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SUBJECT: ZIRCONIUM DIBORIDE, BORON NITRIDE, AND BORON CARBIDE
COMPATIBILITY WITH AUSTENITIC STAINLESS STEEL

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ABSTRACT

The compatibility of zirconium diboride, boron carbide, and boron nitride with type 304 stainless steel was evaluated as a function of temperature (1000–1200°C), time (1–3 hr). Appropriate loadings of the boron compounds and stainless steel powder were blended and fashioned into a compact powder metallurgically. Each compact was roll clad into a plate and subsequently heat treated at a temperature equal to the initial sintering temperature. Metallographic examination of the fabricated and heat-treated plates demonstrated that none of the systems were metallurgically stable. The instability was generally manifested by the (1) interaction of the discrete boron compounds with the matrix and (2) precipitation of a hypothetically boron-rich phase throughout the stainless steel matrix material.

Of the three compounds, boron nitride was relatively the most stable in a stainless steel matrix under the test conditions.

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ZIRCONIUM DIBORIDE, BORON NITRIDE, AND BORON CARBIDE
COMPATIBILITY WITH AUSTENITIC STAINLESS STEEL

INTRODUCTION

Operational observation of the Army Package Power Reactor Core I (APPR), demonstrated the desirability of decreasing the peak-to-average power ratio along the core to achieve a more uniform uranium-235 burnup. This objective could be facilitated by reducing the number of control rods in the reactor from seven to five and controlling the initially high excess reactivity of the 15 Mwyr reactor by increasing the burnable poison loading per plate. It was therefore proposed that the natural boron concentration in the fuel-bearing section¹ of APPR fuel plates be increased from 0.11 to 0.25 wt %.

To observe the effects of the proposed boron increase, fuel plates originally containing 0.25 wt % boron as boron carbide were fabricated and heat treated to simulate established APPR manufacturing procedures. Metallographic examination of the fuel plates showed that a considerable amount of boron had diffused from core to clad and subsequently precipitated there. This was considered undesirable since its effect on the stability of the plate during reactor operation could not be predicted.

A second requirement of projected loadings was the minimization of sensitization of the fuel plate cladding. Although the corrosion resistance of the fuel plate in pressurized water is not impaired by sensitization,² its minimization or elimination was advisable in order to lessen the danger of inadvertent damage to the plate during processing. In Core I plates, carbon had diffused from a relatively high-carbon type 304B stainless steel core into the type 304L cladding and, as a result of processing condition, sensitized the plate. It was anticipated that substitution of low-carbon type 304LB core-matrix material for the type 304B would prevent the sensitization.

Experimental samples of this low-carbon materials combination could not pass the Strauss test demonstrating that some degree of sensitization persisted. Since

¹26 wt % enriched UO₂ dispersed in stainless steel.

²D. J. DePaul, Corrosion and Wear Handbook, TID-7006, p 225-228 (1959).

silicon can increase the thermodynamic activity of carbon in an iron base alloy,³ the high-silicon content of the core can promote carbide precipitation in the cladding either by carbon diffusion from the core to the clad or by silicon diffusion into the cladding and thereby lowering the carbon solubility.

In light of the boride precipitation in the cladding and the desire to minimize sensitization, boron carbide was obviously not the most desirable mode of boron addition; but, since it was incorporated in the Core I loading, it was carried in this program as a reference material. Two other compounds, zirconium diboride and boron nitride, were selected as alternatives.

Throughout the investigation boron losses arising during thermal treatment were not evaluated per se.⁴ However, this does not invalidate any conclusion relating to the compatibility of the systems and the morphology of the reactions under the test conditions since the material system can be explicitly defined as boron compound-stainless steel-hydrogen.

PROCEDURE

Mixtures of -325 mesh B_4C , ZrB_2 , or BN analyzing 75.9, 18.8, and 44.4 wt % B, respectively, equivalent to 0.254 g of natural boron and 99.8 g of -100 mesh, type 304B stainless steel powder, were individually blended in 4-oz jars on an oblique blender for 3 hr. Table I lists the composition of each mixture produced. Type 304LB stainless steel powder was substituted for type 304B when it became available after the initiation of experimental work. Table II lists the composition of the stainless steel used. The blended powders were transferred into the cavity of a 1.8-in. x 2.4-in. double-acting die and cold pressed at 33 tsi to yield green compacts ~ 0.235 in. thick. One compact of each type and loading was then sintered in hydrogen of < -60°F inlet dewpoint for 75 min at 1000, 1100, 1150, and 1200°C, respectively. The cores were subsequently coined in the original pressing die by two applications of a load equivalent to 33 tsi. Coined core thickness varied from 0.214 in. to 0.217 in. The cores were inserted in

³L. S. Darken and R. W. Gurry, Physical Chemistry of Metals, 462, McGraw-Hill 1953.

⁴Met. Div. Ann. Prog. Rep., Oct. 10, 1958, ORNL-2632, p 140-141 (Classified).

TABLE I

COMPOSITIONS OF MIXTURES OF ZrB_2 , B_4C , AND BN
WITH 99.8 g STAINLESS STEEL

Stainless Steel, (Type)	Burnable Poison	Compound (Grams)	Designation
304LB	B_4C	0.374	B_4C -304LB
304B ^a	ZrB_2	1.159	ZrB_2 -304B
304LB	BN	0.686	BN-304LB

^aExcept sample cycled at 1000°C contained type 304LB.

TABLE II

COMPOSITION OF STAINLESS STEEL POWDERS

Type	Ni	Cr	C	Si	Mn	S	P
304B	8.52	18.22	0.07	2.39	1.00	0.012	0.010
304LB	8.64	18.28	0.02	2.38	0.93	0.013	0.013

NOMINAL COMPOSITION OF THE TYPE 304L
WROUGHT STOCK USED

Ni	Cr	C	Si	Mn	S	P
9	19	0.03	0.05	0.7	0.01	0.01

4-7/16 in. x 4-1/2 in. x 0.218 in. frames, 0.054 in. cover plates attached by welding, and the assembly hot rolled to 0.040 in. using the standard APPR fabrication schedule at a hot-rolling temperature equivalent to the core-sintering temperature.⁵

After hot rolling, the plates were cold rolled to 0.030 in. and sectioned into four equal lengths. Three were subject to one, two, and three thermal cycles, respectively, to simulate the APPR fuel plate heat-treating processes. A thermal cycle consisted of furnace heating ($\sim 150^{\circ}\text{C}$ per hr) a section in hydrogen to its respective fabrication temperature, holding for one hour, and furnace cooling. A longitudinal metallographic specimen was examined after each cycle.

Certain thermal treatments and material combinations, which were originally planned, were deleted as trends became apparent. Table III outlines the material combinations and heat treatments performed.

Samples were designated as follows: boron compound - matrix material - processing temperature - number of thermal cycles.

For example: B_4C -304LB-1150-2C would refer to B_4C in type 304LB thermally cycled twice at 1150°C .

RESULTS AND DISCUSSION

Boron Carbide-Type 304 System

Figure 1 (Y-28110), sample No. B_4C -304LB-1150-0C, illustrates the microstructure of the hot-rolled B_4C sample in the core area. Boron carbide, the heavily etched phase, has begun to react with its surroundings yielding small globs of a secondary phase believed to be a metallic boride or borocarbide. Figure 2 (Y-28111), shows the microstructure of a similar specimen after one thermal cycle at 1150°C . Here the reaction products have distributed themselves into two groups; a grain boundary precipitate and a globular, uniformly distributed fraction. The grain boundary phase, although present in all thermally cycled material combinations, was most prevalent in the B_4C -304LB case, suggesting that

⁵J. E. Cunningham et al., Specification and Fabrication Procedures for APPR I Core II, Stationary Fuel Elements, ORNL-2649. (1959).

Fig. 1 (Y-28110) Sample No. B_4C -304LB-1150-OC. Initiation of the B_4C -stainless steel reaction. Etchant: electrolytic oxalic acid. 500X.

Fig. 2 (Y-28111) Sample No. B_4C -304LB-1150-1C. Appearance of the grain boundary phase. Etchant: electrolytic oxalic acid. 500X.

TABLE III

HEAT TREATMENTS AND LOADINGS OF SPECIMENS

Boron Compound	Compound Loading (%) ^a	Thermal Treatment Temperature (°C)	Number of Thermal Cycles Investigated		
			1	2	3
B ₄ C	0.37	1000	x	x	x
B ₄ C	0.37	1100	x	x	
B ₄ C	0.37	1150	x	x	x
B ₄ C	0.37	1200	x	x	
ZrB ₂	1.16	1000	x	x	x
ZrB ₂	1.16	1100	x	x	
ZrB ₂	1.16	1150	x	x	x
ZrB ₂	1.16	1200	x	x	
BN	0.69	1000	x	x	x
BN	0.69	1100	x	x	
BN	0.69	1150	x	x	x
BN	0.69	1200	x	x	

^aWith respect to stainless steel.

it might be carbon dependent. The globular phase was observed in all material combinations suggesting an analogous reaction mechanism in each case. Figure 3 (Y-28121), sample No. B_4C -304LB-1000-2C, shows similar products in the core area, although to a lesser degree. It was therefore concluded that B_4C is not stable in type 304LB stainless steel in the temperature range investigated and the extent of reaction increases with an increasing number of thermal cycles and processing temperature.

Figure 3 (Y-28121), and Fig. 4 (Y-27514), sample No. B_4C -304LB-1150-3C, demonstrate a grain boundary precipitate throughout the cladding and the "boride band." The "boride band" is defined as that area in the cladding adjacent to the core where a band of hypothetically boron-rich material has precipitated. The band width was found to increase and its leading edge approach the outer clad surface with increasing processing temperature and number of thermal cycles. This suggests a diffusion-controlled mechanism. Also evident is the smaller grain size in the specimen processed at a lower temperature. A large portion of the grain boundary precipitate, especially that occurring past the "boride band," probably metallic carbides as is evidenced by earlier experiments demonstrating that plates of this type are sensitized. The large amount of carbon in the cladding is made available by the decomposition of the boron carbide in the core and subsequent diffusion. Figure 5 (Y-25928), sample No. BN-304LB-1150-3C, illustrates the "boride band" more clearly since the effect of carbon is minimized.

Zirconium Diboride-Type 304 System

Zirconium diboride was found to be unstable in a type 304B matrix in the temperature range investigated. Figure 6a (Y-28626), 6b (Y-25977), 6c (Y-25976), and 6d (Y-25975), photomicrographs of the core region of ZrB_2 in type 304B (type 304LB in 1000°C case) in the as-rolled condition processed at 1000, 1100, 1150, and 1200°C, respectively, illustrate a temperature-dependent solid-state reaction manifested by a dark reaction band originating at the ZrB_2 -type 304 stainless steel interface and progressing into the original particle. The extent of reaction is dictated by processing temperature and number of thermal cycles. Also evident in this series of photomicrographs is the globular phase similar to that found in the B_4C -304LB system.

← Core-Clad
Interface

Fig. 3 (Y-28121) Sample No. B₄C-304LB-1000-2C. Illustrating grain boundary precipitate in the cladding. Etchant: electrolytic oxalic acid. 500X.

← Core-Clad
Interface

Fig. 4 (Y-27514) Sample No. B₄C-304LB-1150-3C. The "boride band."
Etchant: electrolytic chromic acid. 500X.

← Core-Clad
Interface

Fig. 5 (Y-25928) Sample No. BN-304LB-1150-3C. The "boride band."
As-polished. 500X.

Fig. 6a (Y-28626) Sample No. $\text{ZrB}_2\text{-304LB-1000-OC}$. Zirconium diboride reaction at 1000°C . As-polished. 750X.

Fig. 6b (Y-25977) Sample No. $\text{ZrB}_2\text{-304B-1100-OC}$. Zirconium diboride reaction at 1100°C . As-polished. 750X.

Fig. 6c (Y-25976) Sample No. $\text{ZrB}_2\text{-304B-1150-OC}$. Zirconium diboride reaction at 1150°C . As-polished. 750X.

Fig. 6d (Y-25975) Sample No. $\text{ZrB}_2\text{-304B-1200-OC}$. Zirconium diboride reaction at 1200°C . As-polished. 750X.

Figure 7a (Y-28120), a photomicrograph of the cladding of sample No. $\text{ZrB}_2\text{-304LB-1000-2C}$, illustrates a rather heavy grain boundary precipitate similar to that in the case of B_4C . However, the "boride band" is not clearly defined in this sample treated at 1000°C . Figure 7b (Y-25973), sample No. $\text{ZrB}_2\text{-304B-1150-3C}$, demonstrates that the phenomena persists at higher processing temperatures.

Boron Nitride-Type 304LB System

Of the three boron-bearing compounds considered, boron nitride was the most stable although a certain amount of instability persists. This is illustrated in Fig. 8a (Y-28108) and 8b (Y-25978), the core area of sample Nos. BN-304LB-1150-2C and BN-304LB-1150-3C , respectively. The primary disadvantage associated with the BN-type 304LB system is the gross stringering of the BN particles during fabrication. At 1000°C processing temperature, the system exhibits a remarkable degree of stability as depicted in Fig. 9a (Y-28122) and 9b (Y-28125), sample Nos. BN-304LB-1000-2C and BN-304LB-1000-3C , respectively. In Fig. 9a, a "boride band" is not apparent as it is in a sample treated at a higher temperature (see Fig. 5), and in Fig. 9b, only a small amount of secondary boride precipitate can be found.

Reaction Mechanism

The metallographic examination of all the boron-bearing specimens revealed that the ovate precipitate was present in all cases. To ascertain if the precipitate is characteristic of the boron compound-stainless steel reaction or inherent in high-silicon, type 304 stainless steel, a boron-free sample was examined. It was fabricated from type 304LB stainless steel powder and type 304L wrought stock employing techniques identical to those previously utilized. Figure 10 (Y-30950), the boron-free sample cycled twice at 1150°C , illustrates the typical nonmetallic inclusions inherent in the system and that the microstructure is free of the globular precipitate found in the boron-bearing cases. It was therefore concluded that the precipitate in question results from a boron compound-stainless steel interaction.

← Core-Clad
Interface

Fig. 7a (Y-28120) Sample No. ZrB_2 -304LB-1000-2C. Grain boundary precipitate and the "boride band." Etchant: electrolytic oxalic acid. 500X.

← Core-Clad
Interface

Fig. 7b (Y-25973) Sample No. ZrB_2 -304B-1150-3C. The "boride band." As-polished. 200X.

Fig. 8a (Y-28108) Sample No. BN-304LB-1150-2C. Boron nitride reaction and stringing. Etchant: electrolytic oxalic acid. 500X.

Fig. 8b (Y-25978) Sample No. BN-304LB-1150-3C. Boron nitride reaction and stringing. As-polished. 500X.

← Core-Clad
Interface

Fig. 9a (Y-28122) Sample No. BN-304LB-1000-2C. Absence of "boride band." Etchant: electrolytic oxalic acid. 500X.

Fig. 9b (Y-28125) Sample No. BN-304LB-1000-2C. Minimal BN reaction products in core region. Etchant: electrolytic oxalic acid. 750X.

Fig. 10 (Y-30950) Type 304LB Stainless Steel Clad with Type 304L Wrought Stock and Cycled Twice at 1150°C. Etchant: aqua regia. 500X.

Since boron is alleged to be a strong ferrite former,⁶ the possibility of the precipitate being ferromagnetic was examined. A drop of colloidal magnetite in water was placed on a boron-bearing specimen and the system subjected to an interrupted electromagnetic field during microscopic observation.⁷ Magnetic etching was not observed, demonstrating that the precipitate is not ferromagnetic and, consequently, not ferrite.

It was therefore concluded that the precipitate in question is the primary boron-stainless steel reaction product and may be either a metallic boride or borocarbide.

CONCLUSIONS

Dispersions of ZrB_2 , B_4C , and BN in a matrix of type 304LB stainless steel in the 0.25 wt % boron range are metallurgically unstable at the temperatures and times investigated (1000 to 1200°C; 1 to 3 hr).

1. The instability is associated with the formation of a new phase distributed throughout the matrix and occasionally a "boride band" found in the specimen cladding.
2. The extent of instability increases with increasing processing temperature and number of thermal cycles.
3. The "boride band" increases in width with increasing processing temperature and number of thermal cycles.
4. Metallographically, the hypothetically boron-rich reaction product is similar in all cases, suggesting an analogous reaction mechanism.
5. In all the thermally cycled samples, a discontinuous grain boundary phase is found in the core area and sometimes in the cladding. This grain boundary phase was present in the greatest amount in the B_4C -type 304LB system suggesting a dependence on carbon.
6. No positive signs of a molten phase in any of the systems were observed.
7. At 1000°C, boron nitride in type 304LB is the most stable system investigated.
8. In comparison with the other compounds investigated, boron nitride stringers severely during fabrication.

⁶J. H. G. Monypenny, Stainless Iron and Steel, 1, 139-140, Chapman and Hall 1951.

⁷H. S. Avery et al., "Metallographic Identification of Ferromagnetic Phases," Metals and Alloys (Nov. 1939).

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