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PRELIMINARY MICROSCOPIC STUDIES OF CERMETS AT HIGH TEMPERATURES

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THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

APRIL 1955

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Approved for Public Release

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WRIGHT AIR DEVELOPMENT CENTER

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MATERIALS LABORATORY

CONTRACT No. AF 33(038)-16911

PROJECT No. 7350

**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This report was prepared by the Ohio State University Research Foundation under USAF Contract No. 33(038)-16911. This work was accomplished during the period of September 1952 to September 1953. The contract was initiated under Project No. 7350 "Ceramic and Cermet Materials", Task No. 73500 "Ceramic and Cermet Materials Development", formerly RDO No. 605-233, "Ceramic and Cermet Materials Development", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. Robert S. Thompson acting as the project engineer.

Personnel participating in the research and preparation of the report include T. S. Shevlin, H. M. Greenhouse, H. W. Newkirk, L. J. Trostel, Jr., G. A. Bole and E. T. Montgomery.

WADC TR 54-33

ABSTRACT

This report covers the determination of some of the physical properties of cermet IIIB not previously reported. It also covers the design, construction, and testing of special equipment required for the study of the microstructure of TiC base cermets.

The initial study of possible phase changes and changes in microstructure of some TiC base cermets, with time, at high temperatures is reported. A tentative theory is advanced in explanation of the steep slope of the stress-rupture curves for TiC+Ni cermets of the type produced by Kennametal, Inc.

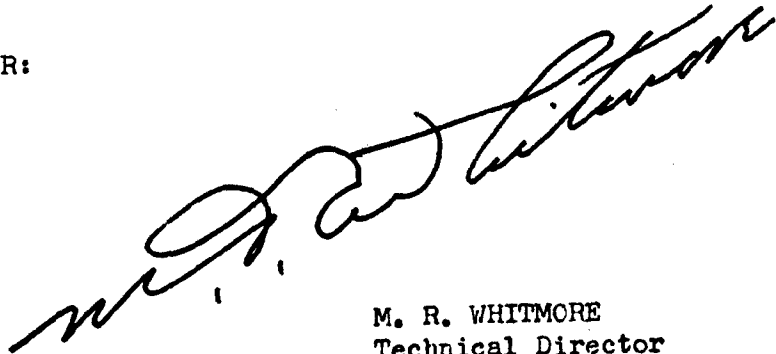
In preparation for this study the following special equipment was built: a high-temperature x-ray camera, a vacuum quench furnace, and apparatus for the determination of coefficients of thermal conductivity at temperatures to 1700° F. This equipment is described in detail.

A preliminary evaluation of the potentialities of TiB_2 and $MoSi_2$ as components of a cermet is discussed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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INTRODUCTION

This is a summary report and consists essentially of the material contained in six bimonthly reports submitted under the contract to the Materials Laboratory, Directorate of Research, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The research and development program covered by the report is a continuation of the work reported in WADC Technical Report No. 53-287. The principal studies were two in number.

1. The evaluation of the physical properties of the promising cermet III B having the composition $55.4 \text{ TiC} + 17.9 \text{ TiB}_2 + 10.0 \text{ Si} + 16.7 \text{ Co}$ was continued. The stress-to-rupture curve for 1800°F was determined and solid nozzle-diaphragm partition blades of airfoil contour were fabricated and tested by the Power Plant Laboratory, Directorate of Laboratories, WADC.

2. One of the best cermet compositions developed to date is composed of titanium carbide bonded with 20 to 30 per cent of nickel, a nickel-molybdenum alloy, or a nickel-chromium alloy. A cermet of this type produced by Kennametal, Inc., Latrobe, Pennsylvania, has been extensively tested in the form of both nozzle blades and rotor blades. This type of cermet meets most of the requirements for a blading material except that it is quite brittle and its stress-to-rupture curve shows as steep a slope as the curves for the better blade alloys. It was considered highly desirable to determine the cause of this rapid loss of strength, with time, at temperatures between 1600° and 1800°F .

Extensive preparations were made for this study, and preliminary data together with a tentative explanation of the cause of strength deterioration are included in this report. In preparation for this study, a high-temperature x-ray camera was built and a special vacuum quench furnace was designed and constructed. As supplementary equipment for the evaluation of this and other cermets, an elaborate apparatus has been designed and built with which to determine coefficients of thermal conductivity at temperatures to 1700°F .

A third study has been initiated during this period and carried on as time has permitted. It involves a study of the possibilities of using MOSi_2 and TiB_2 , singly or in combination, as the ceramic component of a high-temperature cermet. This study is closely tied to efforts to improve the heat-shock resistance of cermet III B, which proved to be unsatisfactory in this respect presumably because the cobalt binder metal is converted, in sintering, to brittle cobalt monosilicide leaving no ductile metal phase in the cermet.

SECTION I

STRENGTH DATA FOR CERMET III B

The development of cermet body III B has been covered in a previous report. Further data on the strength of this cermet and its resistance to thermal cycling are given here.

1. MATERIALS

The following materials were used in making the test specimens:

- TiC: Minus 325 mesh containing 80.4% Ti; 19.5% total C; 0.10% free C; 0.08% total Fe; Norton Company.
- TiB₂: Minus 20 mesh containing 66.51% Ti, 31.1% B and 1.7% C + 0.69% minor impurities. (1.2% estimated free C); Norton Company.
- Si: Minus 325 mesh, 97% Si; Charles Hardy, Inc.
- Co: Minus 300 mesh, 97.5% Co; Charles Hardy, Inc.

2. COMPOSITION

The composition in weight per cent is 55.4% TiC, 17.9% TiB₂, 10.0% Si, 16.7% Co.

3. PROCESSING

(a) Milling

Batches containing 500 grams of the above composition were milled 50 hours in a one-quart steel mill, using benzene as the vehicle and cobalt-bonded tungsten carbide slugs as the grinding medium.

(b) Forming

Following air drying and drying overnight at 100°C the above batch was pressed hydrostatically at 35,000 psi in the form of a blank. This blank was crushed in a mortar and screened through a 65-mesh screen. The prepressed granulated batch was then packed in thin-walled rubber tubes retained in

appropriate lengths of perforated brass pipe. The air was evacuated from the powder and the ends of the rubber tubing closed. As a result of subjecting this assembly to a hydrostatic pressure of 35,000 psi, cylindrical rod blanks approximately 0.6 inch in diameter by 12 inches long were obtained.

(c) Firing

The rod blanks were fired in a furnace consisting of a gas-tight refractory porcelain tube heated within a tubular Globar element surrounded with suitable insulating refractories. They were heated at a rate of approximately 400°F per hour to a soaking temperature of 2760-2790°F, and held at this temperature for 1.5 hours.

(d) Grinding

The fired rod blanks approximately 0.5 inch in diameter by 10 inches long were ground on a modified lathe specially designed for this purpose to form tensile test specimens approximately 9 inches long by 0.375 inch in diameter containing a necked center section ground on a 4.69-inch radius. This produces a necked length 1.5 inches long containing a minimum center section 0.250 inch in diameter.

SHORT-TIME TENSILE TESTS

The tensile test specimens were sandblasted on the ends and wrapped with two turns of 1-inch wide asbestos tape cemented with sodium silicate to provide for gripping and accommodation in the jaw assemblies. The tensile test machine employs cold grips and incorporates pneumatic loading, jaw aligning, and furnace heating features of proven value in the tensile testing of brittle materials. The load is applied smoothly by cylinder-gas pressure acting on a hydraulic piston and cylinder. Alignment between the heads which contain the jaws is preserved during mounting and throughout the loading cycle by guide rods press-fitted into one head, and sliding in the other head. A small platinum-wound furnace fits around the specimen and between the heads, which are cooled with dry ice for these tests. Specimens were tested at 75°F, 1800°F, 2000°F, and 2200°F and the results are shown in Table I.

TABLE I. SHORT-TIME TENSILE STRENGTHS

Temperature °F	Breaking Stress, psi
75°F	26,700
	28,100
1800°F	26,822
	28,914
2000°F	39,363
	33,567
2200°F	20,109
	13,380

STRESS-RUPTURE TESTS

1. SPECIMENS

Standard rod specimens identical with those described for short-time tensile tests were prepared for stress-to-rupture testing.

2. TESTING

The equipment used is similar to that described for short-time tensile testing and in addition provides for maintenance of a constant mechanically applied load and a constant sustained temperature, with the necessary auxiliary equipment for temperature check purposes and timing the duration of the test run. This equipment has been previously described in detail.¹

The rods initially tested failed at relatively low loadings and at the relatively cool locations between the furnace and the water-cooled grips where the temperature is between 800 and 900°F. This type of failure is attributed to low-temperature oxidation. Since this composition develops oxidation resistance upon heating to a relatively high temperature, through the production of a borosilicate glass skin, the practice of subjecting all rods to a preoxidizing treatment for 24 hours at 2000°F was adopted.

The final stress-to-rupture data at 1800°F for this cermet are shown in Table II and the stress-to-rupture curve is shown in Figure 1. For comparison there are shown in this same

¹A. Rief Blackburn and Thomas S. Shevlin: Equipment for Processing and Testing Cermet Solid Bodies. J. Am. Ceram. Soc., Nov., 1949.

figure the curves for two chromium - alumina cermets and for three Kennametal TiC base cermets.

TABLE II

Stress-Rupture Strengths in Tension at 1800°F

Test No.	Stress, psi	Time to failure	Remarks
117	28,000	1.5 minutes	Broke in the neck
118	27,000	202 hours	" " " "
WADC*	25,000	2,700 "	Broke outside neck
115	22,000	1,058 "	" " "
114	20,000	1,253 "	" " "

* This rod tested by Materials Laboratory, Directorate of Research, WADC.

NOZZLE BLADES

Solid nozzle blades of a simulated airfoil shape conforming to Air Materiel Command drawing X51D9692 were fabricated of composition III B and sintered in a new furnace conforming in all respects to the furnace used for sintering the tensile-test rods.

Thin bar specimens of this composition displayed good heat-shock resistance in laboratory tests but when the solid nozzle blades were subjected to the present standard cycling test at the Power Plant Laboratory, Directorate of Laboratories, WADC, they failed completely in the first few cycles.

As the study of this composition progressed it was determined that, as the end product of sintering, the cobalt is converted entirely to cobalt monosilicide. The fact that in the sintered product there is no metal left, as such, but is replaced by a brittle silicide which serves as the binder phase, may explain why this composition is not resistant to heat-shock.

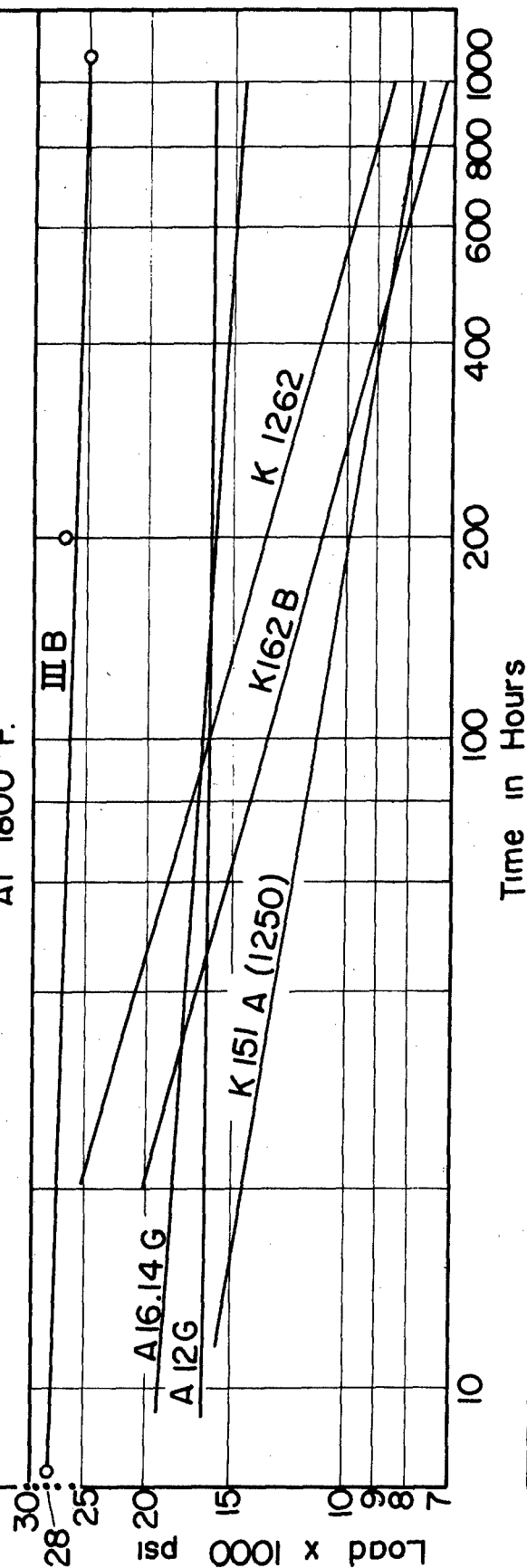
DISCUSSION WITH RESPECT TO CERMET III B

This composition first attracted favorable attention because it is a cermet with a TiC base which is remarkably resistant to high-temperature oxidation by virtue of a borosilicate glass skin which develops on the surface upon heating in an oxidizing atmosphere.

Further development disclosed excellent short-time tensile strengths to 2200°F and a stress-rupture curve at 1800°F higher and flatter than the curves for any other known cermet. Nozzle blades of this composition failed in standardized thermal cycling tests. It is also anticipated that these blades will be brittle because they contain no ductile metal phase.

Continuing research will undertake to get a sufficient metal content into this composition to overcome its present deficiencies without too great a sacrifice in high-temperature strength, particularly stress-rupture strength.

FIGURE 1 STRESS - RUPTURE IN TENSION

CERMET III B VS. Al_2O_3+Cr and SOME KENNAMETAL TiC BASE CERMETS
AT 1800°F.

LEGEND

Code	Composition, Weight %	Hours	Reference
A-12-G	30 Cr + 70Al ₂ O ₃	10 100 1000	O.S.U. Report 60 May '50
A-16.14-G	72Cr + 28Al ₂ O ₃	16,500 16,450 16,000	O.S.U. Let.Rep. 21 Nov. '51
K-151A	65TiC+15(Ti,Ta,Cb)C+20Ni	19,000 16,800 14,500	Kennametal Let.Rep. 3 Oct. '51
K-1262	72TiC+8(Ti,Ta,Cb)C+15Ni+5Mo	15,500 11,000 7,000	" " " " "
K-162B	62TiC+8(Ti,Ta,Cb)C+25Ni+5Mo	16,500 8,500	" " " " "
III B	55.4TiC+17.9TiB ₂ +10.0Si+16.7Co	13,000 7,000	" " " " 5 Apr. '52
		28,000 27,000 25,000	O.S.U. Laboratory Data

SECTION II

HIGH-TEMPERATURE VACUUM X-RAY CAMERA

A high-temperature x-ray camera was built to permit a study of the phases present in carbide base cermets at gas turbine engine operating temperatures or other significant high temperatures.

Drawing No. 441-4, Figure 2, is the assembly drawing of the camera. It is essentially a 114.6 mm powder camera utilizing thin rod specimens which rotate slowly. The operating temperature range of this camera is from room temperature to 2732°F (1500°C).

The brass case, Detail No. 27, Figure 3, consists of an upper and a lower half. The lower half was machined in one piece. The upper half was made in two parts, the cylinder with the flange being one part and the top plate being the other. The cooling coil in the upper half also consists of two parts, the coil on the inside of the cylinder and the coil attached to the top plate. All cooling coils were soft-soldered in place. The top plate was soldered in place concurrently with the joining of the two cooling-coil sections.

The furnace, Detail No. 10, Figure 4, consists of two identical parts which are connected in series outside the camera. A suspension of alumina in water was used to paint over the platinum wire windings to about 1/8-inch thickness.

Beryllium foil windows, Reference No. 16, Figure 2, are used in the camera. Low-vapor-pressure hard black wax (Apiezon W) was used to cement the beryllium foil windows to the brass case and experimentation under vacuum indicates this cementing medium to be satisfactory.

The film holder, Detail No. 11, Figure 5, slides over the outside of the camera. The film holder can be removed without affecting the vacuum or the temperature, thereby permitting the photographing of the same sample at different temperatures without the necessity of shutting down the apparatus each time.

The collimator, Detail No. 29, Figure 4, is of the circular pinhole type, while the beam-trap, Detail No. 28, Figure 4, is simpler and different from the usual type in that it does not extend inward to the sample. This simple design is possible because in a vacuum there is no scattering of the x-ray beam by air or other gasses.

The vacuum is obtained using a 1403 Welsh mechanical pump and a two-inch National Research Corp. (NRC) oil diffusion pump. The vacuum is measured using a NRC 501 thermocouple gauge and a NRC 507 ionization gauge. A single NRC combination thermocouple and ionization control circuit is used with these gauges.

A Pt, Pt-Rh thermocouple, Reference No. 34, Figure 2, is used to measure the temperature.

Operation of the Camera

Operation of this camera and accessories indicates that all major difficulties have been overcome and that it will operate successfully. Before heating the platinum-wire resistance furnace, the camera was evacuated to a pressure of 1×10^{-6} mm Hg. When this furnace was heated, even at the rapid rate of 900°F per hour, the first outgassing did not cause the pressure to rise above 5×10^{-5} mm Hg. At 2000°F (1093°C) the cooling coils kept the temperature of the beryllium-foil window, as well as the entire camera, well below room temperature. The Apiezon "W" wax kept the beryllium-foil window vacuum tight, and at 2000°F the pressure did not rise above 1×10^{-5} mm Hg.

The camera furnace was originally wound with 31-gauge platinum wire. At 2000°F it drew 3.5 amperes at 35 volts. When we proceeded to raise the temperature above 2000°F the winding of the upper half of the furnace burned out. This may have been due to some flaw in the wire or to too light a gauge, and not to contamination of the wire by the cement covering it, since only 100% Al_2O_3 was used with no binder of any kind. A 26-gauge platinum + 20% rhodium wire was used for the new winding. It is of some interest to note that after the burn-out it took about one hour for the furnace temperature to reach approximately room temperature. It is of considerable interest to note that after the first thorough outgassing, a vacuum of 5×10^{-7} mm Hg could be maintained.

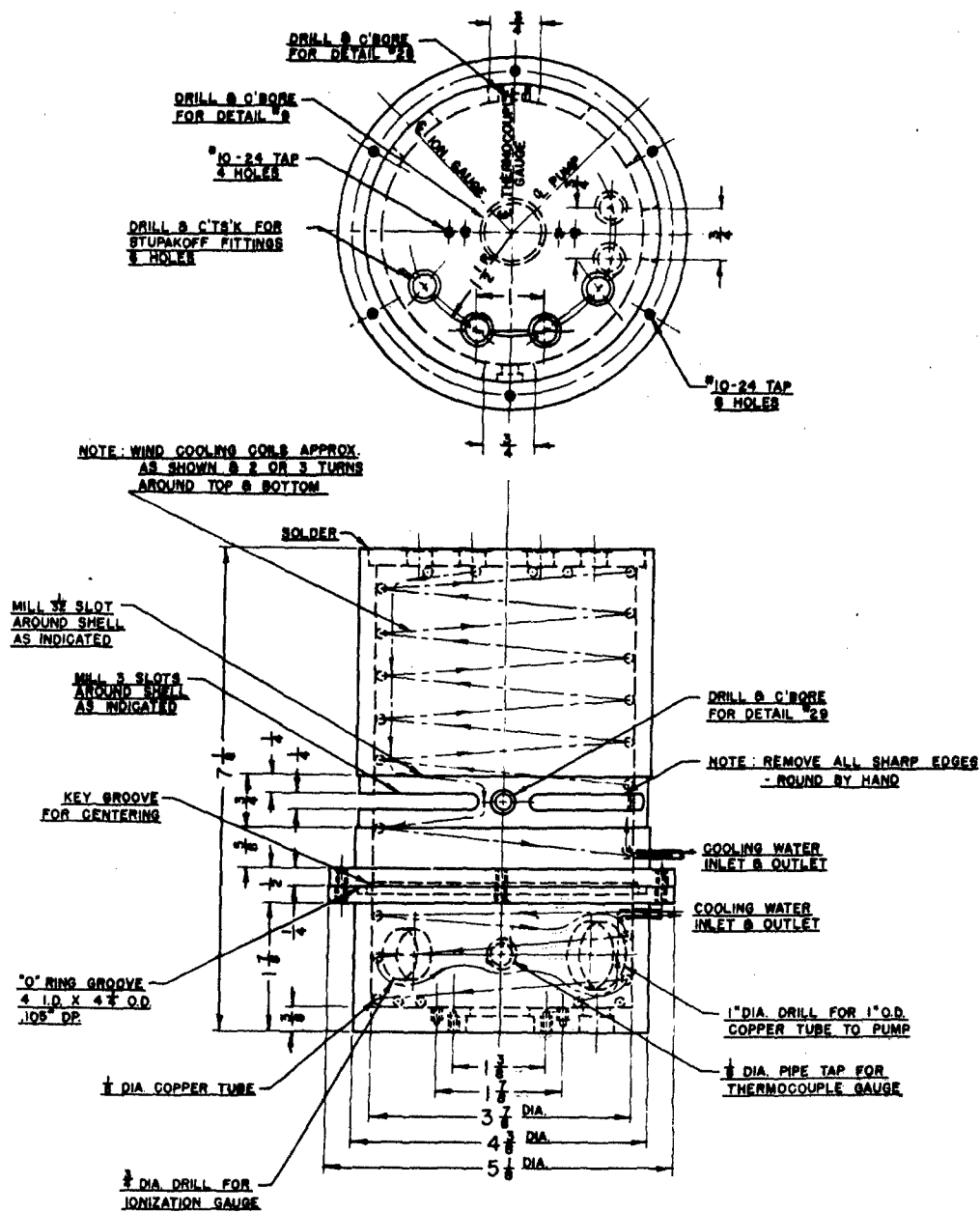
It was originally planned to calibrate the Pt, Pt-Rh thermocouple against the thermal expansion of MgO . Calculations indicated that this method of temperature calibration would be unsatisfactory as the thermal expansion of MgO is known with insufficient accuracy for this purpose. Calibration could be made using the known melting points of pure metals. It is our opinion that the accuracy of the thermocouple is sufficient for the present intended purposes.

The identification of new phases as well as the determination of the amount of solid solution in the system $\text{Ti} + \text{metal}$ at elevated temperatures necessitates preliminary

high temperature x-ray work. This involves the separate determination of the thermal expansion of TiC and of the metal. These data must be known so they can be correlated with the high temperature x-ray data for the cermet under investigation.

Reference Numbers - Figures 2, 3, 4, 5 and 6

1. Stupakoff Fittings - 6 required
2. Steel holder for alumina thermocouple tubing
3. 2 hole alumina thermocouple tubing
4. Alumina sample holder
5. Brass plate - 2 required
6. Alumina tubing - 2 required
7. Alumina rod
8. Thumb screw
9. Brass bushing for Garlock seal and shaft
10. Platinum wire-resistance furnace
11. Film holder
12. Black paper
13. Film
14. Brass sheet
15. Brass sheet
16. Beryllium foil 0.012 inch thick
17. "O" Rings - (1/8" W) 4" I.O. x 4-1/4" O.D.
18. Brass Post - 2 required
19. Holder for centering sample
20. Steel shaft
21. "O" Ring - (1/16" W) 1/2" I.D. x 5/8" O.D.
22. Garlock Klosure, Model 51, Part #51X3863
23. Pulley
24. Washer
25. Brass plate
26. Brass ring
27. Brass Shell
28. X-ray beam-trap assembly
29. Collimator assembly
30. Base support---beam-trap end
31. Base support---collimator end
32. Thumb screws - 2 required
33. Steel springs - 2 required
34. Pt, Pt-Rh thermocouple



(27) 1 ASS'Y REQ - BRASS

SCALE 1" = 1"	THE OHIO STATE UNIVERSITY	
DATE 1 Sept 52	RESEARCH FOUNDATION for	
DRAWN - P. Rempes	WRIGHT AIR DEVELOPMENT CENTER	
APPROVED <i>[Signature]</i>	WRIGHT - PATTERSON AFB, DAYTON, OHIO	
ENGINEERING	HIGH TEMPERATURE VACUUM X-RAY	
EXPERIMENT STA.	CAMERA	
OHIO STATE UNIV.	PROJECT 441	
COLUMBUS, OHIO	DETAIL	REVISED
	DRAWING NO.	441-4D

Figure 3

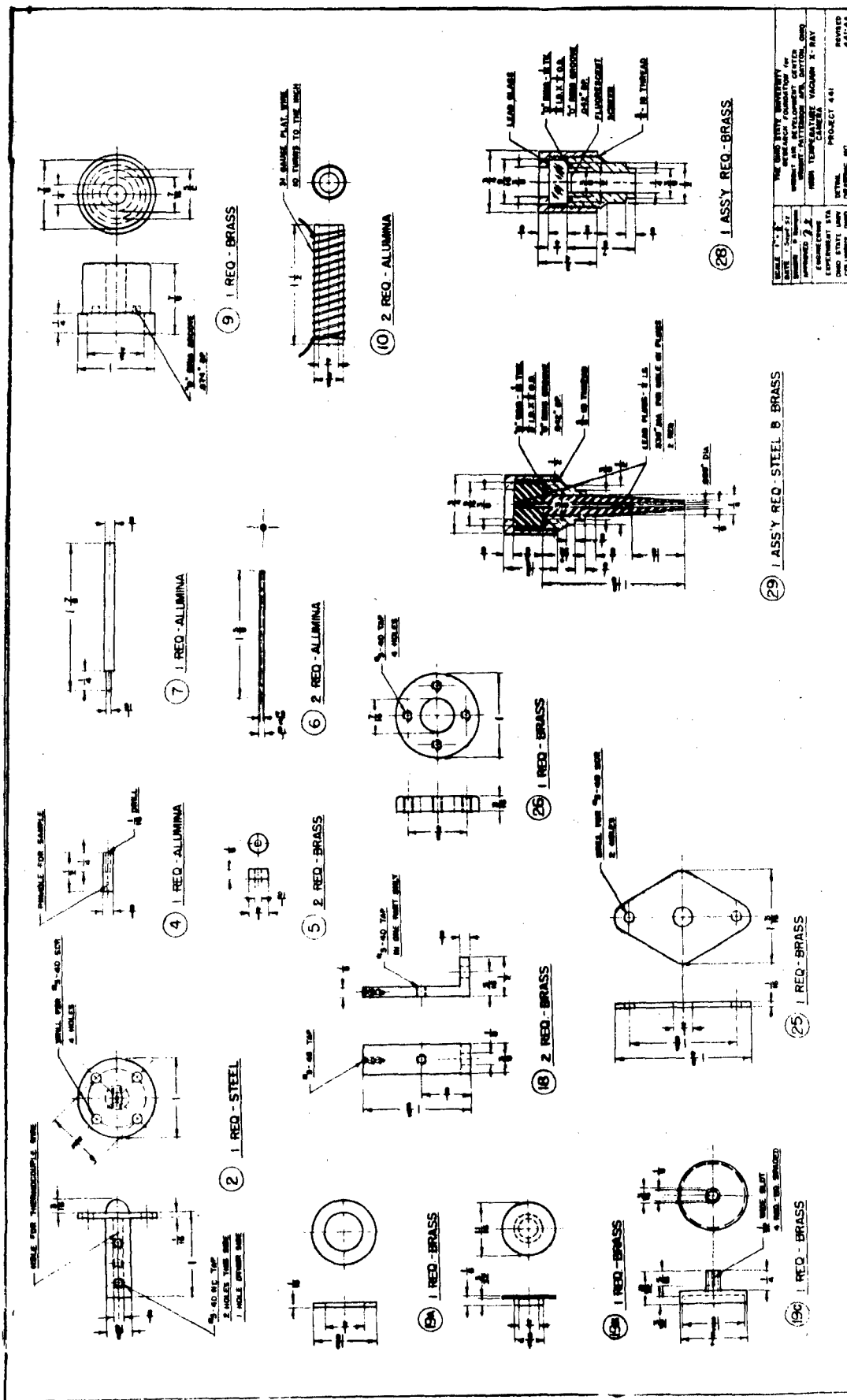
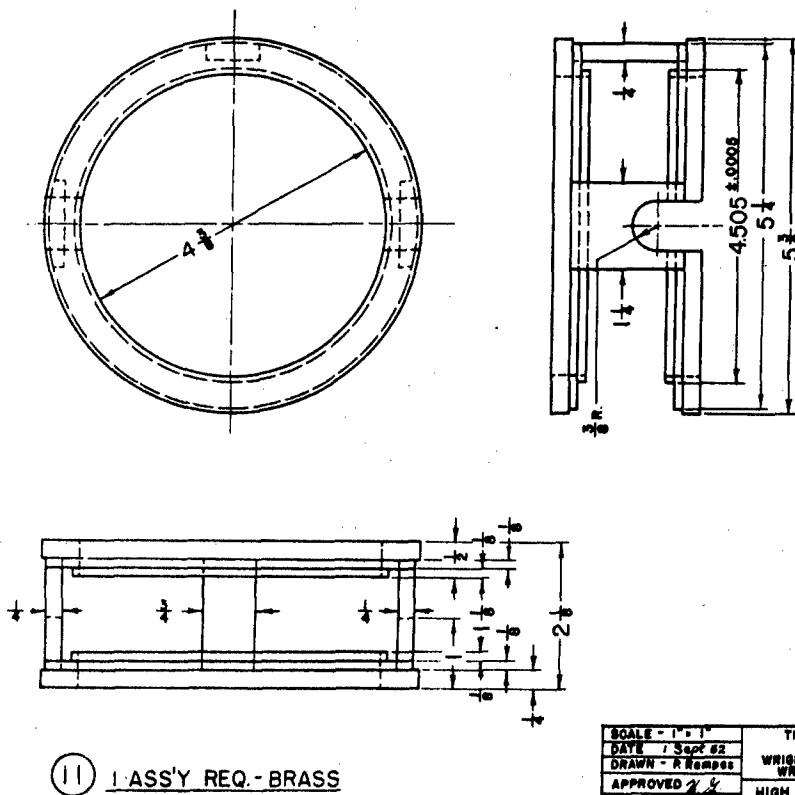
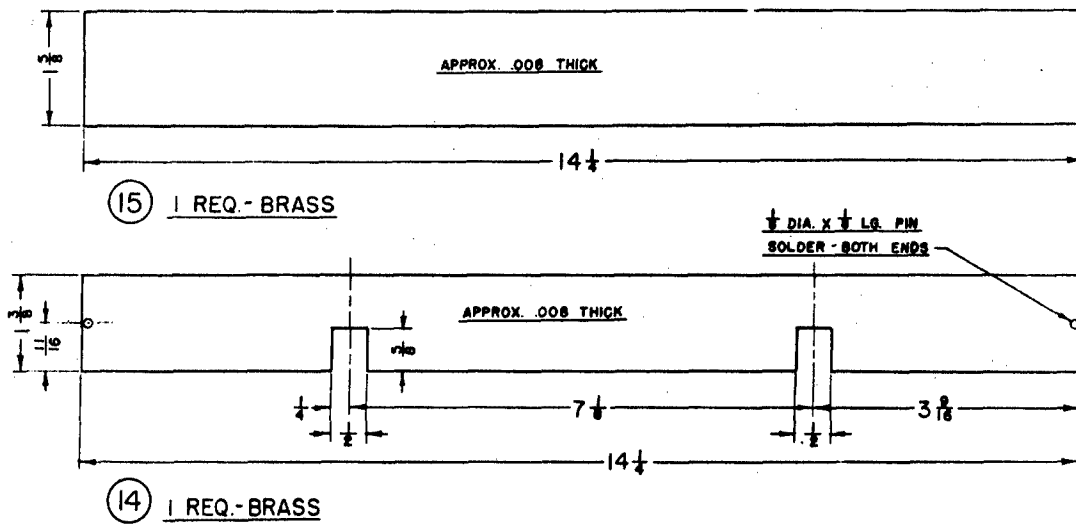


FIGURE 4



SCALE - 1" = 1"	THE OHIO STATE UNIVERSITY	
DATE 1 Sept 62	RESEARCH FOUNDATION for	
DRAWN - R. H. H. 62	WRIGHT AIR DEVELOPMENT CENTER	
APPROVED 2/4	WRIGHT-PATTERSON AFB, DAYTON, OHIO	
ENGINEERING	HIGH TEMPERATURE VACUUM X-RAY	
EXPERIMENT STA.	CAMERA	
OHIO STATE UNIV.	PROJECT 441	
COLUMBUS, OHIO	DETAIL DRAWING NO.	REVISED 441-4C.

Figure 5

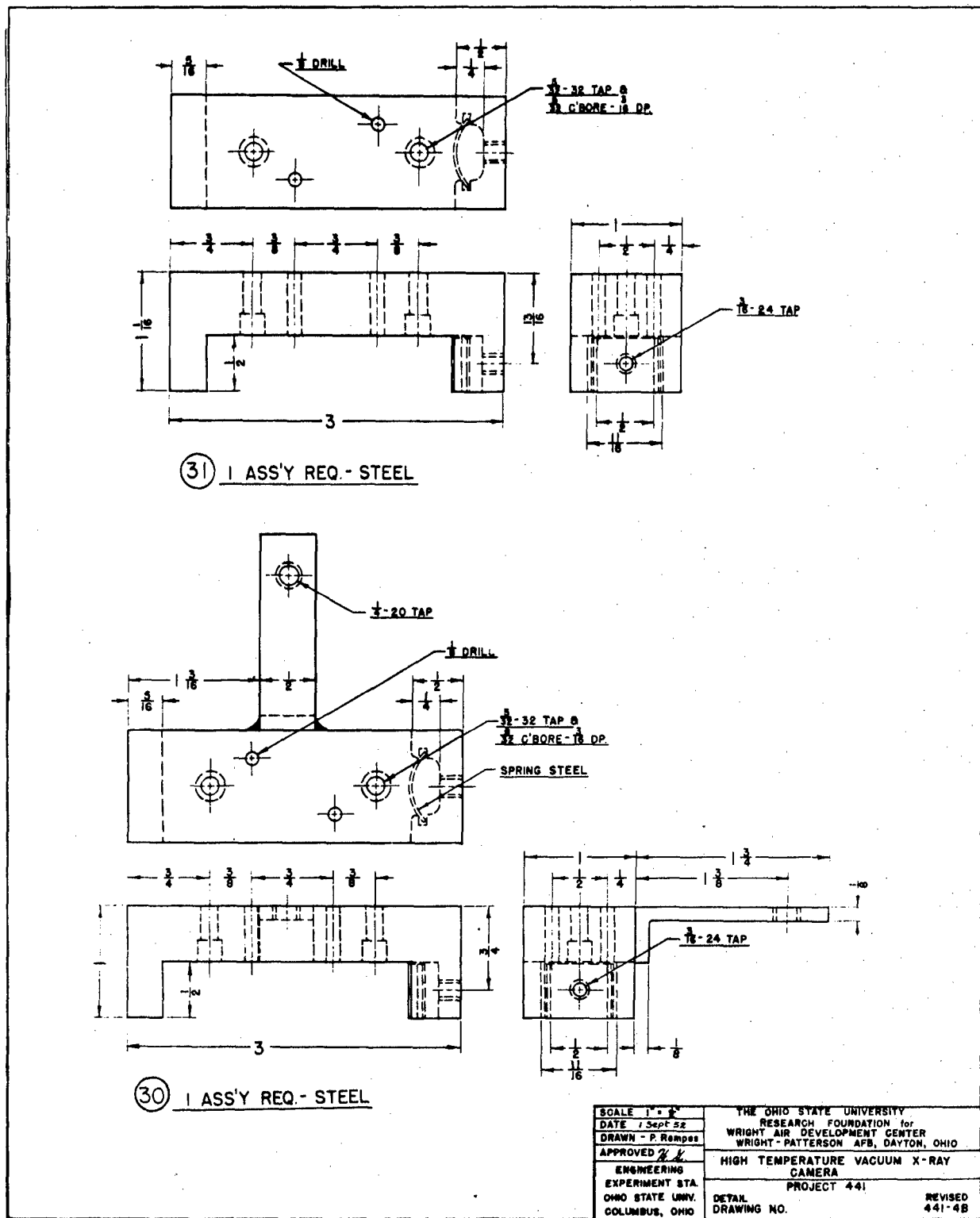


Figure 6

SECTION III

VACUUM QUENCH FURNACE

A furnace was designed and built to permit heating specimens in vacuo and then quenching them in vacuo for the purpose of freezing any high-temperature phases and significant physical characteristics.

Drawing No. 441-5, Figure 7, shows the vacuum quench furnace and accessories. For purposes of description it may be considered as consisting of the furnace, the heating chamber, the quenching system, the vacuum system, and the temperature control system.

The vertical, split-type furnace contains a firing zone 4.5 x 4.5 x 6.0 inches, appropriately insulated and designed for service to 2500°F. It is resistance heated by means of four standard Globar elements. These are in a series circuit with an electrical power source which was readily available. The split feature was incorporated to facilitate loading, making the specimen support assembly and the heating chamber removable as a unit.

The heating chamber is a McDanel refractory porcelain tube. This is sealed to the specimen support assembly at the top and to the vacuum pumping system at the bottom, through the use of "O" rings. The convenient removal and replacement of the tube, necessary in the loading of specimens, is thus provided for.

The quenching system is shown in the detail of Figure 7. It consists of a quenching receptacle and a specimen support-release device. The quenching receptacle is a drilled copper block resting on a water-cooled support, which may or may not contain a liquid quenching medium. However, common practice is to use vacuum-pump oil within the receptacle. One to four specimens may be supported in the furnace at one time and can be dropped into the receptacle independently. Each specimen, provided with a bail, is supported by threading the bail over a fine tungsten wire stretched between the common lead and one of the four electrically insulated leads located around the common lead. These leads are 0.050-inch molybdenum wire. The electrically insulated wires are contained in fine alumina tubes from the end in the hot zone of the chamber to near the end which emerges from the fixture at the top of the chamber. A vacuum seal is effected by embedding the ends of these tubes and the protruding wires in Apiezon "W" wax at the point where they emerge from the fixture. The common lead is uninsulated and is connected

to the fixture built up from a standard wrought-copper tee. It is positioned in the hot zone by attachment to a two-hole thermocouple insulating tube which is centrally located. The wires of the supporting system are positioned relative to one another by their manner of mounting in the copper tee fixture at the top of the McDanel tube.

Any one specimen can be dropped by fusing the wire over which its bail is hung. This is done by passing a sufficiently heavy current through the supporting tungsten wire.

The vacuum system is made up of vacuum pumps, gauges, and the heating chamber. The pumping system consists of a Distillation Products Industries MC275 oil diffusion pump backed by a Welch 1403B mechanical pump. Three vacuum gauges are used. A McLeod gauge is used for intermittent measurement of the pressure in the forearm of the diffusion pump, a thermocouple gauge is used to follow the pressure changes near the throat of the diffusion pump during boiler heat-up, and a Philips gauge is used to measure the pressure at the copper tee fixture on top of the heating chamber, during operation at low pressure. This location of the Philips gauge was selected so that the pressure measured during operation would be the highest permanent gas pressure in the system. The gauge is mounted in the tubulation seal attached to the copper tee fixture. This fixture, in conjunction with the heating chamber, completes the closed vacuum system.

Titanium chips are located in the hot zone of the tube which serves as the heating chamber for the specimens. These chips are used as a getter for the permanent gases oxygen and nitrogen which may be present in small amounts. In one sense they may be considered a part of the pumping system.

The temperature control system consists of the power transformer, a bank of resistors, sensing thermocouple, and a Foxboro control-point controller. Manual setting or adjustment of the three power-regulating components allows any desired temperature up to approximately 2500°F to be maintained for long periods of time. To establish and control at a given temperature, the desired temperature is set on the control-point controller. Power is increased manually over a period of time by advancing the setting of the power transformer until slightly more power is supplied than is required to maintain the control temperature with the furnace at equilibrium. At this time the sensing couple signals the control instrument which activates a switch placing power-dissipating resistors in series with the transformer and the furnace. These can be adjusted to dissipate approximately 10% of the power supplied by the transformer. When the furnace temperature falls below the control point, the instrument, signaled by the sensing couple, again

activates the switch and shunts the series-connected resistors so that all the power available from the transformer is applied to heat the furnace. This temperature control system might appear to require anticipators to smooth out the fluctuations accompanying signalling and response. However, the specific heat and insulating effects of the tube, and the vacuum within the tube which is used as the heating chamber, are so effective in stabilizing the temperature of the specimens that a check thermocouple with its junction in the midst of these specimens indicates no temperature fluctuation.

In operation, four specimens provided with bails are supported on four wires stretched between the common lead and each of the four surrounding leads. The system is assembled, the gauges are mounted, and the vacuum pumps started. The furnace is brought to temperature and allowed to equilibrate at the control point which has routinely been 2000°F. After a time lapse, usually 24 hours or longer, one or more specimens are dropped by fusing the support wire, using a 110-volt source at less than 15 amperes. To do this, the grounded support fixture serves as the terminal for the common lead, and the appropriate independently insulated lead serves as the other terminal. The specimen drops into the quenching receptacle.

As pointed out earlier, the selected operating temperature is usually 2000°F, and this can be controlled very closely in the vicinity of the specimens. Fluctuations, being so small as to be undetectable with the ordinary portable laboratory potentiometer, are believed to be less than 10°F.

Pressures of 2×10^{-5} mm Hg are maintained at 2000°F as a matter of routine. These are measured at the tabulation seal shown in Figure 7.

Two methods of dropping the specimens have been used: (1) by slowly melting the supporting wire with a gradually increasing current, and (2) by vaporizing the wire with a direct application of full current. The first method is less positive, in that the wire may fuse through at one point but still support the specimen. The second method is positive and preferred. The resulting deposition of vaporized metal within the heating chamber may prove to be a disadvantage, but so far has not proven troublesome.

Operation of the Furnace

A vacuum of 2×10^{-5} mm Hg can be maintained when the furnace is at 2000°F. Although this vacuum results in an oxygen pressure of less than 1×10^{-5} mm Hg, there is sufficient

oxygen passing through the system in a 24-hour period to form a very thin oxide layer on a polished specimen being held at temperature. Calculations taking into account the pressure in the system and the pumping speed of the oil diffusion pump agree with the experimental evidence. A static helium atmosphere was used in the hope of reducing the total oxygen content so that no oxidation could take place. Results indicate that more oxidation takes place when using helium than when using a vacuum. Therefore, the furnace will be used in conjunction with the vacuum system and a titanium getter will be inserted in the furnace to react preferentially with the small amount of oxygen that enters the system.

The specimen finally adopted is a disc $3/8$ inch in diameter by $3/16$ inch thick, polished on one face. After being held at temperature for the desired period of time, the sample is quenched by dropping it into the water-cooled cup containing diffusion pump oil. To determine the efficiency of quenching in oil, five identical specimens of Kennametal composition K152B were heat-treated and quenched as follows:

- (1) Sample heated to 2000°F in vacuum, held there 42 hours, and quenched in oil.
- (2) Sample heated to 2000°F in vacuum, held there 42 hours, and allowed to cool with the furnace.
- (3) Sample heated to 2000°F in air, held there 42 hours, and quenched in oil.
- (4) Sample heated 2000°F in air, held there 42 hours, and quenched in salt water.
- (5) Sample heated to 2000°F in air, held there 42 hours, then removed from the furnace and allowed to cool in air.

Results indicate that for specimens held at temperature for 42 hours the method of quenching has no effect on the resulting microstructure of the cermet. At the moment neither the method nor the speed of quenching appears to be significant.

These 42-hour samples were investigated metallographically giving results as follows:

- (1) No distinct new phase has appeared.
- (2) No change in the carbide grain size was found.
- (3) No rounding of the carbide grains was noted.
- (4) The nickel phase appears more mottled.

There is some mottling of the nickel phase before the cermet has undergone any heat treatment, but this effect is much more pronounced after heat-treating and quenching. Further investigations will be conducted to determine what causes this mottled appearance.

SECTION IV

NEW APPARATUS FOR THE DETERMINATION OF COEFFICIENTS OF THERMAL CONDUCTIVITY AT TEMPERATURES TO 1700°F

The apparatus, shown in Drawing No. 441-6, Figure 8, built to determine the coefficients of thermal conductivity of specimens at temperatures to 1700°F, makes use of a standard specimen and an unknown specimen. It consists of an input heater unit, a system of guard heaters, a throughput water calorimeter, a system of thermocouples for temperature measurement, and a number of variable external resistors for temperature control. Drawing No. 441-6A, Figure 9, shows the electrical wiring diagram for the apparatus and the circuits for the thermocouples.

The standard specimen, whose thermal conductivity is known, and the unknown specimen, whose thermal conductivity is to be determined, are cylinders 1.0 inch in diameter and 5.0 inches long. They are joined end to end by a thin slurry of alumina cement to form a composite specimen 1.0 inch in diameter by 10.0 inches long. The joint between the top of the specimen and the calorimeter is Wood's metal.

The input heater unit consists of 15 inches of 24-gauge nichrome resistance wire wound as a toroid coil embedded in an alumina plaque. The amount of heat that is generated is controlled by an external dropping resistor in series with the heater winding. A Simpson ammeter, Model 57, is used to measure the current for the purpose of calculating the amount of heat furnished.

An input bottom guard heater also consists of 15 inches of 24-gauge nichrome resistance wire in an alumina plaque. Its temperature is controlled by external variable resistors to match the temperature of the bottom of the input heater unit.

The input lateral guard heater is made of 29 inches of 22-gauge nichrome resistance wire wound on a 1.875-inch O.D. McDanel refractory porcelain tube. This winding is covered with a cement composed of alumina and plastic fire clay. The temperature of this heater is matched to that of the side of the input heater unit by the same method as in the input bottom guard heater.

A specimen lateral guard heater also is made of 1.875-inch O.D. McDanel refractory porcelain tube wound with 235 inches of 22-gauge nichrome resistance wire and covered with the alumina and plastic fire clay cement. This continuous winding, however,

is divided into five equal parts by the addition of four intermediate taps, permitting the temperature of each individual section to be matched to that of the specimen opposite it at that point. The temperatures of the sections of the specimen lateral guard heater are controlled by a series of voltage dividers in parallel with the winding.

The entire assembly is surrounded with a split-type furnace insulation made of C-20 insulating brick held together by a hinged case.

The temperatures of the specimens and the various heaters are measured and compared by means of chromel-alumel thermocouples. The temperatures at the side and bottom of the input heater unit and at points along the specimen corresponding to the steps of the specimen lateral guard heater are measured. The temperatures of these points are compared with the temperatures of points on the guard heaters opposite them by connecting together the thermocouples at the two points being compared and reading the resulting differential voltage.

The throughput water calorimeter, of the constant-flow type, is constructed of copper. This calorimeter is used to check the amount of heat transmitted through the composite specimen and to maintain the cold end at room temperature.

Since the temperature difference between the water flowing in and the water flowing out of the calorimeter is small, a differential thermopile is used to measure this temperature difference. This thermopile is composed of 50 iron-constantan thermocouples connected together so as to multiply by a factor of 25 the actual temperature difference between the two water temperatures. These thermocouples pass through rubber stoppers which seat in copper cups. The sections of the thermocouples that are immersed in water are waterproofed by painting a covering of General Electric black air-drying varnish, No. 457, over the bare wires.

Under ideal equilibrium conditions the heat passing through the unknown specimen in a given time may be expressed as any one of the following equivalent values:

- (1) The heat equivalent of the electrical energy input at the input heater.
- (2) The heat passing through the standard specimen for which the thermal conductivity is known and for which the temperature gradient is measured during test.
- (3) The heat absorbed in the calorimeter.

Since $K = Hl/A\Delta T$, and we have three independent measurements of H , we can calculate three independent values of K from H , the physical dimensions of the unknown specimens and the temperature measurements that give ΔT . Thus, three values of thermal conductivity which should check one another are obtained as a result of measurements made under a single equilibrated heat-flow condition.

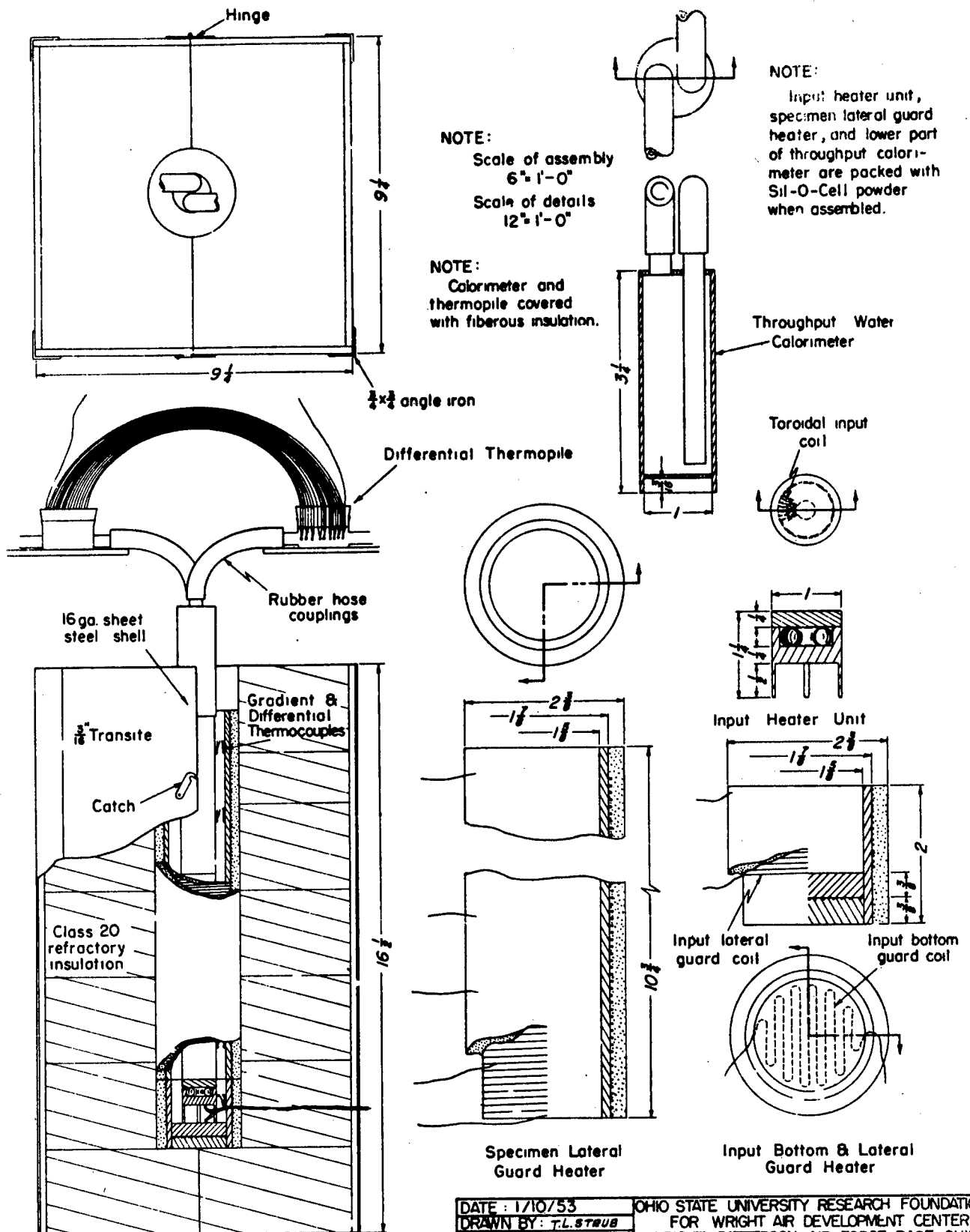
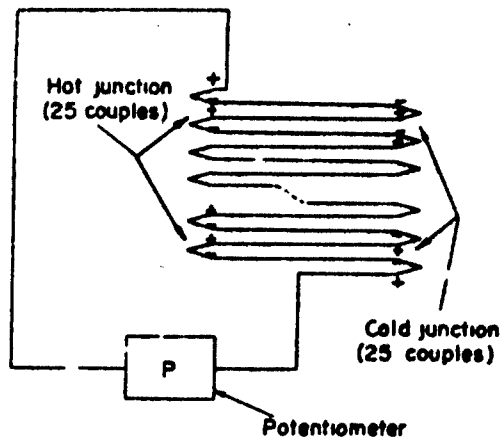


Figure 8

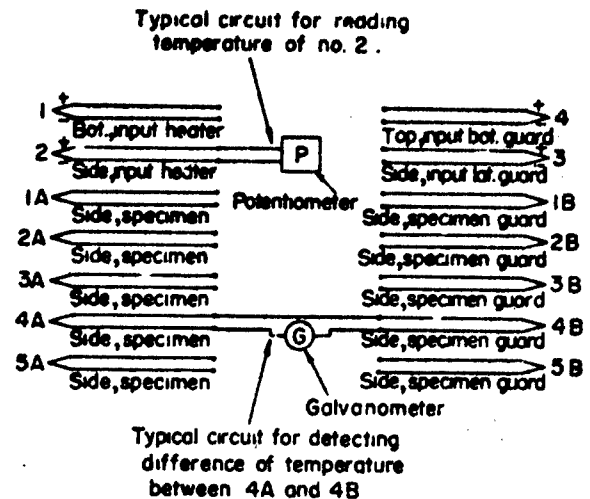
DATE: 1/10/53	OHIO STATE UNIVERSITY RESEARCH FOUNDATION
DRAWN BY: T.L. STUBB	FOR WRIGHT AIR DEVELOPMENT CENTER
APPROVED: J.L. STUBB	WRIGHT-PATTERSON AIR FORCE BASE, OHIO
ENGINEERING	COEFF. OF THERMAL CONDUCTIVITY APPARATUS
EXPERIMENT STATION	PROJECT 441
OHIO STATE UNIVERSITY	DRAWING NO. 441-6
COLUMBUS, OHIO	

DIFFERENTIAL THERMOPILE



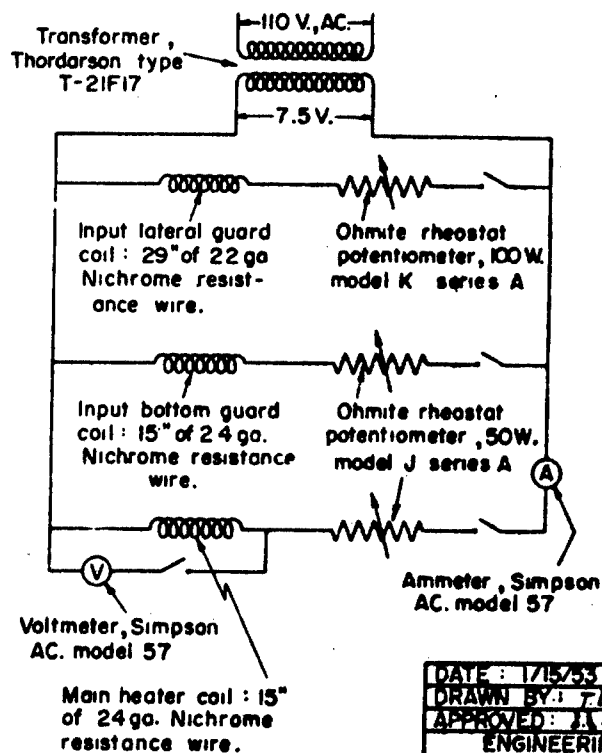
Thermopile is 50 iron(+) - constant(-) thermocouples in series.

TEMPERATURE MEASURING AND COMPARISON CIRCUITS



Thermocouples are chromel(+) - alumel(-).

INPUT LATERAL GUARD HEATER, INPUT BOTTOM GUARD HEATER AND INPUT HEATER CIRCUIT



SPECIMEN LATERAL GUARD HEATER CIRCUIT

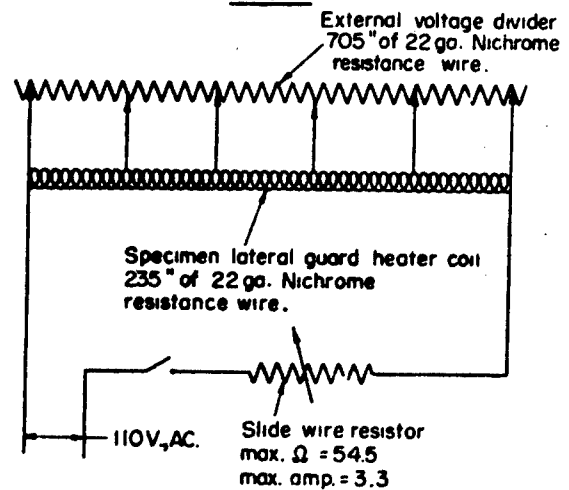


Figure 9

DATE: 1/15/53	OHIO STATE UNIVERSITY RESEARCH FOUNDATION
DRAWN BY: T.L. STUBB	FOR WRIGHT AIR DEVELOPMENT CENTER
APPROVED: J.L.L.	WRIGHT-PATTERSON AIR FORCE BASE, OHIO
ENGINEERING	COEFFICIENT OF THERMAL CONDUCTIVITY
EXPERIMENT STATION	APPARATUS, CIRCUIT DIAGRAMS
OHIO STATE UNIVERSITY	PROJECT 441
COLUMBUS, OHIO	DRAWING NO. 441-6A

SECTION V

STUDY OF PHASES AND MICROSTRUCTURE OF TiC-Ni CERMETS

As stated in the introduction, one of the principal phases of this year's program was a study of phase changes or changes in microstructure with time at high temperatures, which might explain the steep slope of the stress-to-rupture curves for the Kennametal type of TiC base cermets.

The high-temperature vacuum x-ray camera was built to obtain diffraction patterns of the phases present at engine operating temperatures, for comparison with phases present at normal atmospheric temperatures, and also to determine if solid solution of TiC in Ni is taking place at these temperatures.

The vacuum quench furnace was built so specimens might be heated in vacuo at high temperatures and quenched in vacuo to freeze any significant phase changes produced by the combination of temperature and time. It also serves the purpose of freezing the microstructure of these heat-treated specimens for study by use of the metallograph. Where grain growth occurs it is important to know whether the observed grain size was present in the hot specimen or whether the grain growth occurred during cooling.

As discussed in the section of this report dealing with the vacuum quench furnace, no new phase was found in quenched specimens which had been heat-treated 42 hours at 2000°F. This was also found to be true for specimens heat-treated for 200 and 300 hours. This practically eliminates the possibility of any new stable phase in these specimens while still in the hot condition. The determination of x-ray diffraction patterns at high temperatures has therefore been held in abeyance until further fundamental data are assembled which will permit an evaluation of TiC in solution in the nickel. The x-ray diffraction pattern at a given high temperature will show an expanded crystal lattice due to thermal expansion. In addition, there will be a change in the lattice dimensions if there is any substitutional solid solution taking place. The amount of solution can be measured quantitatively assuming a substitution of Ti atoms for Ni atoms in the nickel. It is first necessary, however, to determine separately the thermal expansion of TiC and of Ni at the selected temperature.

With respect to grain growth, the freezing of specimens heat-treated for varying lengths of time at 2000°F assures that grain size shown in photomicrographs of polished sections of the quenched specimens corresponds exactly with the size of the grains while at 2000°F.

Studies were conducted on Kennametal compositions K151A and K152B. Figures 10 and 11 are photomicrographs of K151A and K152B as originally sintered and before they had undergone any heat treatment. It will be noted that the carbide grains are discrete and angular, and the nickel phase shows a little mottling. Figure 12 is a photomicrograph of K152B after a heat treatment of 42 hours at 2000°F in vacuum followed by quenching in oil. The carbide grains have remained discrete and angular but the mottled appearance of the nickel has increased considerably. X-ray diffraction studies of this sample show that it is still a two-phase system, with neither solution of the carbide in the nickel nor the presence of any nickel in the carbide. This seems to indicate that the mottling in the nickel is due to fine grains or a fine precipitate of TiC. Greater resolution of the mottled nickel is not possible with visual optics, and plans are being made to investigate this structure under the electron microscope.

Figures 13 and 14 show specimens of these two compositions heat-treated 100 hours at 2000°F in vacuo and quenched in oil in vacuo. Figure 13 especially shows the carbide grains in the process of coalescing. Boundary lines still show where the original grains are in contact. The electron microscope will be used to study the nature of this incipient interfacial bond.

Figure 15 is a photomicrograph of a specimen of K151A which, for another investigation, had been heat-treated in air for 764 hours at 2000°F and not quenched. This picture shows a very pronounced growth of the carbide grains by coalescing, and a squeezing out of the nickel into large lakes.

2000°F rather than 1800°F was selected as the temperature for heat-treating in order to accelerate the significant changes taking place when specimens are heated for long periods of time. It is assumed that the same changes take place at 1800°F though probably not at the same rate. The preliminary investigations completed this year indicate strongly (1) that no significant phase changes occur in the subject specimens during heating for long periods of time at 1800°F or at 2000°F, but (2) that significant grain growth does occur by coalescing of the TiC grains into large carbide masses, probably through the mechanism of solution of TiC in the nickel and reprecipitation on the larger TiC grains. At the same time the nickel is squeezed out into large interstitial lakes.

Further work must be done to confirm the data and the ideas presented here in preliminary form. Samples will be heat-treated for longer times, and all samples will be investigated metallographically, by x-ray diffraction and with the electron microscope. In addition, cermet III B will also be investigated in an identical manner so that we may compare its microstructure with that of K151A and K152B.

A reasonable explanation of the steep slope of the stress-rupture curve for this material is as follows. The coalescing of the carbide grains and the creation of large nickel lakes causes a decrease in the carbide - metal interfacial area. This results in a decrease in the number of carbide-to-metal bonds, and an increase in the number of metal-to-metal bonds. The metal-to-metal bond is very weak at high temperatures, as is evidenced by the steep stress-rupture curves for metals. The structure formed by the coalescing of TiC grains at 2000°F is not nearly so strong as that formed at the sintering temperature of the cermet (Approx. 3000°F) because of the incomplete bonding at this relatively low temperature. Although the bond strength between carbide molecules is a constant, independent of the sintering temperature, the bonding strength between grains is proportional to the number of carbide-to-carbide bonds formed, the latter being a function of the sintering temperature. It is therefore presently believed that the weakening of the K152B body at 1800°F results from the fact that a decrease in the number of strong carbide-to-metal bonds and an increase in the number of weak metal-to-metal bonds, with only a relatively small increase in the number of strong carbide-to-carbide bonds, produce an over-all decrease in the bond strength in the body.



Figure 10. Kennametal K151A as sintered in production. Unetched. Max. resolution at 2000X.

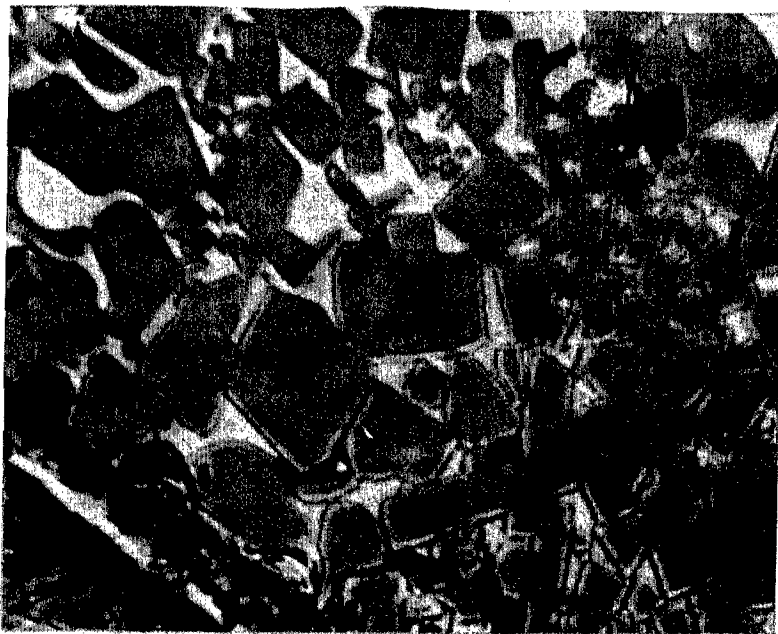


Figure 11. Kennametal K152B as sintered in production. Unetched. Max. resolution at 2000X.

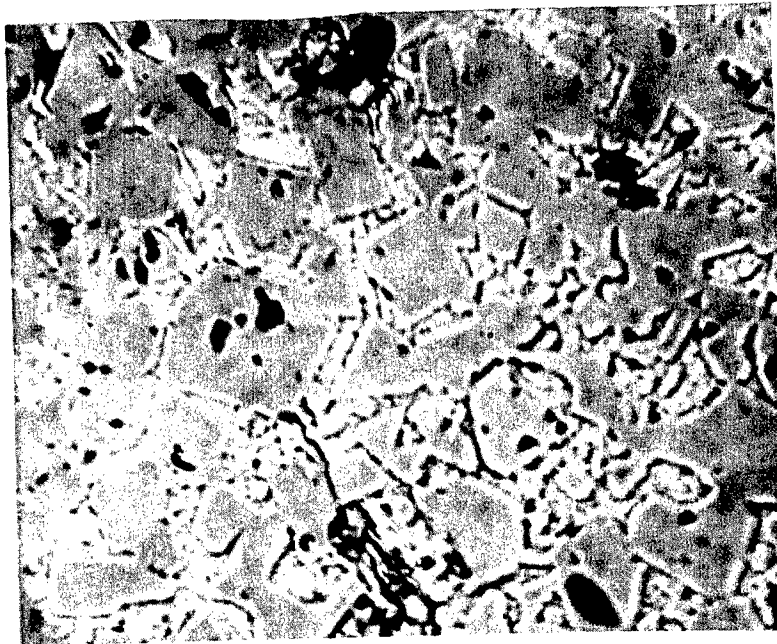


Figure 12. K152B heat-treated 42 hours at 2000°F in vacuo and quenched in oil in vacuo. Unetched. Max. resolution at 2000X.

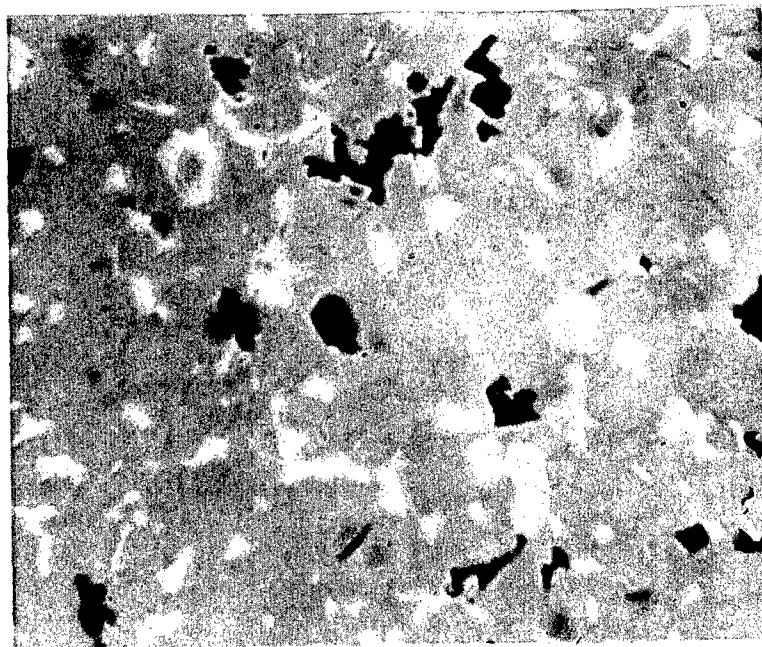


Figure 13. K151A heat-treated 100 hours at 2000°F in vacuo and quenched in oil in vacuo. Unetched. Max. resolution at 2000X.

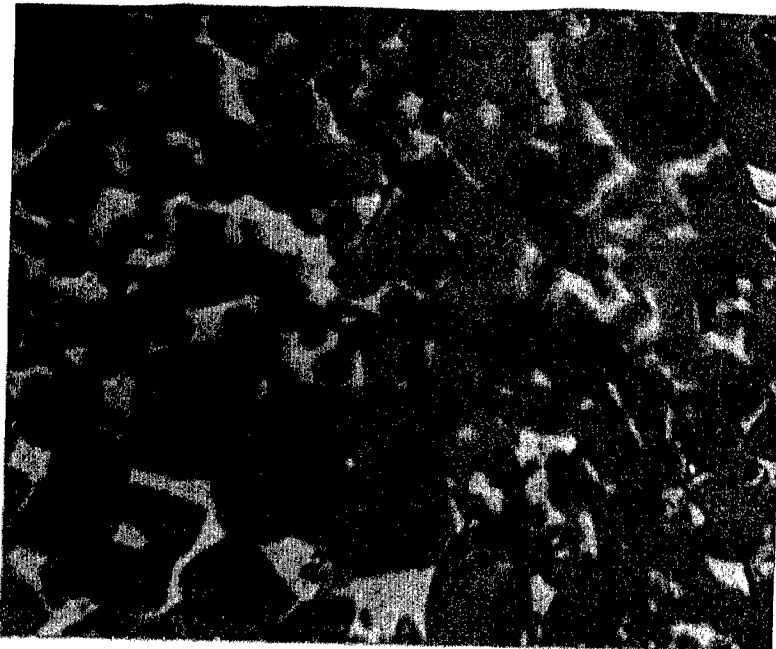


Figure 14. K152B heat-treated 100 hours at 2000°F in vacuo and quenched in oil in vacuo. Unetched. Max. resolution at 2000X.



Figure 15. K151A heat-treated 764 hours at 2000°F in air and cooled in air at 75°F. Unetched. Max. resolution at 2000X.

SECTION VI

PRELIMINARY INVESTIGATION OF TiB_2 AND $MoSi_2$ AS THE CERAMIC COMPONENT OF A CERMET

Investigations of hot-pressed $MoSi_2$ by NACA have indicated that this material has good strength and excellent oxidation resistance.² Work done in this laboratory on sintered $MoSi_2$ resulted in strength and oxidation data which agreed very well with the data for hot-pressed $MoSi_2$. Although this material is very brittle, it was thought, because of its excellent oxidation resistance, that it might be used in conjunction with some metal or alloy in the synthesis of a high-temperature material, or in conjunction with TiB_2 as a ceramic base which could be metal bonded.

There were two general plans of investigation:

- (1) Metal-bonding of $MoSi_2$ to improve its ductility.
- (2) Adding $MoSi_2$ to some component such as TiB_2 to make an oxidation-resistant base which could then be metal bonded; sources of both boron and silicon being needed to form a borosilicate glass in the sintered product.

1. MATERIALS

The following materials were used:

$MoSi_2$: Minus 100 mesh containing 63.44% Mo, 36.45% Si, 0.17% impurities; Electro Metallurgical Division of Union Carbide and Carbon Corp.

TiB_2 : Minus 20 mesh containing 66.51% Ti, 31.1% B, 1.7% total C, 0.69% minor impurities (1.2% estimated free C); Norton Company.

Co: Minus 300 mesh, 97.5% Co; Charles Hardy.

Ni: Minus 300 mesh, 99% Ni; Charles Hardy.

Cr: Minus 325 mesh, 98% Cr; Charles Hardy.

2. COMPOSITION,

The following compositions were investigated initially:

² NACA Research Memorandum E50F22 August 1950.

A. Metal Bonded MoSi₂:

70% MoSi₂ + 30% Cr
70% MoSi₂ + 30% Ni
70% MoSi₂ + 30% Co

B. TiB₂ + MoSi₂ Base:

80% TiB₂ + 20% MoSi₂

3. FABRICATION

(a) Metal Bonded MoSi₂

The MoSi₂ was milled alone for 24 hours in a hardened steel mill using cobalt-bonded tungsten carbide slugs and benzene as the vehicle. All compositions were wet mixed in benzene and then oven dried. Compositions were formed into bars and re-pressed hydrostatically. Separate lots of these bars were fired at 2500°F and at 2700°F in a helium atmosphere with a one-hour soak at temperature.

(b) TiB₂ + MoSi₂ Base

The MoSi₂ and TiB₂ were milled separately for 24 hours in a hardened steel mill using cobalt-bonded tungsten carbide slugs and benzene as the vehicle. The MoSi₂ and TiB₂ were then wet mixed together in benzene and oven dried. Small pellets were formed and re-pressed hydrostatically. These pellets were fired at 2500°F, 2700°F, and 2900°F in a helium atmosphere with a one-hour soak at temperature.

4. FACTUAL DATA

(a) Metal Bonded MoSi₂

The MoSi₂ + Ni and MoSi₂ + Co compositions produced porous bars with very little strength. The maximum modulus-of-rupture was 10,000 psi but most of the bars could be broken easily in the hand. These poor results were due to silicide forming reactions between the MoSi₂ and the Ni or Co. Although the reaction between MoSi₂ and Cr was not as great as with Ni or Co, the bars were still very porous and the maximum modulus-of-rupture in this case was only 14,000 psi. These poor results did not warrant the further testing of these compositions.

(b) TiB₂ + MoSi₂ Base

Pellets of 80% TiB₂ + 20% MoSi₂ fired at 2500°F and at 2700°F were very porous (20-30 percent). The firing at 2900°F resulted in a porosity of 2.0 to 3.0 percent. These latter pellets were tested for oxidation resistance at 2000°F by measuring the weight gain due to oxidation. The oxidation

resistance was excellent; the oxidation parameter K in $\text{mg}^2/\text{cm}^4/\text{min}$ was 0.001 after 100 hours, and over 90% of the gain in weight took place during the first 24 hours. Very little or no volatile oxide is produced. This is comparable to MoSi_2 alone and considerably better than SiC .

The next step was to press and sinter bars of the compositions shown in Table III. These bars were sintered in helium at 2900°F. All showed excellent oxidation resistance at 2000°F. The porosities and strengths are shown in Table III.

TABLE III

Strength of $\text{TiB}_2 + \text{MoSi}_2$ Compositions

Composition %	Sintering Temp., °F, held 1 hr.	Apparent porosity, %	Modulus of rupture, psi
80 $\text{TiB}_2 + 20 \text{ MoSi}_2$	2900	6	34,000
90 " + 10 "	2900	16	42,500
95 " + 5 "	2900	12	32,000

These porosities indicated that a higher firing temperature might be desirable to get maximum strength. Additional bars of 90% $\text{TiB}_2 + 10\% \text{ MoSi}_2$ were made and fired in the induction furnace in a helium atmosphere at 3150°F held for 1 hour. The average modulus-of-rupture was 70,000 psi. While the porosity decreased to somewhat less than that of the specimens fired at 2900°F, the 3150°F specimens were still porous. Further firings of the 90% $\text{TiB}_2 + 10\% \text{ MoSi}_2$ composition failed to reproduce the 70,000 psi modulus-of-rupture. All subsequent moduli of rupture were less than 50,000 psi.

While no phase diagram has been developed for $\text{TiB}_2 - \text{MoSi}_2$, it is known that there is a chemical reaction at about 7 to 8 percent of MoSi_2 which presumably accounts for the porosity of mixtures of these two components when larger percentages of MoSi_2 are present.

It has been found that the 95% $\text{TiB}_2 + 5.0\% \text{ MoSi}_2$ composition can be sintered dense with an apparent porosity less than 0.5% over a reasonable range of temperature and still consistently show cold moduli of rupture of over 50,000 psi. It was therefore decided to concentrate first on the metal bonding of this composition since it is oxidation resistant and appears to be the more promising ceramic component for a cermet body. Work on the metal bonding of this composition with nickel, cobalt, and chromium has been started, but as yet the optimum firing temperatures have not been determined.