C at 850℃ for 2000 hrs

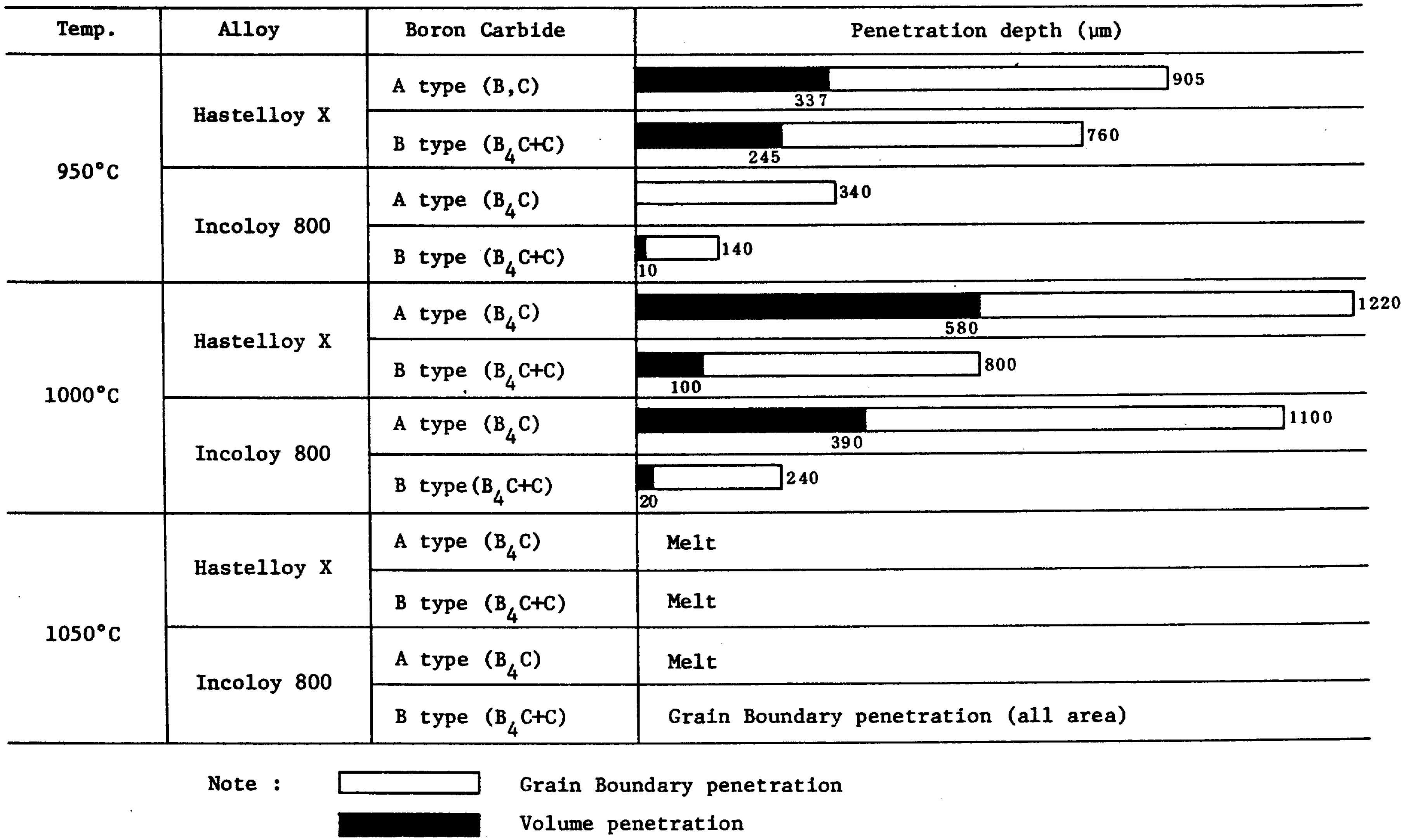


Fig. 11 Comparison of penetration depth data in alloys reacted with different types of B_4C for 500 hrs

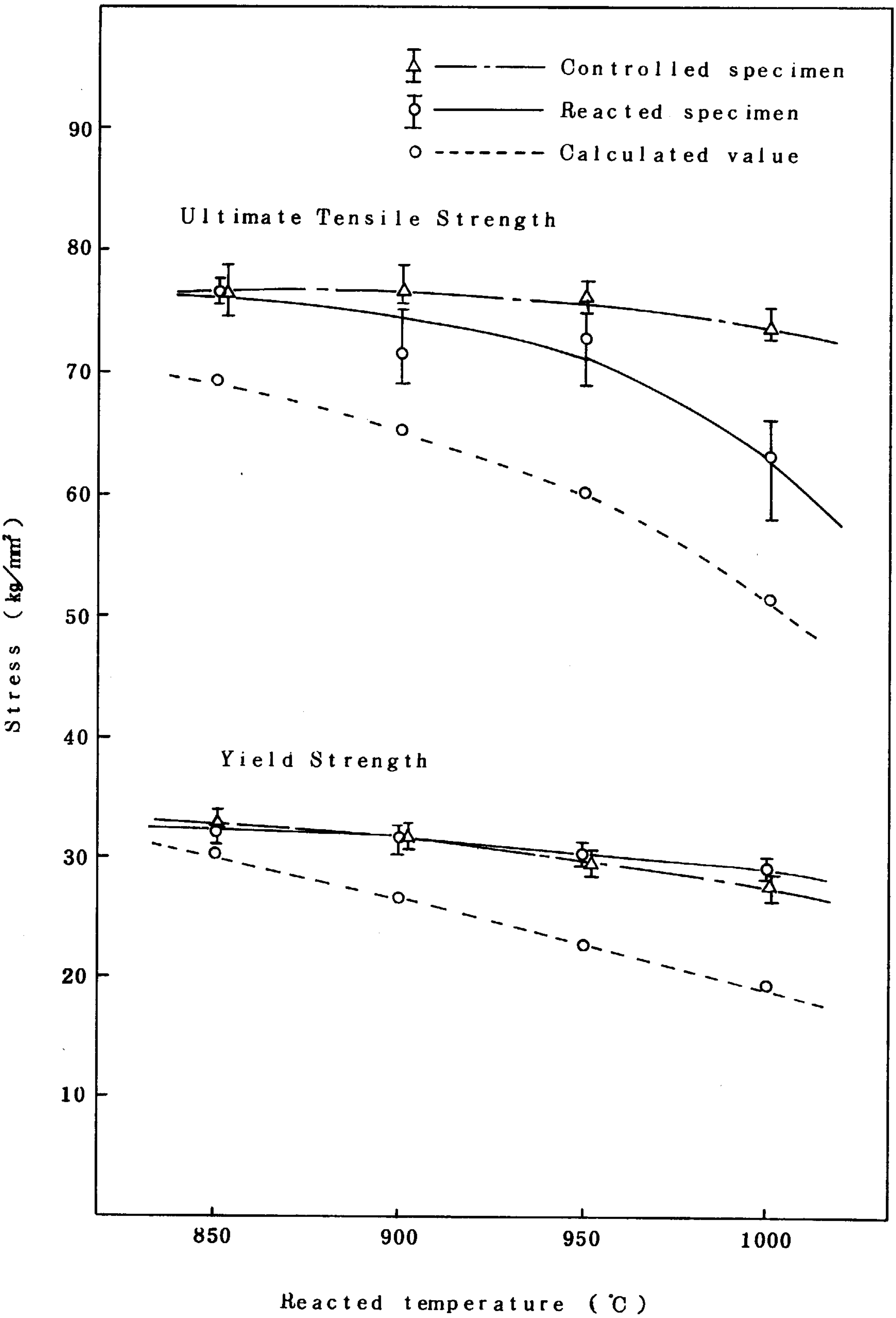


Fig. 12 Effect of reaction temperature on the strength of Hastelloy X