

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 1948

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I - NICKEL, COBALT, IRON, OR CHROMIUM WITH

BORON CARBIDE

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SUMMARY

A qualitative investigation was made of the bonding phenomenon in ceramals after exposure at temperatures above the melting temperature of the metal constituent. Simple bonding experiments were made to indicate the compatibility of various metals and a ceramic to form a ceramal. The temperature, time at temperature, and atmosphere suitable for sintering of the ceramal were indicated by the results of preliminary experiments.

The bonding experiments conducted with boron carbide and each of four metals showed that cobalt, iron, and nickel formed a bonding zone between the metal and the ceramic and that chromium showed satisfactory physical wetting characteristics on the ceramic.

INTRODUCTION

The need of increasing the present allowable gas temperatures of flight-propulsion systems in order to improve performance has stimulated research on refractory materials. Some of the materials under current investigation are mixtures of metal and ceramic material, which are known as ceramals. References 1 and 2 indicate that ceramals may combine the desirable high-temperature strength properties of the ceramic material and the thermal-shock resistance of the metal constituent. Economically, ceramals are also of interest because they frequently have a lower optimum fabrication temperature than pure ceramics.

In order to obtain a ceramal having desirable properties, it is imperative that the proper combination of materials be chosen and that the combining and sintering be done under optimum conditions. An investigation was therefore conducted at the NACA Lewis laboratory to determine whether any significance or value can be attached to a

simple experiment that will permit the investigator to study the behavior of a metal when brought into intimate contact with a ceramic and exposed to temperatures above the melting temperature of the metal. Experiments of this kind can be expected to yield fundamental information concerning the suitability of any combination of a ceramic and metal for use as a ceramal. In addition, the results obtained may serve as a guide in determination of the proper fabrication procedure.

Boron carbide was selected as the basis material because it has a tensile strength of 22,550 pounds per square inch at 1800° F and an apparent density of 2.50 grams per milliliter (reference 3), which results in a high strength-to-weight ratio.

The bonding of cobalt with boron carbide was studied because cobalt has been successfully used for many years in cemented carbides (reference 4). Iron and nickel were included because both materials are abundant domestically whereas cobalt is not. Chromium was selected as a possible constituent because it is known to be resistant to oxidation and because the possibility exists of forming a desirable carbide (reference 5) or boride (reference 6) if any excess carbon or boron is present as impurity in the boron carbide.

ANALYSIS

The type of experiment for the determination of the suitability of a ceramal for service use is dependent on the conditions of intended operation. In aircraft gas turbines, material temperatures of 1800° to 2400° F are present goals. An evaluation of the bonding between the constituents of a ceramal is a primary need before further evaluation is attempted.

All components of a ceramal must be strong and stable at the proposed temperatures in order to have desirable physical properties. Softening of the metal in a ceramal, however, is possible in the temperature range of 1800° to 2400° F because many of the commonly used metal constituents, such as nickel, iron, or cobalt, melt only a few hundred degrees above this range. The temperature at which the metal phase melts can sometimes be raised either by the formation of a new (bonding) phase by making a solution of the metal and the ceramic or by a chemical action between the constituents (references 7 and 8). When highly refractory metals, such as tungsten or molybdenum, are being considered for use in ceramals in the same temperature range, raising the softening

temperature of metal by forming a new phase is probably unnecessary. The prime consideration in the use of highly refractory metals is that during sintering the surface forces between the liquid (metal) and the solid (ceramic) be such that the contact angle between the two constituents be zero for satisfactory wetting (reference 9).

A simple screening experiment enabling investigators to select suitable constituents would eliminate considerable expense and guesswork in the evolution of a new ceramal. A study of the behavior of a metal in the liquid state when brought into intimate contact with a ceramic would probably yield information required for determining whether a bonding phase is formed and also indicate the conditions for sintering in order to obtain optimum properties in the ceramal.

Primary variables that must be considered during the sintering operation are temperature, time at temperature, and furnace atmosphere. During the sintering of a ceramal that is to be produced by the formation of a new phase between the metal and the ceramic, the sintering temperature must be high enough to provide the energy required for the reaction to take place. If the new phase is formed by solution, the time at the sintering temperature is primarily dependent on the limit of solubility of the constituents. When the bonding phase is formed by chemical action, the time at temperature is dependent upon the rate of reaction at the sintering temperature. When only physical wetting is required, the sintering temperature must be high enough for the metal to become fluid and to permit the conditions for wetting to be established. Because this mechanism is dependent only on the wetting between the metal and the ceramic, the time at temperature need only be long enough to permit the metal to fill completely the interstices in the ceramic network.

The behavior of the metal in contact with the ceramic is affected by the furnace atmosphere, which may act as a catalyst, react chemically, or alter the surface of the materials so that wetting, chemical action, or solution is achieved. Sintering of the ceramal in a suitable atmosphere is therefore necessary.

APPARATUS AND PROCEDURE

Specimen Preparation

The study of bonding mechanisms in this investigation was made using disks of hot-pressed boron carbide (fig. 1) to which the various metals were bonded. An indentation in the ceramic

disks was ground using diamond abrasives. The disks were washed in carbon tetrachloride and then cleaned by immersion in ammonium hydroxide, in dilute hydrochloric acid, and finally in distilled water. Metal powders of the following specifications were placed on the specimen, as shown in figure 1:

| | |
|----------|--|
| Cobalt | - minimum of 97.50 percent cobalt 0.60 percent nickel |
| Iron | - minimum of 98.50 percent iron (hydrogen reduced) 0.04 percent carbon 0.18 percent manganese |
| Nickel | - minimum of 99.00 percent nickel |
| Chromium | - minimum of 99.00 percent chromium (electrolytic) approximately 0.10 percent iron approximately 0.01 percent carbon |

Method of Bonding

The electric furnace in which specimens were heated (fig. 2) had a 3-inch-inside-diameter and 5-inch-outside-diameter graphite-resistance tube as the heating element. The furnace atmosphere was dry oxygen-free helium. In order to maintain a positive pressure of approximately 2 inches of water in the furnace, a helium flow rate of 40 cubic feet per hour was required. During the time the door of the furnace was opened to insert or remove specimens, the helium flow rate was increased to 80 cubic feet per hour in order to minimize contamination of the furnace atmosphere.

Specimens were inserted into the preheated furnace for approximately 5 minutes in order to reach the temperature of the bonding experiments. The furnace temperature was controlled with an automatic-recording total-radiation optical pyrometer. This instrument was focused on the end of a closed graphite tube that extended through the protector tube and was located within $\frac{1}{4}$ inch of the graphite-resistance heating element. The temperature of the specimen was measured with an optical pyrometer by sighting through a quartz window mounted in the door of the loading chamber. The sensitivity of the temperature-controlling instrument resulted in a maximum specimen-temperature variation of $\pm 15^{\circ}$ F. The specimen was held at the indicated temperature for 15 minutes and then rapidly cooled in the water-jacketed cooling zone of the furnace; about 5 minutes was required for the specimen to cool to

room temperature. After removal from the cooling zone, the specimens were visually examined and the metal beads were picked using a dental-type probe to determine whether the metal adhered to the ceramic.

The experiments using cobalt, iron, nickel, or chromium in contact with boron carbide were conducted at approximately 300° F above the melting temperature of each element, that is, 3000° F, 3100° F, 2950° F, and 3240° F, respectively. Before any bonding mechanism could be observed using nickel on boron carbide, an additional experiment was required at approximately 600° F above the melting temperature of 2650° F.

Microscopic Examination

All specimens were microscopically examined in order to study the mechanism of the bond between the metal and the ceramic. The specimens were sectioned through the indentation, mounted in bakelite, and polished. The preliminary polishing procedure consisted in grinding the mounted specimens on a facing wheel embedded with 600-mesh diamond abrasive, and then polishing with 1200-mesh diamond abrasive on a canvas polishing mat. The final polishing was accomplished on cloth-covered wheels using diamond abrasive with a particle size of 1 to 5 microns and then diamond dust of 0- to 0.5-micron size.

RESULTS AND DISCUSSION

The boron carbide disks used in this investigation were hot-pressed and possessed a density of 2.50 grams per milliliter, as determined by differential weighing in air and water. This value is close to the density of a single crystal of boron carbide, which is 2.52 grams per milliliter as reported in reference 10. Consequently, at room temperature any adherence between the metal and the boron carbide was not considered to be a result of capillary action of the liquid metal.

The nickel - boron carbide specimen exposed at 2950° F showed no evidence of adherence of the metal to the ceramic. The nickel powder melted and formed an unattached bead of metal in the indentation of the ceramic disk. When exposed to a temperature of approximately 600° F above the melting temperature of the nickel (3250° F), however, the metal bead could not be readily picked from the ceramic; the specimen was therefore sectioned and polished for further examination.

A cross section of the nickel - boron carbide specimen is shown in figure 3. In figure 3(a), three zones are evident: (a) metal, nickel; (b) bonding zone; and (c) ceramic, boron carbide. The bonding zone was formed by the liquid metal selectively dissolving part of the boron carbide and penetrating into the pores formed between the carbide particles that remained undissolved. The depth to which the solution penetrated is a function of the time and the temperature at which the specimen was exposed and of the limit of solubility of the ceramic in the metal at 3250° F.

A magnification of the nickel and bonding-zone interface (fig. 3(b)) shows that the metal penetrated into the capillaries or pores that were formed by selectively dissolving the carbide. In this photograph, the gray particles are thought to be undissolved carbide and the black areas are either voids formed during the experiment or during polishing by the pulling out of some brittle particles.

The interface between the bonding zone and the boron carbide is shown in figure 3(c). The surface of boron carbide adjacent to the bonding zone appears comparatively smooth and no capillaries are evident.

An examination of the microstructure (fig. 3(c)) shows a crack at the interface between the boron carbide and the bonding zone. This crack, may have formed as a result of the thermal stresses induced either during the sudden cooling of the specimen or during the sectioning and mounting operation. The presence of a crack is not of importance in this experiment because only the formation of the bonding zone is significant in determining the suitability of a metal and a ceramic for use as a ceramal.

The interfaces between the cobalt and the bonding zone and the boron carbide and the bonding zone are shown in figures 4(a) and 4(b), respectively. A comparison of these figures with figures 3(b) and 3(c) shows that the bonding zone formed between cobalt and boron carbide was produced in the same manner as that between nickel and boron carbide. Figure 4(a) indicates the selective solution of carbide particles and the penetration of the liquid metal into the formed pores.

Examination of the iron - boron carbide specimen showed two zones: (a) bonding zone; and (b) ceramic, boron carbide (fig. 5). The structure of the interface between the bonding zone and the boron carbide of the iron - boron carbide specimen is similar to that observed for both nickel (fig. 3(c)) and cobalt (fig. 4(b)).

In figure 5, a phase of metallic appearance (white area) surrounds some carbide particles (gray area in the metallic matrix). Because no zone of pure metal could be detected as in the case of both nickel and cobalt, boron carbide appeared to be exceedingly soluble in iron at 3100° F.

During the experiment conducted at 3240° F with chromium and boron carbide, the chromium melted but did not form a bead in the indentation as did the other metals. The metal completely covered the boron carbide specimen evidencing zero contact angle and satisfactory wetting characteristics (reference 9). This phenomenon is similar to that obtained when a wetting agent is added to a bead of water on an oily surface. The adherence, however, was very poor and the metal could be easily peeled from the ceramic. The specimen was sectioned and microscopically examined. No evidence of any bonding phase between the chromium and the boron carbide was present.

Because a bonding phase was formed between nickel, cobalt, or iron with boron carbide, the possibility exists that the melting temperature of the bonding phase might be higher than that of the pure metal. Thus, ceramals consisting of boron carbide with nickel, cobalt, or iron might be suitable for use in the temperature range of 1800° to 2400° F. Chromium, which showed satisfactory wetting characteristics with boron carbide, might be a suitable ceramal constituent provided that softening does not occur below 2400° F.

The results obtained from these experiments indicate that the suitability of a metal and a ceramic for use as a ceramal can be readily determined and that the bonding between the metal and the ceramic can be easily studied.

SUMMARY OF RESULTS

From a qualitative investigation of boron carbide with nickel, cobalt, iron, or chromium, a simple screening experiment was found to facilitate study of the bonding of a metal when brought into intimate contact with a ceramic and exposed to temperatures above the melting temperature of the metal. Examination of the experimental specimens indicated that the suitability of a metal and a ceramic for use as a ceramal could be determined. The temperature, time at temperature, and atmosphere suitable for sintering ceramals of these materials were indicated by the results of preliminary bonding experiments.

Bonding experiments conducted with boron carbide and each of four metals showed that two mechanisms existed: (a) formation of a bonding phase with nickel, cobalt, and iron; and (b) physical wetting with chromium. Formation of a bonding phase was believed necessary for most metals; however, either forming of a bonding phase or wetting might be suitable for highly refractory metals.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 10, 1949.

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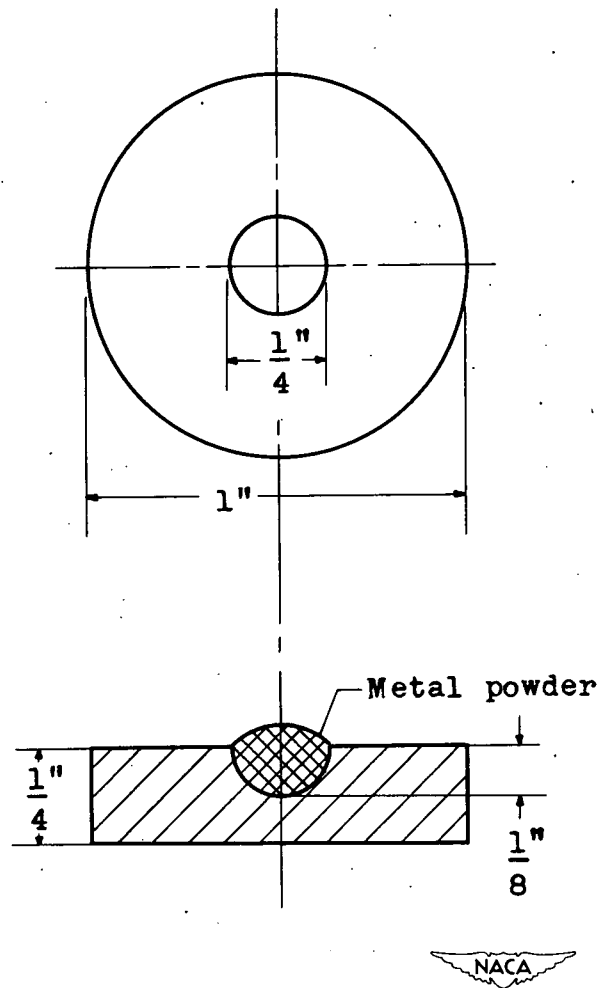


Figure 1. Boron carbide specimen used for study of bonding mechanism.

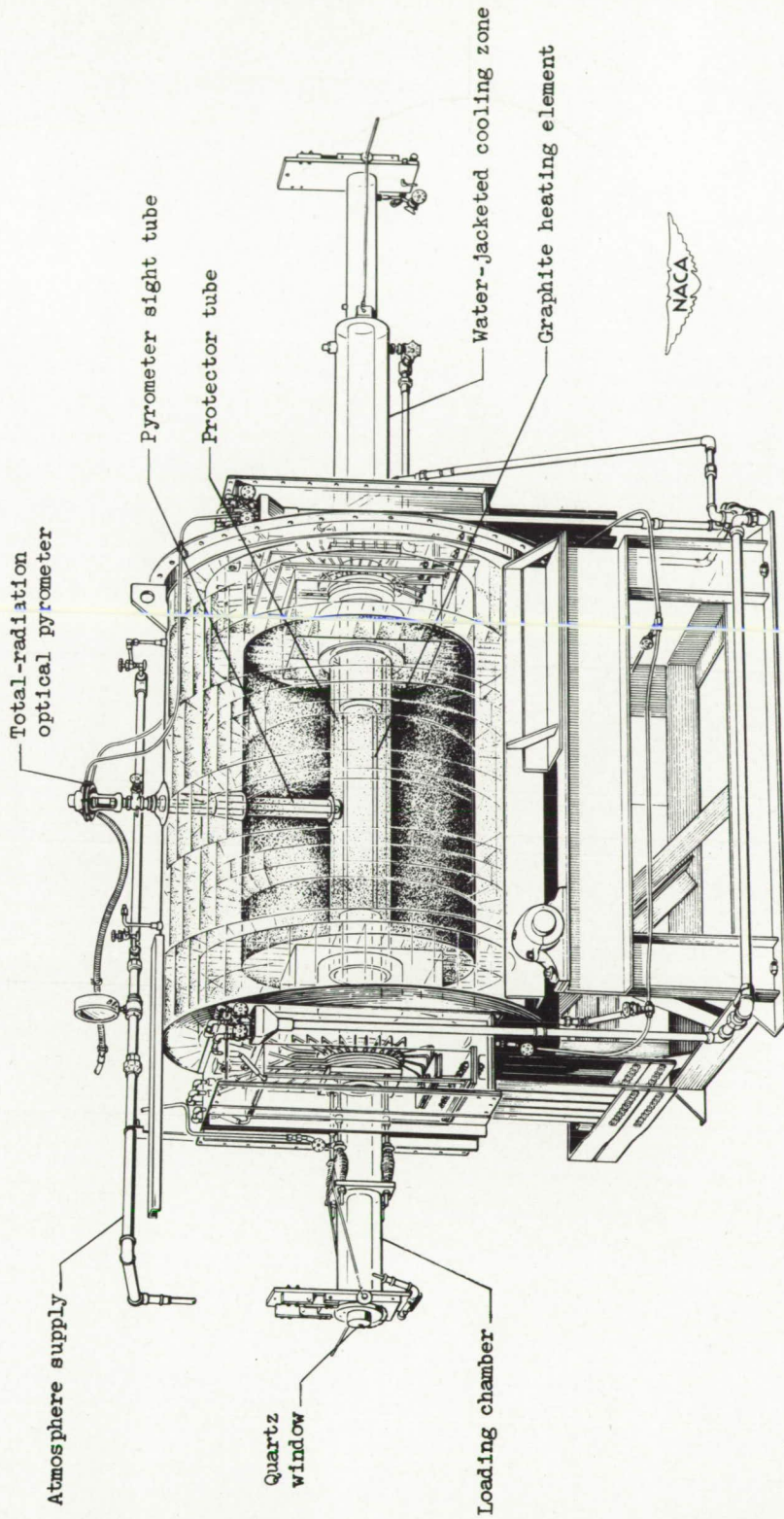
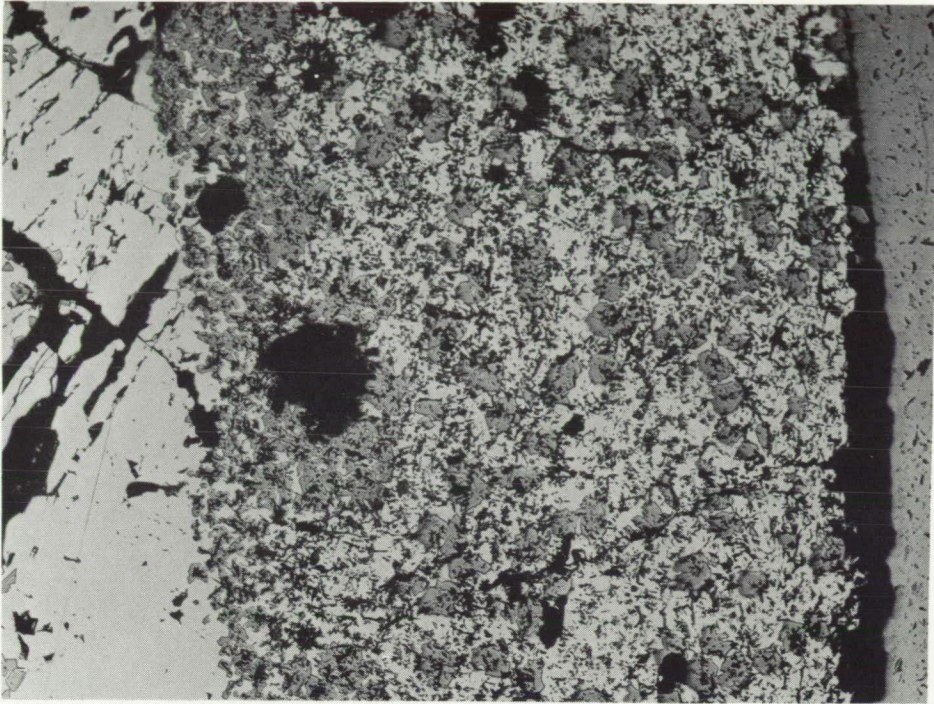


Figure 2. - Graphite-resistance electric furnace used for bonding study.

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— Nickel — | — Bonding zone — | — Boron carbide

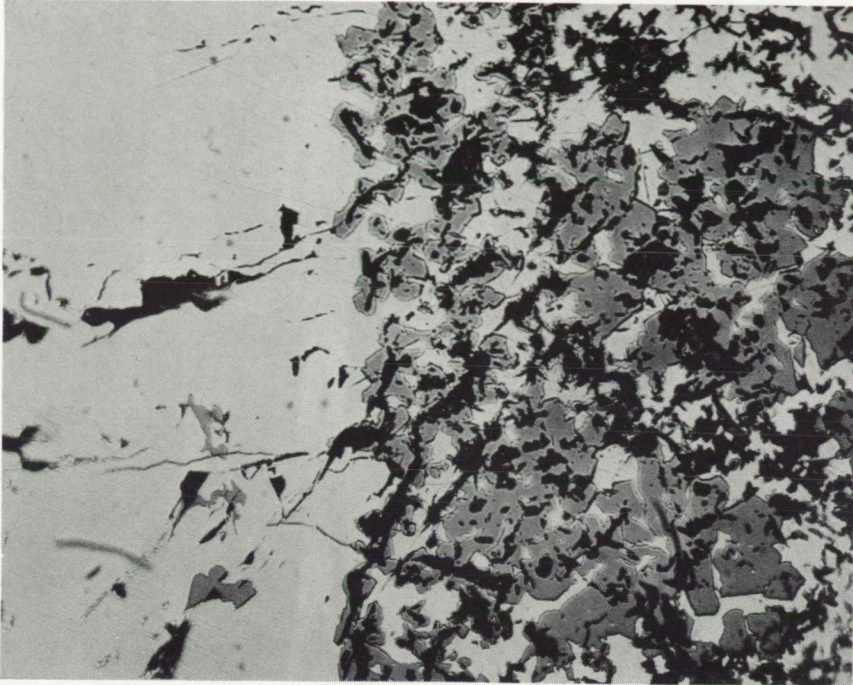
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(a) Cross section of specimen. X50.

Figure 3. - Photograph of nickel - boron carbide bonding specimen after 15 minutes at 3250° F.

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— Nickel — | — Bonding zone —

(b) Interface between bonding zone and metal of specimen. X250.

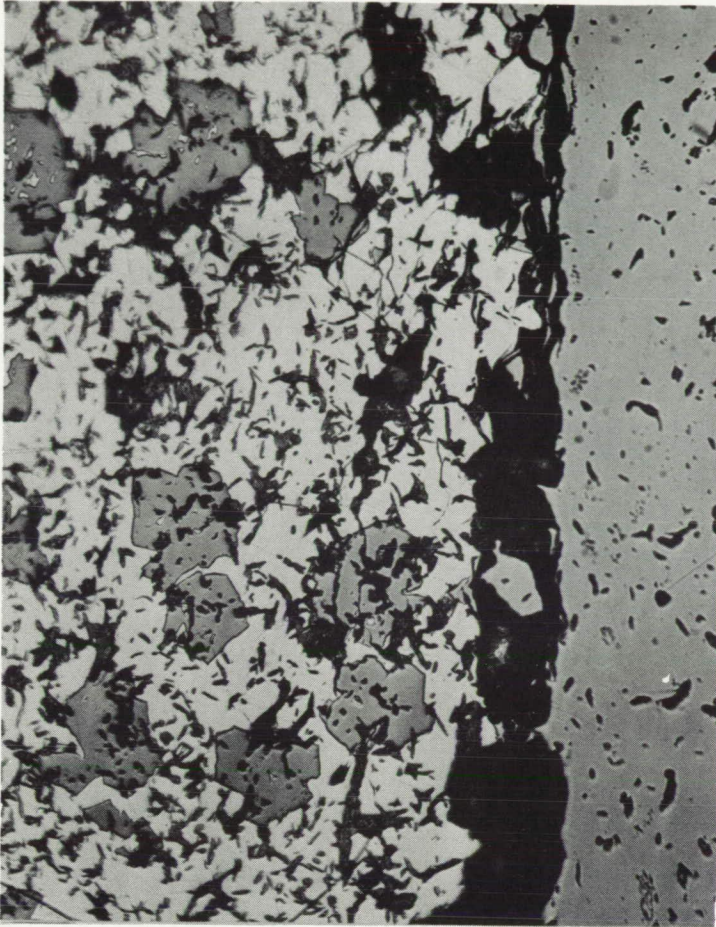


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Figure 3. - Continued. Photograph of nickel - boron carbide bonding specimen after 15 minutes at 3250° F.

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————— Bonding zone ———— | ———— Boron carbide

(c) Interface between bonding zone and ceramic of specimen. X250.

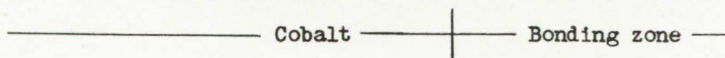
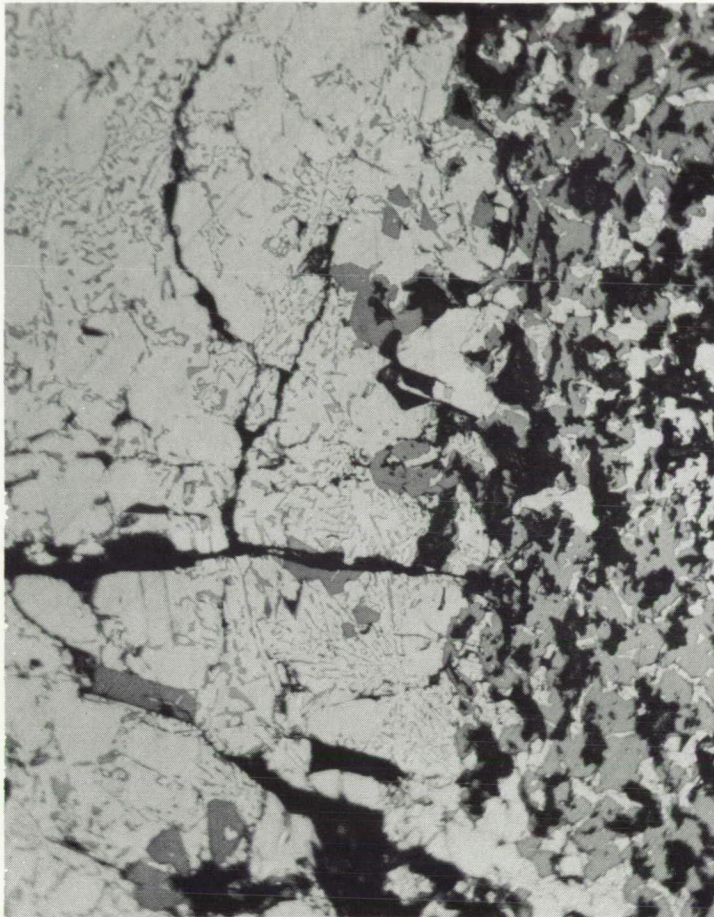


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Figure 3. - Concluded. Photograph of nickel - boron carbide bonding specimen after 15 minutes at 3250° F.

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(a) Interface between bonding zone and metal of specimen.



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Figure 4. - Photograph of cobalt - boron carbide bonding specimen after 15 minutes at 3000° F. X250.

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————— Bonding zone ———— | ———— Boron carbide ————

(b) Interface between bonding zone and ceramic of specimen.

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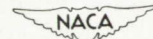
Figure 4. - Concluded. Photograph of cobalt - boron carbide bonding specimen after 15 minutes at 3000° F. X250.

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————— Bonding zone ————— | Boron carbide



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Figure 5. - Photograph of interface between bonding zone and ceramic of iron - boron carbide bonding specimen after 15 minutes at 3100° F. X250.