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Technical Report No. 32-452

Mechanical and Thermal Properties of Hot-Pressed Zirconium Carbide Tested to 2600°C

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September 15, 1963

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ABSTRACT

Tensile, creep, thermal expansion, and modulus of elasticity data were determined for hot-pressed zirconium carbide. The material was relatively impure, containing 1 to 2% nitrogen and 1 to 2% free carbon. Tensile and creep properties, which were measured to 2600°C, indicated that above 2100°C the strength is 2,000 psi or lower and the elongation is 40% or greater, thus signifying little structural usefulness. It is proposed that results were influenced by the presence of impurity at the grain boundaries. Mean coefficient of thermal expansion of this zirconium carbide varied from 5.6×10^{-6} $°C^{-1}$ (for 25 to 400°C) to 7.6×10^{-6} $°C^{-1}$ (for 25 to 2300°C). Room-temperature modulus-of-elasticity values averaging 51.6×10^{6} psi were obtained by dynamic methods.

I. INTRODUCTION

During recent years, there has been a marked tendency to design systems for operation at ever-increasing temperatures. This tendency has severely limited the number of usable materials and has intensified the search for new and better materials. The refractory metal carbides have been considered for such uses because they have the highest known melting points (approximately 4000°C). Such carbides have been considered for reactors, rocket nozzles, heat shields, and thermionic emitters.

In spite of the interest in these materials, very little basic information on their mechanical and thermal properties at the temperatures of interest has been reported. Occasional mechanical property tests have been conducted, and some thermal properties data are available (Ref. 1 and 2). However, the results are not in good agreement, and the materials tested were not well characterized, which would contribute to this lack of agreement among various investigators. A very definite practical interest exists in the physical properties of refractory metal carbides.

From a fundamental standpoint, the carbides are an interesting class of materials because of their chemical and physical nature. Chemically, on the basis of electronic conductivity and metallic luster, they are considered to be metallically bonded materials. However, their mechanical properties are considerably different from those of the metals in that they apparently exhibit brittle failure at all temperatures. The nature of the brittleness has not been determined; it may be a result of the fundamental structure of the material or principally the effect of contamination. It is conceivable that a transition in the mode of failure of carbides might exist as is the case with metals, but this apparently has not been determined.

This program was undertaken in the hope of providing (1) fundamental information concerning the properties of a relatively little understood class of materials and (2) engineering information that might be of value in the design of future high-temperature structures. Since little data were available on the refractory metal carbides, it would be beneficial to obtain information as quickly as possible. Therefore, tests on commercial materials were conducted in test equipment of known capabilities. Using this approach, results could be obtained without resorting to extensive materials and equipment development programs. Concurrently, information would be gained for proper planning of future fabrication programs and for the design of improved test facilities. Zirconium carbide, the material selected for evaluation, was chosen on the basis of cost, availability, and stability. It was felt that the zirconium carbide would be compatible with the test environments available, at least to the anticipated test temperatures.

II. MATERIALS, FABRICATION, AND PURIFICATION

All of the zirconium carbide tested came from the same lot of powder. Most of the test specimen blanks were hot-pressed by the vendor. (The hot-pressing parameters were not available.) Specimens were also hot-pressed at the Jet Propulsion Laboratory (JPL). The specimen characteristics for typical vendor- and JPL-fabricated pieces and for the raw powder are given in Table 1. The techniques employed for these analyses were (1) micro-Kjeldahl for the nitrogen, (2) vacuum fusion for the oxygen, (3) spectrographic analysis for the metallics, (4) acid separation for free carbon, and (5) combustion for total carbon. It should be noted that since the accuracy of the analyses for nitrogen and oxygen in zirconium carbide is subject to question,[1] the values indicated should be taken only as the best indications of the true values rather than as absolutely correct values.

As may be seen in Table 1, the analyses of the vendor-fabricated specimens show high purity for metallics (except for the commonly associated hafnium) but considerable contamination for nonmetallics. These samples contained a relatively large quantity of nitrogen and considerable free carbon. The existence of nitrogen within the lattice of zirconium carbide is assured since zirconium nitride and carbide are isomorphous and form a continuous solid solution. Oxygen can substitute for carbon in the carbide lattice to some unknown extent, although in large quantities it will form a second phase.

With the vendor-fabricated specimens it is believed that nitrogen was dissolved into the carbide lattice during the hot-pressing procedure because of an insuffi-

Table 1. Zirconium carbide material composition and density

Characteristics	As-received powder	Typical as-received commercial test specimens	Typical JPL-fabricated test specimens
Impurity,[a] wt. %			
Co	0.001 to 0.01	0.001 to 0.01	<0.001
Si	0.001 to 0.01	<0.001	0.001 to 0.01
Fe	<0.001	0.01 to 0.1	0.1 to 0.5
Al	<0.001	<0.001	0.001 to 0.01
Ni	0.001 to 0.01	0.001 to 0.01	0.001 to 0.01
Sn	0.001 to 0.01	<0.001	<0.001
Ti	0.01 to 0.1	0.01 to 0.1	<0.001
V	0.001 to 0.01	<0.001	0.001 to 0.01
Cr	<0.001	0.001 to 0.01	0.001 to 0.01
Hf	1.	1.	1.
C_{free}	0.79	1.58 to 2.49	0.85 to 1.0
C_{comb}[b]	10.87	8.81 to 9.41	10.6
N_2	0.24	1.06 to 2.08	0.28 to 0.55
O_2	0.044	0.21 to 0.28	0.22 to 0.56
Density, g/cm^3	Not determined	6.19 to 6.50	6.53

[a] Others observed were less than 0.001 wt. %.
[b] C_{comb} = combined carbon.

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[1] Private communication with Melvin G. Bowman, Group Leader, CMB 3, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

ciently protective atmosphere. This nitrogen caused precipitation of an equivalent amount of carbon which then appeared as free carbon at the grain boundaries (see Fig. 1). Removal of the nitrogen impurity was attempted by annealing the specimens for 1 hr at 2150°C in an argon atmosphere containing carbon from furnace hardware. However, this purification technique was only partly successful, as may be seen by the results of the chemical analyses given in Table 2.

The x-ray diffraction pattern of all of the zirconium carbide used in these tests showed only face-centered cubic zirconium carbide with no other phases resolved; this pattern agreed completely with that published (Ref. 3). The lattice parameter was determined by a standard least-squares analysis (Ref. 4). The lattice parameter for zirconium nitride is reported to be 4.56 (Ref. 5) and that for zirconium carbide, 4.702.[2] The reported value for zirconium carbide may be in error because the quantity of oxygen reported in the sample was not accurately known. The effect of this oxygen is to reduce the lattice parameter, but the magnitude of the change is not known.

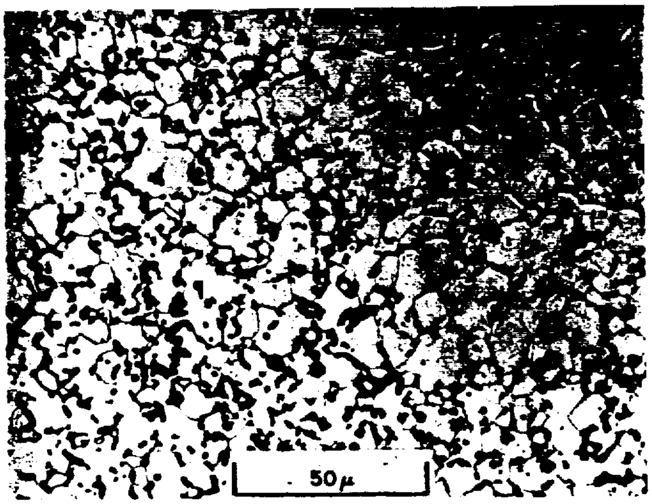

Fig. 1. Typical microstructure of vendor hot-pressed zirconium carbide as received showing free carbon at grain boundaries. Void content was small (<1%). Specimen was polished and etched with 50 parts conc. HNO_3: 50 parts H_2O: 1 part HF

The effect of annealing, under the conditions previously described, on the x-ray diffraction lattice parameter of the zirconium carbide was significant, but not fully explained. As shown in Table 2, a sizable increase in the lattice parameter was noted after annealing, but since this increase could be related to changes in the carbon, oxygen, or nitrogen content, no specific correlation was made. With higher temperature annealing, the lattice constant for any particular specimen remained essentially unchanged, although chemical analysis indicated some changes in composition (see Table 2). These inconsistencies may have resulted from the uncertainty in chemical analysis. Because the highest annealing temperature employed (2700°C) was above any test tem-

Table 2. Effect of heat treatment on zirconium carbide

Characteristics	Commercial specimen 1		Commercial specimen 49			JPL specimens 51, 52, 54	
	As received	1 hr at 2150°C in carbonaceous argon	As received	1 hr at 2500°C in carbonaceous argon	1 hr at 2700°C in carbonaceous argon	As pressed	1 hr at 2250°C in 10^{-5} vac
Impurity, wt. %							
C_{comb}	9.9	9.7	9.07	9.85	9.97	10.67	10.14
C_{free}	1.6	1.4	2.03	1.85	1.41	0.85	1.18
N_2	1.06	0.94	2.08	1.97	1.32	0.32	0.28
O_2	0.21	0.18	0.27	0.08	0.07	0.56	0.017
Lattice parameter, Å	4.6782	4.6911	4.6764	4.6825	4.6832	4.6941	4.6936
Grain size, μ	4.7	6.2	5.4	9.4	10.5	3.8	12.9
Knoop hardness number for 0.2 Kg load	800	1200	900	1200	1300	1600	1400

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[2] Private communication with Melvin G. Bowman.

peratures used in this investigation, it must be concluded that all of the vendor hot-pressed zirconium carbide specimens used contained 1 to 2% nitrogen, 1 to 2% free carbon, and about 0.2% oxygen.

Other physical measurements on the zirconium carbide material correlated with the indicated compositional changes. The increase in Knoop hardness after annealing (see Table 2) was a result of a decrease in nitrogen content in the carbide–nitride solid solution. The grain size increased slightly during annealing. Those grain sizes indicated in Table 2 were determined by the line-count method (Ref. 6).

The zirconium carbide specimens produced at JPL were hot-pressed in graphite dies under flowing argon at 2000°C and 6,000 psi for 30 min. As may be seen in Tables 1 and 2, the chemical analysis results, the lattice parameter, and the Knoop hardness all indicated some contamination from oxygen and nitrogen as a result of hot-pressing. The flowing argon atmosphere was apparently helpful but not entirely sufficient. As also shown in Table 1, iron was introduced into the specimens fabricated at JPL. It was subsequently determined that this contamination could be eliminated by acid leaching of the dies with HCl.

The purification of the JPL hot-pressed material was attempted by annealing in a liquid-nitrogen cold-trapped vacuum system. The limiting conditions are indicated in Table 2. Severe outgassing was encountered at 1400 to 1700°C, and a total weight loss of 0.5% was evident at 1700°C. Since the vapor pressures of zirconium carbide and graphite are $<10^{-6}$ mm Hg (Ref. 7) at these temperatures, the losses should have been a reflection of purification. The chemical analysis, if assumed to be relatively correct, appeared to support this, indicating a 0.04% loss of nitrogen and a 0.55% loss of oxygen.

Although these annealing techniques resulted in some purification of the zirconium carbide, the resulting material was still impure. Most test specimens in this investigation were heated to 2150°C for 1 hr and this fact is noted in appropriate test specimen designation.

III. TESTING PROGRAMS

Because several different mechanical and thermal measurements were made on the hot-pressed zirconium carbide material, each test program will be reported as a unit. Included for each test program are the technique and equipment used, specific specimen configuration, results, and interpretation. The conclusions in Part IV apply to all of the programs.

A. Tension Program

The tension properties of zirconium carbide were measured in equipment originally designed and constructed at JPL for use with graphite (Ref. 8) in a test environment of carbonaceous helium. The specimen grips were graphite and were at the same temperature as the specimen. The configuration of the test specimen is shown in Fig. 2. Note the compound radius employed to reduce stress concentrations to less than 2%. The specimens were machined to this configuration by means of a combination of spark discharge and ultrasonic technique. Test loads were applied by a motor-driven screw, and stress was measured by a standard load cell. The deformation of the specimen, as indicated by relative motion of the grips, was measured by mechanical transmission to the exterior of the furnace where a transducer in the form of a strain gauge was used to produce an electrical signal. In this Report, the total deformation, as determined by the extensometer, will be referred to as recorded strain.

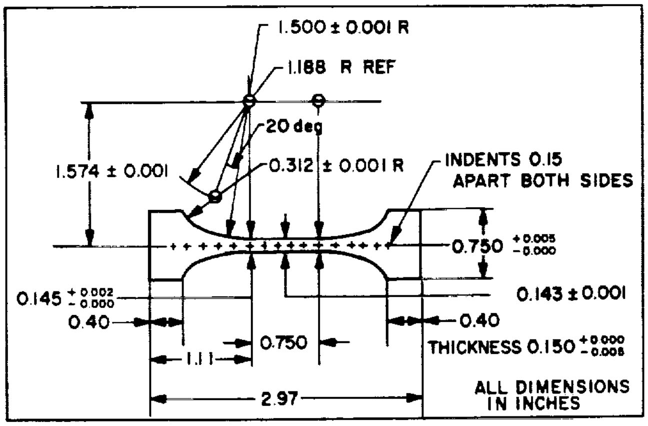

Fig. 2. Configuration of zirconium carbide tension or creep specimen

The distribution of the deformation within the specimen was accurately determined by the measurement of the location of 25-μ wide microhardness indents on each side of the specimen before and after testing (see Fig. 2). From this technique, it was determined that the deformation in the gauge length was equal to 74 ± 10% of the recorded strain over the entire range of deformation. This deformation within the gauge length will be referred to as gauge length strain. Both the consistency of the ratio of gauge length strain to recorded strain and the actual measurement of the distribution of deformation indicated that this deformation was uniform with no localized necking. The appearance of fracture was entirely of a brittle nature even after the large elongations at the highest temperatures employed for these tests. Correlation of the various strain measurements, as determined by the extensometer system, indents, and external dimensions, was generally excellent with variations being less than 5%.

The data were obtained in the form of curves for stress vs. time and for recorded strain vs. time. These were replotted to yield stress vs. gauge length strain curves. The stress vs. gauge length strain curves for tests conducted above 2200°C are typified by that shown in Fig. 3. The stress vs. gauge length strain curves at 1600°C are typified by Fig. 4. Those taken at 2000 and 2200°C lie between these two extremes. Figure 4 shows

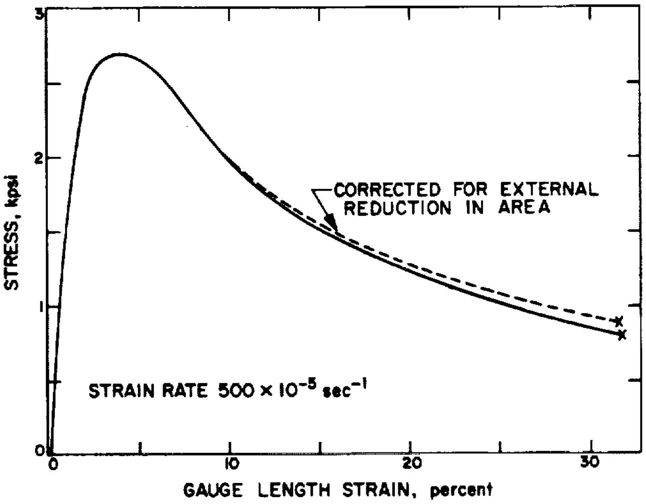

Fig. 3. Stress vs. gauge length strain for hot-pressed zirconium carbide tested at 2600°C

a large stress at zero strain because of inherent insensitivity to small strains in the strain-measuring systems.

The results of the tension tests are shown in Table 3, and they are expressed as a function of various test parameters in Fig. 5, 6, and 7. In all of these instances, the strain rate listed is based on original gauge length. In general, the strength of the zirconium carbide was quite low at temperatures above 2200°C, and gauge length elongation reached 50% or greater at the highest temperature. The nature of the deformation observed was evident from the microstructure shown in Fig. 8. Note

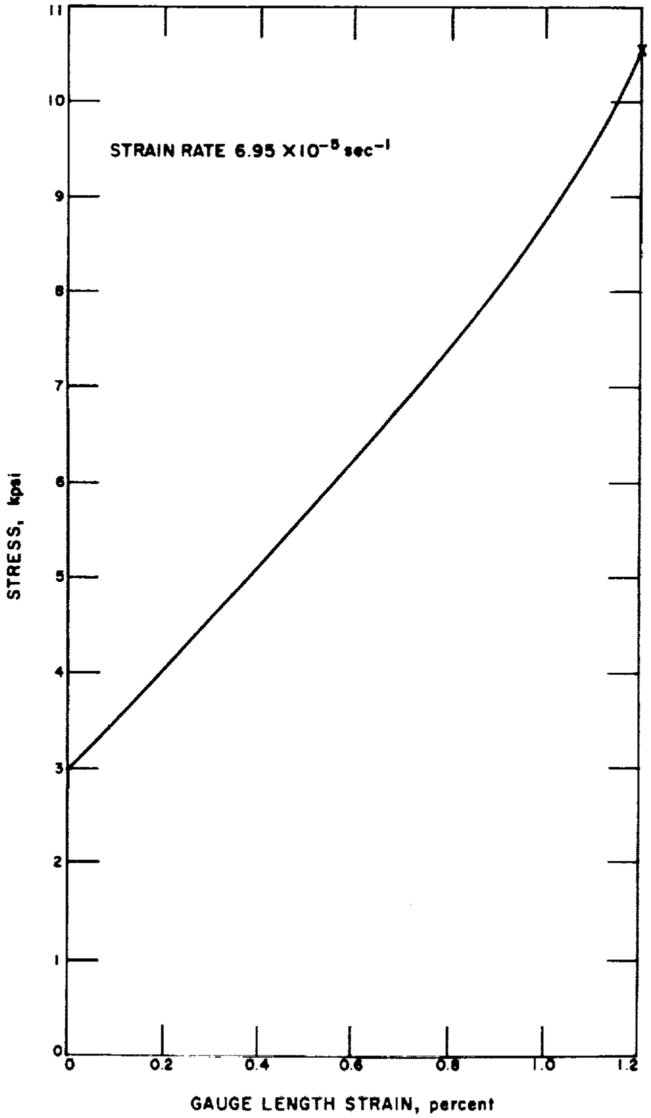

Fig. 4. Stress vs. gauge length strain for hot-pressed zirconium carbide tested at 1600°C

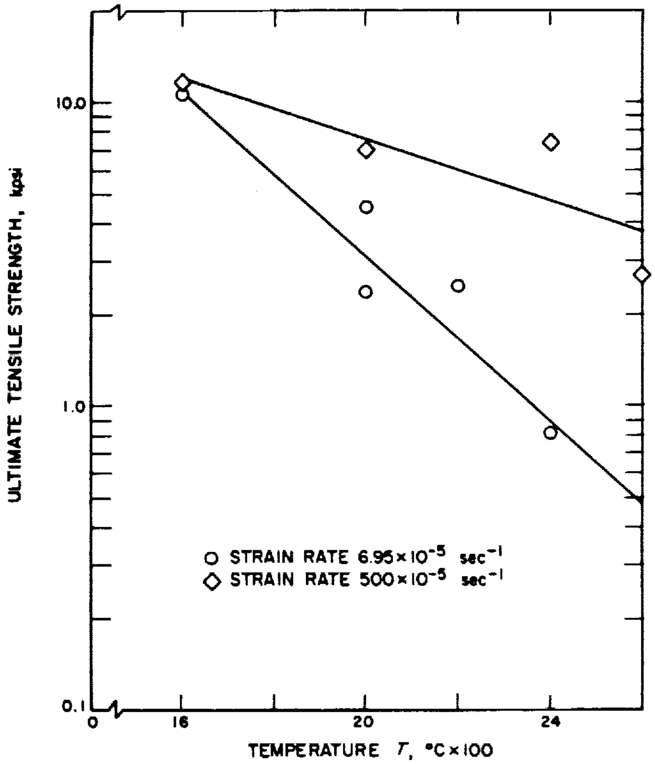

Fig. 5. Ultimate tensile strength vs. temperature for hot-pressed zirconium carbide

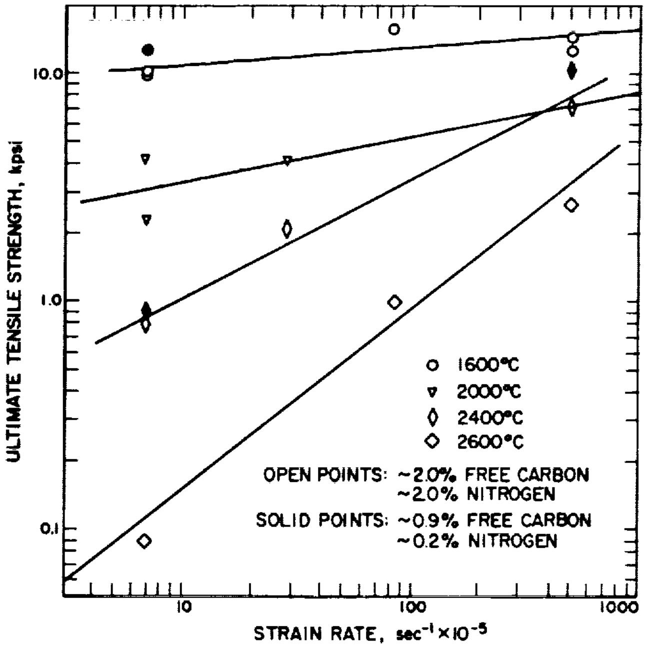

Fig. 6. Ultimate tensile strength vs. strain rate for hot-pressed zirconium carbide

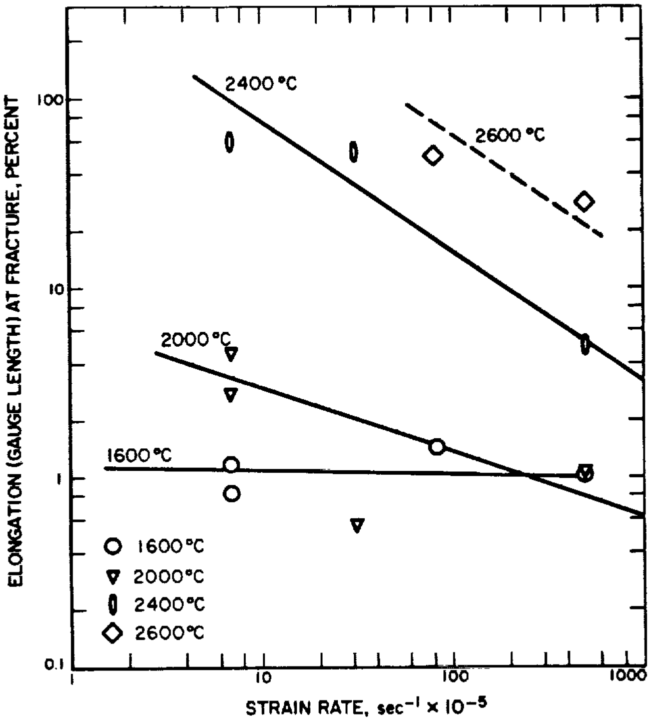

Fig. 7. Elongation (gauge length) at fracture for hot-pressed zirconium carbide

that deformation was in the form of intergranular cracking with no change in the shape of the zirconium carbide grains. Compare these grains with those of the as-received material shown in Fig. 1. These microcracks lay in the plane perpendicular to the direction of loading. Such microcracks resulted in a decrease in density and a reduction in load-carrying area, thus increasing the actual stress. The stress reported was not corrected for either apparent or true reduction in area.

The strain hardening exhibited in the stress vs. gauge length strain curve (see Fig. 4) taken at 1600°C was entirely reproducible at this temperature. Specimen numbers 1, 5, 25, 40, and 52 (see Table 3) all exhibited this strain hardening. In all cases the reduction in area and the gauge length elongation were so small that no correction to true-stress vs. true-strain curves was required. No fundamental significance has been ascribed to this strain hardening since the nature of the deformation exhibited at 1600°C has not been determined.

At temperatures above 2200°C, the material deformed with either constant or decreasing load after reaching a maximum load at a fraction of the total elongation (see Fig. 3). The decreasing load was undoubtedly a result of the crack formation shown in Fig. 8. This reduced the effective area supporting the load beyond that reduction produced by the external reduction of area (see Fig. 3). The basis for this behavior will be discussed further under creep results.

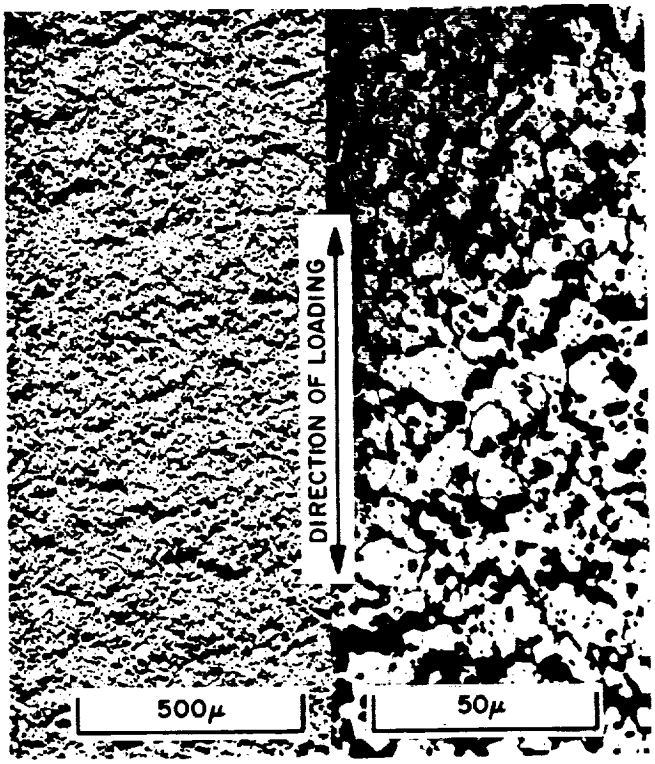

Fig. 8. Microstructure of hot-pressed zirconium carbide after 52% gauge length strain. Specimen was polished in left photo and polished and etched with 50 parts conc. HNO_3: 50 parts H_2O: 1 part HF in right photo

The stress vs. gauge length strain curves for zirconium carbide at temperatures above 2200°C, although exhibiting low ultimate stress, still represented considerable energy for fracture. The result in Fig. 3 exhibits approximately 410 in-lb/in^3 for fracture while that in Fig. 4 is approximately 99 in-lb/in^3. The energy for fracture for these tests is shown in Fig. 9. From these results, a marked increase in energy for fracture, apparently a result of increased ductility, is evident above 2000°C.

B. Creep Program

The creep data were obtained on the same type of system used for tension work with the substitution of a

Table 3. Tensile properties of hot-pressed zirconium carbide

Specimen	Heated at 2150°C 1 hr	Test temperature °C	Strain rate $\mathrm{sec}^{-1} \times 10^{-6}$	Ultimate tensile stress kpsi	Total recorded strain, %	Reduction in area %	Decrease in density[a] %
9	No	20	5.1	>30.[b]	0.0	0.0	0.00
1	No	1600	6.95	10.55	0.82	0.0	1.39
5	Yes	1600	6.95	10.58	1.16	−1.	0.86
52[c]	No	1600	6.95	13.09	1.4	0.0	0.37
25	Yes	1600	83.5	16.00	1.41	−1.	0.91
40	Yes	1600	500.	11.78	1.09	0.0	1.15
2	No	2000	6.95	2.38	4.45	3.0	0.0
36	Yes	2000	6.95	4.496	2.73	0.71	0.52
12	Yes	2000	31.2	4.28	0.55	1.4	0.25
33	Yes	2000	500.	6.94	1.07	0.69	0.12
3	No	2200	6.95	2.48	8.50	0.92	2.0
6	Yes	2400	6.95	0.82	>59.4[d]	>21.7	3.84
51[c]	No	2400	6.95	0.85	46.2	18.0	3.13
13	Yes	2400	31.2	2.20	52.5	19.4	3.07
39	Yes	2400	500.	7.35	4.95	0.67	0.52
54[c]	No	2400	500.	11.04	3.25	0.1	0.83
8-A[e]	Yes	2600	6.95	0.03	—[e]	—[e]	—[e]
8-B[e]	Yes	2600	83.5	1.00	50.4	21.1	5.5
14	Yes	2600	500.	2.69	27.7	10.0	2.60

[a] Based on entire specimen.

[b] Specimen reached this value, then failed in subsequent test due to misalignment.

[c] Hot-pressed at JPL; others were vendor hot-pressed.

[d] Specimen did not fracture.

[e] Strain rate changed during test.

dead weight for the motor drive (Ref. 8); the same deformation measurement procedures and definitions were used. The results were plotted in the form of gauge length strain vs. time and of log gauge length strain vs. log time curves.

Any attempt to analyze the creep behavior of materials soon becomes involved in a choice of which of the many theories of creep is to be applied. Mere representation of the experimentally determined data by a mathematical relationship often does not yield any useful insight into the mechanism controlling it. In fact, data on many materials vastly different in structure may exhibit the same fundamental mathematical relationship. This investigation was designed to determine the creep properties of a particular carbide rather than to evaluate various theories of creep. So that these properties could most easily be related to those of other materials, the simplest form of creep expression, that of linear deformation vs. time, was chosen for the bulk of the analysis. To represent the plot by a simple mathematical expression, a linear region must exist within the creep curve. Such a region was found in almost all cases (see Fig. 10 for typical results); consequently, it was assumed that such a region of creep exists for this material.

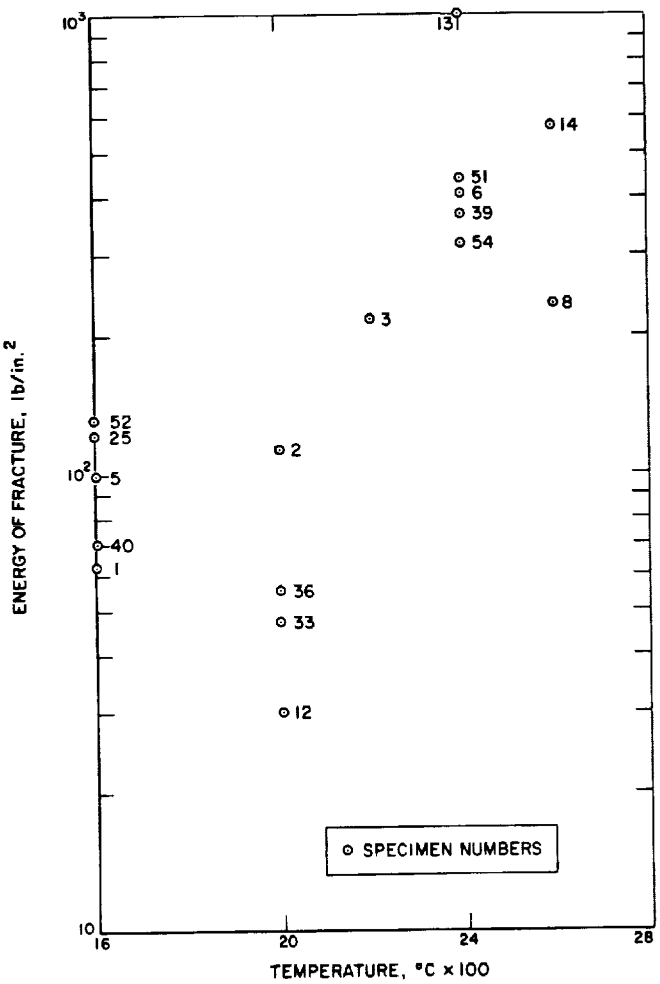

Fig. 9. Energy for fracture in hot-pressed zirconium carbide

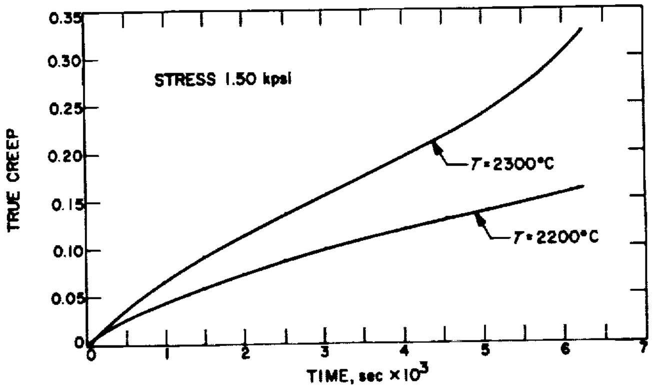

Fig. 10. True creep vs. time for hot-pressed zirconium carbide

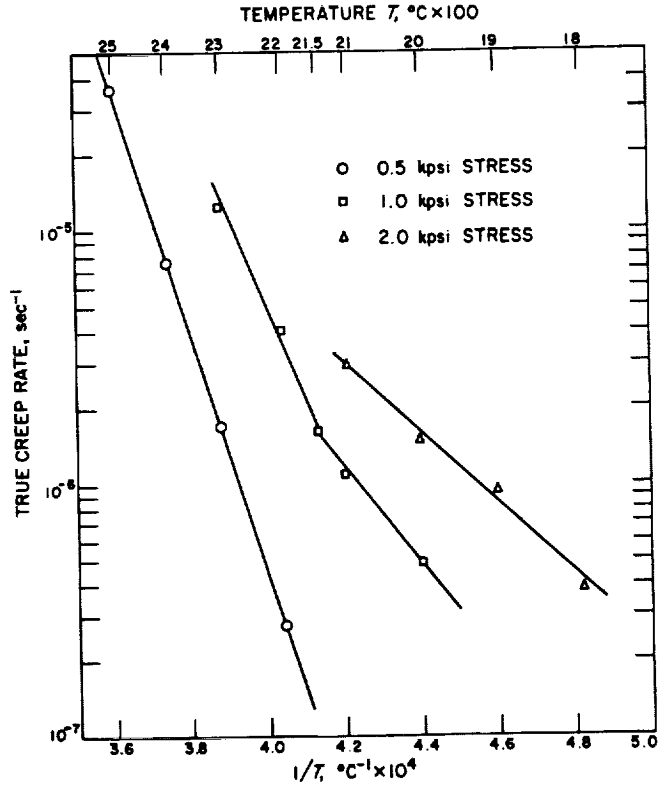

Fig. 11. True creep rate vs. reciprocal temperature for hot-pressed zirconium carbide

The creep rates determined from the linear portion of the deformation–time curves are listed in Table 4. These creep rates are true rates and have been corrected for changes in gauge length and stress level caused by the reduction in cross-sectional area. The reduced load-carrying ability caused by internal cracking was neglected. An Arrhenius plot of the data is shown in Fig. 11. Here it may be seen that a change in creep process was indicated at a temperature of approximately 2150°C. The creep rate below 2150°C exhibited an activation energy of approximately 75 kcal/mole, while above 2150°C the activation energy was approximately 200 kcal/mole. This higher level of activation energy might be evidence of a second process, that of grain boundary deformation, in addition to the unknown process occurring at lower temperatures. The microstructure of the material after large deformation showed no change in the appearance of the grains of the zirconium carbide accompanying the large deformation at the grain boundaries. Since the free carbon is located at these grain boundaries, it is proposed that the large deformation was a result of the effect of the impurities at the grain boundaries – in this case, primarily free carbon. It should be

Table 4. Linear true creep rate for zirconium carbide at various temperatures and stresses

Specimen	Temperature °C	Load kpsi	Linear creep rate[a] $\text{sec}^{-1} \times 10^{-5}$	Exponential creep equation parameters[b]	
				b	*n*
42	1800	2.00	0.0387	0.55	0.092
24	1800	4.50	0.410	0.33	0.13
22	1800	5.00	0.460	0.98	0.04
30-B	1900	2.00	0.0971	0.51	0.10
44	1900	2.00	0.102	0.54	0.072
45-A	2000	1.00	0.0481	0.74	0.033
18-A	2000	2.00	1.5	0.73	0.10
45-B	2100	1.00	0.110	0.74	0.034
18-B	2100	2.00	0.298	0.96	0.04
45-C	2150	1.00	0.163	0.72	0.040
31-A	2200	0.50	0.0278	0.65	0.17
34-A	2200	1.00	0.403	0.79	0.14
23-A	2200	1.50	1.80	0.77	0.54
31-B	2300	0.50	0.170	0.78	0.06
34-B	2300	1.00	1.28	1.04	0.10
23-B	2300	1.50	3.88	0.95	0.48
17	2400	0.50	0.75	0.75	0.70
32	2500	0.50	3.65	0.79	1.10
19	2600	0.37	35.8	1.10	0.25

[a] Slope of linear portion of true creep vs. time curve.

[b] Parameters of $\varepsilon = \varepsilon_0 + bt^n$.

noted that the activation energies of creep determined in this investigation for zirconium carbide agreed with the range of values reported for graphite (Ref. 9); however, the magnitude of the deformation in the zirconium carbide at any temperature was considerably greater than that reported for graphite at the corresponding temperature.

The role of the nitrogen and oxygen in the creep behavior of zirconium carbide was not clear. It has been reported[3] that oxygen has a marked effect on the lattice parameter of zirconium carbide, but whether such an effect of oxygen exists in the deformation mechanisms cannot be reported at this time. It was not possible to obtain material free of these impurities, nor were there adequate methods for determining the quantity of such impurities.

The clear differentiation between the effects of the carbon and the effects of the other impurities was not possible from these data. However, it is believed that the high creep rates and low strengths exhibited at temperatures above 2150°C are related primarily to the presence of carbon at the grain boundaries rather than other contaminants. The oxygen and nitrogen are soluble in the zirconium carbide lattice and thus would not contribute so strongly to grain boundary mobility. Such

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[3] Private communication with Melvin G. Bowman.

solubility is not known to exist for carbon beyond the stoichiometric amount (Ref. 10).

The apparent marked dependence of these results on the presence of impurities, in this case carbon, at the grain boundary could be verified by studying materials without this impurity. Toward this end, some samples of zirconium carbide were hot-pressed at JPL under conditions designed to prevent the solution of nitrogen and the precipitation of carbon. Although this was accomplished, the improved specimens still contained approximately 0.8% free carbon, this amount having been present in the starting material. Tests were conducted on material of this composition, and the results are shown in Fig. 6. A small increase in strength of questionable significance is evident. Reduction of the free carbon to far lower amounts would appear to be necessary. Specimens exhibiting no free carbon have not yet been obtained for testing.

The effect of stress level on linear creep rate is shown in Fig. 12. This creep rate was found to vary with approximately the third power of the stress, and no significant change in the power term seems to occur at 2150°C. However, a vast number of materials exhibit stress dependence of creep of approximately this magnitude, and it may well be that the creep mechanisms existing both above and below 2150°C have approximately this same dependency.

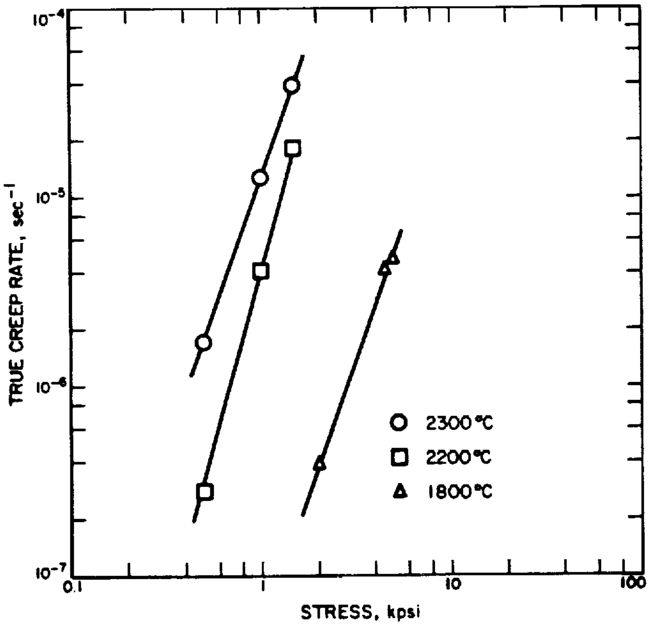

Fig. 12. True creep rate vs. stress for hot-pressed zirconium carbide

An attempt was made to apply an exponential creep equation of the form

$$\varepsilon = \varepsilon_0 + b\,t^n$$

where

ε = total strain

ε_0 = elastic strain

t = time

and

b, n = constants

Some sample plots are shown in Fig. 13, and the values obtained for the parameters of this equation are summarized in Table 4. In all cases, ε_0 was approximately zero. However, no correlation of the other parameters of the equation with conditions in the test could be made.

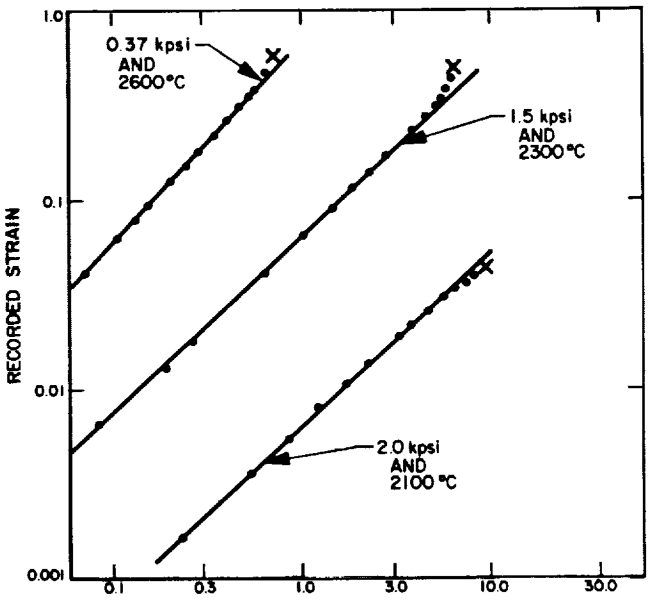

Fig. 13. Recorded strain vs. time for hot-pressed zirconium carbide

C. Modulus of Elasticity

The strain sensitivity of the equipment used for these tension and creep studies was not sufficiently great to permit measurements of modulus of elasticity. However, dynamic techniques were used for measurements at room temperature. The data were obtained using Magnetest Elastomat Type FM-500. The specimen was supported at the nodes by wires, and the excitation and detection of response was by means of wires touching the end of the specimen. Modulus-of-elasticity values obtained were 52.0 ± 0.2 × 10^6 psi for the zirconium carbide in the as-received condition. For material that had been heat-treated for 1 hr at 2150°C in a carbonaceous atmosphere furnace, the value was 51.2 ± 0.2 × 10^6 psi. These values were the averages of results for transverse and longitudinal modes of vibration and were corrected for specimen shapes.

D. Coefficient of Thermal Expansion

Measurements of the coefficient of thermal expansion were made on zirconium carbide from room temperature to 2800°C. Measurements from room temperature to 1000°C were made in an automatic recording fused-silica-tube dilatometer under argon. Measurements from 1000 to 2800°C were made by observing the displacement of the ends of the specimens by means of a filar telemicroscope. The high-temperature tests were conducted in a carbonaceous argon atmosphere. These results indicated no unusual behavior for thermal expansion up to 2400°C; however, at this temperature, scatter in the data became unreasonably large, and so the data are not reported. Whether this scatter was a result of some phenomena in the material or merely an unidentified contribution of the experimental setup is not known. The data are shown in Fig. 14.

During these determinations of thermal expansion, a peculiar phenomenon was noted at about 2750°C: in three independent tests, the zirconium carbide specimen under study underwent catastrophic fracture, causing the specimen to fly into several small pieces. It is believed that this phenomenon was a result of the combination of the oxygen impurity with either free carbon or carbon from the carbide lattice to form carbon monoxide. The temperature at which this occurred (2750°C) is reported to be the eutectic temperature for zirconium carbide–carbon.[4] It would thus seem that the oxygen reacted with the eutectic melt; however, no indication of melting was noted.

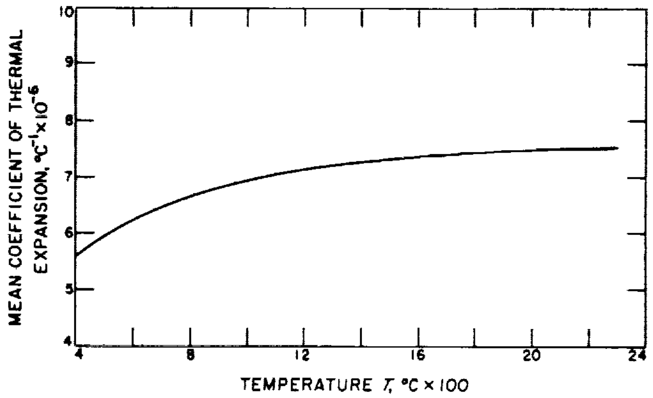

Fig. 14. Mean coefficient of thermal expansion from 25°C to the temperature indicated for zirconium carbide hot-pressed by vendor and heat-treated to 2150°C in carbonaceous argon

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[4] Private communication with Melvin G. Bowman.

IV. CONCLUSIONS

From the data presented here it is proposed that the mechanical properties of zirconium carbide at high temperatures are controlled by the presence of impurities. This, of course, is quite common in materials. These results re-emphasize the necessity for complete characterization of a material before representation of its properties becomes meaningful. For the zirconium carbide used in this study, the principal contaminant appeared to be free carbon; however, the possibility that the presence of nitrogen and oxygen severely affected the mechanical properties measured cannot be overlooked.

Because the properties under study appear to depend so markedly on the impurities, additional analysis of this material would not seem valuable. The engineering data obtained are useful only for material of this particular level of impurity, while fundamental data require better control and knowledge of the qualitative and quantitative impurity level. The data that were obtained showed ultimate tensile strengths as low as 100 psi at 2600°C. Up to 2000°C, strength remains at least 2500 psi. Gauge length elongation ranged from 1% at 1600°C to 50% at 2600°C. The appearance of such large elongation in this material is apparently a new finding. The ultimate tensile strength increased quite rapidly with strain rate at temperatures above 2000°C, whereas strain rate had only slight effect below 2000°C.

The activation energy for creep in this hot-pressed zirconium carbide was approximately 75 kcal/mole below 2150°C and 200 kcal/mole above 2150°C. It is proposed that the higher value is related to the presence of impurities, principally free carbon, at the grain boundaries. The creep rate was proportional to approximately the third power of the applied stress.

Dynamic modulus of elasticity at room temperature was found to be $52.0 \pm 0.2 \times 10^6$ psi for as-received zirconium carbide and $51.2 \pm 0.6 \times 10^6$ psi for zirconium carbide that had been heated for 1 hr at 2150°C in a carbonaceous argon atmosphere furnace. The mean coefficient of thermal expansion was found to vary from 5.6×10^{-6} °C^{-1} (for 25 to 400°C) to 7.6×10^{-6} °C^{-1} (for 25 to 2300°F).

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