STATIC OXIDATION AND COMPATIBILITY OF BORON NITRIDE AND BORON NITRIDE COMPOSITE TO 2000°C

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SUMMARY

Two grades of boron nitride and a boron nitride composite were subjected to temperatures up to 1500°C in air and up to 2000°C in a vacuum of 10^{-5} torr for various periods of time. Compatibility tests were made with four refractory oxides, JTA graphite composite, and five refractory metals at temperatures up to 1800°C. The results showed that composition influences thermal shock and oxidation resistance of boron nitride bodies. Little or no reaction occurred between the boron nitride compositions and the refractory ceramics at temperatures up to 1500°C and the refractory metals at temperatures up to 1000°C.

INTRODUCTION

The Langley Research Center of the NASA has recently completed a study of boron nitride and boron nitride composite. The objective of this investigation was to characterize the thermal shock, oxidation qualities and compatibility of these boron nitride compositions. These materials are homogenious mixtures of boron nitride, boric oxide, and/or titanium diboride with minor addition of calcium oxide and/or calcium borate in one of the compositions. Two boron nitride bodies, HBN and HBR, and one composite, HDA, were investigated in this study.

Interest in new boron nitride compositions is based on a continuing need for improving the effeciency of facilities and structures using these materials. Arc jet engines, plasma accelerators, power supplies for space vehicles, components such as microwave antennas, leading edges for aerospace vehicles, and RF (radio frequency) windows for deep space interplanetary vehicles are facilities and structures which employ or are considering use of boron nitride materials (reference 1-5).

The data presented here are results of thermal shock, static oxidation, and compatibility tests. The thermal shock tests were performed in air; the static oxidation and compatibility tests were performed in air and vacuum. Compatibility was determined between the boron nitride compositions and several commonly used high-temperature refractory ceramics, metals, and metal alloys.

SPECIMENS AND EQUIPMENT

The nominal composition of the three bodies investigated is shown in table I. In addition to the components normally found in these bodies, boron, nitrogen, oxygen, and carbon, a significant amount of titanium was used to produce the boron nitride composite HDA, while a small amount of calcium was added to produce HBR. The specimens used in this study were small, square pieces 1/2-inch on a side by 1/8-inch thick, cut from stock that had been dried and packaged in moisture-proof packages by the vendor. To minimize the hydration of boric oxide, present in the boron nitride compositions. all specimens were placed in a desiccator after machining.

A cold-wall 2000°C combination atmosphere or vacuum furnace and a hot-wall vertical tube furnace were used in all of the tests. Tests in vacuum were performed in the cold-wall furnace while the hot-wall furnace was used for tests at ambient pressure.

TEST PROCEDURES

Thermal Shock Tests

Thermal shock specimens were tested at ambient pressure in air. To observe the effect of a humid atmosphere, normally detrimental to the thermal shock qualities of boron nitride (reference 6), specimens in this investigation were subjected to room temperature conditions of approximately 25°C and a relative humidity of 85 percent for 7 days prior to thermal shock treatment. Specimens were suspended by a platinum wire into a precalibrated hot zone of the vertical tube furnace, soaked at 1500°C for 15 minutes, removed quickly, and cooled in ambient air. Thermal shock tests were repeated until a specimen failed or were concluded if no failure occurred after 10 cycles.

Oxidation Tests

Oxidation tests were performed in ambient air and at 10^{-5} torr.

Specimens tested in ambient air were removed from the desiccator, placed at the end of the platinum wire, and lowered into the precalibrated heat zone of the vertical tube furnace used in the thermal shock tests. All of the specimens were weighed and measured before and after testing. Test temperatures were 500°C, 1000°C, and 1500°C at times varying between 4 and 16 hours.

The procedure followed in the reduced pressure tests was similar to that of the ambient air tests except that specimens were placed in the atmosphere furnace cold, heated to the desired temperature, soaked at that temperature, and then cooled to room temperature in the furnace. Temperature was monitored in the atmosphere furnace with a thermocouple and a micro optical pyrometer. Test temperatures ranged from 1000°C to 2000°C at times varying between 4 and 16 hours.

Compatibility Tests

Compatibility tests were similar to the oxidation tests except that scrap metal or ceramic of the same composition as that of the specimen being tested was used as a buffer between the specimen and the specimen holder surface to prevent contaminating reactions. A specimen consisted of one of the three boron nitride bodies sandwiched between two pieces of ceramic having similar dimensions, or between two pieces of metal or metal alloy 0.5 inches square by 0.02 inches thick. Compatibility was visually determined between the boron nitride bodies and the ceramics, or metals, at temperatures of 500°C and 1000°C, and soak times ranging up to 24 hours at ambient pressure and at temperatures between 500°C and 1800°C for equal periods of time at 10^{-5} torr.

RESULTS AND DISCUSSION

Thermal Shock Tests

Thermal shock tests were made on HBN, HBR boron nitride, and HDA boron nitride composite to observe the effects of composition and hydration of boric oxide (B_2O_3) on spalling.

Figure 1 shows the thermal shock data in a bar graph of thermal shock cycles to failure for the three materials tested. It can readily be seen that grade HBR boron nitride and boron nitride composite HDA have better thermal shock resistance than HBN. The low moisture pickup and thermal expansion of HBR (reference 6) and the good thermal shock qualities contributed by titanium diboride (reference 7) and/or titanium oxide (reference 8) in HDA are believed to be the factors which gave these bodies good thermal shock resistance.

Oxidation Tests

Test results on the boron nitride bodies subjected to elevated temperatures at ambient pressure in the vertical tube furnace are presented in figures 2 and 3. The 500°C tests showed no substantial change in weight due to oxidation. Figure 2 shows weight change percent plotted against time for the three boron nitride bodies tested at 1000°C at ambient pressure (760 torr). The HDA boron nitride composite increased in weight at four hours followed by a gradual decrease in weight with increasing time. The HBN and HBR specimens exhibited a continual decrease in weight with increasing time. The significant

increase in weight noted in HDA was attributed to the formation of titanium oxide resulting from the oxidation of the large amount of titanium diboride (reference 7) present in HDA. The weight loss experienced by HDA in the latter portion of its curve and through the lengths of the HBN and HBR curves was believed to result from a two-step thermochemical reaction: (1) the oxidation of boron nitride producing B_2O_3 (reference 9); (2) the volatilization of the B_2O_3 (reference 10 and 11). Boron nitride bodies heated to 1500°C at ambient pressure showed very little variation in weight change percent (figure 3). The large loss in weight after four hours, noted in all of the boron nitride compositions, was due to the increase in volatilization of the B_2O_3 present in all of these bodies and volatilization of B_2O_3 produced by oxidation of boron nitride at 1500°C (reference 9).

To determine the effect of reduced pressure on the boron nitride compositions, specimens were heated in a vacuum of 10^{-5} torr at temperatures ranging from 1000°C to 2000°C. No significant change in weight was observed in the specimens heated at 1000°C. Figures 4 through 7 show the weight percent change resulting from heat treatment of the boron nitride bodies in the cold wall furnace under vacuum. The curves in figure 4 representing the three boron nitride bodies heated at 1500°C show variation in weight change at four hours but little difference in weight change with increasing time. The increase in weight realized by HBN at four hours was attributed to the oxidation

process of boron nitride being initially stronger than the vaporization process of B_2O_3 (reference 6 and 9). After eight hours, the three boron nitride compositions exhibited similar weight loss. This suggested a decrease in oxidation of boron nitride, particularly in HBN, and an increase in vaporization process of B_2O_3 (reference 9). Curves of specimens heated to 1750°C and 10^{-5} torr in figure 5 exhibit little difference in weight change percent for the HBR and HBN boron nitride bodies. A comparatively large change in weight was observed in the HDA boron nitride composite body. The process responsible for the weight loss in all of the boron nitride compositions is believed to be, as discussed earlier, the oxidation of the boron nitride component, forming B_2O_3, and the vaporization of this B_2O_3 and the B_2O_3 present in the basic composition of these boron nitride materials (reference 6 and 9). The excessive loss of weight observed in the HDA plot in figure 5 was attributed to the added vaporization of the TiO_2 component of the boron nitride bodies produced by the oxidation of titanium diboride (reference 12).

Figure 6 displays data for the three boron nitride bodies heated to 2000°C at 10^{-5} torr. This curve shows that HBR suffered the least weight change of the three boron nitride bodies tested. Weight change varied from a loss of 12 percent for HBR at 8 hours to approximately 36 percent for HDA heated for the same period of time.

Figure 7 varies from the preceding static oxidation curves (figures 4 through 6) in that weight change is plotted against temperature at a constant heating time of eight hours. These curves show that the HBR body was equal or better than HBN or HDA in resistance to oxidation at all test temperatures.

Compatability Tests

In the compatability tests, it was not considered necessary to verify the reactions or to identify new phases, since the object of this part of the investigation was to determine general temperature ranges within which the various refractory ceramics, metals, and metal alloys could be safely used in contact with HBN, HBR, or HDA. Visual evidence of reaction was considered sufficient basis for establishing the inadequacy of a particular combination.

Reactions were observed between the three boron nitride bodies and the following ceramic refractories:

Material	Symbol
Zirconia	ZrO_2
Magnesia	MgO
Alumina	Al_2O_3
Silica	SiO_2
JTA (graphite, zirconium, diboride, and silicon carbide)	C, ZrB_2, SiC

Reactions were also observed between the following refractory metals and metal alloys:

Material	Symbol
Tungsten	W
Tantalum	Ta
0.5% titanium 0.07% zirconium balance molybdenum	TZM
8% aluminum 1% molybdenum 1% vanadium balance titanium	titanium 811
10% tungsten 3% zirconium balance niobium	niobium 752

The degree of reaction between the various refractory materials and the boron nitride compositions was characterized by graphic symbols. as shown on figures 8 through 14.

(1) Slight reaction as designated by cross hatching was characterized by roughening and distortion of interface surfaces that were originally smooth before heat treatment; (2) fusion was characterized by the sticking and, in some cases, diffusion of one or both materials through the material interface; (3) destructive reaction was characterized by extensive distortion or severe fracture on one or both materials making up a test specimen indicating complete incompatibility.

No reactions were observed between the three boron nitride bodies and the refractory ceramics tested at 500°C ambient pressure. Figure 8 shows that reactions did take place between the boron nitride bodies and refractory ceramics at 1000°C and ambient pressure. Silica was the most reactive, while JTA and alumina showed the least reaction.

No visual evidence of reaction between boron nitride compositions and the refractory ceramics was present when exposed to a vacuum of 10^{-5} torr at 500°C or 1000°C for up to 24 hours. Slight reactions, exhibited in figure 9, were observed between HNB and magnesia and HBR and magnesia at 1500°C. Figure 10 shows reactions of the boron nitride bodies, varying from slight reactions with JTA graphite composite at 10^{-5} torr and 1750°C after 24 hours, to destructive reactions with alumina and silica at 10^{-5} torr and 1750°C after four to eight hours. The zirconia and magnesia, except for vaporization, displayed only slight interfacial reactions with the boron nitride bodies. Magnesia exhibited no reaction with HDA.

Results presented in figure 11 show that reactions took place at the interface between the metals and metal alloys and HBN and HDA at 500°C and 760 torr. No reaction, however, was observed between HBR and any of the metal and metal alloys. Visual examination of compatability specimens tested at 1500°C and 10^{-5} torr in figure 12 shows reactions varying from slight to destructive for all of the metal and metal alloys and boron nitride combinations except for niobium 752. The niobium alloy showed no reaction with any of the boron nitride bodies within the 24-hour test period.

In figure 13, it was observed that reactions occurred between all of the boron nitride compositions and the refractory metals and metal alloys at 1800°C and 10^{-5} torr.

CONCLUDING REMARKS

The results of the study of thermal shock, static oxidation, and compatability of HBN and HBR boron nitride and HDA boron nitride composite are as follows:

1. Grade HBR boron nitride and boron nitride composite, HDA, show good resistance to thermal shock when subjected to a humid atmosphere before testing. HBN is very poor in thermal shock under the same test conditions.

2. HDA exhibits good resistance to oxidation at 1000°C and 760 torr. HBR shows better resistance to oxidation and/or vaporization than HBN or HDA with increasing temperature at 10^{-5} torr.

3. HBR is compatible (shows no interfacial reaction) with the refractory metals tested at 500°C and 760 torr.

4. HBN, HBR, and HDA are compatible (show no interfacial reaction) with all of the refractory ceramics tested, except magnesia, at 10^{-5} torr up to 1500°C and with all of the metals and metal alloys tested at 10^{-5} torr up to 1000°C.

REFERENCES

1. Todd, J. P. and Sheets, R. E.: The Development of a Regeneratively-Cooled 30 KW Arc-Jet Engine. AIAA Journal, vol. 3, no. 1, January 1965, pp. 122-126.

2. Carter, A. F.; Wood, G. P.; and McFarland, D. R.: Research On a One-Inch-Square Liniar D-C Plasma Accelerator. AIAA Fourth Electric Propulsion Conference, August 31-September 2, 1964, AIAA paper no. 64-699.

3. Swenski, D. F. and May, J. R.: Advanced Continuous Duty Power Supply for Space Vehicles. In Progress in Astronautics and Aeronautics. Szego, G. C. and Taylor, J. E., ed: vol. 16, Academic Press, New York, 1966, pp. 1161-1184.

4. Judge, J. F.: Hardened Antennas Pose Problems. Missiles and Rockets, vol. 17, no. 18, November 1965, pp. 24-28.

5. Hill, M. L. and Akridge, J. M.: High Temperature Structures and Materials. Applied Physics Laboratory, John Hopkins University U-RQR/65-1, Research and Development Quarterly Report, January-March 1965, 111/12b.

6. Fredrickson, J. and Redanz, W. H.: Boron Nitride for Aerospace Applications. Metals Progress, vol. 87, no. 2, February 1965, pp. 97-101.

7. Battle Memorial Institute: Refractory Ceramics for Aerospace. A materials selection handbook. The American Ceramic Soc. Inc., Columbus, Ohio, 1964.

8. Kingery, W. D.: Property Measurements at High Temperature. John Wiley & Sons Inc., 1959.

9. Ingles, T. A. and Popper P.: Special Ceramics. Academic Press, New York, 1960, pp. 144-167.

10. Selge, P. C.: A Review of the Physical and Thermodynamic Properties of Boric Oxide. NACA RME57B14, 1957.

11. Drowart, J.: Mass Spectrometric Studies of Vaporization of Inorganic Substances at High Temperatures. In Condensation and Evaporation of Solids. Rutner, E.; Goldfinger, P.; and Hirth, J. P., ed., Gordon and Breach, Science Publishers, New York, 1964, pp. 255-310.

12. Touloukian, Y. S., ed.: Thermophysical Properties of High Temperature Solid Materials, Vol. 4: Oxides and Their Solutions and Mixtures, Part I: Simple Oxygen Compounds and Their Mixtures. The Macmillan Co., New York, 1967, p. 479.

MATERIALS AND SPECIMENS

GRADE	ANALYSIS, WEIGHT PERCENT							BULK DENSITY lb/ft^3
	B	N_2	Ti	O_2	C	Ca	OTHER	
HBN	43.4	54.0		3.3	0.3		.03	125
HBR	43.4	54.0		3.3	0.3	0.9	.03	118.6
HDA	36.2	27.6	33.5	2.6	0.6		.03	175

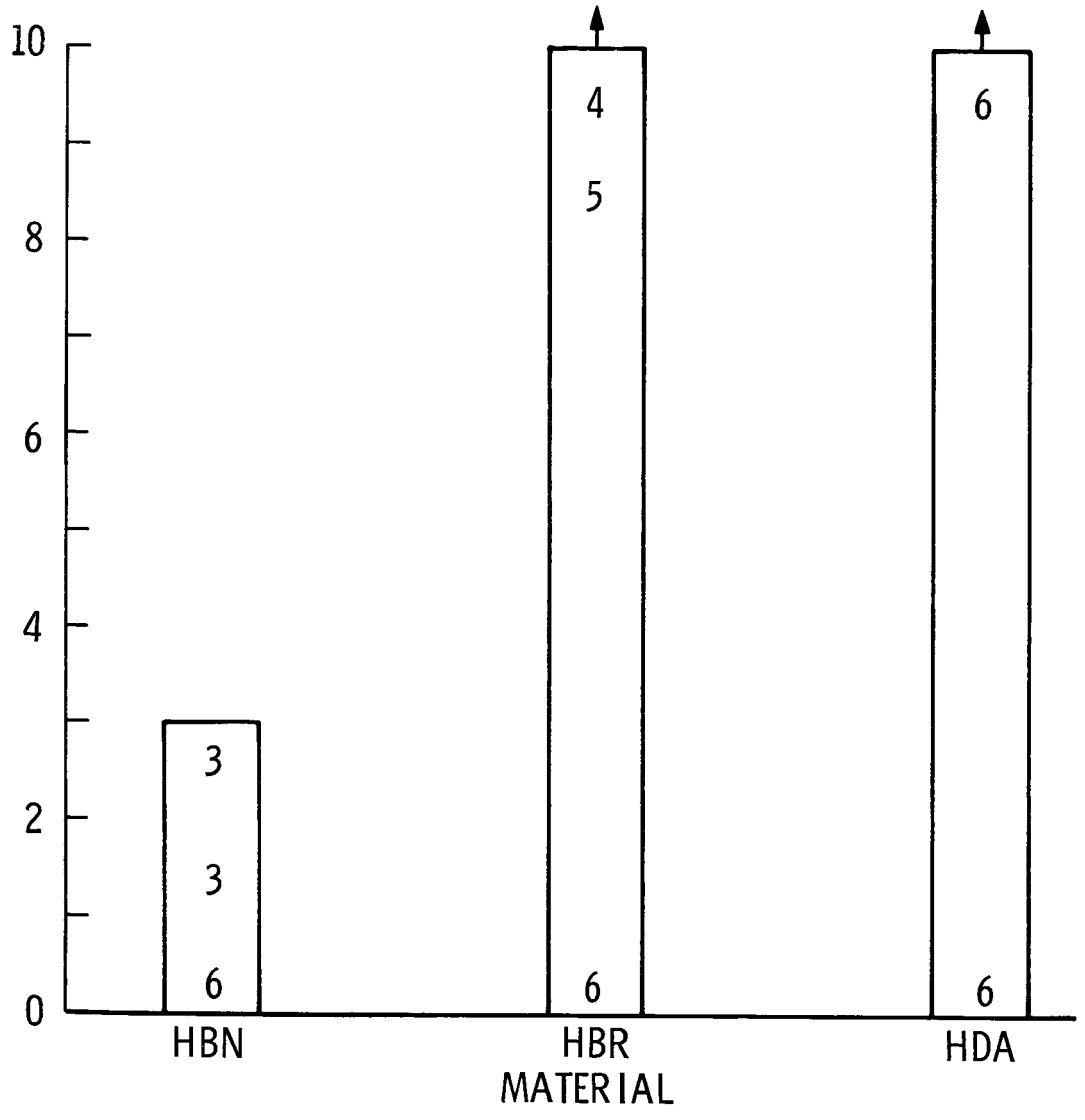

Figure 1.- Thermal shock resistance of HBN, HBR, and HDA, quick heated to 1500° C and cooled in air. (Numbers on bars represent specimens remaining for succeeding tests.)

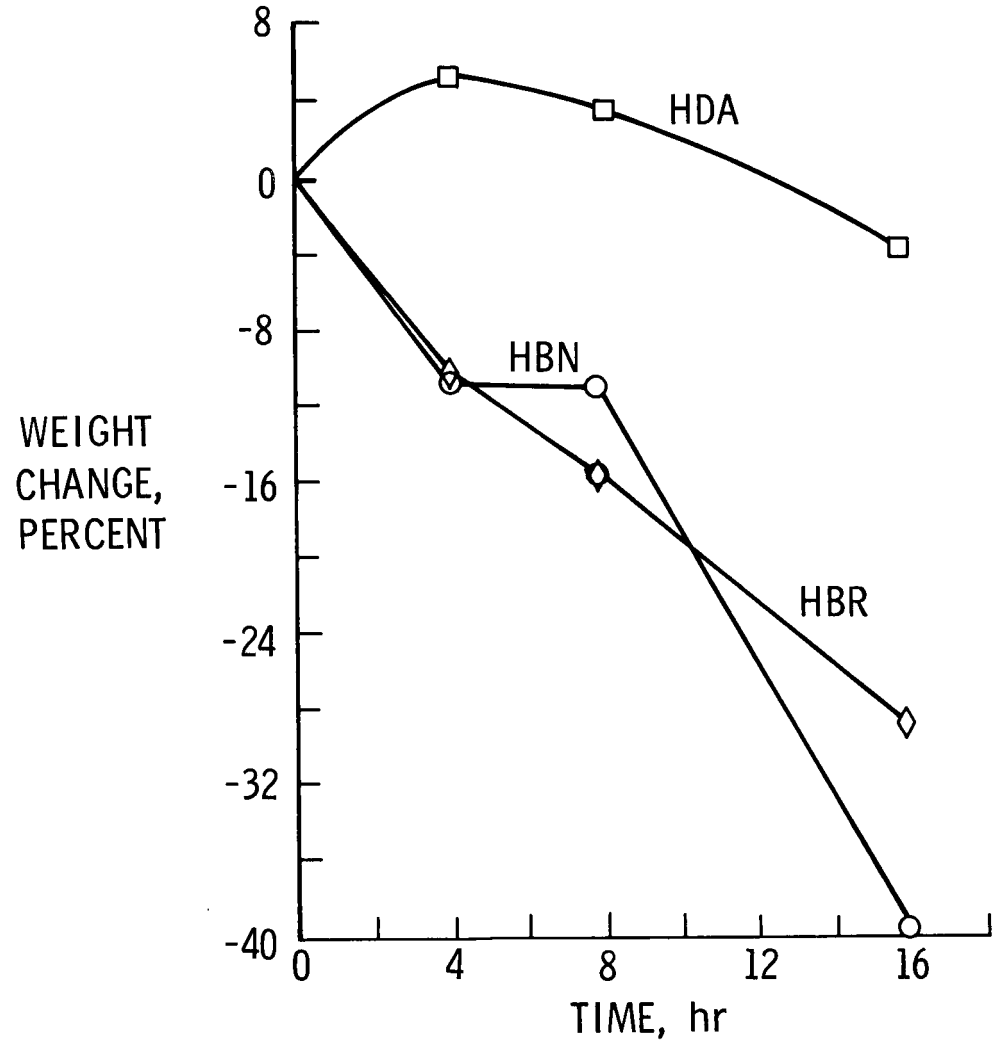

Figure 2.- Static oxidation test results for boron nitride compositions at 1000° C and 760 torr.

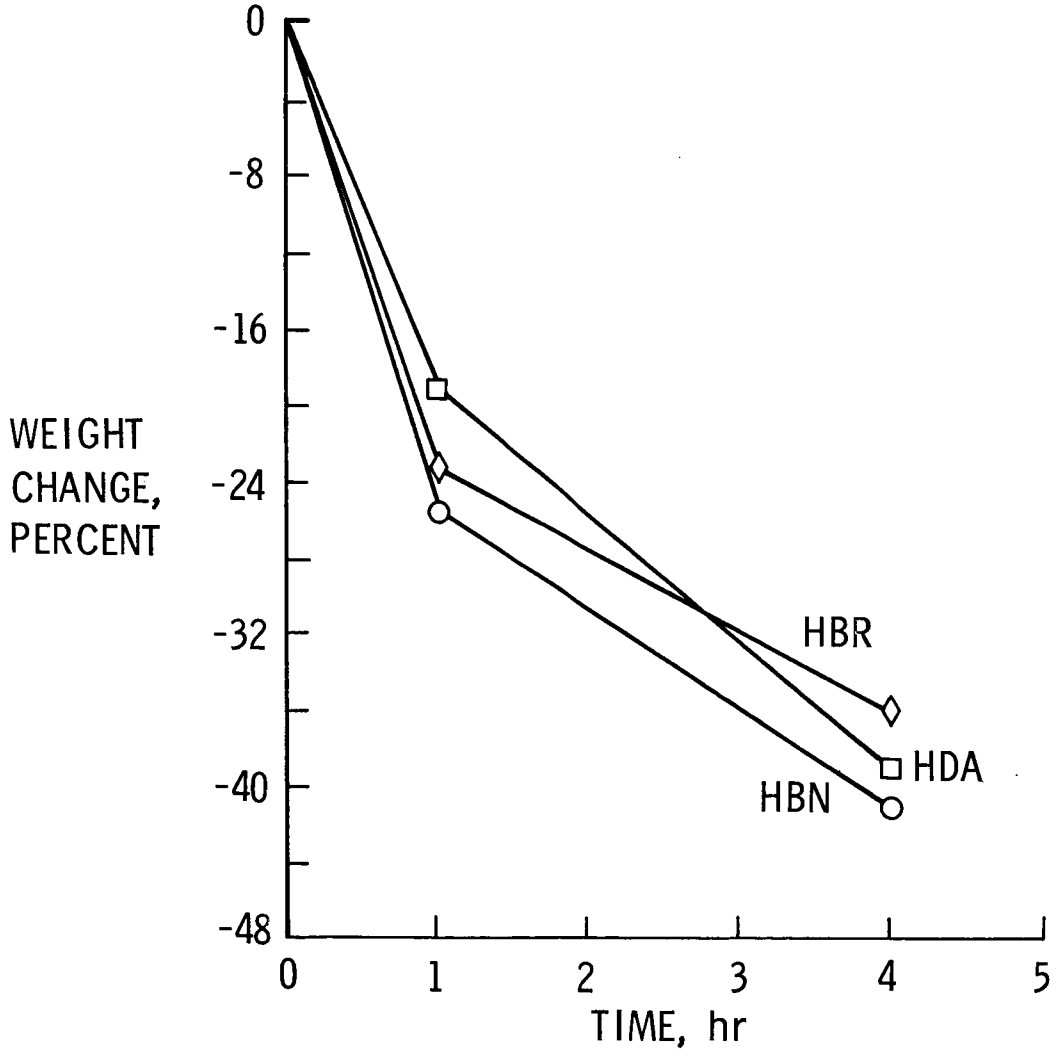

Figure 3.- Static oxidation test results for boron nitride compositions at 1500° C and 760 torr.

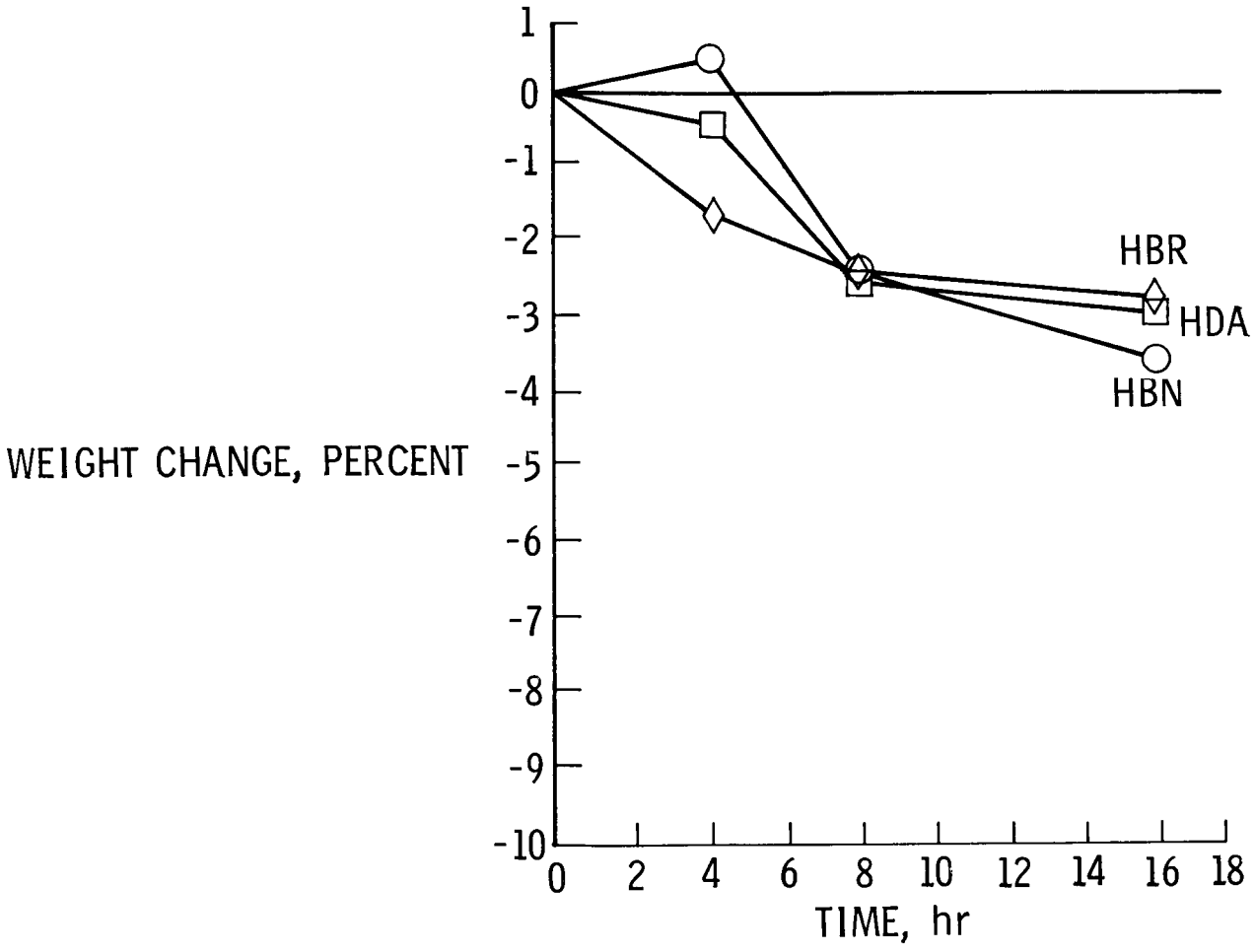

Figure 4.- Static oxidation test results for boron nitride compositions at 1500° C and 10^{-5} torr.

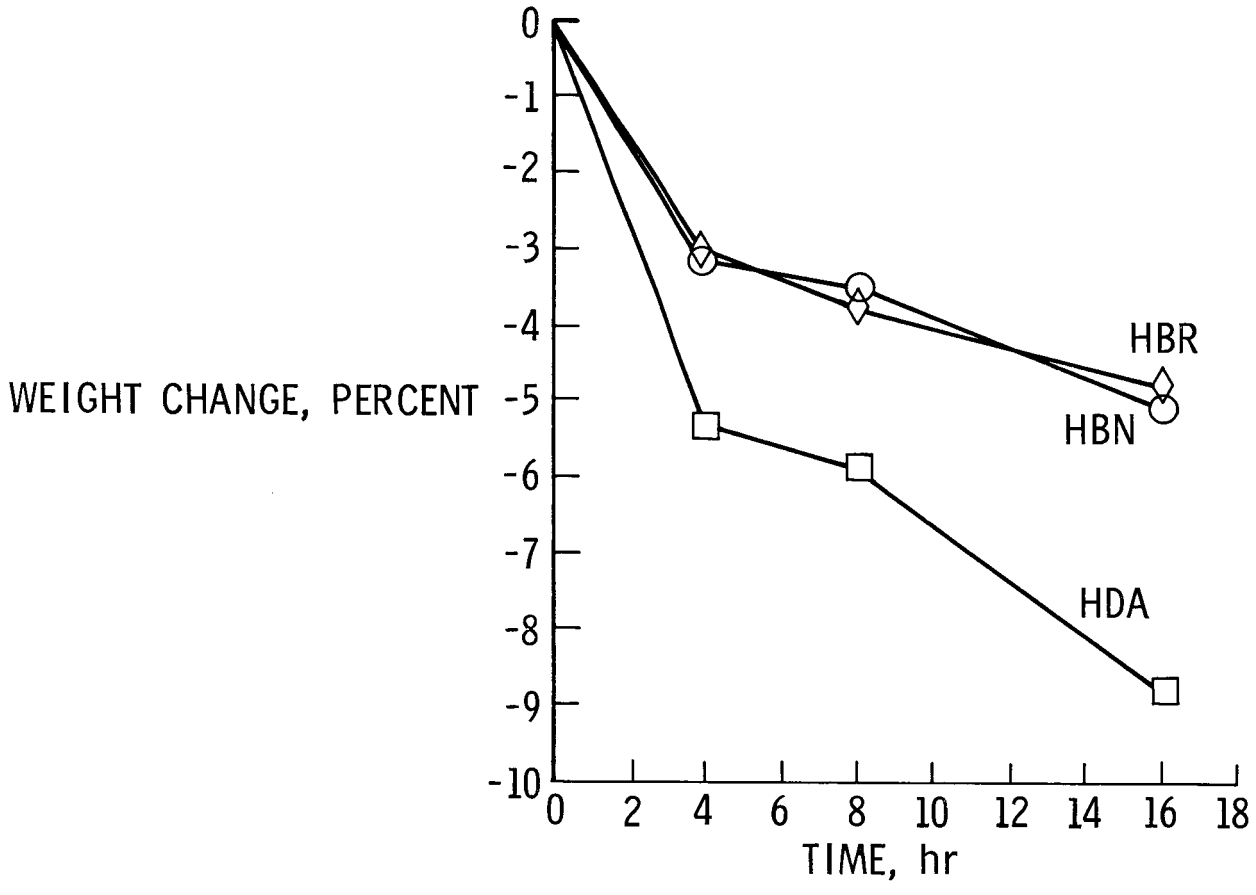

Figure 5.- Static oxidation test results for boron nitride compositions at 1750° C and 10^{-5} torr.

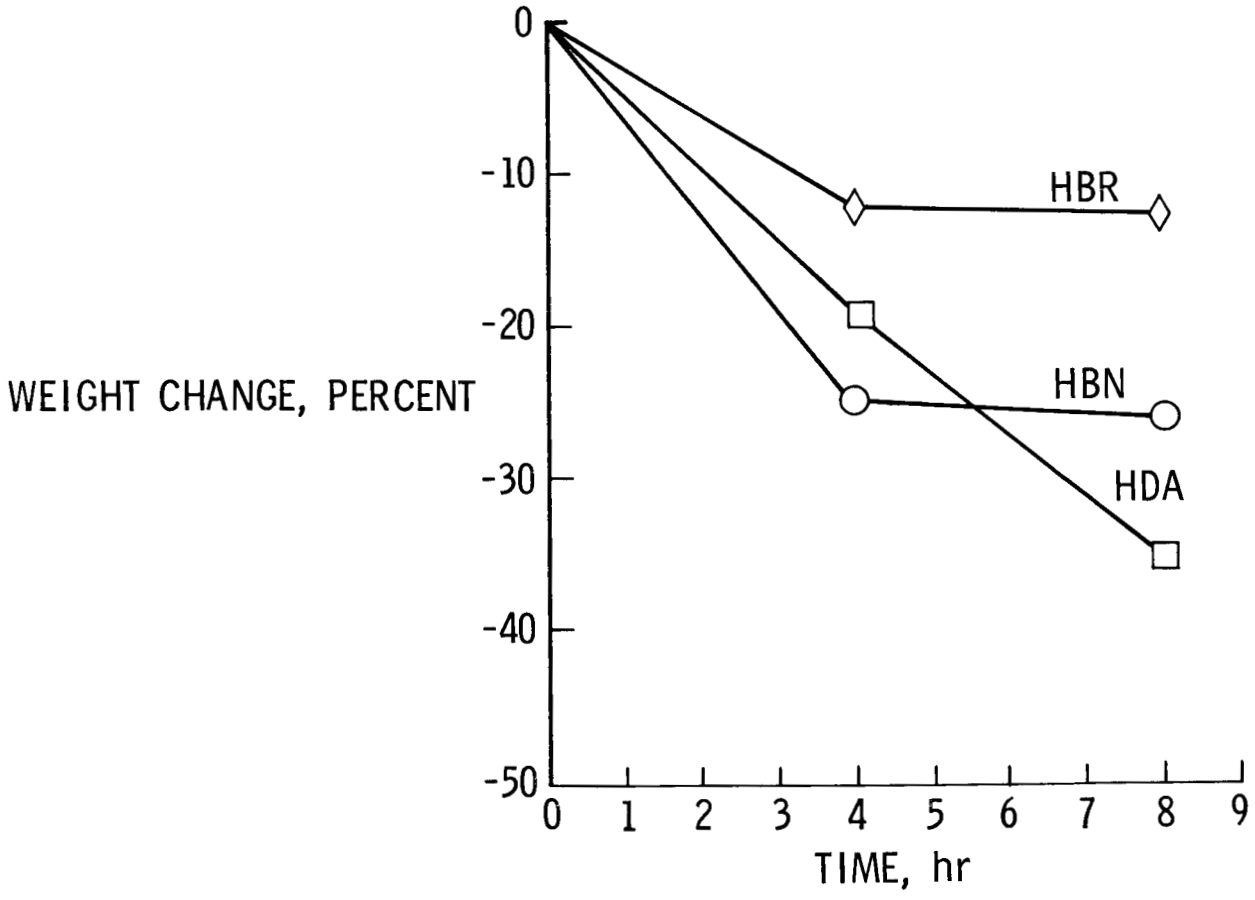

Figure 6.- Static oxidation test results for boron nitride compositions at 2000° C and 10^{-5} torr.

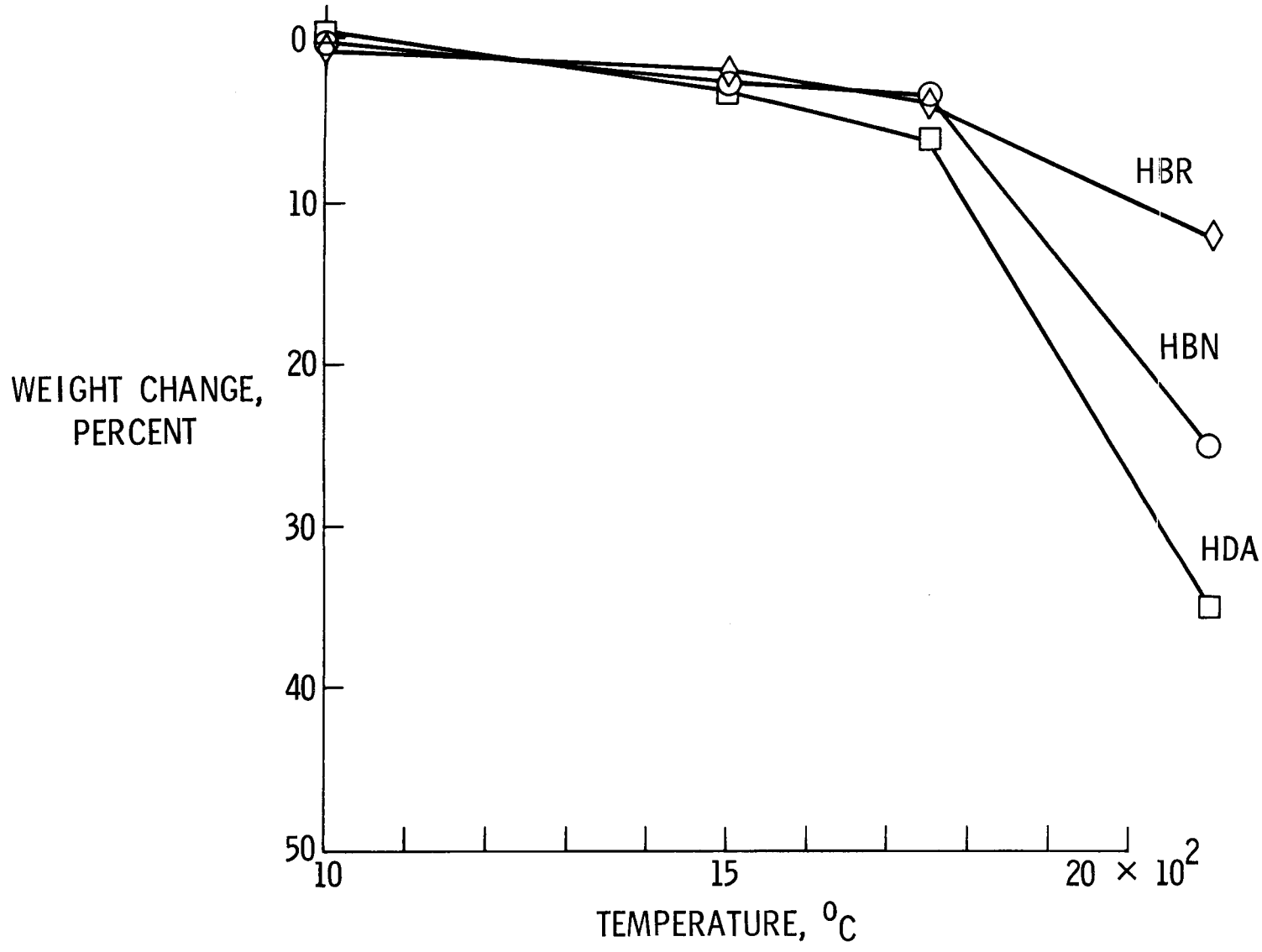

Figure 7.- Static oxidation test results for boron nitride compositions after 8 hours at 10^{-5} torr.

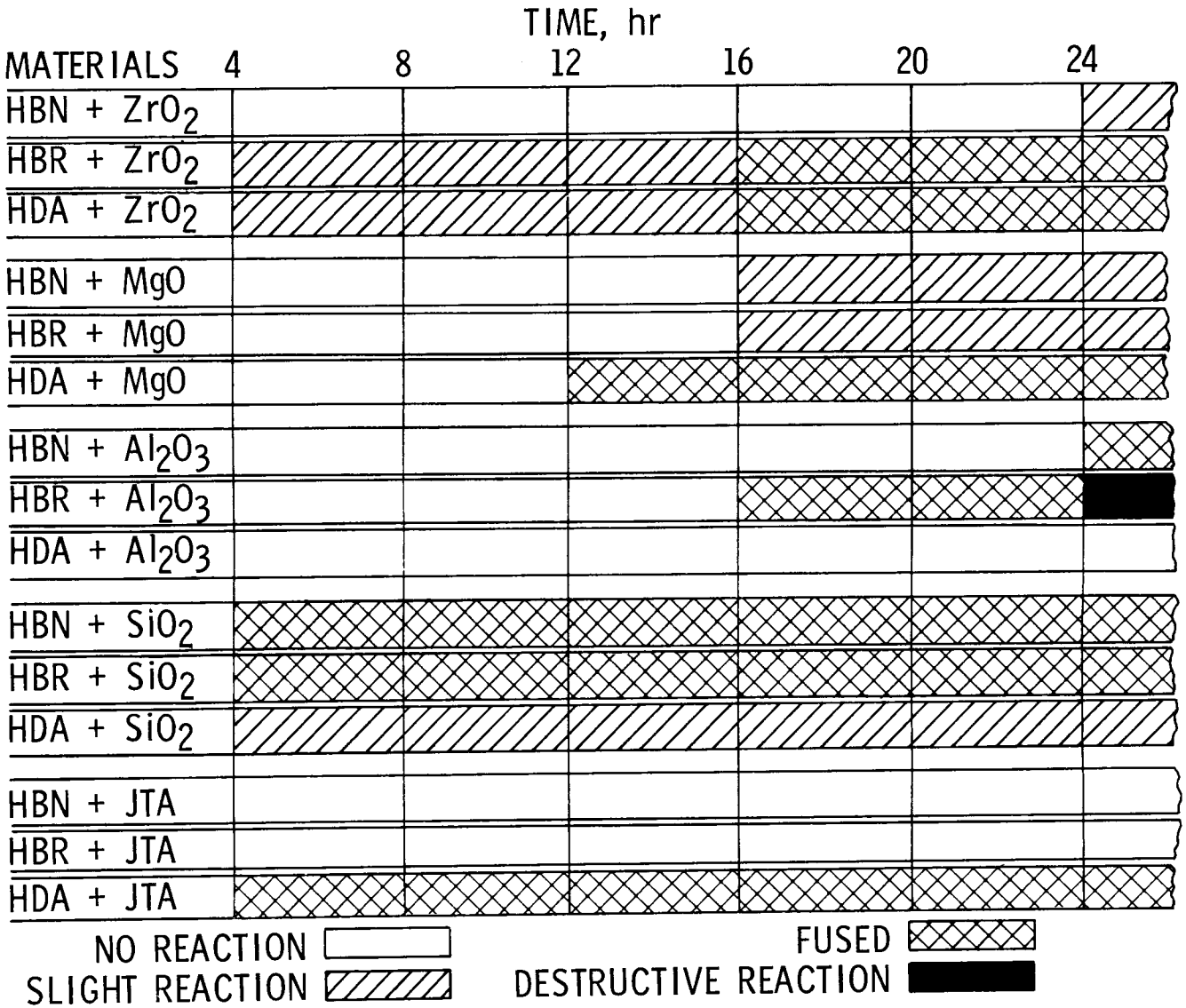

Figure 8.- Reaction of boron nitride compositions with refractory oxides and JTA graphite at 1000° C and 760 torr.

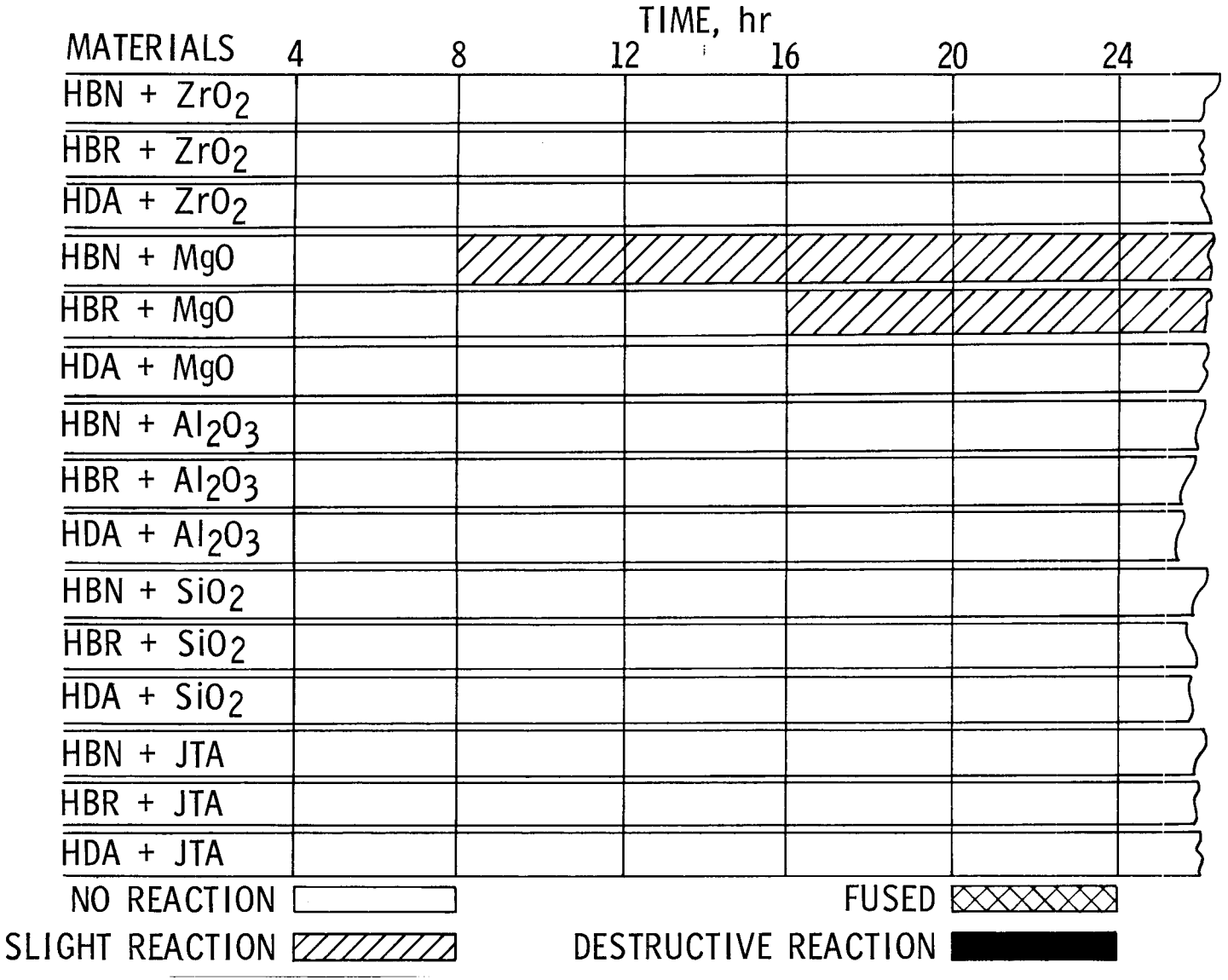

Figure 9.- Reaction of boron nitride compositions with refractory oxides and JTA graphite at 1500° C and 10^{-5} torr.

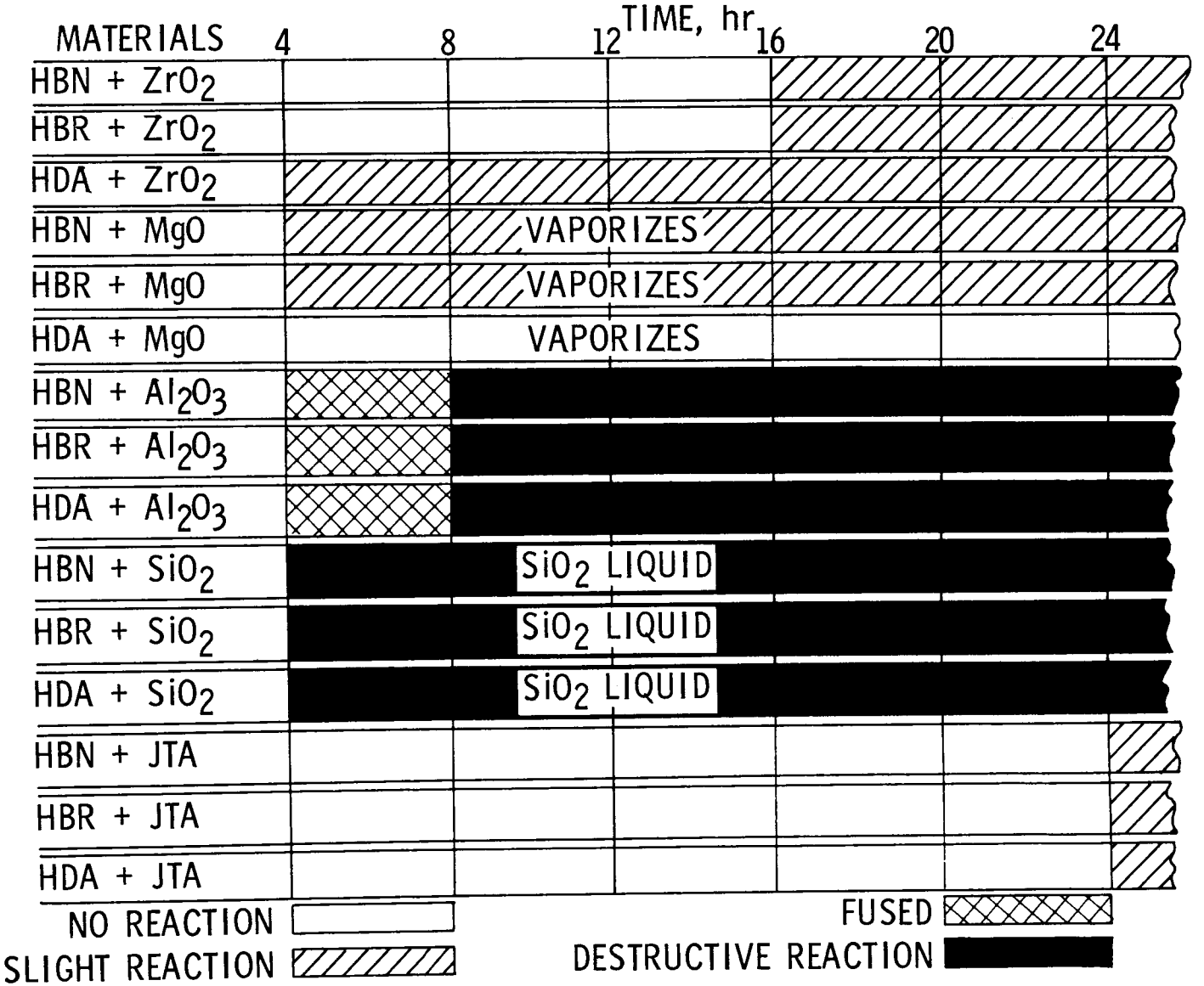

Figure 10.- Reaction of boron nitride compositions with refractory oxides and JTA graphite at 1750° C and 10^{-5} torr.

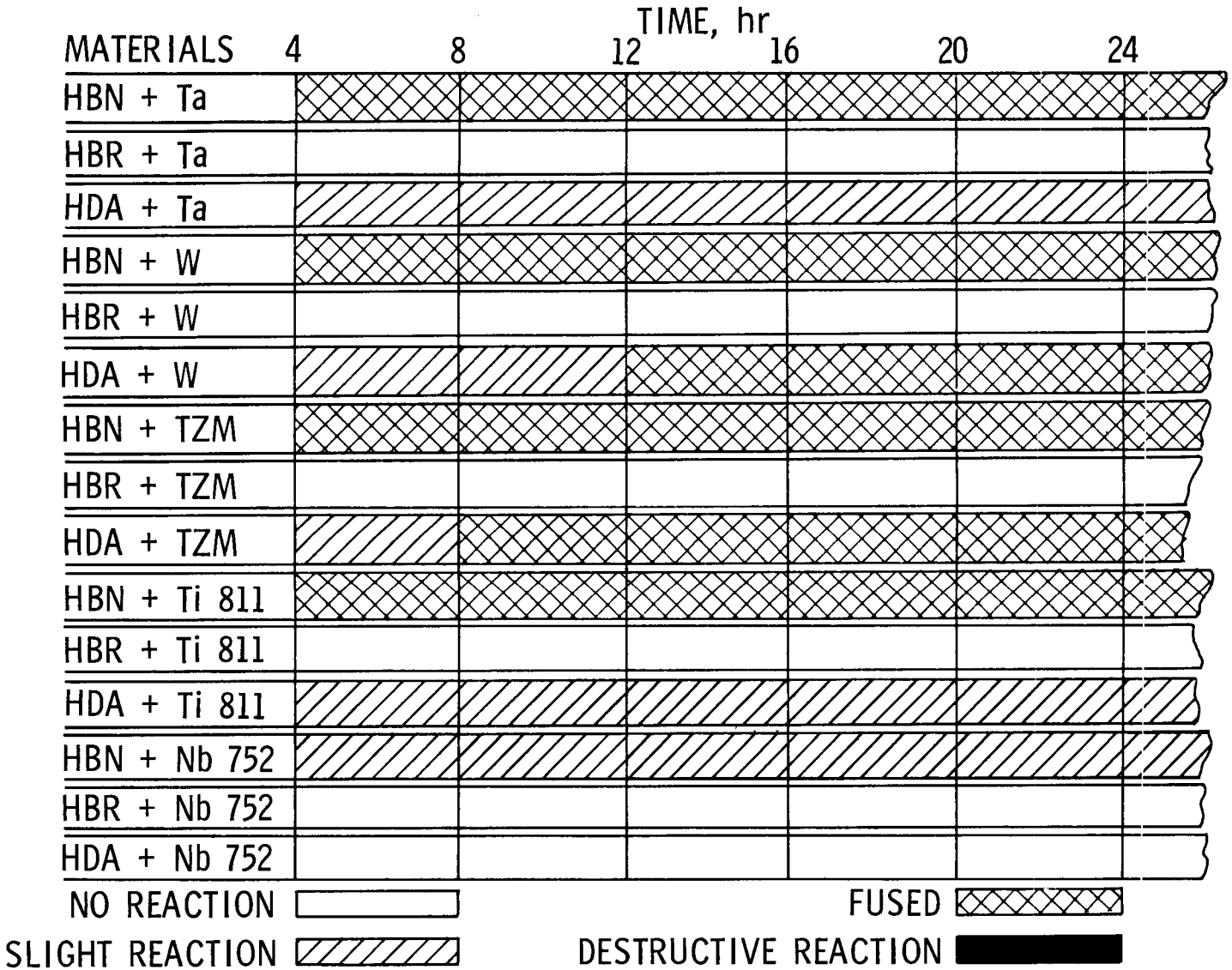

Figure 11.- Reaction of boron nitride compositions with refractory metals and metal alloys at 500° C and 760 torr.

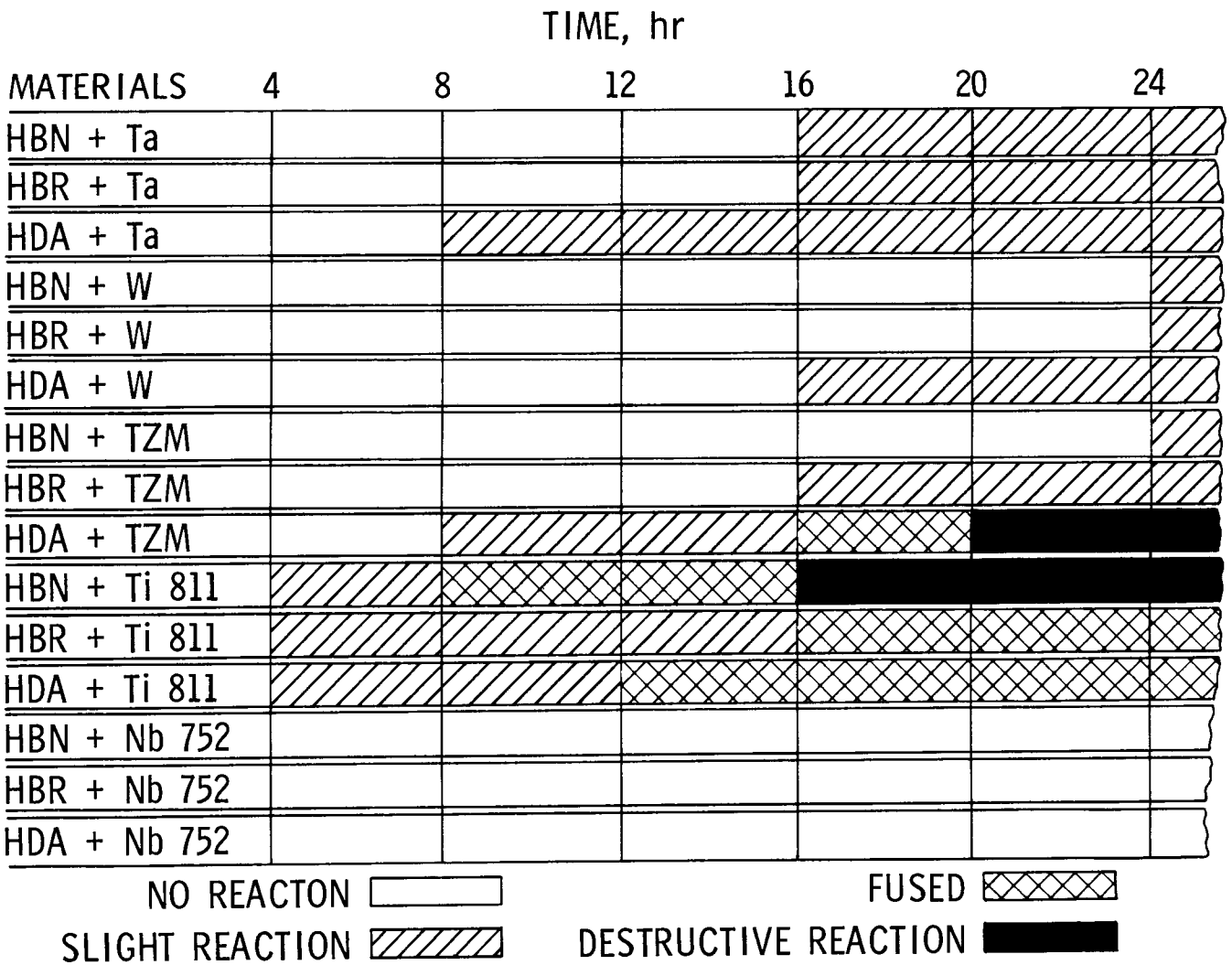

Figure 12.- Reaction of boron nitride compositions with refractory metals and metal alloys at 1500° C and 10^{-5} torr.

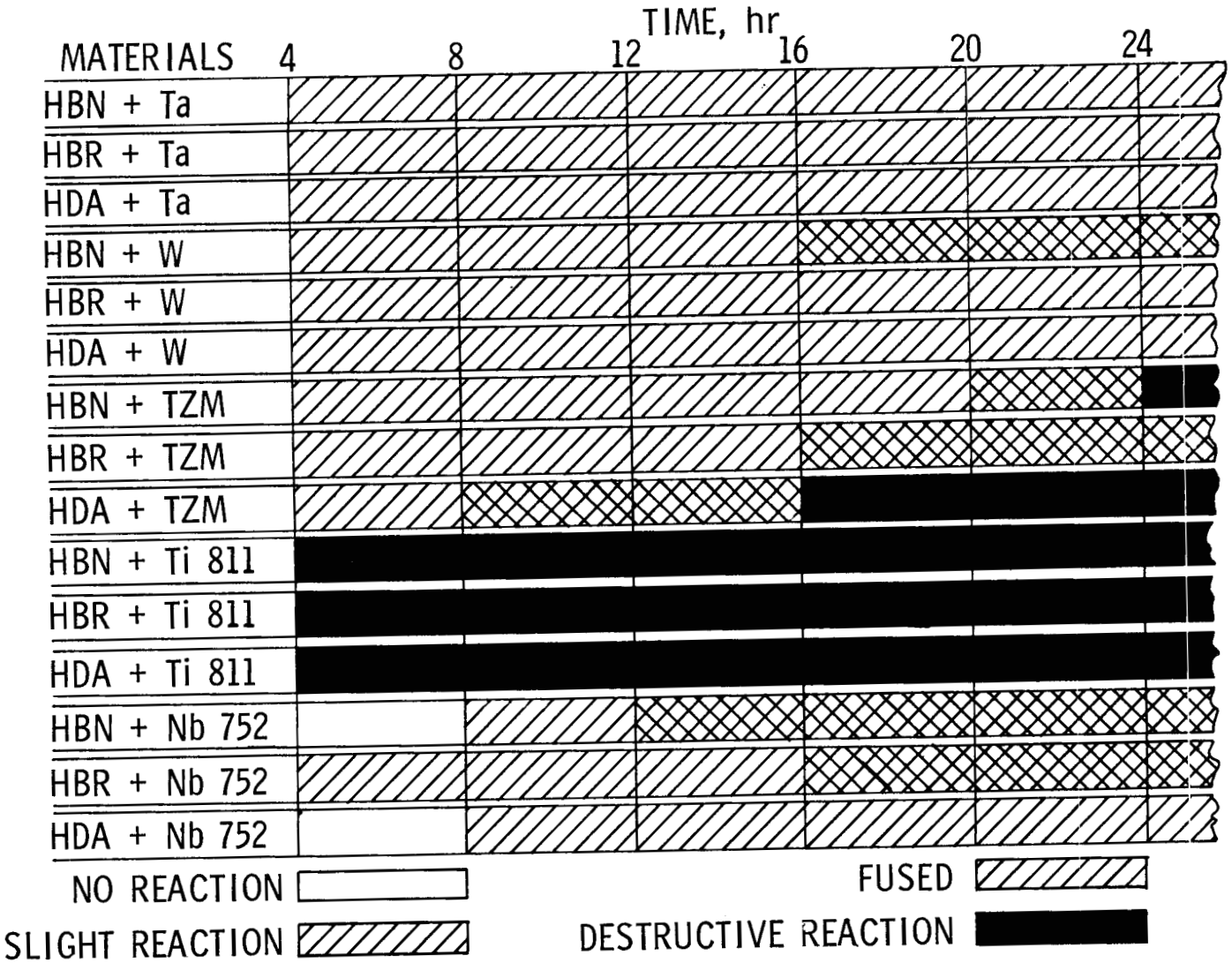

Figure 13.- Reaction of boron nitride compositions with refractory metals and metal alloys at 1800° C and 10^{-5} torr.