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COMPATIBILITY OF BORON CARBIDE WITH POTENTIAL AOMR CONTROL ROD CLADDING MATERIALS

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COMPATIBILITY OF BORON CARBIDE WITH POTENTIAL AOMR CONTROL ROD CLADDING MATERIALS

By

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ABSTRACT

The solid state compatibility of boron carbides with commercial copper, Types 304 and 430 stainless steels, and AISI 4130 steel, for potential control rod application, were investigated at 750, 950, 1100, and 1300°F, for periods of 500, 1000, 5000, and 10,000 hr.

These studies have shown commercial copper and Type 430 stainless steel to be compatible with boron carbide at 1300°F for 10,000 hr. Type 304 stainless steel was compatible with B_4C for 10,000 hr at 1100°F, but not at 1300°F. There were no reactions observed in the AISI 4130 steel for 10,000 hr at 750°F; but a very hard reaction zone, which increased in width from 1 mil at 950°F to 10 mils at 1300°F, was observed. The phase formed in the AISI 4130 steel was identified, by x-ray diffraction, to be primarily Fe_2B. The activation energy for the growth of this phase was calculated to be about 38 kcal/mole.

I. INTRODUCTION

The commercial production of boron carbide (B_4C) was developed as early as 1934 by Ridgway;[1] and, because of its extreme hardness (2800 KHN - 9 Moh), it was initially used as an abrasive. In recent years, with the advent of nuclear reactors, there has been increasing interest in high-purity B_4C, for use in control rods and shielding. Boron-10(B^{10}) has a thermal neutron absorption cross section of 4010 barns,[2] and is the most important stable isotope of boron for nuclear use. Natural boron (18.8% B^{10}) has a relatively high cross section of 755 barns.[2]

The use of B_4C has been extensive in control rods, in reactors at many educational institutions and test sites in the United States and Canada. Since control rods are essential devices for safety, as well as for reactor control, and because of their position in the reactor core, it is necessary to investigate the irradiation performance of boron carbide and the compatibility of boron carbide with potential cladding materials at core temperatures. This study includes only the compatibility of B_4C with copper, Types 430 and 304 stainless steels, and AISI 4130 steel at temperatures near and above those considered for the Advanced Organic Moderated Reactor (AOMR) concept.

II. EXPERIMENTAL PROCEDURE

A. MATERIALS

1. Boron Carbide

The boron carbide used in these experiments was a commercial grade, obtained from the Norton Abrasive Company. Hypo-, hyper-, and essentially stoichiometric B_4C were used for comparative purposes. The stoichiometric composition for B_4C is 78.3 wt % boron - 21.7 wt % carbon. The hypostoichiometric and hyperstoichiometric compositions used in these tests were about 18 wt % carbon and 28 wt % carbon, respectively, with negligible solubility of the boron or carbon in the B_4C. These compositions were used to determine what effects, if any, might be realized from either free boron or free carbon in the B_4C. The hypo- and hyperstoichiometric boron carbides were used only in the diffusion couples which contained copper and Types 304 and 430 stainless steels. The B_4C was either in a powder form or a sintered pellet form. The powder was approximately 200 mesh, and the pellets were 3/8 in. in diameter by 1/2 in. long.

2. Cladding Materials

a. Copper

Copper was selected for these studies, because of a potential application of plating the inside of control rods with copper, to form a diffusion barrier.

b. Type 304 Stainless Steel

This austenitic steel was selected for its oxidation and corrosion resistance, high creep strength up to 1300°F, and availability. Its nominal composition is 18 Cr - 8 Ni - 0.08 C - 2 Mn.

c. Type 430 Stainless Steel

This ferritic nonhardenable stainless steel was selected for comparison with the austenitic Type 304 stainless steel. Type 430 steel has good creep strength at 900°F, and good oxidation and corrosion resistance up to 1500°F.[3] Its nominal composition is 17 Cr - 0.5 Ni - 0.12 C - 1 Mn.

d. AISI 4130 Steel

This low-alloy steel was selected because it is currently being utilized as a B_4C control rod cladding in many organic research reactors. Its nominal composition is 0.28 C - 0.65 Mn - 0.19 Si - 0.16 Ni - 0.66 Cr - 0.22 Mo.

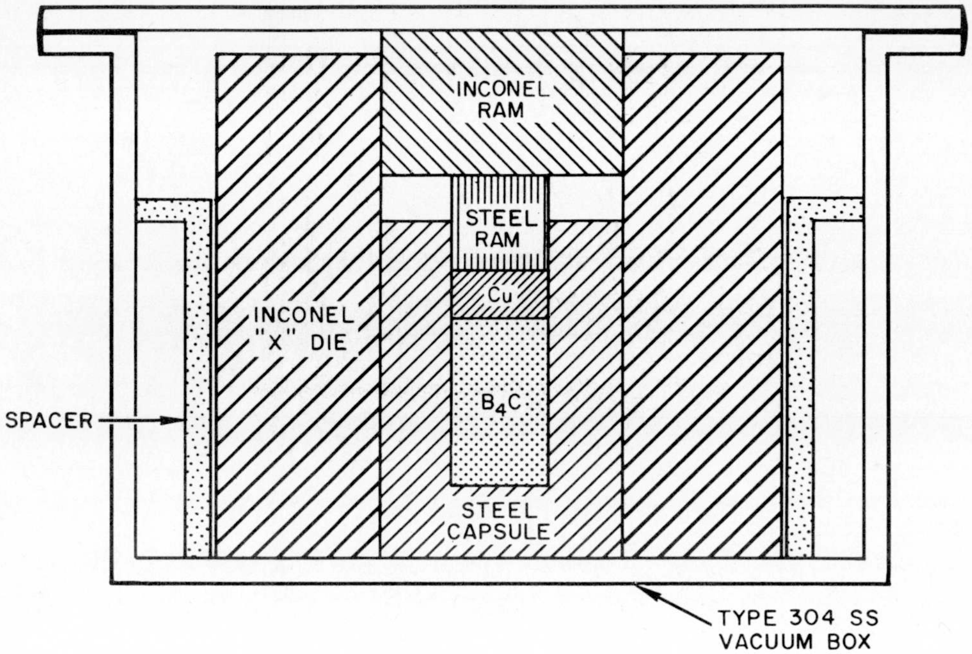
B. DIFFUSION COUPLE ASSEMBLY

The components of a typical diffusion couple assembly are shown in Figure 1a. The diffusion couples consisted of a 3/4-in. diameter by 3/4-in. long rod, in which a 3/8-in. diameter hole was bored 5/8 in. deep. The cavity was filled with B_4C powder or pellets, and then capped with a wafer of copper and a 3/8-in. diameter by 1/8-in. thick plug of the same material as the 3/4-in. diameter rod. The couple was press fitted into an Inconel-X restraining ring, and placed in the vacuum pressing can shown in Figure 1b for weld sealing. The couples were evacuated for 24 hr, prior to hot pressing. Each couple was then pressed under 10,000 lb force (approximately 108,000 psi on a 3/8 in. diameter) for 4 hr at 1200°F, under a dynamic vacuum of approximately 1×10^{-5} torr. The hot press (Pasadena Hydraulic Press), with the furnace (Marshall) mounted, is shown in Figure 2. The cans were then sealed and placed in isothermal soaking furnaces, for periods of 500, 1000, 5000, and 10,000 hr at temperatures of 950, 1100, and 1300°F. The potential cladding materials used were Types 304 and 430 stainless steels and AISI 4130 steel. In addition, a wafer of commercial copper was incorporated in the diffusion couples, to evaluate copper as a diffusion barrier material.

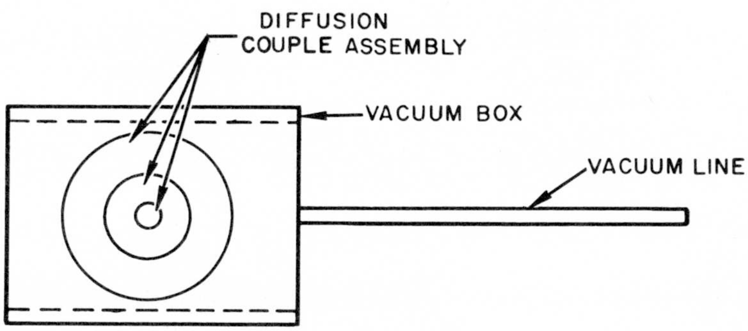
C. DIFFUSION COUPLE EXAMINATIONS

1. Metallography

Following the isothermal heat treatments, the couples were sectioned for metallographic examination and evaluation, as shown in Figure 3. In each specimen section, a major portion of the B_4C was carefully cleaned from the B_4C-metal interface, prior to mounting the specimen in Bakelite. This was done to prevent the B_4C powder particles from spalling, and scratching the specimen during polishing. It was also done to prevent the very hard B_4C (Moh = 9) from causing relief at the B_4C-metal interface, which would reduce the accuracy of the determination of the existence of a reaction zone in the metal.



a. Cross-Section View



b. Top View

Figure 1. Diffusion Couple

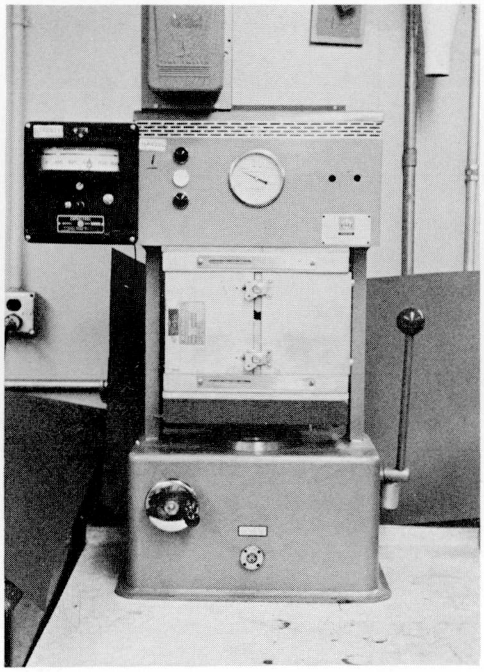


Figure 2. Hydraulic Press and Furnace

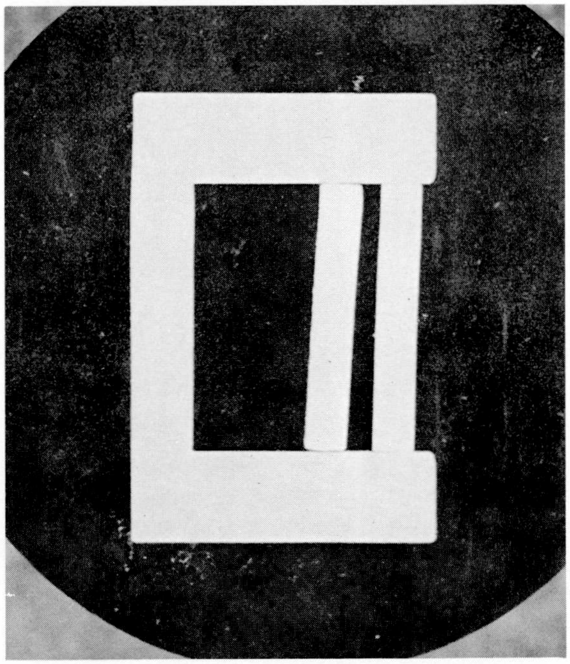


Figure 3. Longitudinal Section of Diffusion Couple

The following are the metallographic procedures used for the AISI 4130 steel, Types 304 and 430 stainless steels, and copper.

a) Grind on 180- , 320- , 400- , and 600-grit paper.

b) Rough polish with 14- , 9- , 6- , and 1-μ diamond paste.

c) Final polish with Linde "B" and water.

d) Etch.

The specimens were examined in the as-polished and etched conditions. The times for the etchants were as required to bring out the reaction zones or grain structure of the specimens. The specific etchants are given in the figures of this report.

2. Hardness

Hardness traverse measurements were taken on a Tukon microhardness tester, using a Knoop indenter with a load of 100 g.

In some cases, the amount of a second phase was so small that it was not possible to isolate for a hardness reading. A very thin reaction zone on the surface of a specimen also reduced the accuracy of hardness measurements. In this instance, the hardness of the same phase in a more extensive reaction zone was reported.

3. X-Ray Diffraction Analysis

The phases observed in the 1300°F, 10,000-hr AISI 4130 steel specimen were chipped off the edge of the specimen, powdered, and analyzed by x-ray diffraction by the Debye-Scherrer powder method, using filtered CrK_2 radiation.

III. RESULTS AND DISCUSSION

Table 1 presents a summary of the results obtained from these studies. The following is a discussion of the compatibility of the individual materials investigated with boron carbide.

A. COPPER

Copper was shown to be compatible with B_4C, after 10,000 hr at 1300°F. Typical metallographic results of these tests are shown in Figure 4. There were no detectable reactions observed in any of the diffusion couples, at magnifications up to 250X.

B. TYPE 430 STAINLESS STEEL

Type 430 stainless steel was found to be compatible with B_4C, after 10,000 hr at 1300°F. The metallographic results of these tests are shown in Figure 5. There was some pitting, of unknown cause, noted at the surface of the specimens. The maximum depth shown is approximately 0.001 in. There were no hardness increases in the specimens, but this type of stainless steel essentially loses its impact strength after long exposures (10,000 hr) at approximately 900°F.[3] Thus, use of this material at this temperature, where transient stress conditions exist, should be avoided.

C. TYPE 304 STAINLESS STEEL

Type 304 stainless steel was found to be compatible with B_4C after 10,000 hr at 1100°F, but not at 1300°F. The metallographic specimens for the 1100 and 1300°F tests are shown in Figures 6a and 6b, respectively. The dark lines in the grains of Figure 6a are due to carbide precipitation on slip bands, but there were no increases in microhardness. Information from the literature has shown that various phases exist in the Fe-B-Cr-C system. Some of these are FeB, Fe_2B, (Fe, Cr)B, and $Fe_3(B, C)$. The phase shown in Figure 6b is probably the iron-chromium boride or the iron borocarbide. There was not enough material in the reaction zone to obtain satisfactory x-ray analyses of the reaction products. The hardness of the solid gray phase was 950 KHN (100-g load), and the basket-weave structure was 470 DPH. The difference in the behavior of the Type 430 stainless steel and Type 304

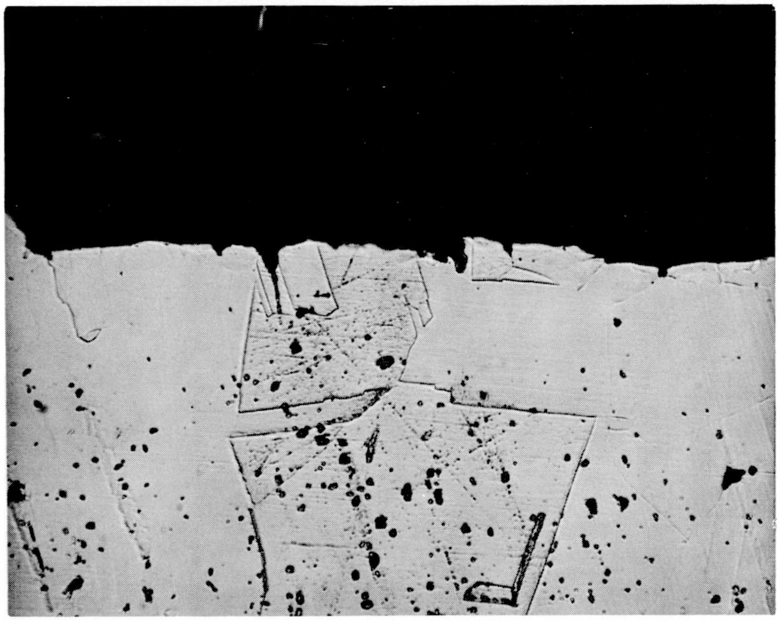
TABLE 1

RESULTS OF DIFFUSION COUPLE EXAMINATIONS

Material	Time (hr)	Temperature (°F)	Zone Thickness (in.)	Knoop Hardness (100 g Load)
AISI 4130 Steel/B_4C	500	1,300	0.0025	
	1,000	1,300	0.004	
	10,000	1,300	0.010	White phase (Fe_2B)—1000 KHN
	1,000	1,100	0.0006	Gray phase—400 KHN
	5,000	1,100	0.0018	
	10,000	1,100	0.0027	
	10,000	950	0.0005	
	10,000	750	None	No change
As-received AISI 4130 Steel	-	-	-	130 KHN
Type 430 SS/B_4C	10,000	1,300	None	No change
As-received Type 430 SS	-	-	-	230 KHN
Copper/B_4C	10,000	1,300	None	No change
As-received Copper	-	-	-	~ 70 KHN
Type 304 SS/B_4C	10,000	1,300	0.004 (2 phase)	Gray phase—950 KHN Basket weave—500 KHN
Type 304 SS/B_4C	10,000	1,100	None	No change
As-received Type 304 SS	-	-	-	250 KHN

CrO_3-NaCl-HNO_3-H_2SO_4-H_2O 3465-4 250X

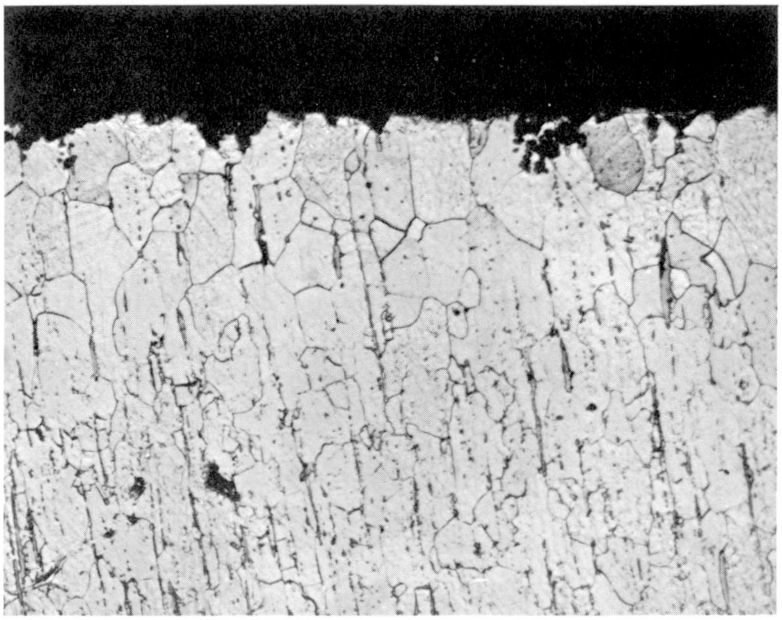
a. Stoichiometric B_4C—10,000 hr (No reaction)



CrO_3-NaCl-HNO_3-H_2SO_4-H_2O 3190-4 250X

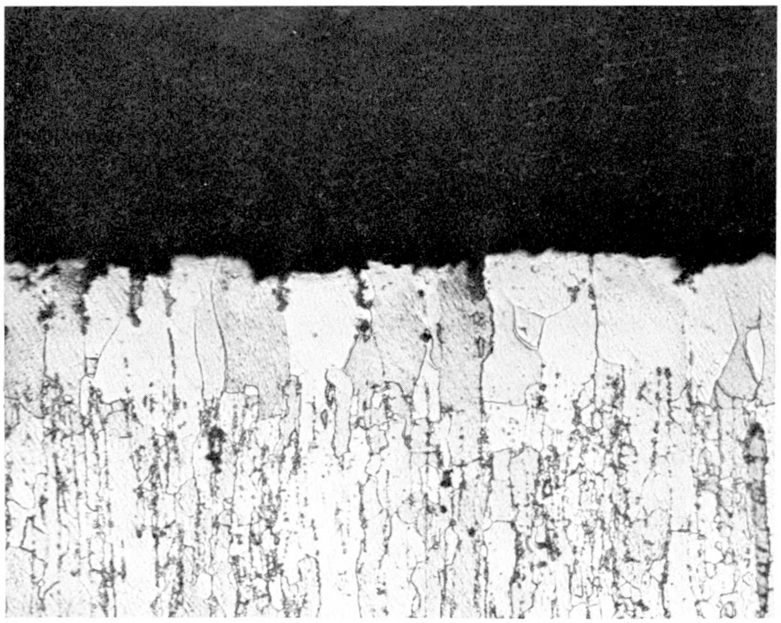
b. Hypostoichiometric B_4C—5,000 hr (No reaction)

Figure 4. Copper/Boron Carbide—1300°F



Picric Acid-$FeCl_3$-$CuCl_2$-Ethanol-H_2O-$CuSO_4$ 3465-2 250X

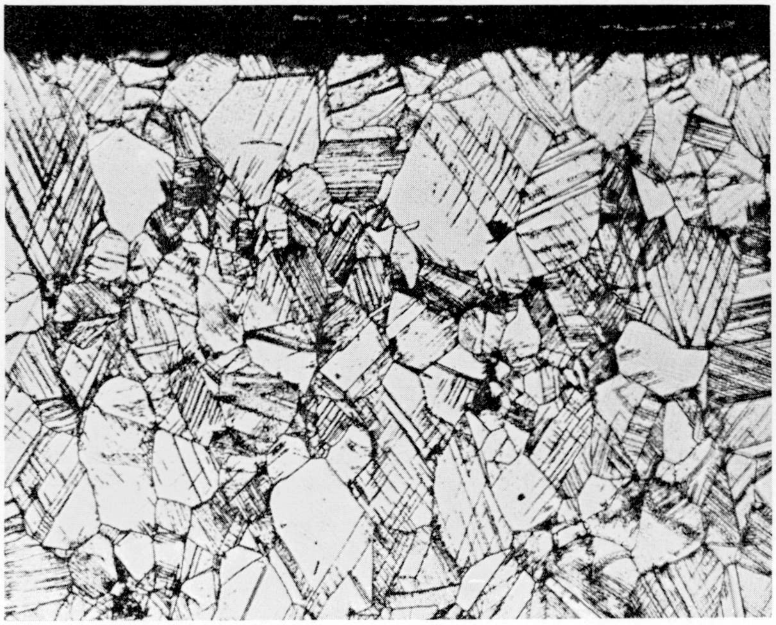
a. Stoichiometric B_4C—10,000 hr (Slight pitting)



Marble's Reagent 3190-3 250X

b. Hypostoichiometric B_4C—5,000 hr (Slight pitting)

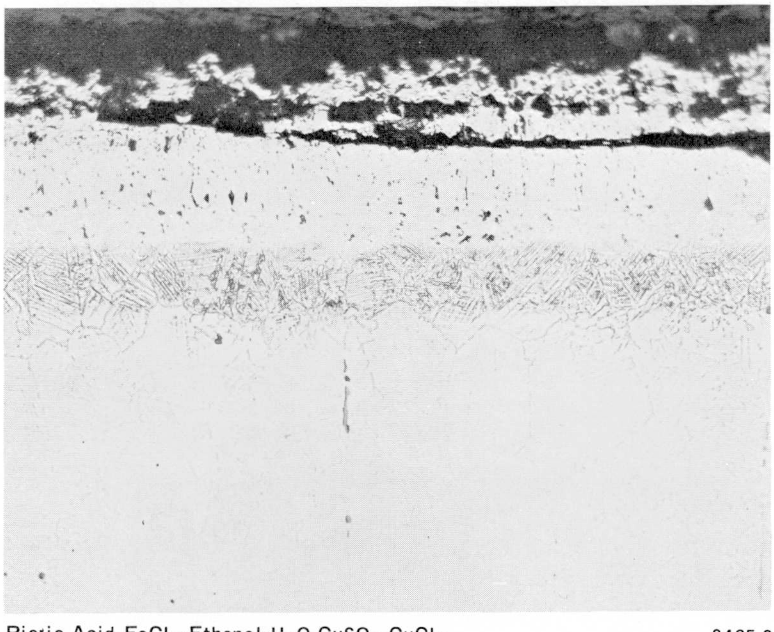
Figure 5. Type 430 Stainless Steel/Boron Carbide—1300°F



2% Oxalic Acid

3428-5
250X

a. 1100°F (No reaction)

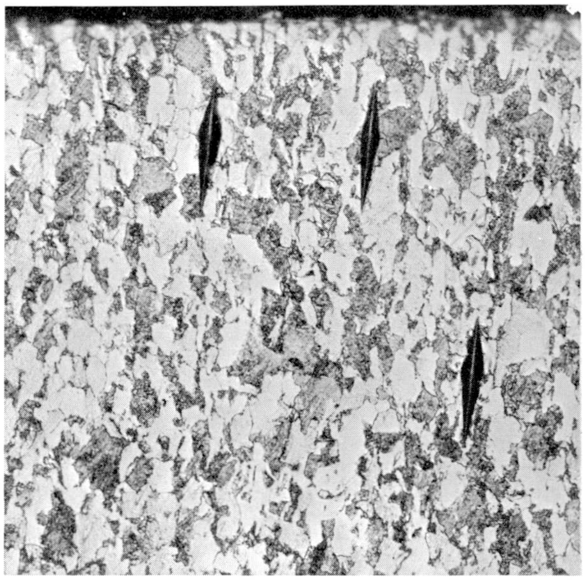


Picric Acid-$FeCl_3$-Ethanol-H_2O-$CuSO_4$-$CuCl_2$

3465-3
250X

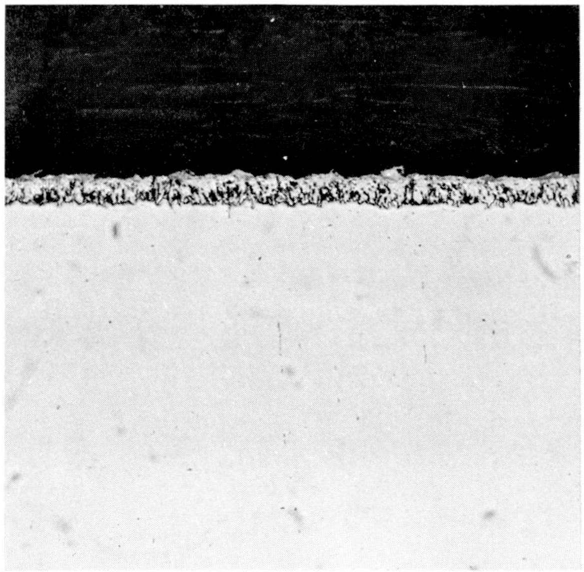
b. 1300°F (Duplex reaction—0.004 in.)

Figure 6. Type 304 Stainless Steel/Hypo-stoichiometric Boron Carbide—10,000 hr



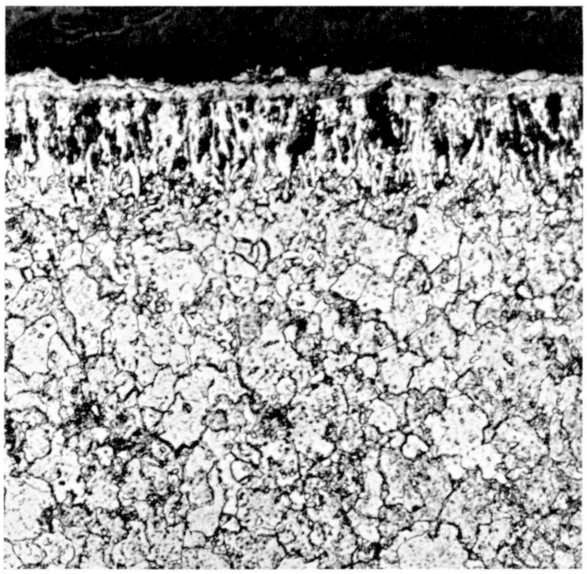
2% Nital 3384-2 250X

a. 750°F (No reaction)



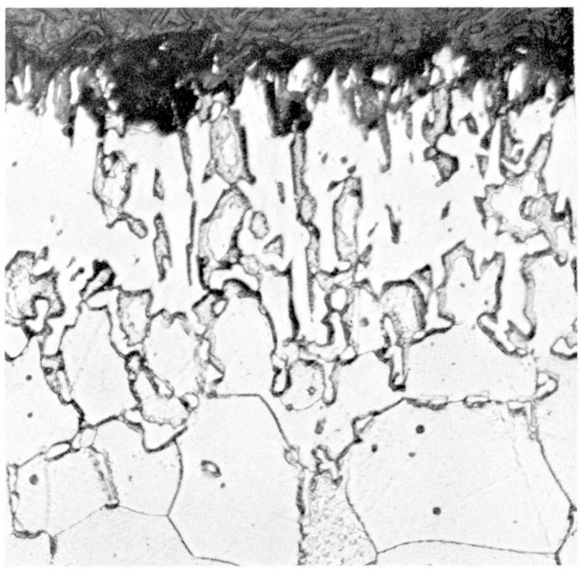
As Polished 3410-2 250X

b. 950°F (Duplex reaction—0.0005 in.)



2% Nital 3428-9 250X

c. 1100°F (Duplex reaction—0.004 in.)



2% Nital 3465-1 250X

d. 1300°F (Duplex reaction—0.010 in.)

Figure 7. AISI 4130 Steel/Stoichiometric Boron Carbide—10,000 hr

stainless steel at 1300°F is unexplained. The only major difference in the composition is that Type 430 stainless steel has ~0.5 wt % Ni and Type 304 stainless steel has 8 to 10 wt % Ni.

D. AISI 4130 STEEL

AISI 4130 steel was found to be compatible with B_4C at 750°F for 10,000 hr, but not compatible at temperatures in excess of 950°F. A hard, two-phase region, identified by x-ray diffraction as primarily Fe_2B, was formed at the B_4C-steel interface after 10,000 hr at 950°F. The reaction zone was uniform in thickness, and was approximately 0.001 in. thick. This reaction layer increased progressively with increasing temperature, as shown in Figures 7a, b, c, and d, which represent 10,000-hr exposure at 750, 950, 1100, and 1300°F, respectively.

The large white phase (Fe_2B), shown in Figure 7d, had a hardness of approximately 1000 Knoop with a 100-g load. The second gray phase, not identified, was about 400 KHN, while the original metal matrix was about 130 KHN.

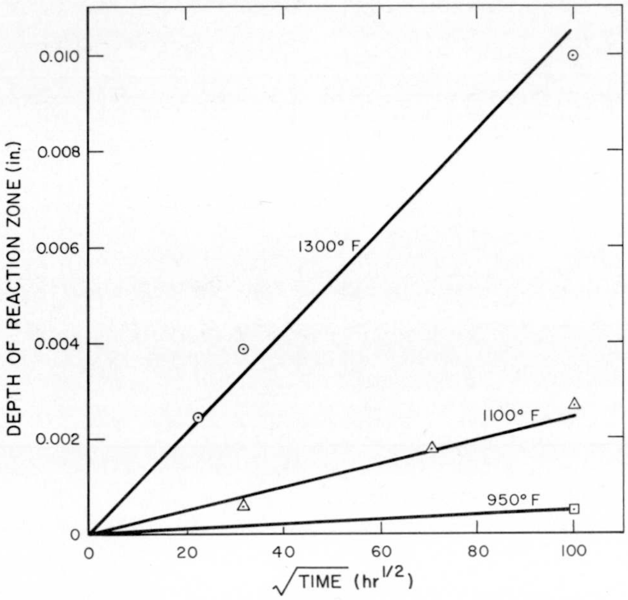
Figure 8a shows the depth of the reaction zones in the AISI 4130 steel vs the square root of the time at temperature for 1300, 1100, and 950°F. The graph shows that the data points fit the required straight line temperature curves well for a diffusion controlled process.

Figure 8b shows the depth of the reaction zone squared, divided by the time at temperature (x^2/t = penetration coefficient), vs the reciprocal absolute temperature. An activation energy of approximately 38 kcal/mole for the growth of the boride reaction zone (Fe_2B) observed in the AISI 4130 steel is derived from the slope of the line.

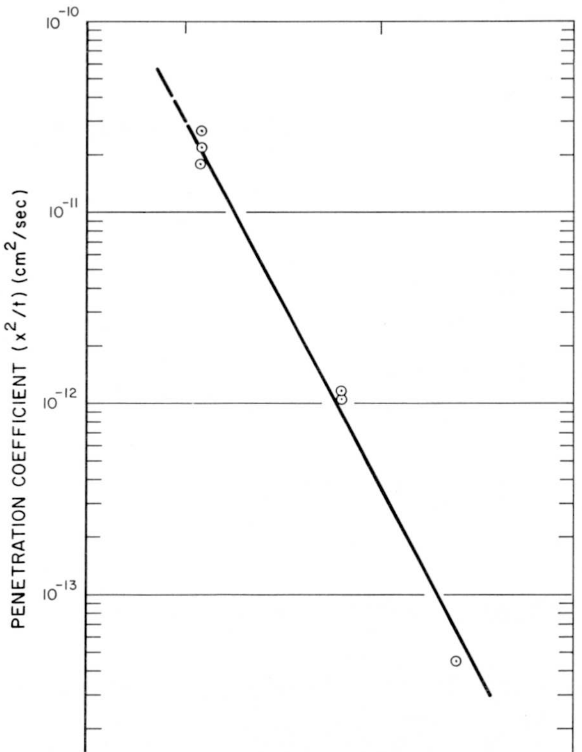
E. HYPO- AND HYPERSTOICHIOMETRIC BORON CARBIDE

Due to the extensive reactions observed in the initial short-time tests between the stoichiometric B_4C and AISI 4130 steel (Figures 7c and 7d), only the most promising materials were investigated in the second stage of these studies. These materials were copper and Types 430 and 304 stainless steel.

The second stage of studies was limited to a maximum of 5000 hr. Therefore, the reaction between the Type 304 stainless steel and stoichiometric B_4C (shown in Figure 6b) cannot be compared to a couple which contained Type 304 stainless



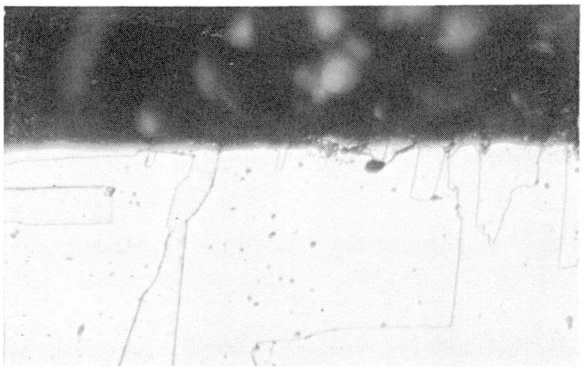
a. Depth of Reaction Zone vs Square Root of Time



b. Penetration Coefficient vs Reciprocal of Absolute Temperature

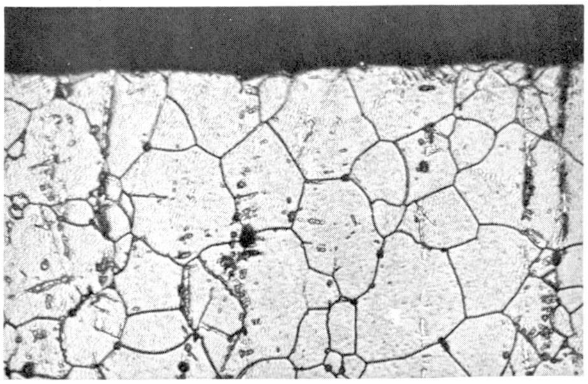
Figure 8. AISI 4130 Steel/Stoichiometric Boron Carbide Diffusion Couples

steel/hypo- or hyperstoichiometric B_4C, exposed for the same time and temperature. However, the other 5000-hr tests show that there were essentially no differences in comptability between the couples which contained stoichiometric B_4C and those which contained hypo- and hyperstoichiometric B_4C at the temperatures investigated. This is shown in Figures 4b, 5b, 9, 10a, 10b, and 11.



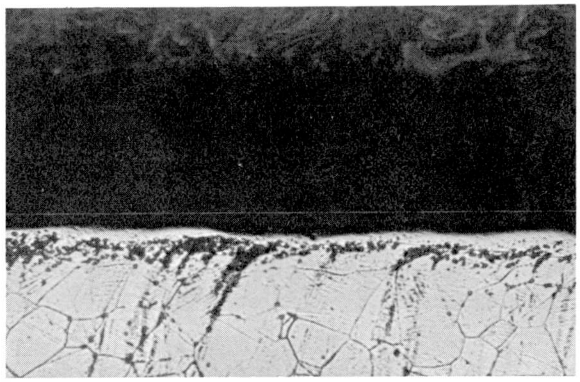
CrO_3-NaCl-HNO_3-H_2SO_4-H_2O 3190-6 250X

Figure 9. Copper/Hyperstoichiometric Boron Carbide—1300°F, 5,000 hr



2% Oxalic Acid 3213-6 250X

a. Hyperstoichiometric B_4C

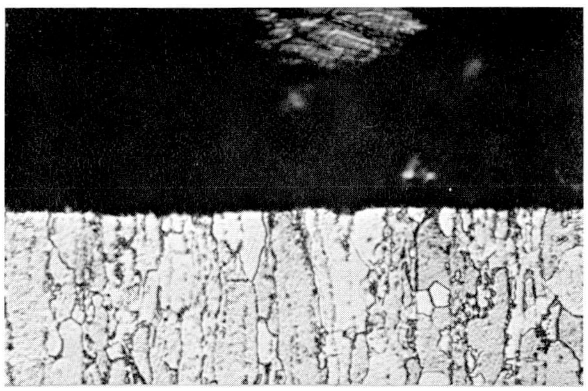


2% Oxalic Acid 3190-9 250X

b. Hypostoichiometric B_4C

Figure 10. Type 304 Stainless Steel/Boron Carbide—950°F, 5,000 hr

Figure 11. Type 430 Stainless Steel/Hyperstoichiometric Boron Carbide—1100°F, 1000 hr



Marble's Reagent 2767-6 250X

IV. CONCLUSIONS

Copper and Type 430 stainless steel were found to be compatible with near-stoichiometric B_4C for 10,000 hr, at temperatures from 750 to 1300°F.

Type 304 stainless steel was shown to be compatible with B_4C for 10,000 hr from 750 to 1100°F, but was shown to react extensively at 1300°F after 10,000 hr.

AISI 4130 steel was compatible with B_4C for 10,000 hr at 750°F, but a duplex boride phase formed at the diffusion couple interface at 950°F for 10,000 hr, and became more extensive with increasing temperature, up to 1300°F. The maximum penetration of the hard phases shown was approximately 0.010 in.

The activation energy for the growth of the iron boride zone in the AISI 4130 steel was calculated to be about 38 kcal/mole.

There were essentially no differences in compatibility between the couples which contained stoichiometric B_4C and those which contained hypo- and hyper-stoichiometric B_4C, at the temperatures investigated.

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