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UNITED STATES NAVY

PROJECT SQUID

FIELD SURVEY REPORT

MATERIALS

DOWNGRADED Volume 1, Part 3

**TO
UNCLASSIFIED**

30 June 1947

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MATERIALS

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PROJECT SQUID

MATERIALS

Field Survey Report

Volume I, Part 3

by
ROYAL C. BRYANT



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Engineering Research Associates, Inc.

Washington, D. C.

30 June 1947

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Princeton University, the central management organization of Project SQUID, arranged for the preparation of the *Field Survey Report* under Contract Number N6ori-105, Task Order III, with the Office of Naval Research, Navy Department.

This report was prepared by the Technical Survey Group of Project SQUID as a cooperative effort of Princeton University and Engineering Research Associates, Inc. Engineering Research Associates was given primary responsibility for the preparation of these reports in accordance with the provisions of Task Order II under Purchase Order Number 08451 with Princeton University.

TECHNICAL SURVEY GROUP

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FOREWORD

The *Field Survey Report* on liquid propellant rockets and pulse jet engines was prepared at the suggestion of the Policy Committee, in order that the fundamental research in Project SQUID might be related to other projects and programs of research in this field, and to problems arising in the development of rocket and pulse jet engine equipment.

In order to fulfill this purpose the *Field Survey Report* had to be more than a brief outline of the work of each contractor, but time did not permit it to be prepared as a monograph in each branch of the field of propulsion. The choice of presentation of the work in each volume of the report was governed in part by the amount of available information and by its relation to the research now being sponsored by Project SQUID.

The Policy Committee will use the *Field Survey Report* as a basis for adjustments in the research program of Project SQUID, in order to ensure a more effective attack on the fundamental problems in the field of propulsion. The Policy Committee hopes that this report may also be useful to scientists conducting research and development in fields relating to propulsion, and to members of government organizations responsible for the planning and integration of research programs in propulsion.

HUGH S. TAYLOR, Chairman
Policy Committee, Project SQUID

PREFACE

The *Field Survey Report* was prepared by the Technical Survey Group, Project SQUID, under the direction of Engineering Research Associates, Inc.

The assembly of the material and the preparation of each part of the report was undertaken as a group effort, to which the staffs of both Princeton University and Engineering Research Associates, Inc., have contributed. Mr. F. A. Parker, Project Organizer, and Mr. W. C. House, Chief Technical Aide, of the central administrative staff of Project SQUID at Princeton served as members of the Technical Survey Group and prepared Volume II. In addition, Prof. J. V. Charyk of the Aeronautical Engineering Department at Princeton visited the California Institute of Technology and furnished basic information concerning the research program there. He also offered many helpful suggestions with regard to several parts of Volume I.

In the preparation of this report the members of the Technical Survey Group have received the assistance, counsel and cooperation of representatives of the War and Navy Departments and other Government agencies, and of representatives of academic and industrial laboratories who are under contract to the government for research and development in this field.

The authors are indebted to a number of scientists who have reviewed each part of the report and have offered much constructive criticism. The authors also wish to express their appreciation for the assistance which was so generously given by representatives of the Office of Naval Research and of the Bureau of Aeronautics.

THE TECHNICAL SURVEY GROUP

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I. SUMMARY

This report summarizes the government sponsored research work on metallic and ceramic materials suitable for use at elevated temperatures. In addition, brief discussions are given of the fields of research important in connection with the development of materials, of the present state of knowledge, and of outstanding problems.

No criterion exists by which the high temperature properties of a material can be predicted, and hence most of the work on the development of materials must be empirical. To furnish a logical basis for the guidance of a research program on materials, it is important that a better understanding of the solid state at elevated temperatures be obtained.

The most satisfactory high temperature alloys available at present are those developed for use in gas turbines. Further improvement of these alloys may be expected, but the requirements for rocket and pulse jet engines are so severe that work on the high melting point metals not commonly used for construction should be emphasized.

The requirements for resistance to thermal shock and for strength at elevated temperature have opened new fields of research in ceramics, about which little is known. High temperature techniques and testing methods need further study. The high melting compounds heretofore used either not at all or only for special purposes should be thoroughly investigated.

II. RECOMMENDATIONS

The research projects described in this report make adequate provision for the development of metallic and ceramic materials for use in the near future by the improvement of the best of the materials now known. It is felt, however, that relatively more emphasis should be placed on the solution of the outstanding problems discussed in Section V. Therefore, the following recommendations are made:

- A. Research on the physical and chemical factors which affect the properties of metals, alloys, and ceramics at high temperatures should be continued and extended.
- B. Basic research to determine the properties which a material must have to give satisfactory performance should be extended. More information on the influence of thermal conductivity of metals

and alloys is urgently required.

- C. The development of high melting point metals, borides, carbides, nitrides, and oxides should be accelerated.
- D. Special provision should be made for the development of high temperature techniques and apparatus to increase the temperature range over which quantitative data can be obtained.
- E. A project should be set up to study testing procedures, particularly for ceramics, and eventually to recommend the most suitable for general use.
- F. More emphasis on investigations to establish the correlation between laboratory tests and service results is considered necessary for both metallic and ceramic materials.

III. INTRODUCTION

The simplified thermodynamic theory of rocket propulsion (3), which assumes that hot gases in the combustion chamber expand adiabatically, shows that the thrust on a rocket increases with increase in the combustion chamber temperature, other factors remaining constant. It is therefore desirable to have the temperature of the gases as high as possible. But a limit to the temperature which can be attained by

the combustion process is set by the dissociation of the products of combustion.¹ In the case of propellants consisting of carbon, hydrogen, nitrogen, and oxygen, a temperature of about 6000°F is the maximum for pressures of the order of 300 pounds per square inch; but other fuel combinations, which have been considered theoretically and which will

¹Reference (3), page 297.

shortly be tested experimentally, give chamber temperatures considerably in excess of 7000° F (2). With construction materials and cooling methods now available, the highest possible flame temperature which is practicable for continuous operation is about 5000° F. The development of materials with better properties at high temperatures or of better cooling methods is therefore necessary if the effectiveness of jet power plants is to be increased.

The most promising method of solving the high temperature problem appears at present to be transpiration cooling, discussed in Part 5 of this report, which will require the development of satisfactory porous materials. However, the addition of a cooling system to a power plant is not the ideal solution because the design is complicated and the weight increased. In the case of short-burning-time power plants, a cooling system is impracticable. Therefore studies of cooling methods and the development of porous materials and materials resistant to high temperature must proceed together.

The two types of materials which have been given the most consideration for high-temperature use are special alloys and ceramics. Before the war, alloys were used at temperatures up to 1100°F, and in the last few years improvements have been made which permit use of alloys up to about 1500°F in gas turbines. Standard refractory materials have fusion points between 3000°F and 4000°F and can be used in this temperature range if the strength requirements are not too great and the heating is not too rapid. The requirements for jet power service are far more severe than these materials can meet. It has already been mentioned that ability to withstand temperatures of 7000° F would be desirable. In addition, it has been found that the average heat flow through walls of a rocket may amount to as much as 6 Btu per square inch per second (35), about 50 times that met in usual furnace practice. Tensile

strength, fatigue resistance, and, most important, the ability to withstand rapid heating (resistance to thermal shock) are additional requirements. It may appear that the material to withstand these operating conditions does not exist, but it should be kept in mind that many elements and compounds with high melting points have never been examined as materials of construction and that any increase in the resistance of materials to high temperatures will make an important contribution to the construction problem.

The high temperature problem in materials has been emphasized because it appears to be the most difficult to solve and because its solution would greatly increase the effectiveness of jet power plants, but materials satisfactory at low temperatures are also necessary because of the use of liquefied gases as propellants. Resistance to corrosion and oxidation at all temperatures and to erosion at high temperatures are further requirements. In addition, there are all the normal constructional problems and design considerations that go with the building of any power plant.

In the following sections a survey of the research projects on high temperature materials is given with emphasis on the work which may be of special significance for liquid rocket and pulse jet power plants. The research on problems of general applicability, such as the strength and behavior of materials at room temperature and stress analysis, and the extensive program on the properties of materials at low temperatures have not been included.

It is recognized that the metals and ceramics industries have had a large part in originating and developing materials which are satisfactory for use at high temperatures and that the work is being actively carried on at the present time. This report, however, is primarily concerned with research under government sponsorship and no attempt has been made to review other work.

IV. SURVEY OF RESEARCH PROJECTS

A. Metals and Alloys

Metals are commonly used for construction purposes in the form of alloys, except for special purposes such as coatings, because it is difficult to remove impurities in a commercial process to produce a pure metal, and because alloys can be made whose mechanical properties are better than those of the pure metals composing the alloy. A system of two or more metals in equilibrium in the solid state is often quite

complicated, consisting of one or more phases which may be the pure metals, solid solutions, intermediate phases of definite composition of the nature of chemical compounds, or intermediate phases of variable compositions. The basic information required in the scientific study of alloys is the equilibrium phase diagram, which gives the phases at equilibrium as a function of composition and temperature. The phase diagrams of many binary systems are not yet accurately

determined. In the case of ternary systems, the relations are so complicated that only a few phase diagrams have been completely worked out.

The structure of alloys is further complicated by the fact that equilibrium is often not attained in the commercial product and that many valuable properties result from non-equilibrium conditions. When the solid alloy in equilibrium at a high temperature is cooled, phase changes may take place in the solid state, involving precipitation of a component whose solubility decreases with the temperature, phase transformation from a form stable at high temperatures to one stable at low temperatures, or the eutectoid decomposition of one phase into two different phases. The phase changes require considerable time, and it is often possible to cool an alloy rapidly enough to retain at room temperature a phase stable only at high temperatures. Rapid cooling may also cause a transition phase to form, intermediate between the high temperature and low temperature phases or similar to the high temperature phase but not related to the low temperature phase.

The phase changes which occur on change of temperature are the basis of the development of desired properties by various heat treatments, such as solution heat treatment to attain equilibrium at a high temperature, quenching, and aging. A fundamental approach to the problem of alloy properties will require the detailed study of phase changes as a function of time and temperature and a correlation of physical properties with the nature and distribution of the phases. The effect of time and temperature on certain phase changes has been investigated for steels, leading to the development of curves (5) which are useful in determining the heat treatment a given steel should receive to develop required properties. Similar studies are needed for other alloys.

The properties of a metal or alloy depend not only on the nature of the phases present but also on the number, size, shape, orientation, and distribution of the individual crystallites or grains. It is known from experiment, for example, that for each alloy system there is an optimum grain size for mechanical strength and that in some cases the proper orientation of crystals has important effects. The properties of a cast alloy depend to a large extent on the nature of the intercrystalline network, and the accumulation of even small amounts of some phases in the grain boundaries will cause important alterations in those properties. Certain alloys are hardened by the precipitation of small particles throughout the body of the material, thought to be due to a keying action in the grain boundaries or to residual stresses in the

crystal lattice. In general, effects due to the macrostructure are known and used, but the physical basis of the action is not understood.

Although most of the work on alloys has been experimental, theoretical investigations have been made which show promise of leading to a better understanding of the structure and properties of materials. From quantum mechanical considerations of the energy of valence electrons, recently reviewed by Hume-Rothery (21), the phase boundaries for certain alloy systems have been calculated, giving rough agreement with experimental values. It has been possible to explain, qualitatively at least, the mechanical properties of pure single-crystal and polycrystalline metals in terms of "dislocations," a particular type of lattice defect (33). It has not been possible yet to extend this theory to the complicated metallic systems met in practice. Other workers have attacked the problem from a different point of view, by developing mathematical expressions, from theory or experiment, for observed phenomena such as creep and rupture. Dushman and co-workers have found an expression for creep rate as a function of temperature and stress from experiments carried out up to about 1000°C (6, 33). Nowick and Machlin (28) have developed an equation for the creep of metals by the application of the theory of rate processes. Other expressions relating strain, stress, and time have also been investigated recently (20, 29). Studies of the effect of grain size on internal friction, showing that grain boundaries exhibit viscous behavior (23), may lead to an expression for the effect of grain size.² It is hoped that eventually the fundamental characteristics of a metal or alloy can be correlated with the parameters of the mathematical expressions describing the behavior and thus allow the mechanical properties of a given system to be predicted.

The experimental investigation of the mechanism of failure of materials is an important part of the attempt to correlate the structure of a metal or alloy with its mechanical properties. The most common types of mechanical failure are normal ductile failure, brittle fracture, creep, and fatigue. Brittle fracture is usually an intergranular separation. Creep may occur along slip planes of the crystal, by flow along the grain boundaries because of some property of the boundaries themselves, or by flow along the grain boundaries because of a property of intergranular material. One explanation of fatigue failure is the development and growth of a small crack at a point of stress concentration because of a non-homo-

²University of Chicago, Chicago, Illinois; T. S. Kê; ONR Contract N6-ori-20, T.O. -4; *Unclassified*.

MATERIALS

geneity or of a lattice imperfection. In this connection it may be noted that theoretical calculations of mechanical strength give results many times as great as observed values. This is an indication of the importance of intergranular conditions, micro-flaws, and lattice imperfections.

The purpose of the above general discussion is to point out the type of problem involved in the development of satisfactory metals and alloys. For further details, reference should be made to a standard text book on metallurgy, such as reference (31).

1. ALLOYS OF CHROMIUM AND OF COBALT. Most of the work on high temperature alloys has been done in connection with the development of materials suitable for use in gas turbines. During the war the National Defense Research Committee, War Metallurgy Division (Div. 18), investigated many alloy systems in a preliminary way in order to find those which appeared most promising for further development. In one project (8), for example, the following systems were investigated: (a) tungsten-titanium-iron; (b) tungsten-chromium-nickel, tungsten-chromium-cobalt, and tungsten-chromium-nickel-cobalt with additions of carbon, boron, beryllium, vanadium, titanium, aluminum, silicon, iron, and molybdenum; and (c) tungsten-chromium-nickel-cobalt with one or more elements replaced by molybdenum, manganese, aluminum, vanadium, iron, or copper. The results of preliminary investigations of this type have lead to the development of alloys of chromium and of cobalt as the most heat resistant metallic materials of construction available today.

Many variations in composition have been studied, but the alloys 18-8 stainless steel, Inconel-X, Nimonic, N-155, and Vitallium or Haynes Stellite 21 may be chosen as representative of the types of alloys which are being considered. The main components of these alloys are given in Table 1. Other components which are present in small percentages, not shown in Table 1, may have important effects on the properties of the alloys.

Table 1. Main Components of Certain High Temperature Alloys.

Alloy	Percentage composition					
	Iron	Chromium	Cobalt	Nickel	Molybdenum	Titanium
18-8 Stainless Steel	72	18	—	8	—	—
Inconel-X	7	15	—	73	—	—
Nimonic-80	—	21	—	75	—	2.5
N-155	33	20	20	20	3	—
Vitallium or Haynes Stellite 21	—	25	65	—	6	—

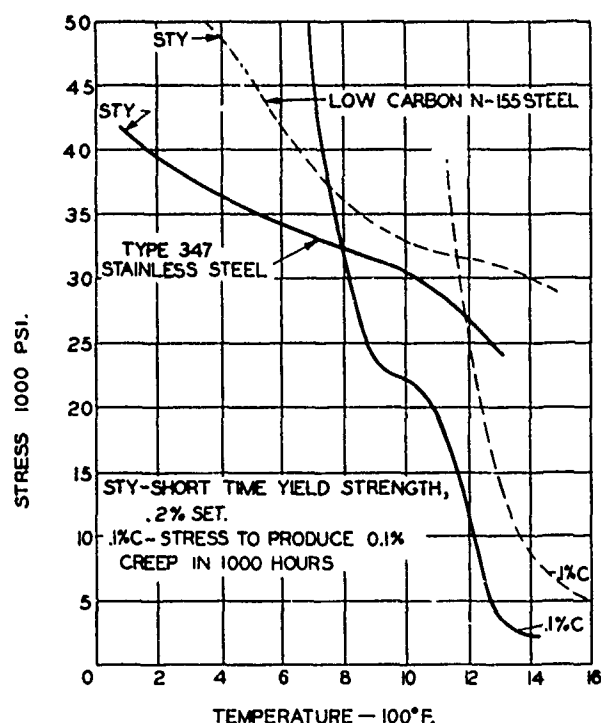


Figure 1. High temperature properties of two alloy steels.

Stainless steel is commonly used for construction purposes, although its strength decreases rapidly above 1100°F. Vitallium or Haynes Stellite 21 and N-155 have relatively good tensile strength at 1500°F and have been used for turbine blades. Nimonic is low in hot tensile strength but it has good creep resistance and has given satisfactory service in gas turbines. As an illustration of the properties to be expected of alloys of this type in high temperature service, the short-time yield strength, 0.2% set, and the stress required to give 0.1% creep in 1000 hours are given in Figure 1 for a stainless steel and an N-155 alloy, taken from reference 25. A bibliography of high temperature alloys is given in reference 1. Compilations of data on some of the alloys which appear to be most useful for jet power plants will be found in references 9, 25, 34. More extensive compilations are being prepared by Battelle Memorial Institute³ and the M. W. Kellogg Company.⁴

The development of heat resistant alloys must be carried on by experiment at high temperatures be-

³Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; ONR Contract N5-ori-111, T. O. -1; *Unclassified*.

⁴M. W. Kellogg Company, Jersey City, N. J.; G. H. Meserly; AAF Contract W-33 038-ac-13916; *Restricted*.

cause performance at room temperature is not a criterion for performance at high temperatures and because the fundamental data and techniques for predicting high temperature performance do not exist. The alloys of chromium and of cobalt are usually of the precipitation hardening variety, in which one component of the system forms a phase whose solid solubility decreases with temperature. A heat treatment, consisting of solution heating, quenching, and aging, is required for the development of the best properties, and studies of mechanical properties as functions of the temperature history and of fabricating techniques are important.

Research projects, the ultimate objective of which is to develop improved chromium and cobalt alloys, are being carried on at Battelle Memorial Institute, the Polytechnic Institute of Brooklyn, the M. W. Kellogg Company, Massachusetts Institute of Technology, the University of Michigan, the National Research Corporation, the Naval Research Laboratory, Ohio State University, Stevens Institute of Technology, and various industrial research laboratories. As a result of this program, a better understanding of the properties of alloys at high temperature and the eventual development of alloys satisfactory for use at, say, 2000°F may be expected.

Battelle Memorial Institute⁵ is engaged in a study of the factors which promote high-temperature properties in alloys of the Vitallium type. Because of the lack of fundamental data it was first found necessary to study the cobalt-chromium phase diagram over the whole composition range, with particular emphasis on establishing the correct boundary lines for the epsilon-beta transformation and the solubility limit of gamma in epsilon. A sample heat-treated to give the pure epsilon phase, for example, was heated at constant temperature within the epsilon plus beta field, and the appearance of the beta phase was studied as a function of time by metallographic and X-ray techniques. At 808°C it required 31 days to reach equilibrium, but for practical purposes a time of 50 hours was considered to give conditions sufficiently close to equilibrium. These studies have indicated boundaries of the epsilon, beta, and epsilon plus gamma fields which are different from those previously reported. After the study of the cobalt-chromium system is complete, the effect of adding the other elements used in Vitallium (singly and together) on the phase relations will be investigated.

⁵Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; ONR Contract N5-ori-111, T.O.1; *Unclassified*.

The preparation of metallurgical samples must be carefully controlled if test results are to be reproducible, and in extreme cases results for samples supposedly prepared under identical conditions may differ by a factor of 100. In the case of chromium-base alloys, contamination and chemical action by the air are thought to be factors affecting the consistency of test results and the ultimate properties of the alloy. In order to eliminate the effect of the air, Battelle Memorial Institute⁵ is melting and casting a chromium-base alloy, chromium 60%, molybdenum 25%, iron 15%, in beryllia or zirconia crucibles in a vacuum. This alloy was first developed by the Climax Molybdenum Corporation for the Army and is being further studied by the Union Carbide and Carbon Corporation. The specimens tested to date by Battelle Memorial Institute have shown high temperature properties which are better than those of any other alloy. Not enough work has been done to show whether the techniques which have been developed will result in consistent test results.

In a third project, Battelle Memorial Institute⁵ is collecting and presenting in convenient form engineering test data on high-temperature alloys, in order to assist the designer of high temperature devices. These data include stress-rupture, creep, and fatigue over a temperature range from 1350° to 1600°F in most cases. Some data are obtained at 1800°F. Particular attention has been paid to disc alloys, because most of the data readily available are for bar stock. This work is largely completed for alloys low-carbon N-155, S-590, S-816, and Inconel-X disc form.

A study of the chromium-beryllium system has been started at the Polytechnic Institute of Brooklyn.⁶ Little is known about this system, but it may have some interest because of the possible high melting point of the alloys and possible low specific gravity. It is planned to construct the equilibrium diagram over the whole range of composition from cooling curves. Phases will be identified, where necessary, metallographically and by X-ray techniques. This project is in its preliminary phase, attention being concentrated on devising suitable heating techniques. A method which looks promising is to heat the sample in an inert atmosphere in a refractory crucible surrounded by a carbon ring. The carbon ring is heated by induction and hence the crucible and the sample become heated.

Up to the present, metals have rarely been used in

⁶Polytechnic Institute of Brooklyn, Brooklyn, N. Y.; O. H. Henry; ONR Contract N6-ori-98, T.O.2; *Unclassified*.

continuous service at temperatures above 1500°F, although some testing has been carried out at temperatures up to 1800°F. If the useful temperature range of special alloys is to be extended, it is necessary that testing be carried out at higher temperatures, and the M. W. Kellogg Company has set up a laboratory equipped for metallurgical testing at temperatures up to 2200°F. Machines are available for the following tests: tensile strength, creep, stress-rupture, rotary fatigue, tension fatigue, torsion creep, and torsion rupture. The tension fatigue, torsion creep, and torsion rupture tests are not conventional tests, and preliminary work will be necessary to determine what kind of correlation can be obtained with other tests and with service results. In addition, a biaxial stress-to-rupture test has been developed. In this test the sample is in the form of a hollow tube, and internal pressure can be developed by a gas while the sample is under tension. The work on these special tests is in a preliminary stage, and plans for future research will depend on the initial results.

The research program at the M. W. Kellogg Company⁷ is just now getting under way. A survey of all available data in the open and in the classified literature on the properties of high temperature metals and alloys has been completed. The first phase of the experimental work will be to determine what heat treatment will give the best high temperature properties. Alloys such as low carbon N-155, Inconel-X, S-816, and S-588 will be solution treated to give both fine and coarse grain. Unaged samples, and samples aged 48 hours at 1500°F and at 1800°F will be tested in stress-rupture. From this series of tests it is hoped to determine what solution and aging treatment will give maximum properties at 1800°F. The best of these samples will then be tested in stress-rupture and rotary fatigue at 1800°F, 2000°F and at higher temperatures up to 2200°F if the materials still show strength at these high temperatures. A similar series of tests will be run on aged and unaged samples of cast alloys, which cannot be solution treated.

The investigation of the behavior of alloys at high temperatures is the main concern of an investigation at the Massachusetts Institute of Technology⁸ under Dr. Nicholas J. Grant. This work includes the study of pertinent binary systems, the results of various

metallurgical treatments, and the development of superior alloys (13, 14).

Equilibrium systems which were investigated include cobalt-chromium and chromium-carbon, in which it was desired to reconcile conflicting diagrams, especially as to the nature of the epsilon-beta transition in high-cobalt alloys, and to verify if possible the existence of chromium carbide.

The erratic mechanical properties of some alloys led to the study of casting variables. It was found that both mold and metal temperature have an important effect on hot strength and ductility through their influence on grain size and carbide spacing. In addition, the factors which interfere with soundness in hot-investment casting were evaluated and the effects of porosity on high temperature strength determined.

The aging characteristics of several high temperature alloys were investigated. In general, precipitation began to form at 1350°F, was a maximum at 1500-1600°F, and resolution of the aging precipitate, along with some of the carbide, gradually occurred with increasing temperature. The precipitation rates at temperatures ranging from 1000° to 1650° F were also determined.

An extensive program of alloy development has continued since the inception of the project. Alloys of the N-155 type have been investigated, but the major effort has been on cobalt-base alloys. A study of the effects of alloying elements has led to the "J" alloys, which are stronger than any other reported cobalt-chromium alloys in the range of 1350-1800°F. At the present time, the elements in small amounts which appear to do the most good in the cobalt-chromium-molybdenum system are manganese (1 or 2%), carbon (up to 1%), nickel (up to 15%), tantalum (up to 2%). For 100 hours rupture life at 1500°F, this "J" alloy will withstand 35,000 p.s.i.

The University of Michigan obtained measurements some time ago at 1700°F and 1800°F on two precision cast alloys prepared at Massachusetts Institute of Technology (30). The samples studied were variants of N-155 and Vitallium which had particularly good properties, relative to other alloys, at 1600°F. Stress-rupture tests were run, with stress from 9000 p.s.i. to 27,000 p.s.i., and rupture times from 1 hour to 500 hours at 1700° and 1800°F. The elongation at break varied from 2% to 22% and the reduction in area from 4% to 37%. The variant of N-155, which contained 30% nickel, 2% tantalum, and 0.9% carbon, showed particularly good properties at these temperatures. In agreement with modern theory, it was found

⁷M. W. Kellogg Company, Jersey City, N. J.; G. H. Meserly; AAF Contract W-33-038-ac-13916; *Restricted*.

⁸Massachusetts Institute of Technology, Cambridge, Mass.; N. J. Grant; BuShips Contract NObS 25391, T.O.-2; *Unclassified*.

that a plot of stress vs. log rupture time represented the data better than a plot of log stress vs. log rupture time.

The National Research Corporation⁹ is studying the effects of impurities on the high temperature physical properties of metals and alloys. The initial work is concerned with a comparison of the physical properties obtained by adding commercial chromium to refractory metals with those obtained by the addition of highly purified chromium. The techniques for preparing pure chromium and for melting and casting it are being developed. The tensile strengths of the two sets of alloys will be measured at several temperatures and strain rates. If any differences in properties are noted, the effects of adding impurities such as nitrogen, hydrogen, oxygen, boron, and carbon to the pure chromium will be investigated.

The Naval Research Laboratory has started a study of the fundamental characteristics of the cobalt-chromium system. Three cobalt-chromium systems were investigated, 20%, 25%, and 27% chromium, by dilatometric and X-ray techniques. This project has not been active recently because of lack of personnel.

An investigation of the chromium-titanium binary alloys has just begun at Ohio State University.¹⁰

Stevens Institute of Technology¹¹ is investigating powder metallurgy techniques for making gas turbine blades to operate at high rotational speeds and dynamic stresses at temperatures up to 1800°F in oxidizing atmospheres. Samples are being made of representative alloys in the chromium-nickel-cobalt, chromium-nickel-cobalt-iron, and chromium-molybdenum-iron systems. Studies of methods of powder preparation and of the effects of initial pressing, sintering temperature and atmosphere, and coining pressures are being carried on. The materials are evaluated by hardness and density measurements and by microstructural and diffusion analyses. Stress-rupture tests at high temperatures are being made in cooperation with Massachusetts Institute of Technology.

2. METALS OF HIGH MELTING POINTS. Most of the work on high-temperature metallurgy has been concentrated on a small group of special alloys which

have been found useful for gas turbines. Other metals which have the obvious advantage of a high melting point have been largely neglected because of their cost or rarity. Battelle Memorial Institute¹² is investigating these less familiar metals. A preliminary survey of the data available in the literature has been made, and on the basis of melting point alone the following metals are thought to deserve consideration as materials of construction: titanium, tungsten, tantalum, zirconium, molybdenum, boron, and columbium (12). The melting points of these metals range from about 6200°F down to 3800°F, while platinum melts at about 3200°F and nichrome and the stainless steels, often used in high temperature service, melt below 2700°F. When the survey of these and other promising metals is completed, it is planned to start an experimental program to develop methods of using them, either pure or as alloys, in bodies or in coatings.

The Jet Propulsion Laboratory of California Institute of Technology¹³ is engaged in studies of rocket nozzles made from such metals as molybdenum, tungsten, and tantalum. Experimental liners of molybdenum sprayed on graphite and of molybdenum sheet have been prepared at Massachusetts Institute of Technology.¹⁴

3. TESTS AT HIGH TEMPERATURES. At room temperature, metallic materials are used under conditions such that creep usually may be neglected. At high temperatures, however, plastic flow becomes important, and any evaluation of mechanical strength must include time. Creep tests, measuring strain as a function of stress, time and temperature; stress-rupture tests, measuring the time to rupture as a function of stress and temperature; and short time yield tests, measuring the stress required to cause a given permanent set in a given short time, are frequently used. These, however, are not sufficient to describe the suitability of the material for all service conditions. Furthermore, experts do not agree on the criteria to be used because the factors which influence the ability of a substance to perform satisfactorily are not known in fundamental terms. Until such time as more fundamental information is available, it will be necessary to devise special tests and

⁹National Research Corporation, Boston 15, Mass.; J. H. Moore; Army Ordnance Contract W-19-066-Ord-1046; *Unclassified*.

¹⁰Ohio State University, Columbus, Ohio; M. G. Fontana; AAF Contract W-33-038-ac 16368 (17278); *Unclassified*.

¹¹Stevens Institute of Technology, Hoboken, New Jersey; G. J. Comstock; BuShips Contract NObs 45091; *Restricted*.

¹²Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; Materials, Fuels, and Combustion Project, Project RAND; *Confidential*.

¹³Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

¹⁴Massachusetts Institute of Technology, Cambridge, Mass.; J. Wulff; BuOrd Contract NOrd 9661; *Confidential*.

to correlate them with the results obtained under actual service conditions.

In a rocket power plant, materials reach a high temperature in a very short time, and no data are available on the behavior of metals under these conditions. Because of this lack of data, Battelle Memorial Institute¹² is designing and constructing apparatus for a short-time high temperature test (4). Suitable experimental arrangements are being considered to provide for heating and temperature control, strain measuring and recording, control and measurement of loading, and other instrumentation. It is hoped that samples can be heated up to the final temperature in four seconds. The temperature range from room temperature up to about 2600°F is to be covered. The work will be concentrated on sheet metals and will include tests on commercially available magnesium-base and aluminum-base alloys, carbon and alloy steels, and high temperature alloys such as Inconel and Vitallium. It is proposed also to develop, fabricate, and test titanium-, molybdenum-, tungsten-, and columbium-base alloys. Welded joints and ceramic-coated metals will also be studied. At the time of writing, this project was in the design and construction stage and no results are available.

Certain parts of jet power plants are subjected to periodic strains, and the fatigue life at elevated temperature is a property which may affect the performance of a material. Although it is not clear from the evidence available at present that fatigue is an important cause of failure in jet power plants, except perhaps for special parts such as the valves in a pulse jet, it is important to investigate materials from this point of view. Equipment has been devised, mainly in industrial research laboratories, to measure fatigue life of metals and alloys at room temperature and at elevated temperatures, and recently a large engine manufacturer has developed a new test which appears to give satisfactory results.

The Polytechnic Institute of Brooklyn¹⁵ is interested in the fatigue properties of metals, and a new fatigue test is being studied to determine if it can be adapted for use at high temperature. In this machine the specimen (1/4 inch by 1/8 inch by about 5 inches) is clamped at one end and the free end is made to vibrate by the passage of magnets. The sample must be clamped so that its natural frequency is 18,000 vibrations per minute. Present work consists in an analysis of the stresses in the sample and experiments at room temperature on metal whose fatigue prop-

erties at room temperature are known. If suitable correlations can be established, this machine might be useful in high temperature studies.

Cornell Aeronautical Laboratory¹⁶ is also interested in the life of metals at high temperature and is designing and constructing a fatigue machine which will vibrate a specimen at its natural frequency while it is at high temperature. In addition, a high-temperature metaloscope is being developed by means of which it will be possible to examine samples metallographically while being heated in a vacuum or in a controlled atmosphere. The work at the Cornell Aeronautical Laboratory is still in the relatively early stages of equipment design and construction, although a few trial runs have been made with the fatigue machine.

The dynamic behavior of a metal at high temperature does not necessarily correlate with its dynamic behavior at room temperature nor with its static behavior at high temperature. Evidence for this has been found in the failure of Inconel tensile specimens in rupture under dynamic test conditions without any of the expected elongation. Consequently, the Cornell Aeronautical Laboratory¹⁷ is undertaking a study of the characteristics of metals under dynamic load at high temperatures. A survey of the literature showed no significant data on this problem. Tensile tests have been run on specimens at 2700°F vibrated at frequencies from 1500 to 3600 cycles per minute. Under these conditions it is found that fracture takes place without elongation of the sample, whereas under static conditions considerable necking-down occurs before rupture. Further investigation of this phenomenon is planned.

In a service test being carried out for the Bureau of Ships at the Engineering Experiment Station, Annapolis, Maryland, 142 General Electric B-2 turbo-supercharger blades are mounted on a turbine wheel. The turbine is run at 15,000 r.p.m. at temperatures from 1200° to 1500°F. The temperature of the turbine blades as calculated from the inlet gas temperature, by an empirical method developed experimentally, is believed to be correct within 20°F. At the present time, blades made from 12 different alloys are being tested. The next run will be made at 1500°F using Vitallium alloys.

In rocket motor design, the type of problem of immediate concern is the maximum stress a metal can

¹⁵Polytechnic Institute of Brooklyn, Brooklyn, N. Y.; O. H. Henry; ONR Contract N6 ori 98, T.O.-2; *Unclassified*.

¹⁶Cornell Aeronautical Laboratory, Buffalo, N. Y.; L. W. Smith; ONR Contract N6 ori-119, T.O.-1; *Unclassified*.

¹⁷Cornell Aeronautical Laboratory, Buffalo, N. Y.; L. W. Smith; BuOrd Contract NOrd 8993; *Confidential*.

stand under given conditions of temperature, time of operation, and maximum permissible strain. The Jet Propulsion Laboratory at California Institute of Technology¹⁸ is investigating the properties of metals from this point of view. The sample is heated to the desired temperature in a furnace, the stress is applied as quickly as possible, and the elongation is recorded as a function of time at constant stress for a maximum of ten minutes. Among the alloys being tested are Allegheny Ludlum 46-M (type 501) and 12-W (type 418), Universal Cyclops 19-9-DL, N-155, and International Nickel Inconel-X.

A study of static and dynamic creep of high temperature alloys has recently been started at Syracuse University.¹⁹ Equipment is being designed and built, and no measurements have yet been made.

4. CORROSION AND EROSION AT HIGH TEMPERATURES. The corrosion and erosion conditions which the materials of construction must withstand in jet power plant service are severe. The word *corrosion* is used here in its general sense, referring to deterioration by chemical action, including oxidation. The hot exit gases, which have velocities up to 12,000 feet per second in a rocket, may mechanically erode the surfaces on which they impinge. The atmosphere may be oxidizing in some parts of the motor and reducing in other parts, and it may even be possible that rapid oscillations between oxidizing and reducing conditions take place. The hot chamber walls and nozzle must withstand occasional splashes of liquid fuel or oxidant. It is not surprising, therefore, that material is removed from a rocket nozzle during the firing. The precise mechanism of this action is a matter of controversy. It is usually assumed to be a combination of corrosion and erosion, but the statement has been made that true erosion does not take place with a pure gas and that the failures which appear to be erosion are due to thermal spalling, local melting, or the presence of solid particles in the gas stream (2). However, so little is known about the resistance of materials to the conditions in a jet power plant that one can only theorize about the causes of failure.

Metals and alloys are subject not only to general corrosion due to chemical action, but also to corrosion in the grain boundaries. Intergranular corrosion occurs because of small quantities of a phase of different composition from the parent metal in the

grain boundaries, thus setting up an electrolytic cell. Some alloys are particularly subject to corrosive attack when under stress, corrosion taking place usually along the boundaries but sometimes across the grain. Very little quantitative work has been done on corrosion at high temperatures because the chromium alloys are resistant to oxidation and the most serious failures had mechanical rather than chemical causes. With the continued improvement of heat resistant alloys, studies of corrosion will become more important.

The Alloy Casting Institute, which is an organization composed of most of the producers of heat and corrosion resistant castings in the United States, sponsors two research programs at Battelle Memorial Institute. These have been active for about ten years and provide a considerable reservoir of technical information, much of which has not yet been published. Research activities of this organization are frequently outlined and summarized in the Alloy Casting Bulletin²⁰.

The High Temperature Research Program of the Alloy Casting Institute has included surveys of the 12% chromium-60% nickel, 16% chromium-35% nickel, and 25% chromium-12% nickel heat resistant alloys, the last two having been covered in considerable detail. An intermediate temperature alloy for service up to 1400°F was also developed during the war. More general research efforts have covered oxidation and scaling studies over the range from 1400° to 2200°F, hot gas corrosion resistance in oxidizing and reducing flue gases containing a range of sulphur contents, pack and gas carburizing studies, creep testing, stress-rupture testing, metallographic studies in the broad chromium-nickel-iron field, and investigation of the problem of thermal fatigue. The hot gas corrosion program is probably the most extensive that has yet been undertaken on commercial heat resistant alloys.

The corrosion research program has included some general survey work on a range of chromium-nickel-iron alloys, a comprehensive program relating the composition of the 19% chromium-9% nickel alloys to their performance in oxidizing media, an investigation of modifications that are somewhat more machinable than the conventional grades, and a general study of the effect of composition on cast 12% chromium steels. A number of other minor subjects have also received attention.

Erosion and corrosion are being investigated by two

¹⁸Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

¹⁹Syracuse University, Syracuse, N. Y.; B. J. Lazan; AAF Contract W-33-038-ac-15941; *Unclassified*.

²⁰Inquiries concerning the Alloy Casting Bulletin should be addressed to Howard S. Avery, Member Metallurgical Advisory Committee, P.O. Box 251, Mahwah, New Jersey.

different techniques at the Jet Propulsion Laboratory, California Institute of Technology.²¹ The first involves the insertion of strips or rods of appropriate metals in the various sections of the chamber of a rocket motor. The metal samples are then subjected to an examination of the extent and nature of the erosion. Parallel work is carried on with these metals in vacuum tubes in the presence of controlled atmospheres in order to obtain accurate thermodynamic information regarding the chemical reactivity. Two applications of the results of these investigations would be the proper choice of nozzle inserts for various propellant combinations and the selection of thermocouple materials.

A study of the kinetics of reactions of metals with gases at high temperature has just started at the Illinois Institute of Technology.²² It is planned to determine the orders, mechanisms, and energies of activation of the reactions of air, steam, nitrogen, carbon dioxide, hydrogen, and other suitable gases with metals and alloys used in the construction of missiles. The first phase of the project will involve the development of experimental techniques by which the reactions can be followed, perhaps by measurement of the change in pressure which occurs during the reaction.

The corrosion resistance of most metals and alloys at normal and elevated temperatures is thought to be due to the formation of a passive film on the surface of the material. The factors which influence the formation, the corrosion resistance, and the breakdown of the passive films are being investigated at Ohio State University.²³ Specimens of stainless steel, with and without molybdenum, are passivated by exposure to an acid (sulfuric, nitric, or chromic) and then to air. The passivated specimens are tested for general corrosion resistance in sulfuric acid solution and for pitting corrosion in ferric chloride solution and synthetic ocean water. It was found that the degree of passivation is a function of the length of exposure to air, and this suggests the possibility that the passivating film may be a layer of adsorbed gas. The fact that passivity breaks down under vacuum and that the metal can be repassivated by exposure to air is strong evidence that adsorbed gas is an important factor. Preliminary work is under way on studies of

the breakdown potential of the film, the combined effects of erosion and corrosion, and the formation and properties of the film at elevated temperatures. It was found that the films formed at high temperatures exhibit varying protective characteristics depending upon the conditions under which they are formed. The mechanism and nature of films or scales formed at high temperatures are being studied.

In another project at Ohio State University²⁴ the intergranular deterioration of 16-25-6 alloy at high temperatures is being investigated. This project is just getting started. A literature survey and preliminary tests have been made.

A group at Purdue University²⁵ under the direction of Professor H. J. Yearian, is investigating the process of corrosion as affected by the chemical and physical properties of the materials and the conditions of exposure. Work to date has included a study of the oxidation of 18% chromium steel by oxygen at a pressure of one atmosphere and a temperature of 775°C. The oxide film formed is studied by X-ray and electron diffraction techniques. Initial work has indicated that the layer first formed is rich in chromium oxide and that the iron atoms diffuse through the layer more rapidly than the chromium atoms, with the result that the percentage of chromium in the layer decreases as the oxidation proceeds. The rate of film formation becomes very small after 20 hours. These same techniques will be used in the future to examine the corrosion of pure binary alloys of chromium and iron and of nickel and iron over a range of compositions. Work in this field has already been reported by Gulbransen and Hickman (15, 17, 18).

The opinion has been expressed that the kind of atmosphere has little influence on the failure of alloys under stress at high temperatures, and yet there is some evidence to the contrary. Stanford University²⁶ is investigating the effect of atmosphere and will attempt to determine the magnitude and cause of the effect if it exists. Rod-shaped specimens, necked down, will be tested in stress-rupture over a temperature range of 1200° to 1800°F in atmospheres of argon, air, and steam at a pressure of one atmosphere. The smallest loads applied will be calculated to give a life of about 1000 hours. After rupture the samples will be examined microscopically and

²¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

²²Illinois Institute of Technology, Chicago, Illinois; H. J. MacDonald; ONR Contract N7-onr-329, T.O.-2; *Unclassified*.

²³Ohio State University, Columbus, Ohio; M. G. Fontana; ONR Contract N6-ori-17, T.O.-2; *Unclassified*.

²⁴Ohio State University, Columbus, Ohio; M. G. Fontana; AAF Contract W-33-038-ac-16308; *Unclassified*.

²⁵Purdue University, Lafayette, Indiana; H. J. Yearian; ONR Contract N6-ori-104, T.O.-1 *Unclassified*.

²⁶Stanford University, Palo Alto, California; O. C. Shepard; ONR Contract N6-ori-154, T.O.-5 *Unclassified*.

metallographically to see what changes have taken place at the grain boundaries. The first tests will be made on a Timken low-carbon steel whose properties in air at elevated temperature are known, and later Timken 16-25-6 and Hastelloy "C" will be investigated. In addition, it is planned to study flat strips of Hastelloy "C" in an electrically heated silica tube furnace in atmospheres of air and steam.

5. POROUS METALS AND ALLOYS. In the present design of long-burning-time liquid rockets, some form of cooling is necessary. Usually either the fuel or the oxidizer is circulated around the combustion chamber and nozzle, but preliminary work has indicated that transpiration cooling, which involves forcing a liquid or gas through porous walls, offers definite advantages. If enough cooling can be provided by this means, metals may be more satisfactory than ceramic materials because of their greater mechanical strength and resistance to thermal shock.

In the investigation of methods of fabricating porous metals, the following progress has been made at Battelle Memorial Institute:²⁷

(a) In making porous metals by displacement casting, two alloy systems have been investigated—nickel-bismuth and nickel-cobalt-copper. In the first system bismuth is the phase displaced, and in the second system copper is the displaced phase. The nickel-bismuth system has been abandoned because a brittle nickel-bismuth compound left after displacement of the bismuth makes the porous structure too fragile. The second system is still under investigation.

(b) Extensive studies of the fabrication of powder metal porous elements made without applications of pressure indicate that satisfactory porous elements can be made by this method. It is hoped that large porous elements can be made without the necessity for large hydraulic presses. Investigations of this method of fabrication are continuing.

(c) Electrolytic methods of making porous elements have been investigated. These do not show promise except for thin layers, and methods of plating a porous layer on porous materials made by other methods are now being investigated with the idea that the porous plate will allow a more precise control over permeability.

(d) Vapor-blasting methods have been abandoned as unsuitable for this purpose because the pore sizes that can be made by this method are much too large.

(e) The investigation of porous elements made by laminating corrugated washers, etc., has not been started.

The Jet Propulsion Laboratory at California Institute of Technology²⁸ has been successful in producing porous metals using mixtures of the metal powder and a "blowing agent" such as ammonium bicarbonate (7). The mixture is pressed in a die and sintered in a suitable atmosphere, usually hydrogen or helium, at a suitable temperature depending on the metal. Any desired porosity can be produced by this method. In addition to porous metals, various porous alloys, such as copper-tin, copper-zinc, copper-beryllium, nickel-iron, nickel-iron-molybdenum, aluminum-copper, 18-8 stainless steel, copper-titanium, and nickel-copper have been produced. The samples of porous materials are tested for tensile strength, and if the stress-strain characteristics appear promising, further tests are run to determine fatigue properties and thermal conductivity.

An extensive research program has been undertaken by the Jet Propulsion Laboratory to study the factors which influence the properties of the porous materials which have been prepared. Various pressing techniques have been investigated in order to develop ways of fabricating articles of complicated shapes. The powder pressing problem is of interest in that little is known of the mechanism by which pressure is transmitted through the powder. In this connection a special die has been constructed to study in detail the pressure distribution along the sides and bottom of the die. The influence of powder grain size on the porosity is being investigated by means of a photocell scanning device for measuring pore size and distribution. The mechanism of sintering is being studied theoretically and experimentally, in connection with which the changes in thermal expansion and specific heat which occur during sintering are being measured.

Professor J. Wulff and his group, working at Massachusetts Institute of Technology²⁹ have found that porous metals with controlled permeability can be fabricated by spraying a metal coating onto a rotating mandril. The deposit which is built up consists of minute spherical masses, the permeability being controlled by the distance between the spray gun and the mandril and the speed of rotation of the mandril. The coated mandril is heated in a suitable atmosphere at

²⁷Battelle Memorial Institute, Columbus, Ohio; H. C. Cross, Materials, Fuels, and Combustion Project; Project RAND; Confidential.

²⁸Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-a-20260; Restricted.

²⁹Massachusetts Institute of Technology, Cambridge, Mass.; J. Wulff; BuOrd Contract NOrd J661; Confidential.

the proper temperature and for the proper time to give the desired strength and permeability. The mandrel can then be knocked out and the porous body is ready for use. It appears that this method can be used for any metal. For example, a sample of Vitallium with 15% permeability has been fabricated.

The Aerojet Engineering Corporation has made some preliminary tests on porous bronze, tungsten, molybdenum, stainless steel, and Haynes Stellite 21 obtained from commercial sources (35).

6. FABRICATING TECHNIQUES. A number of miscellaneous fabricating techniques have been studied which may be of interest in connection with this survey of the work on metals and alloys.

Considerable difficulty has been experienced in welding the new alloys which have been developed for high temperature service. Battelle Memorial Institute³⁰ has been making a fundamental investigation of the causes of cracking in welds and adjacent parent metal. Welding properties as a function of wheel composition, bucket composition, and electrode composition were investigated. Four types of defect were found: (a) microfissures in the weld metal; (b) fusion line cracking; (c) intergranular cracking in the heated zone; and (d) interbucket notch extension cracking. The last type of failure was found to be the most serious. The investigation is continuing.

A simple technique for the rapid hot compacting of a metal powder is being investigated at the Polytechnic Institute of Brooklyn³¹. The metal powder is first compacted lightly when cold. It is placed in a furnace and heated to the desired temperature, and is then transferred quickly to a cold die, where it is immediately compacted by the impact of a weight falling onto the plunger. The experimental techniques are just being worked out. Initial work will be on copper and iron powder, and this will later be extended to more refractory metals if the results justify further efforts.

An interesting powder-metallurgy technique for fabricating heat resistant alloy is being developed at Rensselaer Polytechnic Institute.³² The powdered metal is first pressed green at 50 tons per square inch and is then inserted in a die with a ceramic liner. An electric current is sent through the sample while the sample is under pressure. The results obtained to date

have been very satisfactory, a density of 98½% of the theoretical having been obtained with an 80-20 nickel-chromium alloy. However, stress rupture tests at high temperatures have not been made because it has not yet been possible to make large enough samples. In this electric resistance sintering process, the magnitude of the current and the pressure, and the time of flow of the current, can be accurately controlled. Pressures of 2, 5, 10, 20, and 30 tons per square inch have been applied, and it has been found that a pressure of 5 tons per square inch gives as good results, so far as density is concerned, as the higher pressures. There seems to be a definite correlation between the structure of the material and the electric power input. This work is being continued, and a study of the density, hardness, and microstructure of the final material and an investigation of the diffusion of the constituents will be made.

The Ryan Aeronautical Company has developed a nickel base brazing alloy for stainless steels. The brazing is carried out at 2000°F. After brazing, melting takes place only at 2200°F and the shear strength of the bond may be as high as 4000 pounds per square inch at 2000°F. The alloy is austenitic in structure and is useful for brazing the higher austenitic alloys. Another development by the Ryan Aeronautical Company which may be of interest is an acid bath which will take the oxide film off Inconel in 20 minutes at room temperature.

7. LIGHT METAL ALLOYS. The strength of the present alloys of aluminum and of magnesium decreases quite markedly when the temperature exceeds 400°F. Hence these alloys may be expected to have only a limited application to liquid rocket and pulse jet power plants, although some of them have been used in short-burning-time solid-propellant rockets. It may be of interest, however, to review briefly some of the work on the magnesium alloys which appear to be better than other light alloys at 600°F.

The cast magnesium alloy CM-62, magnesium 92%, cerium 6%, manganese 2%, is of particular interest because its properties at room temperature are worse, and at 600°F are better, than those of other magnesium- and aluminum-base alloys. Battelle Memorial Institute³³ has studied this alloy with the object of improving the creep strength of light alloys. Creep and tensile strengths at 600°F were measured and methods of controlling grain size to give small grains were investigated. Modifications in composition of the

³⁰Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; ONR Contract N5-ori-111, T.O.-1; *Unclassified*.

³¹Polytechnic Institute of Brooklyn, Brooklyn, N. Y.; O. H. Henry; ONR Contract N6-ori-98, T.O.-2; *Unclassified*.

³²Rensselaer Polytechnic Institute, Troy, N. Y.; W. F. Hess; BuShips Contract NObs 31493; *Restricted*.

³³Battelle Memorial Institute, Columbus, Ohio; C. H. Lorig; AAF Contract W-33-038-ac-7202; *Unclassified*.

alloy were considered in an endeavor to obtain better room-temperature and elevated-temperature properties. The effect of melting and casting the alloy in inert atmospheres was also studied.

A careful comparison of creep properties of the coarse- and fine-grained CM-62 alloy was made, and it was found that the fine-grained material is at least as resistant to creep as the coarse-grained material. Grain-refinement methods were investigated, and it was found that zirconium was quite effective. With additions of only a few hundredths of a per cent of zirconium, the grain size at a pouring temperature of 1400°F is reduced from approximately 0.2 inch to 0.02 inch. This grain refinement is accompanied by an increase in room-temperature tensile strength from an average of 14,000 pounds per square inch to approximately 18,000 pounds per square inch.

In addition to zirconium, other elements were added to the magnesium-cerium alloys in an attempt to improve the creep and tensile strengths at 600°F. Most of the elements investigated had a very adverse effect upon the creep rate under the conditions of a test for 150-500 hours at 600°F with a load of 2,500 pounds per square inch. It was found, however, that cadmium, beryllium, and barium added separately to CM-62 alloy reduced the creep rate under conditions of the test. The optimum amounts of these elements for best creep properties have not been established.

A melting technique for the magnesium-cerium alloys was developed which was the advantage over the previous methods employing salt fluxes in that higher metal recoveries are obtained and flux inclusions avoided. The metal is melted in dry nitrogen in a pot having a closely fitted cover. Provision is made to hold the metal quietly in the pot before pouring, to provide opportunity for heavy nonmetallic particles which form during melting to settle to the bottom.

While the above project terminated March 1, 1947, arrangements have been made to continue the development of the cast magnesium-cerium alloys starting July 1, 1947, under the sponsorship of Navy Department, Bureau of Aeronautics. The object will be to study the magnesium-cerium alloys to which have been added combinations of elements which were previously found to have the most beneficial effect on high-temperature properties. Optimum compositions for best creep and high-temperature tensile properties will be sought. The additions for optimum effects appear to be relatively critical, and an endeavor will be made to establish limits for such elements as zirconium, cadmium, beryllium, and barium.

Battelle Memorial Institute is also investigating the

properties of wrought magnesium-base alloys at elevated temperatures for the National Advisory Committee for Aeronautics. An investigation is being conducted on the magnesium-cerium alloys in an endeavor to improve the existing compositions. High-temperature testing of existing forging alloys to obtain data on their creep and tensile properties is now in progress. In addition, new alloy compositions which are essentially modifications of the magnesium-cerium alloys are being investigated in order to improve the high-temperature properties, particularly above 400°F. As compared with cast magnesium-cerium alloys, the wrought alloys of the same type have twice the room-temperature properties, equivalent tensile properties at 600°F, but creep rates that are 200 times those of the cast alloys in the standard test of 150 hours at 600°F with a load of 2,500 pounds per square inch. The importance of improving the creep resistance of the wrought alloys is, therefore, apparent.

Progress has been made in determining the optimum temperature and speed for extruding the magnesium-cerium alloys. The proper base composition has likewise been established and the optimum heat treatment has been determined. A large number of experimental compositions have been prepared and tested for tensile properties at room temperature and at 600°F. Creep testing of the experimental alloys has only recently been under way.

B. Ceramics

In the last few years an extensive research program has been organized to study the properties of ceramic materials at high temperatures and to develop them for use in jet power plants. In effect this investigation opened a completely new field. Previous work on the high-temperature properties of ceramics had been concentrated on the properties of interest in connection with their principal use in the construction of furnaces. The melting point, compressive strength, thermal expansion, thermal conductivity, permeability, and electrical resistance of the conventional ceramic materials were known, but only a few scattered measurements had been made at elevated temperatures of creep, tensile strength, modulus of rupture by bending, torsion behavior, and thermal shock resistance—the properties of particular interest in connection with jet power plants. As a result the program had to start with the design of testing apparatus, the empirical evaluation of ceramic materials in terms of the new requirements, and the investigation of ceramic formulations making use of the less common but more refractory minerals such as zirconia, zircon, thoria, ceria, and beryllia.

The conventional ceramic material is made from naturally-occurring minerals, which are mainly complex silicates, metallic oxides, or mixtures of the two. Chemical analyses of the minerals most commonly used show high percentages of water and of one or more of the oxides of aluminum, silicon, magnesium, chromium, calcium or iron, and very low percentages of other compounds. When the material is fired, water is lost, and chemical reactions and phase changes take place, resulting in crystal phases bonded by a glassy phase. The crystal phases may be, as in the case of metals, chemical compounds, solid solutions, or intermediate phases of variable composition. In general the structures of the phases which may be present and the changes which occur on heating a pure mineral have been worked out by the mineralogist and crystallographer. The phase diagrams, showing the phases present at equilibrium as a function of composition and of temperature, have been established for many but not all of the systems of interest. The crystal chemist has learned a great deal about the ionic replacements which may take place in ionic crystals and about the growth of crystals. Hence the changes that occur on firing a ceramic composition are understood in many cases, and the chemical composition and structure of the resulting product are known or can be determined by standard techniques. Details concerning ceramic compositions and properties and references to the literature may be found in reference 27 and a general discussion of important fields of investigation in reference 24.

The high-temperature properties of the standard ceramic materials are limited by the softening of the glassy phase which occurs over a range of temperatures noticeably below the melting point of the crystalline phase. To improve the high-temperature properties, a more refractory bonding phase must be devised; and metals, ceramic crystalline phases, and high melting point glasses have been suggested. This is a new line of investigation for ceramics, and the fields of research which are important are the same as for metals. The properties of the material will depend on the amount and physical and chemical properties of the phases and on the number, size, shape, orientation, and distribution of the crystals. In order to obtain the fundamental knowledge on which to base a logical development program, each of these factors must be studied and correlated with physical properties at high temperatures, phase diagrams must be established, chemical reactions and phase changes in the solid state must be studied as functions of temperature and time, and the nature of the bonding forces must be investigated.

1. **SURVEYS.** A continuing survey is being carried on by Battelle Memorial Institute³⁴ in the field of ceramic materials of construction for supersonic vehicles. Progress is briefly indicated in quarterly reports (32), and topical reports will be prepared to present the complete results of the survey.

Pennsylvania State College³⁵ has made a literature survey of the properties of the oxides of aluminum, beryllium, calcium, cerium, chromium, magnesium, silicon, thorium, titanium, and zirconium. It appears that the thermal expansions of the crystalline forms of these oxides are larger than desirable for use in a material to resist thermal shock, but that the fused amorphous forms of zircon and zirconia may be suitable.

A symposium on *High Temperature Ceramics for Gas Turbines, Jets, and Rockets*, sponsored jointly by the Office of Naval Research and the Bureau of Aeronautics of the Navy Department and the Air Materiel Command of the Army Air Forces, was held at the National Academy of Sciences, Washington, D. C., on February 25 and 26, 1947. The minutes of this symposium (2) give a discussion of requirements for ceramic materials and a review of the ceramics research program.

2. **STUDIES OF THE PROPERTIES OF CERAMIC MATERIALS.** Studies made during the war have indicated that refractory bodies with high thermal shock resistance and high tensile strength can be made from mixtures of ceramic and metal powders. The fundamental behavior of such systems is being studied at Alfred University.³⁶ Pressed briquettes of the ceramic powder, the metal powder, and the mixture will be heated in atmospheres of air, nitrogen, and helium, and the chemical and physical changes which occur will be followed. In addition the pressed ceramic powder will be heated in contact with the pressed metal powder in order to study the phenomena which occur at the interface. This work is still in its early stages, due to the delay in delivery of needed apparatus. Initially a briquette of cobalt powder was pressed into contact with a briquette of alumina, and the combination heated at 1350°C. The sample is to be examined by microscope, X-ray, and spectrograph at

³⁴Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; Materials, Fuels, and Combustion Project; Project RAND; Confidential.

³⁵Pennsylvania State College, State College, Pennsylvania; E. C. Henry; AAF Contract W-33-038-ac-13506; Unclassified.

³⁶Alfred University, Alfred, N. Y.; V. D. Frechette; ONR Contract N6-ori-143, T.O.-1; Unclassified.

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³⁵Pennsylvania State College, State College, Pennsylvania; E. C. Henry; AAF Contract W-33-038-ac-13506; Unclassified.

³⁶Alfred University, Alfred, N. Y.; V. D. Frechette; ONR Contract N6-ori-143, T.O.-1; Unclassified.

importance because completely crystalline materials should be serviceable all the way up to the melting point, whereas many common ceramics which depend on a glassy bond for their strength soften over a range of temperatures. It is planned to continue the previous work and to extend it to new binary and ternary combinations. The determination of the phase relations of the ternary system magnesium oxide-beryllium oxide-zirconium oxide will be completed, and then a study of the system beryllium oxide-magnesium oxide-thorium oxide will be undertaken. For details of the techniques used and measurements made, see reference (11).

In another project at the National Bureau of Standards, ceramic bodies composed of refractory oxides have been tested extensively over a temperature range up to 1800°F (10). Four of the six bodies which appeared most promising were composed of varying percentages of the oxides of magnesium, beryllium, and zirconium. The other two were composed largely of beryllium oxide, one with small percentages of the oxides of calcium, aluminum, and zirconium, and the other with small percentages of the oxides of titanium, aluminum, and thorium. The following tests were made on these materials: modulus of rupture in bending, thermal shock, short-time tensile, and creep. Particular emphasis was placed on the creep tests because resistance to creep is important for turbine applications. The best sample could withstand a tensile stress of 15,000 pounds per square inch at 1700°F with a creep of less than 1×10^{-6} inches per inch per hour. This work gave indications that the stress-temperature history of a sample is important in determining the creep properties.

Metal-bonded ceramic bodies, which previous work has shown to have good high temperature properties, are being studied at Ohio State University,⁴² under the general supervision of Dr. G. A. Bole. A mixture of powdered alumina, 325 mesh and finer, and powdered chromium is formed under pressure and sintered at 2850°F in an atmosphere of argon and hydrogen. The range of composition from 10% chromium to 70% chromium by weight has been examined, and good properties appear to be given by a composition of about 30% chromium. A ceramic containing 30% chromium and 70% alumina has a water absorption of 0.5%, a Rockwell "C" hardness of 55, a modulus of rupture at room temperature of 33,600 p.s.i., and a modulus of rupture at 2400°F of 12,500 p.s.i. It is believed that the greatest strength will be obtained by

using finer powders and just enough metal to coat each alumina grain with a molecular film. It is planned to carry out work along these lines in the near future.

At Pennsylvania State College,⁴³ ceramic bodies have been made of the following combinations: beryl and refractory clay, magnesium oxide bonded with the hydroxides and phosphates of cerium and zirconium, zircon and beryl, tin oxide and beryl, and zirconium phosphate and beryl. The effects of time and temperature of firing and of composition are determined. Porosity, water absorption, and bulk specific gravity of the specimens are measured. Tests are made for heat shock resistance. Tests on these bodies were not complete at the time of writing, but the preliminary work has indicated that beryl-clay and beryl-zircon bodies can be used as heat shock resistant materials over the temperature interval from 1500°F to room temperature. In addition, a study is being made⁴⁴ of the following oxide systems: thorium oxide-thorium pyrophosphate; thorium oxide-chromium oxide; thorium oxide-silicon oxide; thorium oxide-tin oxide; zirconium oxide-titanium oxide; and the compound $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$.

3. CERAMIC LINERS, COMBUSTION TUBES, AND BLADES. A group at Battelle Memorial Institute⁴⁵ is investigating the application of ceramic materials to the construction of rocket liners and nozzles. Both properties of the materials and methods of fabrication are considered. The program will involve oxides, ceramic-metal powder mixtures, carbon or carbonaceous materials with or without metal powder additions, and ceramic materials impregnated with metal, mixtures of oxides, and materials which decompose endothermically at high temperatures to produce refractory substances. The present emphasis is on the use of oxides, on the use of graphite, and on means of protecting graphite from oxidation.

A study of ceramic liners for liquid propellant rockets is under way at the Jet Propulsion Laboratory, California Institute of Technology.⁴⁶ Initial tests are being confined to acid-aniline motors, but it is planned to extend the tests to hydrogen peroxide

⁴³Pennsylvania State College, State College, Penna.; E. C. Henry; AAF Contract No. W-33-038-ac-13506; *Unclassified*.

⁴⁴Pennsylvania State College, State College, Penna.; E. C. Henry; AAF Contract W-33-038-ac-16374 (17284) (a continuation of W-33-038-ac-13506); *Unclassified*.

⁴⁵Battelle Memorial Institute, Columbus, Ohio; C. R. Austin; AAC Contract W-33-038-ac-14320; *Unclassified*.

⁴⁶Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

⁴²Ohio State University, Columbus, Ohio; G. A. Bole; AAF Contract W-33-038-ac-14217; *Unclassified*.

and nitromethane units. Attempts are being made to correlate the endurance and insulating qualities of the liners with such parameters as composition, melting point, thermal conductivity, thermal expansion, and tensile strength. The study has included bodies made from alumina, zirconia, beryllia, thoria, and zirconia-silica. In the case of the use of zirconia, a basic question is the effect of the transformation of the ordinary monoclinic form to the tetragonal at 1800°F, accompanied by a discontinuity in thermal expansion. The cubic form is stable at all temperatures up to the melting point. Further study of these phenomena is felt to be necessary to guide further development work.

At the University of Illinois,⁴⁷ considerable attention has been given to the fabrication of combustion tubes and testing them for resistance to thermal shock. Combustion tubes have been made by ramming, solid casting, and pressure casting from materials like fireclay grog, calcined flint clay, zirconia, zircon, alumina, and silicon carbide, bonded with calcium aluminate, alundum cement, nepheline syenite, talc, bentonite, zirconium hydrate, clay, feldspar, and other materials. These tubes showed promise of usefulness for temperatures not exceeding 2500°F. It is planned to study similar tubes made of more refractory materials, particularly oxides. In addition, slip-cast tubes of silicon carbide with feldspar, zircon, cobalt oxide, and chromium oxide have been tested for resistance to thermal shock. The tubes containing the metallic oxides withstood five cycles of heating to about 2000°F and cooling to room temperature and were the most promising of the compositions investigated. Slip-cast tubes of other materials will be investigated.

The spray coating of rocket liners appears to offer advantages in the construction of jet power plants, and the practical application of this technique is being investigated at Massachusetts Institute of Technology,⁴⁸ under the direction of Professor J. Wulff. Liners will be constructed from a molybdenum mesh base, sprayed with refractory metals, ceramics, or a mixture of both, and from graphite with the surface protected by a sprayed coat of metal or ceramics. These liners will be tested in actual use.

Studies of methods of fabricating ceramic bodies and of resistance to thermal shock are being carried out at the Flight Propulsion Research Laboratory of the National Advisory Committee for Aeronautics. High beryllia, zirconia, and alumina bodies are being in-

vestigated, and hot pressing appears to be a promising fabrication technique. Bodies which will stand thermal shock at 2600°F have been found to fail at lower temperatures due to mechanical shock. The emphasis of this work is on the application of ceramic materials to turbine blades.

Ohio State University⁴⁹ is interested in the evaluation of liners by use tests. Rocker liners have been prepared from alumina, beryllia, magnesia, zirconia, spinel, and zircon, some of them in the laboratory and some by commercial producers of refractories. It is planned to test these in nitric acid-aniline and hydrogen-oxygen rocket motors. Another type of liner to be tested is a graphite liner coated inside with silicon carbide prepared by the Carborundum Company. The coat was applied by heating the graphite in an inert atmosphere in the presence of powdered silicon, allowing the latter to evaporate and then condense on the carbon to form silicon carbide. In addition the Carborundum Company has also submitted a metal-bonded silicon carbide liner for test.

A type of liner which appears to show particular promise is constructed of a refractory material on a coarse wire screen. Ohio State University has prepared a liner of this type, using a nickel-chrome alloy screen with mullite cement. The overall thickness of the wall was $\frac{3}{16}$ inches and the diameter was 6 inches. This liner gave satisfactory service at 1800°F for 150 hours. Furthermore, 50 cycles of heating to 1800°F and cooling down to 200°F, using five minutes to heat and three minutes to cool, did not crack the liner.

4. CERAMIC COATINGS. Ceramic coatings have been developed recently to serve several purposes in the construction of jet power plants. An increase in the thermal insulating power of the construction materials cuts down the heat loss and increases the efficiency. A refractory coating is known to increase the high-temperature life of a base metal, probably because of protection against oxidation and other corrosion, although some reduction in the temperature of the base metal has been observed. Radiation from a motor can be diminished by the use of suitable coatings. The success already achieved with ceramic coatings has made it desirable to continue a research program along these lines. The main problem is to develop formulations with the desired properties which will show satisfactory adherence to metals and alloys and resistance to thermal shock.

⁴⁷University of Illinois, Champaign, Illinois; D. G. Bennett; AAF Contract W-33-038-ac-14520; *Unclassified*.

⁴⁸Massachusetts Institute of Technology, Cambridge, Massachusetts; J. Wulff; BuOrd Contract NOrd 9661; *Confidential*.

⁴⁹Ohio State University, Columbus, Ohio; G. A. Bole; AAF Contract W-33-038-ac-14217; *Unclassified*.

MATERIALS

Work was instituted at Battelle Memorial Institute⁵⁰ during April 1947 on the development and evaluation of coatings resistant to high temperatures which might be used to protect or to insulate the skins of supersonic vehicles during high-velocity flight through the atmosphere.

Materials and methods for coating sheet metal with air-setting refractories are being studied at the Cornell Aeronautical Laboratory,⁵¹ and considerable success has been achieved in prolonging the useful life of the material at high temperatures. The most successful coating developed to date consists of a primary coat of Johns Manville refractory #20, approximately 0.0006 inches thick, sprayed on shot-blasted metal, followed by successive coats of Hiloset cement to a thickness of approximately 0.020 inches. Under given test conditions this coating lowered the metal temperature from 100°F to 200°F in the temperature range above 2000°F. In another test, coated stainless steel withstood for 90 seconds an oxy-gas torch flame that would cut a 1-inch hole in 0.042 inch thick sheet steel in less than one second. In general it has been found that rapid heating will cause blistering if the total thickness is too great. Blistering occurs during drying if the individual coats are too thick. During this work many commercially available materials have been tested, among them porous metal aluminum sprayed on by the metallizing process. A sprayed aluminum coat, whose surface oxidized readily, proved to be a good insulator; but cost, disintegrating effect on the steel, and poor bonding made it unsatisfactory in practice.

Ceramic coatings of various kinds have been studied extensively at the University of Illinois,⁵² under the supervision of Prof. D. G. Bennett. In this study temperature-resistant ceramic base coats have been developed for metals such as steels, stainless steels, Vitalium, Inconel, and others. In general the frits have been variants of standard frits and different refractory substances have been used for mill additions. Various firing cycles and methods of preparing the metal surface have been studied. As a result of this work it was concluded that a coating must be especially formulated to fit and adhere to the particular metal to be used and to withstand the specified operating

conditions. Any change in these factors necessitates a corresponding change in coating formulation.

The University of Illinois has had considerable success in the development of thermal insulating and radiation suppressive coatings. A base-coat top-coat combination was used, and it was found that a top-coat thickness of 4 to 5 mils was resistant to thermal shock, while a thickness of 10 to 14 mils was better for insulating properties. Zirconia, magnesia, or Uverite, as ingredients of the top-coat, were helpful in suppressing radiation. Ceramic paints have also shown promise in suppressing radiation and reducing temperature. One successful paint is composed of Uverite 90 parts, white mica 10 parts, sodium silicate 46.8 parts, and water 36 parts. Work on these paints is to be extended to include studies of other promising ingredients.

In work at the M. W. Kellogg Company⁵³ it is hoped to improve the properties of graphite and of stainless steel by a surface coating of refractory oxides such as alumina, zirconia, and thoria, using small amounts of metals as a binder. It has been found that powder can be sprayed with a "powder-weld gun", using an oxyacetylene flame with a gas envelope to keep the powder from oxidizing. This work is in the early stages. The strength of the bond will be tested by bending in the case of the coatings on metals, and by a thermal shock test in the case of coatings on ceramics. The relative efficacy of the various coatings will be determined by observing the behavior of samples placed in the exhaust gases from a rocket motor.

Tests have shown that ceramic coated high temperature metals have a longer life than the base metal alone under high temperature conditions, perhaps because of protection against corrosion. This problem is being investigated at the National Bureau of Standards, by Dr. W. H. Harrison who is particularly interested in developing suitable enamels and in studying methods of application (16). Variations of typical commercial frits with mill additions of refractory oxides have been found promising. The thickness of the coats used varies from 1 mil to more than 10 mils. In some cases it has been found necessary to fire the enamels in a controlled atmosphere to prevent oxidation of the base metal. Future work will involve the development of coatings for molybdenum alloys.

A coating of a mixture of aluminum oxide and sodium silicate has been found by the Naval Ordnance Test Station at Inyokern to be effective in reducing the wall temperature of solid rockets. The coating,

⁵⁰Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; Materials, Fuels, and Combustion Project; Project RAND; Confidential.

⁵¹Cornell Aeronautical Laboratory, Buffalo, N. Y.; J. L. Beal; BuOrd Contract NOrd 8993; Confidential.

⁵²University of Illinois, Champaign, Illinois; D. G. Bennett; AAF Contract W-33-038-ac-14520; Unclassified.

⁵³M. W. Kellogg Company, Jersey City, N. J.; G. H. Meserly; AAF Contract W-33-038-ac-13916; Restricted.

0.020 inches thick, is sprayed on the liner and baked at a moderately low temperature. Under certain test conditions the coating on the inside reduced the temperature of the outside of a solid rocket chamber from 900°F to 500°F. Of course the wall conditions in a solid rocket motor are much less severe than those for a liquid rocket or pulse-jet motor, but the above technique might be useful to protect special parts which are not subjected to extremely high temperatures.

A ceramic coating consisting of silicon carbide bonded with metallic cobalt, has been studied at Ohio State University.⁵⁴ After the coating has been applied to the metal base, it is either sintered in a controlled atmosphere furnace or "fired on" by using a "powder-weld gun." This coat has been tested on iron and Inconel. In the case of iron samples the base metal had swelled and crumbled beneath the coating after 16 to 17 hours at 1800°F, although the coating itself was in fairly good condition. For Inconel, the coating offered complete protection for 50 hours at 1850°F. Longer tests have not been made.

Three base coats of enamel type for Inconel which can be applied in a Globar furnace at 2200°F, 2300°F, and 2400°F respectively, have also been developed at Ohio State University. This method works well on a laboratory scale, but it is not yet known how well the Inconel will withstand 2400°F in a fabricated part. Applications of a base coat enamel have been made with a "powder-weld flame gun." This method results in a rather rough surface, but it should be entirely satisfactory for work on rockets, particularly for repair jobs.

A project has just started at Rutgers University⁵⁵ to study the preparation of glass-free refractory coatings. The coatings are to be deposited in any appropriate manner, such as by electrolytic process, by dipping or spraying, or by condensing from the vapor state. The first method to be tried is the deposit of the compound from a flame, which can be done by injecting the metal dust or oxide dust or a volatile compound of the metal into the flame. This technique appears promising because it is believed that coatings of copper oxide and even of alumina on steel can be made in this way. In order to obtain the high temperatures desired it will be necessary to use an atomic hydrogen burner. Attempts will be made to prepare coatings of spinel, magnesia, beryllia, titania, zirconia, mul-
lito, alumina, and silica. It is proposed also to do some

work on powder metal bases and metal-bonded oxides, using a series of intermediate mixes of graded compositions in order to get better adhesion to the metal base and to get better thermal shock resistance throughout the structure.

5. METHODS OF MEASURING PHYSICAL PROPERTIES.

The development of methods for making measurements at high temperatures and of tests satisfactory for evaluating refractory materials are major problems in the field of ceramics research. Only a few quantitative measurements have been made above 2500°F, and the proper development of ceramic material requires the extension of test methods to much higher temperatures. The engineer needs test data from which he can design with confidence, and the laboratory worker would like to have simple tests by which he can distinguish satisfactory from unsatisfactory materials. It is usually assumed that measurements of mechanical strength, creep, and resistance to thermal shock as functions of temperature describe a ceramic material adequately for many practical purposes; but different laboratories do not always give the same relative ratings to a series of ceramic compositions nor do laboratory test results necessarily agree with practice. Under these circumstances it may be necessary for the present to rely on empirical tests or on laboratory tests which have been correlated with results of actual use until the fundamental factors which determine satisfactory performance at very high temperatures are better understood.

A brief description of some of the tests being used or developed for ceramics research is given in this section. The discussion does not necessarily include all the methods of measurement being used, but it is meant to be illustrative of the main techniques now being considered.

a. Bending Tests. The mechanical strength of a ceramic body is commonly described in terms of the modulus of elasticity or of rupture determined by the bending of a bar supported by two knife edges and loaded midway between the supports. The sample and associated equipment is placed in a furnace to be heated to the desired temperature. At the National Bureau of Standards the samples (6 inch $\times$ 1 inch by $\frac{1}{4}$ inch) are heated to 1800°F by four Globar elements symmetrically placed around the sample (10). The load is applied at the midpoint of a span of about 5 inches and the deflection is measured by a gauge reading to 0.0001 inches. In one set of tests, the observed modulus of rupture varied from 6000 pounds per square inch to 38,000 pounds per square

⁵⁴Ohio State University, Columbus, Ohio; G. A. Bole; AAF Contract W-33-038-ac-14217; *Unclassified*.

⁵⁵Rutgers University, New Brunswick, N. J.; R. B. Soesman; AAF Contract W-33-038-ac-15800; *Unclassified*.

inch. Ohio State University⁵⁶ in a similar test uses a sample $4\frac{1}{2}$ inches by $\frac{1}{2}$ inch by $\frac{1}{4}$ inch loaded at the center of a span of $3\frac{3}{4}$ inches. The deflection at the end of a lever arm giving a magnification factor of ten is measured. Tests can be made at temperatures up to 2800°F. The modulus of rupture by bending is determined by Battelle Memorial Institute up to 2000°F and by the Jet Propulsion Laboratory, California Institute of Technology, up to 2200°F. Alfred University⁵⁷ has designed and is now constructing apparatus for measuring modulus of rupture up to temperatures of 3000°F.

b. *Tensile Tests.* The modulus of elasticity of ceramic materials has been determined in tensile tests by the Flight Propulsion Research Laboratory of the National Advisory Committee for Aeronautics, the National Bureau of Standards, and Ohio State University. In this method care must be used in the preparation of the sample and the alignment of the apparatus to keep bending stresses to a minimum. The experimental complications are such that bending tests are usually preferred, particularly for preliminary screening tests in the development of ceramic materials.

In the Flight Propulsion Research Laboratory test (26) samples are ground to specific dimensions and a gasket of woven asbestos cloth is inserted between the specially designed grips and the sample to insure uniform application of stress. In a preliminary alignment test two strain gauges are mounted on opposite sides of the specimen and the elongations of the two sides of the sample are measured for stresses up to 3000 p.s.i. at room temperature. If the calculated bending stress is greater than 2% of the tensile stress, the apparatus is aligned again. This method has given consistent test results.

The samples used at the National Bureau of Standards for tensile tests are circular in cross-section and screw into ceramic adapters (10). The adapters screw into brass holders which are connected to the loading system through universal joints. A gauge length of 100 mm. is used, and measurements are made with a Gaertner extensometer-viewing device which makes possible measurements with a precision of 1 micron. Ten furnaces are available for experiments up to 1800°F and two for work at 2400°F. The air temperature over the entire gauge length of the specimen can be maintained constant to within 5°F. This apparatus was designed particularly for long-time creep

tests and it has proved to be quite satisfactory for this purpose. A few short-time tensile tests have been made with rather unsatisfactory results, most of the breaks occurring in the adapter.

A method of measuring tensile strengths up to 2400°F is being developed at Ohio State University.⁵⁸ It is planned to use a cylindrical sample $\frac{3}{8}$ inches in diameter and 8 inches long and to heat the center 2 inches of the sample in a small wire resistance furnace or an induction furnace, using a chromium sleeve as the heating element. Insulation is placed between the ends of the sleeve and the ends of the sample. This work is in its early stages and no results are available at this time.

c. *Spin Tests.* The determination of the mechanical strength of a ceramic material by spinning a suitably shaped sample at increasing angular velocities until rupture occurs is suggested by possible turbine applications. However the stresses to which a rotating sample is subjected are not simple because of superposed vibrations and possible stress concentrations at the point of attachment to the rotor, and whether the results of spin tests will be generally applicable must be decided by future experimentation.

A vacuum spin test is being developed at the University of Illinois.⁵⁸ The sample is a disc (diameter 10 inches, thickness at edge 0.70 inches, thickness at center 1.60 inches) formed by dry pressing in a mold at 5000 p.s.i. The sample is spun in a vacuum at speeds up to 60,000 r.p.m. by an air turbine operating at 90 p.s.i. air pressure in a chamber 24 inches in diameter. The walls of the chamber are 5 inches thick and are protected on the inside by blocks of hard wood. Resistance heaters placed above and below the sample will have to be replaced after each test. Work on this project is in a relatively early stage, and it is not yet possible to evaluate the spin test as a means of studying the physical properties of ceramic materials.

Ohio State University⁵⁶ is designing apparatus for a spin test in which the sample will be heated by air friction. It is hoped that temperatures as high as 2400°F can be attained by this means. This project is in its early stages and no results are available yet.

d. *Thermal Shock Tests.* Resistance to thermal shock is required for nearly every application of ceramic materials to the construction of jet power plants, and many tests, mostly of empirical nature, have been devised to measure this property. It would be expected that the coefficient of expansion, the thermal

⁵⁶Ohio State University, Columbus, Ohio; G. A. Bole; AAF Contract W-33-038-ac-14217; *Unclassified*.

⁵⁷Alfred University, Alfred, N. Y.; L. I. Shaw; AAF Contract W-33-038-ac-15903; *Unclassified*.

⁵⁸University of Illinois, Champaign, Illinois; D. G. Bennett; AAF Contract W-33-038-ac-14520; *Unclassified*.

diffusivity, and the strength of the material in tension and in shear would be important factors in determining resistance to thermal shock; but there is not general agreement as to the relative importance of these quantities nor as to the possibility of combining these factors into a single expression to describe resistance to thermal shock. Some workers consider thermal conductivity the most important single factor, and others emphasize thermal expansion. Preliminary work at the Flight Propulsion Research Laboratory of the National Advisory Committee for Aeronautics indicates a correlation between thermal shock resistance and coefficient of expansion and tensile strength (2). The tendency of a refractory material to spall on heating has been considered to be directly proportional to the coefficient of expansion and inversely proportional to the shear strain and the thermal diffusivity (2). A detailed investigation of the nature of thermal shock will be necessary to settle the questions which have been raised.

In connection with the development of ceramic liners, Battelle Memorial Institute⁵⁹ has used an empirical test in which a sample of standard dimensions is heated by a natural gas-oxygen flame to a temperature of about 4000°F in ten seconds or less, depending on the thermal properties of the sample. The material is considered satisfactory for additional study if the sample lasts for three minutes in the flame without melting or spalling. Materials which withstand successfully the first three-minute test are further screened by repeating the test until failure occurs.

A theoretical and experimental investigation of thermal shock is being carried out at the Jet Propulsion Laboratory, California Institute of Technology.⁶⁰ Studies are being made of the temperature variation at two points in a ceramic body as a function of time and rate of heating. The test samples are of such a shape that temperature stresses can be computed in order to determine the stresses at failure. The thermal expansion and critical points of the material can be determined up to 2200°F by a special automatic recording dilatometer. Apparatus is available to measure thermal conductivity up to 2000°F.

In the thermal shock test used at the University of Illinois,⁶¹ a natural gas-air flame is directed along

the axis of the ceramic cylinder to be tested. The flow of the gases is carefully regulated in order to maintain constant temperature. Oxygen may be introduced into the air stream if it is desired to increase the temperature. A measure of the temperature is obtained by replacing the test cylinder with an Inconel cylinder of the same dimensions and determining the temperature of the outside of the metal cylinder. Any desired cycle of heating and cooling can be used, of course. A convenient cycle consists of five minutes heating followed by five minutes cooling in an air blast. For special purposes the sample may be allowed to cool without air blast or it may be quenched in water.

Prof. F. H. Norton at Massachusetts Institute of Technology⁶² is investigating the correlation of the tendency of a refractory to spall with thermal diffusivity, coefficient of expansion, and shear strength. It is planned to determine the maximum rate of heating which a tubular specimen can withstand without cracking. The temperature gradient in the sample will be measured by means of thermocouples connected to the inside and outside surfaces of the tube. The shear strength will be determined by a specially designed optical apparatus which can measure the torsion in a rod at elevated temperatures with a precision of 0.001 degrees. Special precautions will be taken to eliminate bending stresses. The thermal diffusivity can be calculated from the density, specific heat, and thermal conductivity of the material or it may be measured directly by observing the temperature change along the axis of a heated cylindrical specimen when the sample is plunged into a bath which is hotter than the sample. The coefficient of expansion will be measured by standard techniques. Quantitative results have not yet been obtained by this project, but the approach to the problem of thermal shock is logical and the results should be significant.

The Flight Propulsion Research Laboratory of the National Advisory Committee for Aeronautics has used three methods for evaluating the thermal shock resistance of ceramic discs and turbine buckets: (a) the maximum temperature achieved without cracking; (b) the number of cycles of heating and cooling without cracking; and (c) the maximum rate of heating or the number of cycles at a constant rate of heating without cracking (2).

At the National Bureau of Standards resistance to thermal shock is determined by heating a bar sample for 30 minutes at 1700°F and then placing it quickly

⁵⁹Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; AAF Contract W-33-038-ac-14320; *Unclassified*.

⁶⁰Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

⁶¹University of Illinois, Champaign, Illinois; D. G. Bennett; AAF Contract W-33-038-ac-14520; *Unclassified*.

⁶²Massachusetts Institute of Technology, Cambridge, Mass.; F. H. Norton; BuOrd Contract NORD 9661; *Confidential*.

in an air blast for 15 minutes (10). The cycle is repeated a given number of times, or to failure, if desired. Three of the special compositions developed could stand 10 cycles without failure. A similar technique is used at Ohio State University, in which a sample is heated to 1850°F in five minutes in a natural gas-air flame and cooled to 150°F in three minutes in an air blast.

e. *The "Foil Test."* It is important that the jet power plants to be constructed in the near future be built of the best possible materials now available. Accordingly, the M. W. Kellogg Company⁶³ has set up a project to devise suitable test methods and to discover commercially available materials which can be used for combustion chambers or liners. It was first considered necessary to set up empirical tests which would correlate with the behavior of the materials in use, to serve as the first rough screening test. In the "foil test" which has been devised for this purpose, a sample is made up to standard shape and dimensions and is mounted 1/2 inch from the nozzle of a 200-pound thrust acid-aniline rocket motor. After the rocket has been fired, the sample is examined qualitatively. Under these test conditions, stainless steel (18% chromium-8% nickel) is almost completely eaten through in 12 1/2 seconds, while some graphites, electrolytic copper, tungsten, and molybdenum have resisted erosion at high temperature for 12 1/2 seconds. "Foil" have been made up of the best ceramic materials which are available commercially—zirconia, beryllia, NBS 4811, magnesia, silicon carbide, and alumina—and tests will be made of these materials in the near future. Tests which have been run to date indicate that high thermal conductivity and ductility are desirable properties for good thermal shock resistance.

The materials which show up best in the "foil tests" will be made up into nozzles for testing in a rocket motor. The nozzle will be mounted in a stainless steel block but insulated from it, to prevent cooling. It is planned to design this apparatus so that a stainless steel nozzle will burn out in 12 1/2 seconds, a time equal to the life of stainless steel in the "foil test." By this means it may be possible to correlate the results of the nozzle insert test with those of the "foil test."

f. *Structure.* Standard apparatus for studying structure by microscopic and X-ray techniques is available at many of the institutions working on ceramic problems. The X-ray diffraction patterns for most of the interesting ceramic compounds have been ob-

tained by the Jet Propulsion Laboratory, California Institute of Technology⁶⁴ and charts of lattice spacing have been drawn up to aid in the rapid identification of constituents.

6. POROUS CERAMICS. There appears to be little work under government sponsorship on the properties of porous ceramic materials and on methods of fabricating them with suitable permeability. If methods of transpiration cooling can be developed to the point where they are effective in keeping the wall temperatures down to the temperature of a liquid fuel, porous ceramics would have no advantage over porous metals. Nevertheless it is possible that a need for porous ceramics in cooling systems will arise in the future.

The Aerojet Engineering Corporation has made some preliminary tests in rocket motors of porous carbon, graphite, and silicon carbide liners, fabricated commercially (35). The M. W. Kellogg Company⁶³ has obtained porous silicon carbide, mullite, and beryllia liners from commercial sources and will test them to determine whether the permeability is suitable. Battelle Memorial Institute⁶⁵ started work on January 1, 1947, on the development and evaluation of ceramic bodies available commercially for media in transpiration cooling.

C. Other Refractory Compounds

There are a number of compounds of high melting point which have not been used for high temperature service and about which little is known. From the standpoint of melting point these compounds offer distinct advantages, and the fact that some of them are rare and expensive should not be considered a legitimate reason for not evaluating them. If some of these materials should prove to be considerably better than conventional substances in high temperature service, ways can be found to produce them.

1. CARBIDES, NITRIDES, AND BORIDES. A literature survey of the properties of metallic carbides, nitrides, and borides has been made by Pennsylvania State College.⁶⁶ Several of the compounds are very refractory and it is planned to investigate some of them experi-

⁶³M. W. Kellogg Co., Jersey City, N. J.; G. H. Messerly; AAF Contract W-33-038-ac-13916; *Restricted*.

⁶⁴Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; L. G. Dunn; AAF Contract W-33-038-ac-20260; *Restricted*.

⁶⁵Battelle Memorial Institute, Columbus, Ohio; H. C. Cross; Materials, Fuels, and Combustion Project, Project RAND; *Confidential*.

⁶⁶Pennsylvania State College, State College, Penna.; E. C. Henry; AAF Contract W-33-038-ac-13506; *Unclassified*.

mentally and to fabricate appropriate shapes for test. Table 2 lists the compounds with melting points above 5000°F.

TABLE 2. COMPOUNDS MELTING ABOVE 5000°F (22).

Compound	Approximate Melting Point (°F)
Hafnium carbide	7020
Tantalum carbide	7000
Zirconium carbide	6390
Columbium carbide	6330
Titanium carbide	5680
Tungsten carbide	5190
Vanadium carbide	5125
Thorium oxide	5500
Magnesium oxide	5100
Hafnium oxide (19)	5100
Boron nitride	5430
Zirconium nitride	5400
Titanium nitride	5300
Tantalum nitride	5070-5450
Hafnium boride	5540
Zirconium boride	5450
Tungsten boride	5300

Preliminary investigations have shown that chromium borides cemented with nickel or cobalt have excellent corrosion resistance and maintain their hardness at temperatures as high as 2300°F. These materials are being studied and developed further in a project at the American Electro-Metals Corporation.⁶⁷ This work has just begun and the results are not yet available. The initial phases involve obtaining the necessary materials, developing methods of chemical analysis and studying fabricating techniques. The best materials as judged by preliminary screening tests will be fabricated into bodies, such as turbine blades, and tested. The long-range plans for this project include the determination of the factors which influence the behavior of the cemented compacts at high temperatures, in connection with which the effect of the properties of the constituents and of various fabricating techniques will be investigated. In particular the chromium-boron, nickel-chromium-boron, and cobalt-chromium-boron phase diagrams will be established in regions of interest and the solubilities of the various chromium borides in cobalt and nickel will be determined. The effect of particle size, hot pressing

techniques, and compacting temperature and pressure will be studied.

A material composed of a high-melting carbide or nitride cemented with a refractory metal such as chromium, tungsten, or platinum might have suitable properties at high temperatures. It is planned to investigate such materials at the Polytechnic Institute of Brooklyn.⁶⁸ Initially the work will involve qualitative studies of the wetting characteristics. Small quantities of the materials will be put in holes in a carbon block which will be made one electrode of a carbon arc. The resulting beads will be sectioned, the structure will be studied metallographically, and hardness measurements will be made. This work has just begun, and no results are available yet.

2. METALLIC SALTS. The physical and chemical properties of metallic salts, both naturally occurring and made in the laboratory, are being investigated at elevated temperatures by Pennsylvania State College⁶⁹ in order to pick out those which might be suitable as high temperature materials. In order to be at all useful the compound must have a high enough melting point, 3000°F or above. If this property is satisfactory, the thermal expansion is next measured. It is considered that a compound with too great expansion will not resist thermal shock and hence only those compounds with a satisfactorily low expansion are given further consideration as high temperature materials. If a compound appears promising, its chemical properties and crystalline forms are studied, and measurements are made of thermal expansion, water absorption, strength, heat shock resistance, and the effect of various heat treatments. Compacted bodies of the promising powdered materials, alone and mixed with other ceramic compounds, are made up and tested.

Phosphates of aluminum, beryllium, cerium, and zirconium have been studied. Beryllium phosphate has too low a melting point. All the phosphates decompose at high temperatures, losing phosphorous pentoxide. But the coefficient of thermal expansion of zirconium phosphate is so low, smaller than that of fused silica, that it should be a useful material, and it is planned to investigate methods of lowering the vapor pressure of phosphorous pentoxide. In addition the chromates (chromites), phosphates, silicates,

⁶⁷American Electro-Metals Corporation, Yonkers, N. Y.; Paul Schwartzkopf; ONR Contract N6-ori-256; T.O.-1; *Unclassified*.

⁶⁸Polytechnic Institute of Brooklyn, Brooklyn, N. Y.; O. H. Henry; ONR Contract N6-ori-98, T.O.-2; *Unclassified*.

⁶⁹Pennsylvania State College, State College, Penna.; E. C. Henry; AAF Contract W-33-038-ac-13506; *Unclassified*.

stannates, and tungstates of calcium, cerium, magnesium, thorium, and zirconium are being prepared and studied. Some of these compounds have already been found to be refractory, and further work will be done on the most promising.

In connection with the work on zirconium phosphate, it should be mentioned that preliminary meas-

urements at the Bureau of Standards have not checked the reported low thermal expansion of the compound and that further work is necessary to reconcile the apparently conflicting experimental results.

In recent work at Pennsylvania State College⁷⁰ studies have been made of the relation between crystal structure and thermal expansion.

V. OUTSTANDING PROBLEMS

1. FACTORS AFFECTING PROPERTIES OF MATERIALS. It has been noted several times in the discussion of materials that the physical and chemical factors influencing the properties of materials are not well understood, even at room temperature. Hence in the development of new high temperature materials all materials of satisfactorily high melting point must be tested in all possible combinations with all possible fabricating techniques and heat treatments, even though it is known that melting point does not correlate with mechanical strength at high temperatures. This is a time-consuming costly process with no guarantee of achieving optimum results. The determination of the factors responsible for high temperature strength must be regarded as a major objective of any long-range research program on materials, a fact long recognized in studies of metals and alloys and recently emphasized for ceramics by King (24) and Duckworth (2). A brief discussion of the present state of knowledge and of important factors for future investigation was given in the previous section of this report.

2. DEVELOPMENT OF MATERIALS. It appears now that the new fuels which are being considered will be available for test and use before satisfactory materials or methods of cooling are devised for utilizing them efficiently in a power plant. The development of materials, then, is a matter of primary and immediate importance. An effort must be made to improve the materials now in use, but the ultimate requirement for resistance to high temperatures in jet power plants is so far beyond the performance of the present materials that the development of likely but unconventional elements and compounds, the high-melting metals, borides, carbides, nitrides, and oxides, must be vigorously prosecuted.

3. HIGH TEMPERATURE TECHNIQUES. A temperature of 3000°F is still considered to be high, and methods of obtaining, measuring, and controlling temperatures in excess of 3000°F are technical problems of some magnitude. It will be noted in the previous discussion of materials that very few measurements are being made of the properties of materials above 2500°F, and hence there is no quantitative information about the behavior of materials at the high temperatures which are attained in actual practice. High temperature techniques must be developed to provide the needed data.

4. DEVELOPMENT OF SUITABLE TESTS. In attempting to increase the useful temperature range of metallic and ceramic materials, a large number of tests have been devised, the results of which are sometimes difficult to interpret in fundamental terms and which have been of doubtful value to the engineer. Their main use has been as a screening test for the development of new materials. This, of course, is a reflection of the lack of knowledge of the properties of materials at high temperatures and the factors which determine satisfactory performance. There is therefore a need for the study, development, and standardization of testing procedures, a need which is particularly important in the ceramic field.

In the development of suitable tests the several needs of the engineer and designer should be considered. For example, in high temperature testing the time interval involved is important, and emphasis has been placed on long-time tests. Such data, however, are not directly applicable to the design of a device which is meant to last a matter of minutes. In many cases,

⁷⁰Pennsylvania State College, State College, Pennsylvania; E. C. Henry; AAF Contract W-33-038-ac-16374 (17284) (a continuation of W-33-038-ac-13506); *Unclassified*.

short-time tests have given inconsistent results in the laboratory, and it would appear that a special study of such tests is desirable.

At the present stage of development of testing procedures and of general high temperature techniques in ceramics work, it is necessary for each project to carry out its own design and development of apparatus for routine measurements, thus diverting effort from the main objective of the research. The establishment of a project specifically to study testing methods and to develop and produce suitable testing equipment should result in a considerable saving of time and effort.

The ultimate test for a material is its performance in actual service. Unfortunately the measurements of physical properties and the results of laboratory tests designed to simulate service conditions often do not correlate with service performance, and there is a real danger that laboratory evaluations of a material are incorrect. It is therefore of considerable practical im-

portance to provide for service tests of new ceramic and metallic materials and to establish the correlation between laboratory tests and service results.

5. PROPERTIES OF MATERIALS REQUIRED FOR SATISFACTORY PERFORMANCE. The properties which a material must have to give satisfactory performance are not definitely known and must be investigated. High mechanical strength at elevated temperatures has usually been considered to be the most important property. In regeneratively cooled rocket motors, however, it has been found that the metals which give the best service do not necessarily have the best mechanical strength at high temperatures, and the indications are that thermal conductivity may be an important consideration. A determination of the basic properties required for satisfactory service, with particular attention to thermal conductivity, is necessary, especially in connection with the building of large regeneratively-cooled rockets in which thick material must be used to obtain the necessary mechanical strength.

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ABBREVIATIONS OF GOVERNMENT AGENCIES

AAF	Army Air Forces, War Department, Washington 25, D. C.
AAF-AMC	Army Air Forces, Air Materiel Command, Wright Field, Dayton, Ohio.
BuAer	Bureau of Aeronautics, Navy Department, Washington 25, D. C.
BuOrd	Bureau of Ordnance, Navy Department, Washington 25, D. C.
BuShips	Bureau of Ships, Navy Department, Washington 25, D. C.
EES	Engineering Experiment Station, Annapolis, Maryland.
NACA	National Advisory Committee for Aeronautics, 1724 F Street, N.W., Washington, D. C.
NBS	National Bureau of Standards, Washington 25, D. C.
NOL	Naval Ordnance Laboratory, White Oak, Maryland.
NOTS	Naval Ordnance Test Station, Inyokern, California.
NRL	Naval Research Laboratory, Washington 20, D. C.
ONR	Office of Naval Research, Navy Department, Washington 25, D. C.
OSRD	Office of Scientific Research and Development, 1424 16th Street, N. W. Washington, D. C.

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ABSTRACT:

Research work on metallic and ceramic materials suitable for use at elevated temperatures. Variations in composition of the alloys 18-8 stainless steel, Inconel-X, Nimonic, N-155, and Vitallium are being considered. Ceramic materials made from naturally occurring minerals such as complex silicates and metallic oxides are being studied. Other problems discussed are resistance to corrosion and oxidation and design and construction. Recommendations for future work are included.

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