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RESEARCH MEMORANDUM

PROPERTIES OF CERTAIN INTERMETALLICS AS RELATED TO ELEVATED-TEMPERATURE APPLICATIONS

I - MOLYBDENUM DISILICIDE

By W. A. Maxwell

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
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PROPERTIES OF CERTAIN INTERMETALLICS AS RELATED TO ELEVATED-TEMPERATURE APPLICATIONS

I - MOLYBDENUM DISILICIDE

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SUMMARY

A method for the preparation and purification of the intermetallic, molybdenum disilicide, was developed and the following properties were determined for the sintered material:

	Temperature		
	Room	2000° F	2400° F
Modulus of rupture, lb/sq in.	50,700	35,700	20,700
Total elongation calculated from flexure tests, percent	0.09	0.72	3.2
Plastic elongation calculated from flexure tests, percent	none	0.39	1.4
Density:			
Theoretical (X-ray data), grams/ml			6.24
Powdered, grams/ml			6.2
Sintered, grams/ml			5.68
Rockwell hardness (superficial)			C-57
Crystal structure	tetragonal body-centered		
Oxidation resistance, surface effect in air		2000° F	2400° F
(gram gain/sq cm)/hr		-0.0000004	0.000005

Chemical properties of molybdenum disilicide were found to be: highly inert, unattacked by boiling hydrochloric acid, sulfuric acid, or aqueous sodium hydroxide; slightly attacked by nitric acid; dissolved by molten sodium hydroxide.

The sintered material is silvery white in color, possesses high electric conductivity, and is resistant to thermal shock. Molybdenum disilicide melts at 3500° ±100° F with decomposition.

Plastic deformation of the intermetallic at temperatures well below the melting point was observed although only brittle behavior was apparent at room temperature.

From the investigation of properties of molybdenum disilicide, it appears that:

1. Molybdenum disilicide has excellent oxidation resistance, low plastic elongation, and high comparative strength at 2400° F. These properties suggest the use of the material, as currently prepared, in moderate-stress high-temperature parts.

2. Higher densities resulting from improved fabricating techniques may increase the strength of the disilicide.

3. The oxidation resistance and resistance to attack by aqueous acids may be explained as a result of the formation of a protective silica coating. The high-temperature plastic behavior and other properties may be related to the unusual crystal structure of molybdenum disilicide.

INTRODUCTION

The search for materials having satisfactory mechanical properties at elevated temperatures has led to the investigation of several heretofore little-studied types of material. There exists a large class of substances, the intermetallics, which, despite a lack of information concerning their mechanical properties, is known to include compounds that possess properties of value in the field of high-temperature materials. These properties are:

1. High melting points

2. Extreme hardness at room and elevated temperatures

3. Chemical inertness and oxidation resistance

4. High thermal conductivity, indicating satisfactory thermal-shock resistance

The desirable properties appear to be especially evident in what might be called a subclass of the intermetallics - the carbides, borides, nitrides, and silicides of the transition metals (vanadium, chromium, titanium, zirconium, manganese, iron, cobalt, nickel, molybdenum, tungsten, osmium, iridium, platinum, and other elements). This classification is not merely one of convenience because a theoretical basis exists for differentiating these compounds from a larger field. Hägg (reference 1) discusses the similarities of the transition-metal nitrides, carbides, and borides, stating that whereas these compounds are strongly metallic in nature, analogous compounds with other metals are nonmetallic. Ephraim (reference 2) and others group the silicides with the carbides and borides of the transition metals and discuss their similarities.

In considering the properties listed, questions arise concerning what strength the members of this subclass of intermetallics possess at various temperatures and whether they are ever ductile or can be so prepared as to deform plastically at useful temperatures. A thorough survey (reference 3) of recent literature (including Chemical Abstracts, British Iron and Steel Abstracts, and Science Abstracts for 1930-47), for information concerning the possible ductility of these and other intermetallics, reports neither useful data concerning the elevated-temperature strength of intermetallics nor any direct evidence that intermetallics of possible interest for high-temperature use could deform plastically at useful temperatures.

A general survey of the literature on borides, carbides, nitrides, and silicides of the transition metals disclosed that a few of the compounds might possess both good oxidation resistance at high temperatures and high melting points even though quantitative data were lacking. An investigation to determine what elevated-temperature strength could be expected from certain of the more promising compounds and to investigate such points as the high-temperature plastic behavior appeared justified. The compound selected for investigation was molybdenum disilicide $MoSi_2$, which was known to have marked resistance to oxidation at high temperatures. The properties of an impure form of the material indicated that some degree of mechanical strength was possible.

The available information on molybdenum disilicide may be briefly summarized. The disilicide was prepared and described in 1906 by Watts (reference 4), who suggests that earlier preparations may have been molybdenum trihemisilicide Mo_2Si_3. Mellor (reference 5) describes the preparation of the disilicide by a few early investigators, who noticed the marked resistance of the material to oxidation at high temperatures. Indirect methods of preparation were employed and no attempts to form the material for mechanical testing were found. An impure form of the disilicide (approximately 90 percent molybdenum disilicide with iron and other impurities) has been a commercial product of molybdenum producers for several years and is sold as an addition alloy similar to ferromolybdenum.

A program conducted at the NACA Lewis laboratory included a study of methods of preparing molybdenum disilicide by the silico-thermic reduction of molybdenum oxide and by direct combination of the constituent elements. Methods of purification and fabrication were developed. The general properties were studied but the greatest emphasis lay in the high-temperature mechanical properties.

APPARATUS AND PROCEDURE

Preparation and Purification of Molybdenum Disilicide Powder

For the silico-thermic experiments and for the purification of the disilicide powder, conventional methods and equipment were used. Silico-thermic charges were prepared from mixtures of high-purity reagents and fired in fire-clay crucibles. A small quantity of a mixture of chromium trioxide and silicon was used as an igniter.

The first attempt to prepare molybdenum disilicide by direct combination of the elements was made in a vacuum-induction furnace. A compressed pellet containing stoichiometric proportions of molybdenum and silicon was heated slowly in a 5-micron vacuum. At 1800° ±50° F, a violent reaction occurred. This reaction appeared sufficiently strong so that it might go to completion in air or in a neutral atmosphere such as argon. Because the reaction in air had the advantage of retaining the reacted mass at a red heat in an oxidizing atmosphere for several minutes and thereby assured the conversion of excess silicon and molybdenum to the more easily soluble oxides, further preparations were made in air.

Purification of the disilicide is simplified by its unreactive nature. Because neither hot concentrated caustic solutions nor hydrochloric acid or sulfuric acid attack the silicide and because the effect of hot dilute nitric acid is slight, molybdic oxide, silica, and other impurities can be selectively dissolved. Inasmuch as high-purity materials were used, the impurities expected were localized excesses of molybdenum, silicon, and their oxides.

The methods used for preparation and purification were:

(1) Mixture: High-purity silicon and molybdenum in the gram-atomic-weight ratio of 2:1 were mixed by prolonged ball-milling.

(2) Reaction: The mixture was tamped into fire-clay crucibles and ignited with a small quantity of a chromium trioxide - silicon

mixture. In order to preclude contamination, the outside shell of the button thus formed was scraped away and the friable core broken up for ball-milling.

(3) Purification: Iron contamination from the ball-milling operation was removed by leaching the powder with several successive portions of dilute hydrochloric acid. The material was then treated with hot dilute nitric acid to secure oxidation and then with hot concentrated sodium hydroxide to dissolve silica and residual molybdic oxide. After being washed with distilled water, the material was dried and passed through a 400-mesh sieve to secure a uniform particle size.

Forming of Molybdenum Disilicide Bodies

Pressing and sintering. - Powder compacts were prepared by the following procedure: Thin-walled rubber tubes were used as forms and the powder, prepared as described, was poured into them. Stirring and shaking were avoided to minimize segregation. After stoppering, the tube was submerged in oil in a pressure vessel and pressure applied. The pressed green compacts were easily cut free from the rubber tube. The prepared powders gave compacts of sufficient green strength for easy handling so that no binder was considered necessary.

Samples were sintered in a carbon-resistance furnace in an atmosphere of commercial helium. Although it is known that this atmosphere is not completely inert, no oxidation effects were noticed. The pressed samples were separated from contact with the carbon boats by wedges of alumina refractory. The heating cycle of the samples followed that of the furnace, which required $3\frac{1}{2}$ to 4 hours to reach sintering temperature and about $1\frac{1}{2}$ hours to cool below 2000° F.

Modulus-of-rupture specimens were prepared by grinding the sintered compacts with diamond-embedded wheels.

Melting. - Melting of the disilicide was first attempted in an induction furnace in a beryllium oxide crucible. The melting point was not reached but decomposition phenomena, as subsequently described, were observed. Actual fusion was accomplished by high-frequency induction heating in an argon atmosphere and by heating in a carbon-resistance furnace under helium. Carbon crucibles were used in both methods. The melting point was determined on specimens supported on a zircon refractory in a carbon-resistance furnace. The temperature at fusion was read on an optical pyrometer.

Hot-pressing. - Hot-pressing of the disilicide was accomplished with a carbon die in a low-frequency induction coil. The die consisted of a graphite block sized to fit the coil and drilled with a 2-inch hole. Pressure was applied through upper and lower plungers by a hydraulic apparatus capable of exerting a maximum pressure of 3500 pounds per square inch.

Evaluation Methods

Modulus of rupture. - The modulus-of-rupture apparatus and methods described in reference 6 were used. The apparatus consists of a set of supporting knife edges and a movable loading knife edge placed within a resistance furnace, as shown in figure 1. A specimen having a width equal to twice the depth was placed on the knife edges and the counterbalanced loading knife edge brought down in contact with it. Loading was accomplished by a controlled flow of water into a receiver connected to the loading knife edge through a lever system. Upon failure of the specimen, the flow of water was automatically cut off. The specimen load may be calculated by multiplying the weight of the water by the lever ratio. Deflection can be measured on a graduated scale at a lever ratio of 5:1 to an accuracy of 0.01 inch.

Because the disilicide has such excellent oxidation resistance, no protective atmospheres were used. Soaking was done at the evaluation temperatures for a minimum of 1 hour.

Modulus-of-rupture strengths in table I were calculated from the breaking loads by the formula

$$S = \frac{3}{2}\left(\frac{pd}{wt^2}\right)$$

where

S modulus-of-rupture strength, pounds per square inch

p load on specimen, pounds

d distance between supporting knife edges, inches

w specimen width, inches

t specimen thickness, inches

The convenience and the great saving in time made possible by the modulus-of-rupture evaluation furnishes a strong argument for its use as a substitute for high-temperature tensile determinations for preliminary investigations.

The deflection and the elongation of the specimens were of great interest. It was thought that errors in measuring the deformation as described might occur, however, owing to a possible "play" in the lever system or because of deformation of the knife edges. In order to determine the magnitude of these errors, a cathetometer was set up and the telescope sighted through a peephole in the furnace on the specimen and the knife edges. Deflections could be measured to 0.01 centimeter by this method. Use of the cathetometer showed that the aforementioned errors were not of great significance for the accuracy desired; the accuracy was considered sufficient for the present work to prove the existence of plastic deformation and to estimate the amount of deformation.

Accurate measurements of plastic deformation must await high-temperature tensile and stress-rupture measurements. As an approximation, calculations were made on the change in length of the outer fibers as shown by the sketch in table II. If the specimen is deformed by the pressure of the upper knife edge, the bottom fibers will be elongated and may be considered to assume a length equal to an arc of a circle drawn through the knife edges and the bottommost fiber. For small deformations, the length of the arc of this circle approximates the sum of the lengths of the hypotenuses e and e' of the triangles of deformation. In terms of d and δ, the percentage elongation becomes

$$E = \left[\frac{2\sqrt{\left(\frac{1}{2}d\right)^2 + \delta^2} - d}{d}\right]100$$

where

E percentage elongation

δ total deflection, inches

When δ is small in comparison with d, this expression may be simplified by discarding higher-order terms so that

$$E = 2\left(\frac{\delta}{d}\right)^2 100$$

which is a convenient equation used for small deflections.

Elongations as determined from the total deflection represent the combination of plastic and elastic deformation. Reasonably accurate determinations of plastic deformation were possible by reassembling the broken specimens, measuring the permanent set (plastic deformation δ'), and calculating the elongations from the foregoing equation.

In modulus-of-rupture evaluations, only one load, the final load at failure, is actually measured. The rate of loading is uniform, however, and the load at any given time during the evaluation may be determined by the ratio

$$\frac{\text{load at time } t}{\text{load at failure}} = \frac{\text{time } t}{\text{total time to failure } T}$$

From this ratio, loads may be calculated to correspond to deflections measured during the evaluation. With plastic materials, the stresses so calculated using the modulus-of-rupture equation represent only nominal stresses but may be used for comparison purposes, as is done in figure 2.

Modulus-of-rupture values at room temperature were determined on the standard apparatus, using a tensile machine for loading. The order of magnitude of the elongation of the specimens under bending was determined by a strain gage affixed to the bottom of the specimen. The strain was measured at 25-pound increments of continuous loading; such measurements give percentage elongations directly.

Oxidation resistance. - The oxidation resistance of molybdenum disilicide was measured as a function of weight change, dimensional change, and penetration of the oxidized surface layer.

Small rectangular specimens with polished surfaces were used. The specimens were weighed, measured with a micrometer to 0.0001 inch for all dimensions, and measured to 0.01 centimeter on one face with a micrometer-stage microscope. The specimens were placed on refractory boats within a furnace in which circulation of air was assured. Upon removal, the specimens were reweighed and remeasured with the micrometer. The previously measured face was then polished and the dimensions of the clean metal surface measured with the microscope. The micrometer measurements indicate the over-all dimensional changes, and the difference in microscope measurements before and after oxidation determines the penetration, if any, of the oxide coating.

X-ray analysis. - Powder patterns were made by the conventional Debye-Scherrer method and compared with the A.S.T.M. data for molybdenum disilicide. From the pattern, the lattice parameters were calculated and the theoretical density and the crystal structure determined.

Density. - The theoretical density was calculated from the following equation based on reference 7

$$\rho = \frac{KnM}{V'}$$

where

ρ	density, grams per milliliter
K	constant, 1.650×10^{-24}
n	number of molecules per cell
M	molecular weight
V'	volume of unit cell computed from lattice dimensions, cubic milliliters

The powder density was determined by the pycnometer method for fine powders, and the as-sintered density was determined on small bars weighed in water and in air.

Hardness. - Because the specimens were small and brittle, superficial-hardness tests were made. Inasmuch as the specimens came from the interior of sintered bars, no reason appeared for expecting a difference between surface hardness and core hardness.

Thermal-shock resistance. - A rapid but rigorous test was devised that consisted simply in heating the specimen in an oxyacetylene flame to 2000° F (as determined by an optical pyrometer) and quenching in water. The cycle was completed in $1\frac{1}{2}$ minutes or less.

Electric resistance. - Electric sintering of pressed bars was undertaken in an apparatus consisting of two water-cooled flexible-copper clamps connected to a high-amperage current source. These experiments made possible the qualitative estimation of the electric resistance of the sintered and unsintered bars.

RESULTS

Silico-thermic preparation. - Preparation of molybdenum disilicide by direct reaction of silicon and molybdic oxide after ignition with the silicon — chromium trioxide mixture, using quantities required by the reaction

$$2MoO_3 + 7Si \rightarrow 2MoSi_2 + 3SiO_2$$

was unsuccessful. The reaction was sufficiently exothermic to give a semisintered mass, but neither fusion nor separation of slag and metal resulted with the small quantities used.

When fluxing agents were added in quantities equivalent to 10 grams of calcium oxide and 1 gram of calcium fluoride for every 100 grams of the reactants (MoO_3 and Si), the reaction could not be made to support itself.

When the heat available for the reaction was increased by adding chromium trioxide and an equivalent amount of silicon in quantities sufficient to give a product containing 10 percent of chromium, the charge burned well and gave a fair separation of slag and metal. The metal button produced was qualitatively determined to have good oxidation resistance.

Preparation and purification. - Samples from the first material prepared and from the final lot were submitted for chemical analysis. The molybdenum content, as determined in two analyses, is given in table III with a qualitative estimation of the iron-aluminum group and other impurities reported in one analysis. Also included in table III are the results from a spectrographic analysis on the material of lot 6.

Forming of Molybdenum Disilicide Bodies

Pressing and sintering. - Metallographic examination of sintered specimens was made to determine the quantity of voids and to find whether other phases existed. With potassium hydroxide — potassium ferricyanide solution used as an etchant, a yellow second phase was disclosed in the first material examined. This yellow phase was not found in later specimens. Although several etching solutions were tried, including concentrated caustic, hydrofluoric acid of various concentrations, aqua regia, and mixtures of hydrofluoric and nitric acids, no solvent was found that would satisfactorily define grain boundaries except in areas of failure or high stress. The voids disclosed by the microscope were numerous, evenly distributed, and in general rounded. The quantity of voids appeared to be in agreement with the density of 5.68, a density equivalent to 91.0 percent of the theoretical density of 6.24.

Data on the preparation and the properties of three lots of molybdenum disilicide are given in table I. Unless otherwise specified, physical properties, such as hardness and density, given herein are for the material of lot 6.

Melting. - Actual melting was accomplished only in carbon crucibles. All the melts were found to be porous and to contain large gas voids. The work on hot-pressing indicated the possibility of reaction with, or absorption of, carbon, a reaction that might explain the gas evolution. When heated to 3400° F in a refractory crucible in a vacuum-induction furnace, however, a specimen of the compacted disilicide swelled and became porous. These signs of decomposition and gas evolution were present even though the disilicide did not melt and was not in contact with carbon. This decomposition prevents the determination of the true melting point. With use of the method described, molybdenum disilicide was found to become fluid at 3500° ±100° F.

Hot-pressing. - Work to the present time has been limited to the use of carbon dies and difficulty has been experienced with the diffusion of carbon into the disilicide at high temperatures. Results may be summarized as follows:

Pressing temperature (°F)	Density (grams/ml)	Remarks
2700	5.05	Room-temperature modulus of rupture, 20,800 lb/sq in.
2900	5.42	Brittle, easily broken
3000	5.6	Brittle, easily broken; carbon, 0.33 percent

All specimens were pressed at 1115 pounds per square inch for about 5 minutes. While the density increased with pressing temperature, the carbon absorption also appeared to have increased as indicated by the change in brittleness of the specimens. In the brittle specimens, a zone of carbon absorption could be seen on broken surfaces. Hot-pressing with equipment that prevents contact with carbon appeared to offer some possibility of obtaining satisfactory high-density material.

Evaluation Methods

Modulus of rupture and deformation. - Modulus-of-rupture strengths at various temperatures are given in table I, calculated equivalent deformations for both total and plastic elongation are given in table II, and nominal stress is plotted against strain for the material at three temperatures in figure 2. Because comparison of the elastic and plastic characteristics of the material at different temperatures was desired, the calculated percentage elongations have been plotted against the nominal stresses calculated by the modulus-of-rupture equation for the loads corresponding to the measured deflections.

The straight-line curve of figure 2 indicates that the deformation of the material at room temperature is entirely elastic with brittle failure, the approximate total elongation being 0.09 percent. At 2000° F, a change in behavior and a resemblance between this curve and true stress-strain curves for common metals are apparent; that is, for metals, a straight-line, or Hooke's law, portion of the curve is followed by a more slowly rising portion denoting plastic deformation. At 2000° F, the change from elastic to plastic deformation occurs at from 40 to 50 percent of the failure load. At 2400° F, the behavior is similar except that plastic deformation seems to occur at lower percentage stresses and that plastic elongation is much greater.

Oxidation resistance. - Oxidation-resistance values obtained for prolonged tests at high temperatures are given in table IV. Shorter tests made at these and lower temperatures gave results similar to those listed. With a material so highly resistant to oxidation, however, experiments must be continued for long periods of time to obtain measurable results. Definite dimensional and weight changes occurred at 2400° F, but at 2000° F the changes were so small as to approach the experimental error.

Little or no oxidation penetration from smooth surfaces toward the interior was detected in photomicrographs of all oxidation specimens. Examination of smooth and highly polished surfaces was necessary to avoid confusion between penetration darkening and surface voids. From the photomicrographs, it appeared that oxidation took place on a very thin surface layer, which remained stable at 2000° F but which may have gradually vaporized and disappeared at 2400° F.

The appearance of the disilicide specimens after long periods of time at high temperatures was most striking. Specimens held at 2000° F for 75 hours remained shiny with a slight darkening equivalent to a light tarnish on silver. At 2400° F, the effect was more a graying than a blackening and some degree of shininess was retained.

X-ray analysis. - The crystal form of molybdenum disilicide is body-centered tetragonal, the lattice parameters of which were determined to be

$$a = 3.20 \text{ angstroms}$$

$$c = 7.86 \text{ angstroms}$$

$$\frac{c}{a} = 2.45$$

There are two molecules in the unit cell. Atom positions are: for molybdenum (000) and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$; and for silicon $\left(00\frac{1}{3}\right)$, $\left(00\frac{2}{3}\right)$, and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{6}\right)$, $\left(\frac{1}{2}\frac{1}{2}\frac{5}{6}\right)$.

The density as calculated from the lattice parameters was found to be 6.24. All crystallographic values are in agreement with those given by Zachariasen (reference 8).

The structure determined from the foregoing data is unusual in that both the silicon and molybdenum atoms have coordination numbers of 10. Each molybdenum atom is surrounded by ten silicon atoms at an equal distance and the silicon atoms are surrounded by five molybdenum and five silicon atoms at the same distance. The arrangement of atoms in the molybdenum disilicide crystal and the coordination number relations are shown in figure 3.

Density. - Specimens ground from sintered material of lot 6 had densities of 5.68. The powder was found to have a density of 6.2. Consistent results were difficult to obtain with the powder and prolonged boiling of the powder in the pycnometer was found necessary. The difficulties experienced may help explain some of the disagreement in values for the density of molybdenum disilicide found in the literature.

Hardness. - All material of lot 6 was found to have a Rockwell (superficial) hardness number of approximately C-57.

Thermal-shock resistance. - Several thermal-shock tests of a few cycles duration were run on various specimens, all of which showed good thermal-shock resistance. In one prolonged test, 24 cycles from 2000° F to water-quench were completed before any effect could be observed. A few hair-line surface checks were then noticed. Continuing this test to 45 cycles did not increase the checks in size or number. All edges remained clean.

Electric resistance. - The rather limited work on resistance sintering did not produce uniform specimens. The conductivity of the specimens was observed to increase rapidly as sintering progressed, however, and the resistance of the sintered specimens was quite low.

DISCUSSION

Silico-thermic reduction. - The preparation of pure molybdenum disilicide in small quantities by the silico-thermic method was found impracticable. The method, however, does furnish a simple means of preparing alloys such as the chromium alloy discussed. From the results of the silico-thermic work and the preparation of the disilicide by direct combination of the elements, the heat of formation of the compound did not appear particularly high.

Preparation and composition. - The methods of preparation and purification described are somewhat prolonged but otherwise simple and convenient.

The identity of the material as $MoSi_2$ has been proved by X-ray analysis. The results of chemical analysis are in fair agreement with this formula despite wide variation in independent results. The accurate determination of molybdenum content is difficult on the most amenable materials. On substances of this type, difficulties would be expected, but closer agreement in results could be wished. Accurate determination of the composition of the material from these molybdenum analyses apparently is impossible. Inasmuch as it is strongly suspected, but not definitely known, that both molybdenum and silicon are soluble at least in small percentages in $MoSi_2$, the product might contain an excess of either element in a form that would not be readily dissolved by purification reagents. Such excesses, although probably small, can only be determined by accurate chemical analysis because neither X-ray nor light spectrograms can be expected to show small excesses of the principal constituents. An analogous compound, iron disilicide, was found by Phragmen (reference 9) to be a deficiency compound that must contain a slight excess of silicon.

Except for possible excesses of molybdenum or silicon, the material prepared and described is of high purity (table III). The iron introduced in the ball-milling operation might be considered as acting as a "tracer," indicating the behavior of all soluble impurities.

Sintering and fabrication. - Although fabrication techniques are far from completely developed, material of uniform quality has been produced. As indicated in table I, agreement in modulus-of-rupture values is satisfactory for sintered material of lot 6 so that selection of the highest strength value to represent the possible quality of the material is justified. With respect to potential quality, averages of modulus-of-rupture values would be meaningless.

A study of the relation between theoretical and sintered density may indicate the kind of improvement in strength to be expected with new developments in fabricating techniques. The density of the material of lot 6 being 91.0 percent of the theoretical density indicates a quantity of voids, which as stress-raisers throughout the material could be expected to reduce greatly its strength. Although the analogy is not necessarily direct, consideration of the effect on strength of changes in the density of other powder metallurgy products might be useful.

Kieffer and Hotop (reference 10), in discussing the behavior of tungsten and other refractory metals as sintered compacts, state that the physical and mechanical properties of the sintered compacts are governed almost solely by the density. Curves and other data given indicate that for tungsten the tensile strength may increase as much as 1000 percent as the density increases from 90 percent to about 99.9 percent.

Several possible methods for increasing the density of molybdenum disilicide compacts have been indicated by current research. Small increases in density can be expected from the use of finer powders and higher pressures in the formation of the green compacts. Greater improvements can be expected from sintering at more nearly optimum temperature or from increasing the sintering time at the present temperatures. A comparison of the properties of lots 5 and 6 (table I) indicates that the sintering temperature of 3300° F is too high and that the optimum temperature is approximately 2800° F. Kieffer and Hotop (reference 10) state, however, that densities above 95 percent cannot usually be expected from sintering alone. If this generalization applies to molybdenum disilicide, other methods must be used to obtain the best properties. The most feasible method is possibly that of swaging, a standard technique in refractory-metal manufacture where nearly theoretical densities are obtained. Inasmuch as temperatures of 2700° F are used in the swaging of tungsten and the disilicide shows marked plastic deformation at temperatures of 2400° F and below, the method would seem feasible although modified techniques may prove necessary.

Melting. - The decomposition of molybdenum disilicide near the melting point imposes problems in the melting and the casting of this material, although use of either rapid melting and casting or melting under high-pressure inert gases might have some possibilities. The nature of this decomposition is unknown. Because the decomposition occurs above the melting point of silicon (2605° F) and well below the melting point of molybdenum (4760° F), the loss of silicon is assumed.

Oxidation resistance. - The oxidation resistance of molybdenum disilicide is pronounced at all temperatures studied. The material is also resistant to attack by many nonoxidizing acids at room temperature and a relation may exist between the two properties. The behavior in aqueous acids might reasonably be considered analogous to that of the corrosion-resistant high-silicon iron alloys in which the electrochemical behavior and the associated corrosion resistance are determined by the protective film of silica formed on the material (reference 11). That such a film could form on molybdenum disilicide under the same conditions seems quite possible.

If it is hypothesized that a protective coating is also responsible for the oxidation resistance of molybdenum disilicide at elevated temperature, the melting points of molybdic oxide and silica would indicate that the coating must be pure silica or contain a high percentage of silica. This coating must be extremely thin and impervious, and although it remains stable at 2000° F for long periods of time, a slow but evident decomposition and re-formation is indicated at 2400° F. This behavior at 2400° F might be expected as the melting point of silica is more closely approached.

An increase in weight appears to be associated with a decrease in dimension at 2400° F (table IV). This action is the reverse of what might be expected but the weight increase is minute and may be due to surface effects invisible under the microscope.

The transformation of two readily oxidized elements, such as molybdenum and silica, to a compound having exceptional resistance to oxidation demonstrates one of the most interesting and valuable properties of the intermetallics; that is, these compounds may possess valuable properties quite different from the properties of the constituent elements.

Mechanical properties. - The modulus-of-rupture value of molybdenum disilicide at 2400° F is approximately equal to the highest found for three types of titanium carbide ceramal (reference 6), and at 2000° F is only about one-half the value found for the best titanium carbide - cobalt ceramal. At both these temperatures, the disilicide has the advantage of oxidation resistance not possessed by the ceramals.

The results of calculations given in table II indicate rather low but definite plastic deformations. For most applications, a material of limited plastic deformation should be preferable to a completely brittle substance because even small plastic deformations may relieve certain stress concentrations that would cause failure in a brittle material.

The plastic-elastic relations shown in the stress-strain curves of figure 2 are of interest in that they show the transformation of a material brittle at room temperature to a material having metallic deformation characteristics at elevated temperatures. The straight-line portion of the curve at 2000° F combined with the curved portion denotes a combination of both plastic and elastic deformation at this temperature (a conclusion that is also apparent from a comparison of the plastic- and total-deformations given for this temperature in table II). This combined mode of deformation might be designated metallic and differentiated from a softening in which all the deformation would be plastic. Also, the deformation at 2000° F takes place well below the melting point at a temperature at which softening would not be expected.

The material as prepared appears competitive with other high-temperature materials on the basis of strength only at 2400° F. The possible improvements in fabrication discussed may increase the strength at all temperatures, but the present material may prove of value in several uses. The oxidation resistance, ability to retain a finish, and moderate strength of the disilicide suggest its use in gas-turbine stator blades and in moderate-stress high-temperature applications.

Structure and properties. - A search of the literature revealed that coordination numbers of 10 are extremely rare and that

RX_2 compounds in which both elements have the same coordination number are unusual. The high-temperature plastic properties of molybdenum disilicide may be related to the unusual coordination and structure.

SUMMARY OF RESULTS

Satisfactory methods for the preparation and the purification of molybdenum disilicide have been developed and the following properties were determined for the sintered materials:

		Temperature	
	Room	2000° F	2400° F
Modulus of rupture, lb/sq in.	50,700	35,700	20,700
Total elongation calculated from flexure tests, percent	0.09	0.72	3.2
Plastic elongation calculated from flexure tests, percent	none	0.39	1.4
Density:			
Theoretical (X-ray data), grams/ml			6.24
Powdered, grams/ml			6.2
Sintered, grams/ml			5.68
Rockwell hardness (superficial)			C-57
Crystal structure	tetragonal body-centered		
Oxidation resistance, surface effect in air		2000° F	2400° F
(gram gain/sq cm)/hr		-0.0000004	0.000005

Chemical properties of molybdenum disilicide were found to be: highly inert, unattacked by boiling hydrochloric acid, sulfuric acid, or aqueous sodium hydroxide; slightly attacked by nitric acid; dissolved by molten sodium hydroxide.

The sintered material is silvery white in color, possesses high electric conductivity, and is resistant to thermal shock. Molybdenum disilicide becomes fluid at 3500° ±100° F with decomposition.

Plastic deformation of the intermetallic, molybdenum disilicide, at temperatures well below the melting point was observed, although only brittle behavior was apparent at room temperature.

From the investigation of properties of molybdenum disilicide, it appears that:

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1. The oxidation resistance, ability to retain dimensions and finish, moderate strength, and definite high-temperature plastic deformation of the material, as currently prepared, indicate its applicability for use in moderate-stress high-temperature parts.

2. Improvements in fabricating techniques, such as hot-working of sintered material or other methods by which density is increased, may greatly improve the strength of the disilicide.

3. The oxidation resistance and resistance to attack by aqueous acids may be explained as a result of the formation of a protective silica coating. The high-temperature plastic behavior and other properties may be related to the unusual crystal structure of molybdenum disilicide.

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

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TABLE I - PREPARATION AND PROPERTIES OF MOLYBDENUM DISILICIDE

Lot	Preparation		Sintering		Properties			
	Grinding time (hr)	Compression pressure (lb/sq in.)	Temperature (°F)	Time at temperature (hr)	Appearance as sintered	Modulus of rupture (lb/sq in.)		
						Room temperature	2000° F	2400° F
4	5	30,000	2700	$5\frac{1}{2}$	Smooth surface Easily ground	15,000 30,300 17,900	38,600	
5	6	40,000	3300	4	Surface cracks Difficult to grind		15,200	
6	16	40,000	2700	4	Smooth surface Easily ground	50,700 50,400	33,800 35,700	20,700 17,800

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TABLE II - DEFORMATION AND ELONGATION OF SINTERED MOLYBDENUM DISILICIDE SPECIMENS

	Temperature (°F)			
	2000		2400	
Modulus of rupture, (lb)	33,800	35,700	20,700	17,800
Distance between supporting knife edges d, (in.)	2.5	2.5	2.5	2.0
Total deflection δ, (in.)[a]	0.15	0.096	0.23	0.25
Calculated total elongation, percent	0.72	0.29	1.6	3.2
Plastic deformation δ', (in.)[b]	0.11	0.09	------	0.17
Calculated plastic elongation, (percent)	0.39	0.26	------	1.4

[a] Measured on lever-arm scale.

[b] Measured on reassembled broken specimens.

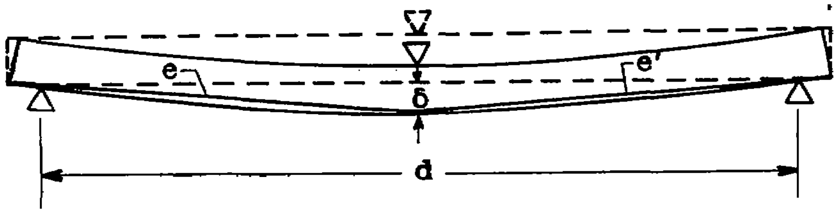

TABLE III - ANALYSIS OF MOLYBDENUM DISILICIDE

Lot	Constituent	Chemical analysis	
		[a]A	[b]B
1	Molybdenum[c]	62.7	64.28
	Iron-aluminum group	present	------
6	Molybdenum[c]	61.5	63.46
	Iron-aluminum group[d]	Not detected	------
	Other impurities[d]	Not apparent	------

[a] NACA Lewis laboratory.

[b] Commercial analytical laboratory.

[c] Molybdenum disilicide $MoSi_2$ theoretically contains 63.1 percent molybdenum.

[d] Of all spectrographically determinable elements, only the following were found as traces in order of decreasing quantity: iron, nickel, copper, cobalt, chromium, vanadium, zirconium, and sodium. (Elements reported as spectrographic traces are considered present to maximum of 0.01 percent and usually much less.)

TABLE IV - OXIDATION RESISTANCE OF SINTERED MOLYBDENUM DISILICIDE

[redacted]

	Temperature (°F)			
	2000		2400	
	Duration (hr)			
	75	150	50	100
External dimensions, (in.)				
Original	0.6300 x 0.3064	0.5645 x 0.2773	0.4700 x 0.6224	0.4696 x 0.5797
Final	.6300 x .3064	.5646 x .2773	.4673 x .6171	.4652 x .5737
Decrease	.0000	.0000	.0027 .0053	.0044 .0060
Cross-section dimensions, (cm)				
Original	0.78	0.70	0.52 x 1.57	0.52 x 1.47
Final unoxidized metal	.78	.70	.52 x 1.57	.52 x 1.46
Decrease	.00	.00	.00 .00	.00 .01
Weight, (grams)				
Original	14.1996	11.3509	5.6505	5.2853
Final	14.1993	11.3502	5.6522	5.2877
Increase	-.0003	-.0007	.0017	.0024
Surface area, approximate (sq cm)	12.62	11.2	6.90	6.38
Unit weight increase ((gram/sq cm)/hr)	-0.0000003	-0.0000004	0.000005	0.000004

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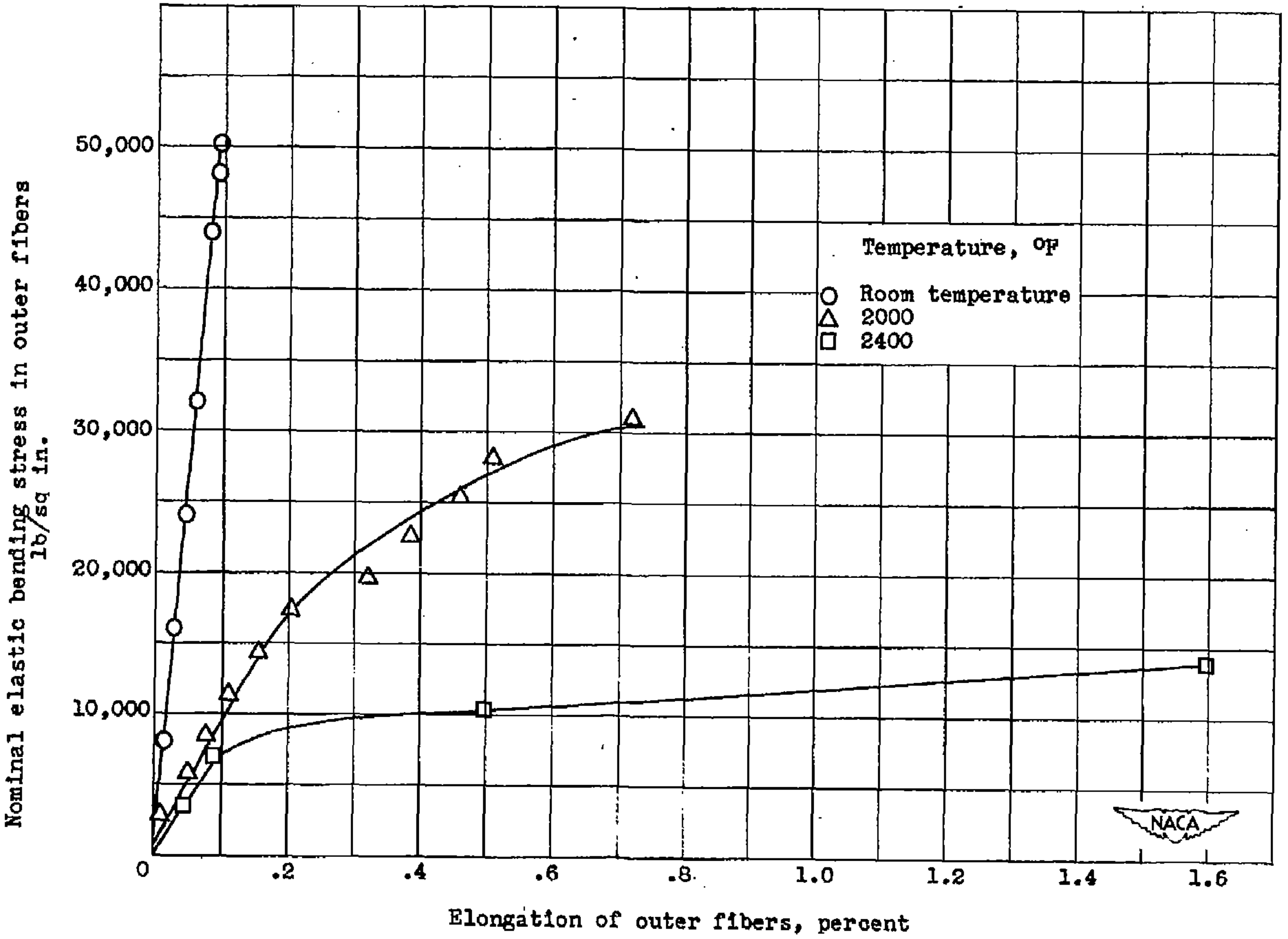
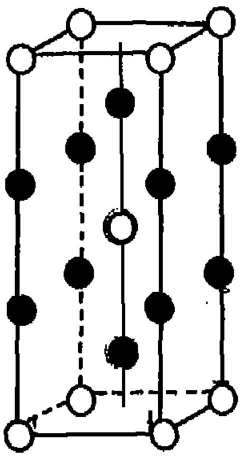
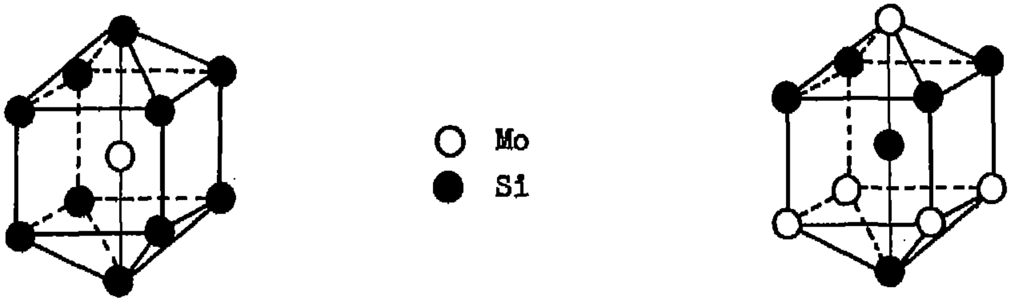


Figure 2. - Nominal stress plotted against strain for molybdenum disilicide modulus-of-rupture specimens at three temperatures.



(a) Molybdenum disilicide $MoSi_2$ structure.



(b) Arrangement of atoms around a molybdenum Mo atom.

(c) Arrangement of atoms around a silicon Si atom.

Figure 3. - Crystal structure and coordination number relations for molybdenum disilicide $MoSi_2$ (after Zachariasen, reference 8).