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Contract No. NASr-65(09)

Gentlemen:

I. INTRODUCTION

This program is concerned with the fabrication of metal carbide-graphite composites by hot pressing at temperatures up to 3200°C, and determination of physical and mechanical properties of these materials. Earlier studies on this project[1,2] have shown that dense, high-strength bodies could be produced by additions of as little as 6 vol% of the carbides of the Group IVA, VA or VIA metals. The strong bonding is obtained through solid and/or liquid (eutectic) diffusion in addition to plastic flow under hot pressing conditions. At a metal level of 50 wt% or higher, all of the carbide-graphite systems studied exhibit room-temperature flexural strengths of over 10,000 psi, and these strength levels persist or increase at 2000°C. Plastic behavior to varying extents are displayed for different compositions at 2500°C.

The greatest potential for high-temperature use has been shown by composites incorporating TaC or NbC. The purpose of this year's program is to fully characterize the properties of various compositions in these systems at temperatures up to 3000°C. Other systems which are of interest as potential high-

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temperature materials are ZrC-C and HfC-C. These compositions are only slightly less refractory than TaC-C or NbC-C and may offer certain advantages. Compositions incorporating ZrC have exhibited strength-to-weight ratios superior to those for TaC-C and NbC-C. HfC-C samples have shown an increase in strength at 2500°C over that at 2000°C; all of the other metal carbide-graphite systems which have been evaluated show maximum strength at about 2000°C. The molybdenum carbide-graphite system is also being investigated to determine the mechanism by which strong orientation of graphite is obtained through formation and migration of the Mo_2C eutectic.

During the present period, property investigations have been conducted on TaC-C and NbC-C compositions of 50 to 90 wt% metal. Flexural tests at temperatures up to 2800°C and compressive deformation studies at 2700°C were performed. Thermal expansion has been measured in the range of room temperature to 2300°C. In addition, evaluation of electrical properties has been continued. Measurements were made to determine if the previously observed linear relationship between electrical conductivity and flexural strength for graphite matrix composites also applied to materials of high metal carbide content.

II. DISCUSSION

The initial phase of this year's program has been devoted to a continued effort of characterization of the TaC-C and NbC-C systems. The compositional range under investigation is from 50 to 85 wt% Nb and from 65 to 90 wt% Ta. These ranges include both graphite matrix and carbide matrix composites, up to the eutectic compositions (81.3 wt% for Nb and 90.6 wt% for Ta). In order to simplify compositional comparisons with the data of other investigators presented as weight percent of the carbide, a plot of wt% metal vs. wt% metal carbide appears in Figure 1. Also presented in the same graph are theoretical densities and volume percent carbide.

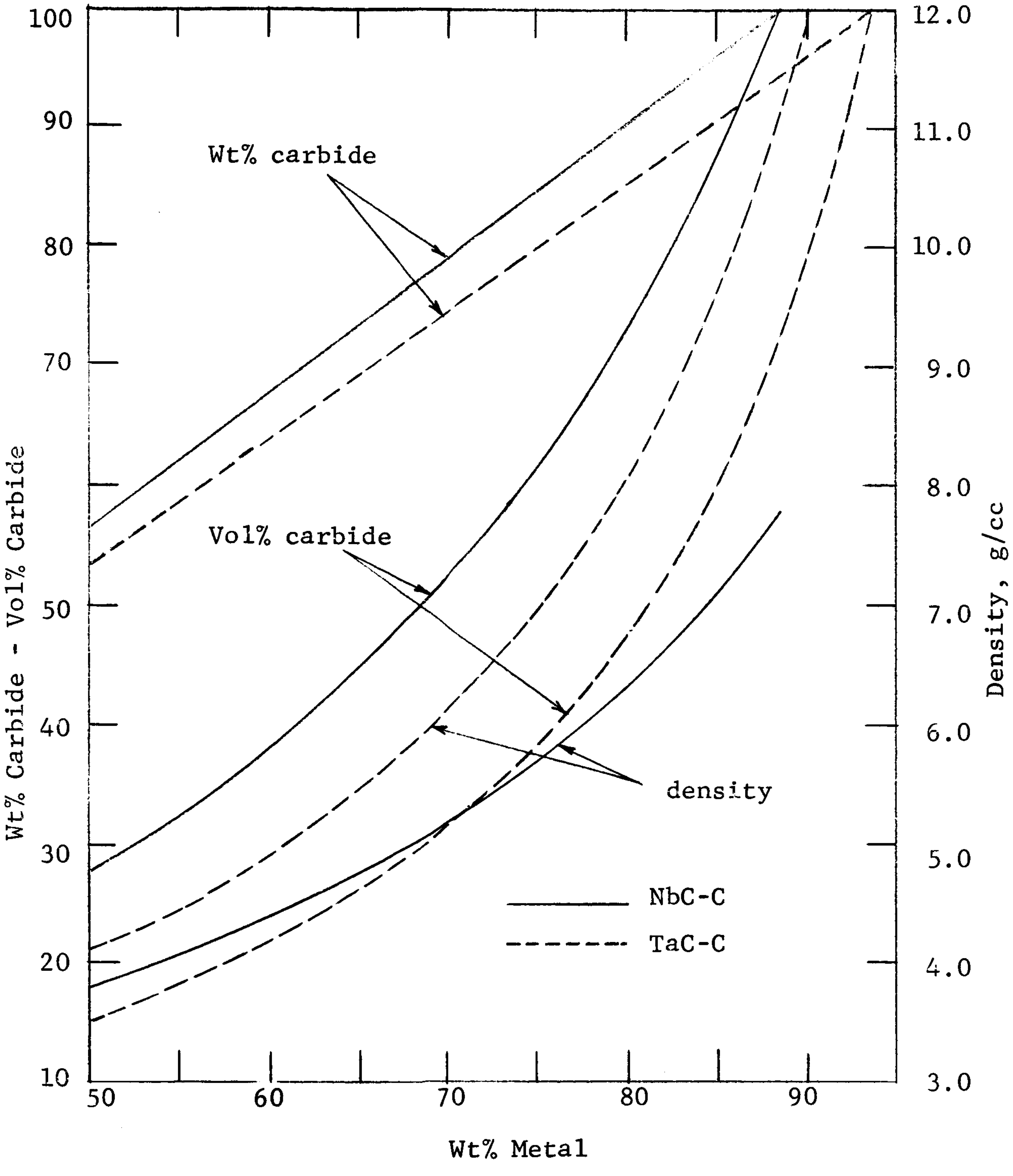


Fig. 1 - WT% CARBIDE, VOL% CARBIDE AND DENSITY AS FUNCTIONS OF WT% METAL

A. Compositional Studies

NbC-C - Earlier work[2] had shown that, for 50 wt% Nb compositions, use of higher processing temperature (≥3100°C) resulted in stronger composites. However, with compositions of high carbide content (greater than 70 vol%), fabrication at about 3200°C yielded poorly bonded composites having long needles of graphite in a eutectic structure. Lowering of the processing temperature resulted in dense, strong carbide matrix composites.

In the present work, a series of low metal content (less than 50 vol% carbide) compositions were processed at 3150°C in an attempt to exploit more rapid diffusion, and hence bonding, afforded by higher temperatures. It was felt that since liquid (eutectic) formation would be in relatively isolated islands, gross melting and loss of material would not occur. Evaluation of these materials (designated C50 Nb, 60 Nb, and C60 Nb; see Table I) revealed a heterogeneity in density. This lack of uniformity is caused by differences in carbide content from one portion of the billet to another. As illustrated in Figure 2, this effect is in the form of a cone which is visible to the eye due to different light-reflecting characteristics.

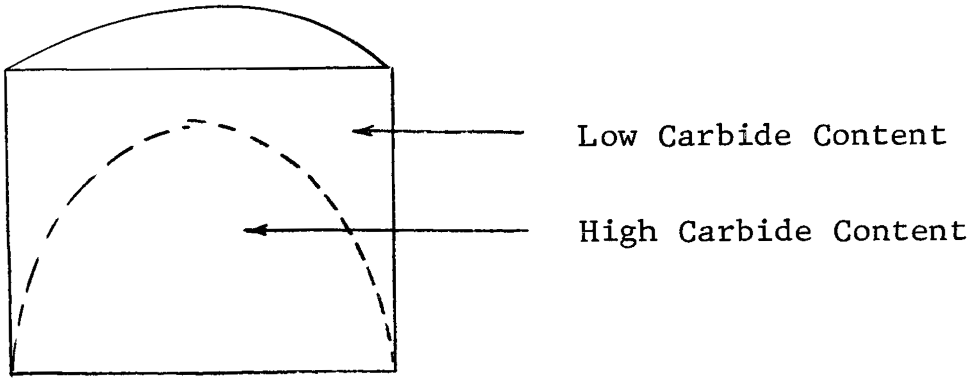


Fig 2 - CONING EFFECT IN NbC-C COMPOSITES REFLECTING DIFFERENCES IN CARBIDE CONTENT

Table I

FABRICATION DETAILS OF METAL CARBIDE-GRAPHITE COMPOSITES

Compositional Designation	Metal Additive		Vol% Carbide	Pressing Temp., °C	Density g/cc	% Theoretical Density
	Form	Wt%				
C 50 Nb	NbC	50	27	3150	*	
60 Nb	Nb	60	37	3150	*	
C 60 Nb	NbC	60	37	3150	*	
90 Ta-A	TaC	90	79	3200	11.79	99.2
80 Zr	ZrC	80	77	2800	5.60	100

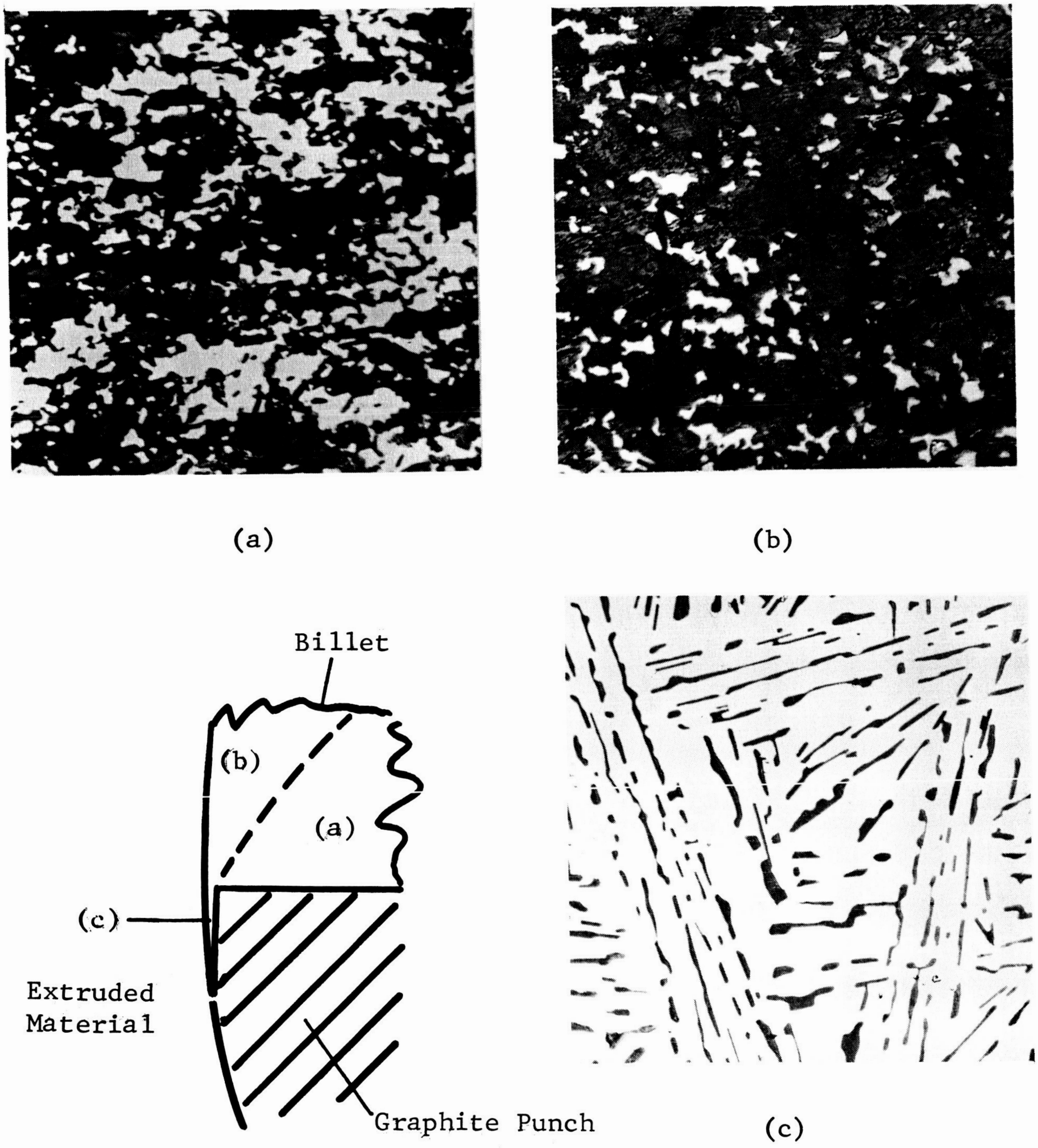
* Heterogeneous body. Quantitative analysis for metal content to be performed for determining percent theoretical density.

The cone contains greater amounts of carbide, and the periphery has lesser amounts. Photomicrographs of these two areas for 60 Nb appear in Figure 3. Also shown is a eutectic structure which existed in the material extruded around the punch during hot pressing, indicating that the eutectic temperature, 3250°C, had been attained.

It is felt that this phenomenon is due to a combination of extrusion around the top punch and reaction with the mold wall of a mobile eutectic phase. The reason the cone has its base at the bottom graphite punch may be due to differences in pressure at the top and bottom punches. Although the system is designed so that the sample is pressed from both ends, the pressure at the bottom may be distributed in part to the carbon black insulation under the bottom of the mold. Thus the carbide-graphite particles toward the top of the charge may be in more intimate contact and more susceptible to eutectic formation.

Recent experiments to eliminate this coning effect by using lower processing temperatures have yielded composites of uniform density. Tests are being conducted to determine if the lower temperature may have had an adverse effect on bonding and strength.

Despite the heterogeneity shown by these materials, variations in flexural strength between "cone" and "non-cone" samples were surprisingly small, being on the order of 10 to 15%. Table II contains the strength at various temperatures for these compositions. All of these low NbC-C composites exhibited large plastic deformation at 2800°C. The 2000°C strengths determined for 60 Nb and C60 Nb appear somewhat low. Although sampling for tests at the various temperatures were made so as to minimize variations in densities and carbide content, the number of specimens tested (3 at each temperature) may not have been adequate considering the heterogeneity. A greater population of data will be gathered to examine this anomaly.



(a) (b)

(c)

Fig. 3 - MICROSTRUCTURE OF 60 Nb COMPOSITE SHOWING HETEROGENEITY IN CARBIDE CONTENT AND FORMATION OF NbC-C EUTECTIC (320x)

Such differences in carbide content in a single billet have also been observed in other niobium compositions when the fabrication temperature was raised above 3200°C. These experiments show that diffusion to produce improved bonding is enhanced by higher temperatures. However, care must be taken to avoid loss of material through extrusion and reaction with the mold in order to obtain a homogeneous system.

TaC-C - The 90 wt% metal level in the TaC-C system is equivalent to 79 vol% TaC. As the data in Table II for 90 Ta-A show anisotropy (W/G:A/G flexural strength ratio of 1.5) still exists at even this high a carbide content. However, this is considerably more isotropic than lower carbide content materials such as 65 wt% Ta (ratio of 5.6) or 82.5 wt% Ta (ratio of 2.6). Microstructural examination of the with-grain and across-grain directions (Figure 4) shows clearly the directional nature of this composition. A trend toward isotropic behavior in flexure tests at higher temperatures is also observed. The W/G:A/G ratios were 1.1 at 2000°C and 2500°C and 1.3 at 2800°C. Such behavior had previously been observed[2] for other compositions in the NbC-C system as well as the TaC-C. This may be due to greater stress relief at higher temperatures in the A/G direction than in the W/G direction.

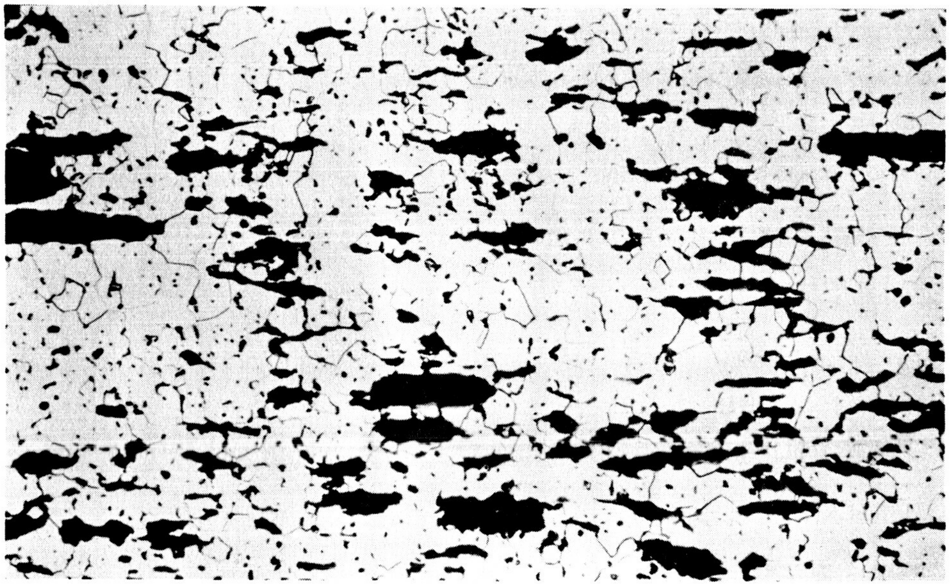
Very high flexural strengths are exhibited by this material at temperatures up to 2800°C. Plastic deformation prior to failure was very slight at 2500°C but was more pronounced at 2800°C. In comparison, deformation occurring for 80 wt% (73 vol%) or 85 wt% (87 vol%) Nb composites at 2800°C did not permit stressing of these materials to failure.

ZrC-C - A hypereutectic composition of ZrC-C was processed at 2800°C (see 80 Zr in Table I). The strength levels of this composition (see Table II) were considerably higher than those for a previously studied eutectic (80.7 wt%) composition, particularly at room temperature (25,000 vs. 17,000 psi). This may be due to greater diffusion and densification in the present

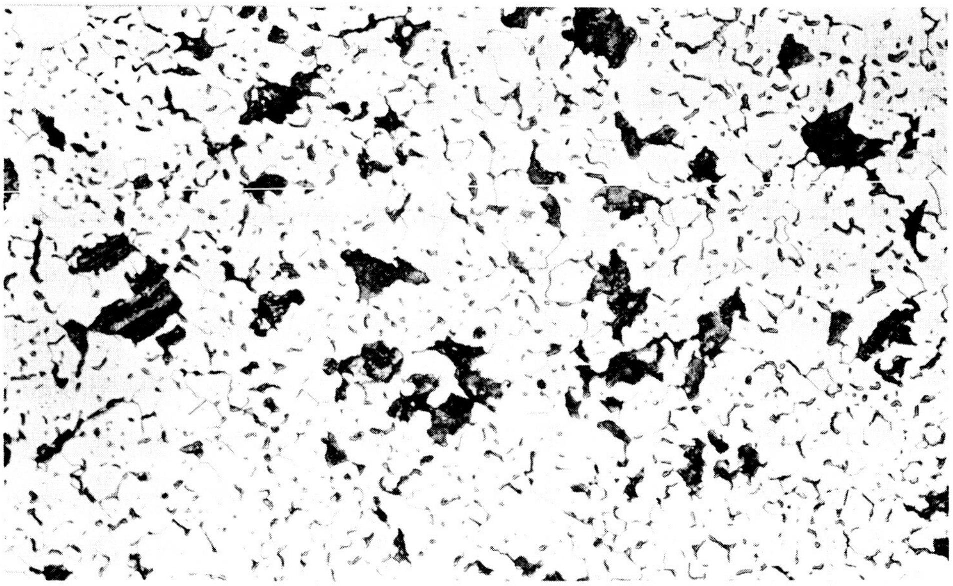
Table II

FLEXURAL STRENGTHS OF METAL CARBIDE-GRAPHITE COMPOSITES

Compositional Designation	Grain Direction		Flexural Strength, psi			Flexural Modulus, x 10^6 psi
		R.T.	2000°C	2500°C	2800°C	
C 50 Nb	W/G	14,960	17,280	14,470	Creep	5.16
	A/G	3590	4230	3300	Creep	1.03
60 Nb	W/G	12,800	13,550	16,520	Creep	5.50
	A/G	3350	5530	4660	Creep	1.42
C 60 Nb	W/G	17,090	15,310	15,430	Creep	8.14
	A/G	5080	5510	5530	Creep	1.90
90 Ta-A	W/G	25,560	32,000	25,450	20,060	34.8
	A/G	16,580	28,000	23,000	15,070	15.2
80 Zr	W/G	25,270	24,480	13,580	Creep	26.1
	A/G	16,820	11,610	9090	Creep	20.2



Perpendicular to Pressing Direction



Parallel to Pressing Direction

Fig. 4 - MICROSTRUCTURE OF 90 Ta-A COMPOSITE SHOWING ANISOTROPY IN GRAIN ORIENTATION (320x, ETCHED)

material resulting from a slightly longer (10 min) heat treatment at 2800°C. However, this material shows a large dropoff in strength at 2500°C which is accompanied by considerable plastic deformation, paralleling the high-temperature behavior of 80.7 Zr. As is the case for 90 Ta, anisotropy (ratio of 1.5) is evident from the strength data despite the carbide being the matrix. The monocarbides of the Groups IVA and VA metals are cubic and may be expected to behave in an isotropic manner. Apparently the presence of even small amounts of graphite, which is an anisotropic material, and/or grain directionality introduced by the uniaxial hot pressing method is sufficient to produce some anisotropy.

B. Thermal Expansion

In the continuing investigations of high-temperature properties, thermal expansion behavior of compositions incorporating TaC or NbC was measured. An optical method was used in which the sample was heated in a graphite tube furnace and expansion monitored visually by sighting on the ends of the sample using Gaertner optical micrometers. Each sample was taken through the heating (to 2300°C) and cooling cycle twice. Sample dimensions were remeasured after removal from the furnace.

Table III contains coefficient of thermal expansion (CTE) values in both grain orientations for a range of graphite-matrix to carbide-matrix compositions in both the TaC-C and NbC-C systems. Compositions in which graphite is the matrix (C 50 Nb and 62.4 Ta-A) exhibit strong anisotropy, not unlike that for ZT (hot pressed) graphite. The CTE values are somewhat higher than those normally seen for ZT, reflecting the influence of the higher thermal expansion carbide.

The trend toward isotropy with increasing carbide content is observed for both systems. Essentially nondirectional behavior is shown by 80 Nb-B and 90 Ta-A. CTE values for pure NbC and TaC in the range RT-2500°C have been reported as 8.75 and 6.81 (in/in/°C x 10^6).[3] The values obtained for our composites

Table III

THERMAL EXPANSION OF NbC-C AND TaC-C COMPOSITES
FROM ROOM TEMPERATURE TO 2300°C

Compositional Designation	Composition Wt% Metal	Composition Vol% Carbide	% Theoretical Density	Coefficient of Thermal Expansion, x10^6 in/in/°C W/G	Coefficient of Thermal Expansion, x10^6 in/in/°C A/G	Ratio A/G: W/G	Permanent Deformation* W/G	Permanent Deformation* A/G
C 50 Nb	50	27	92	4.78	14.22	2.97	-0.4	+0.8
70 Nb	71	54	97	7.12	8.27	1.16	-0.2	+0.1
80 Nb-B	80	73	97	7.49	6.97	0.93	0	0
65 Ta-A	65	26	97	3.29	12.17	3.70	-0.3	+0.6
82.5 Ta-A	83	54	97	6.38	7.98	1.25	-0.2	+0.1
90 Ta-A	90	80	98	7.05	7.32	1.05	-0.3	0

*Permanent changes in sample length due to testing,(%).

appear reasonable in the light of these values. Thermal expansion curves for 90 Ta-A in both directions are presented as Figures 5 and 6. Other investigators[3] have reported a change in slope for NbC in the 2100° to 2200°C region and for TaC at 1900°C. This transition was not observed with the composite materials.

Measurement of samples after testing revealed some dimensional changes which were more pronounced for the graphite-rich materials. Similar permanent deformations in CTE samples have been reported by other investigators.[4] As shown in Table III, these changes were an increase in the A/G direction and a decrease in the W/G direction.

These changes may be due to a relaxation of stresses imparted to the composite during hot pressing. In the cooling process after fabrication, different expansion behavior in the anisotropic graphite crystals build up residual stresses. On subsequent heat treatment such as the CTE measurement, relief of these stresses would occur. It is also possible that further grain orientation may occur upon heating of the sample, thus resulting in these changes. Still another possibility is a change in lattice spacing of the graphite through some limited interaction between the phases.

A study of the mechanism(s) involved to produce these dimensional changes will include x-ray studies, metallographic examination, and strength measurements. If permanent relief of stresses occurs in heat treatment, room-temperature strength of such composites may be expected to change after heating. X-ray techniques will reveal any changes in lattice parameters. It would appear from this preliminary work that heat treatment of composites after fabrication may be desirable for improving room-temperature properties and for obtaining dimensional stability at high temperatures.

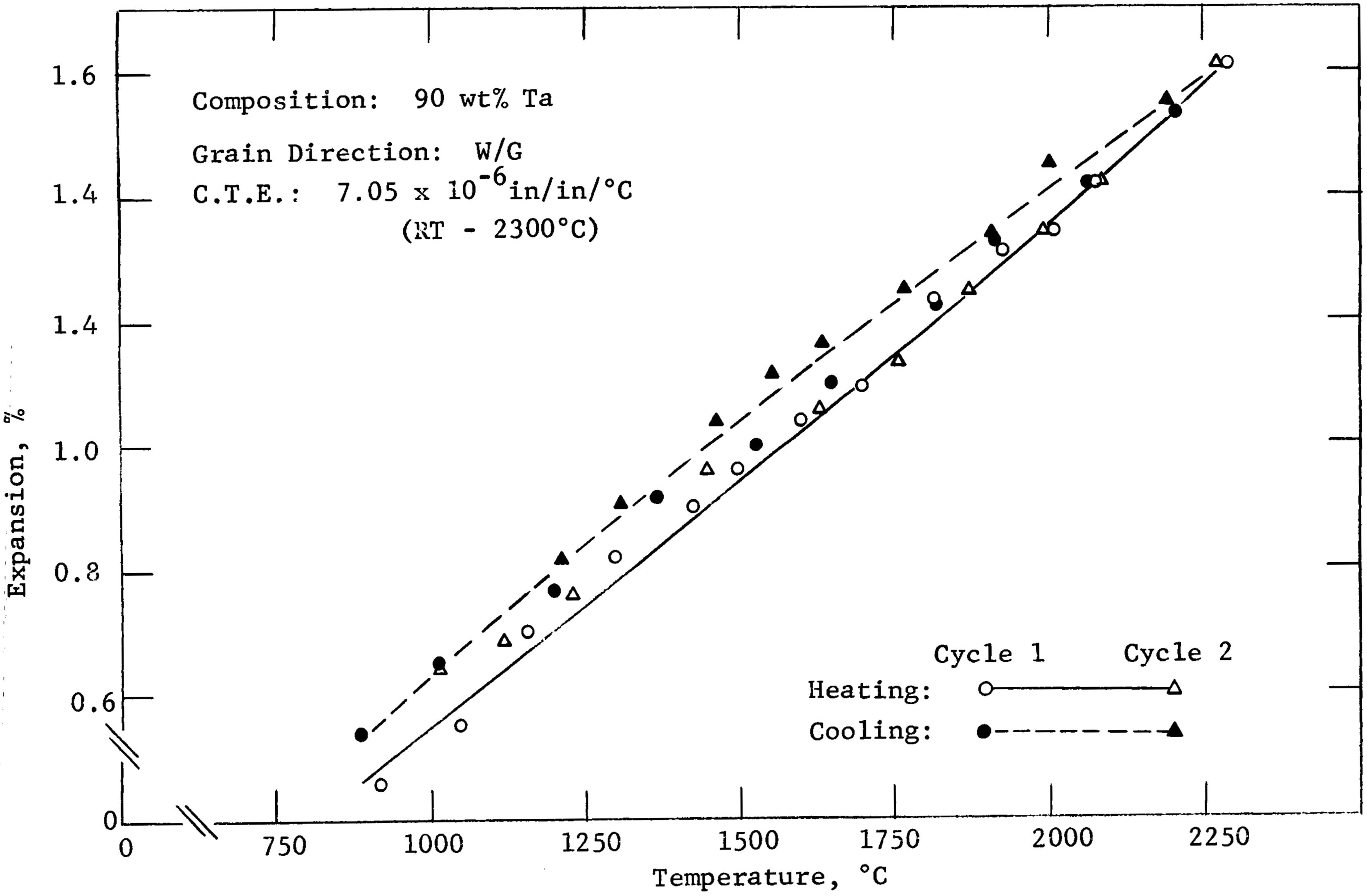


Fig. 5 - THERMAL EXPANSION OF TaC-C (90 WT% Ta, W/G)

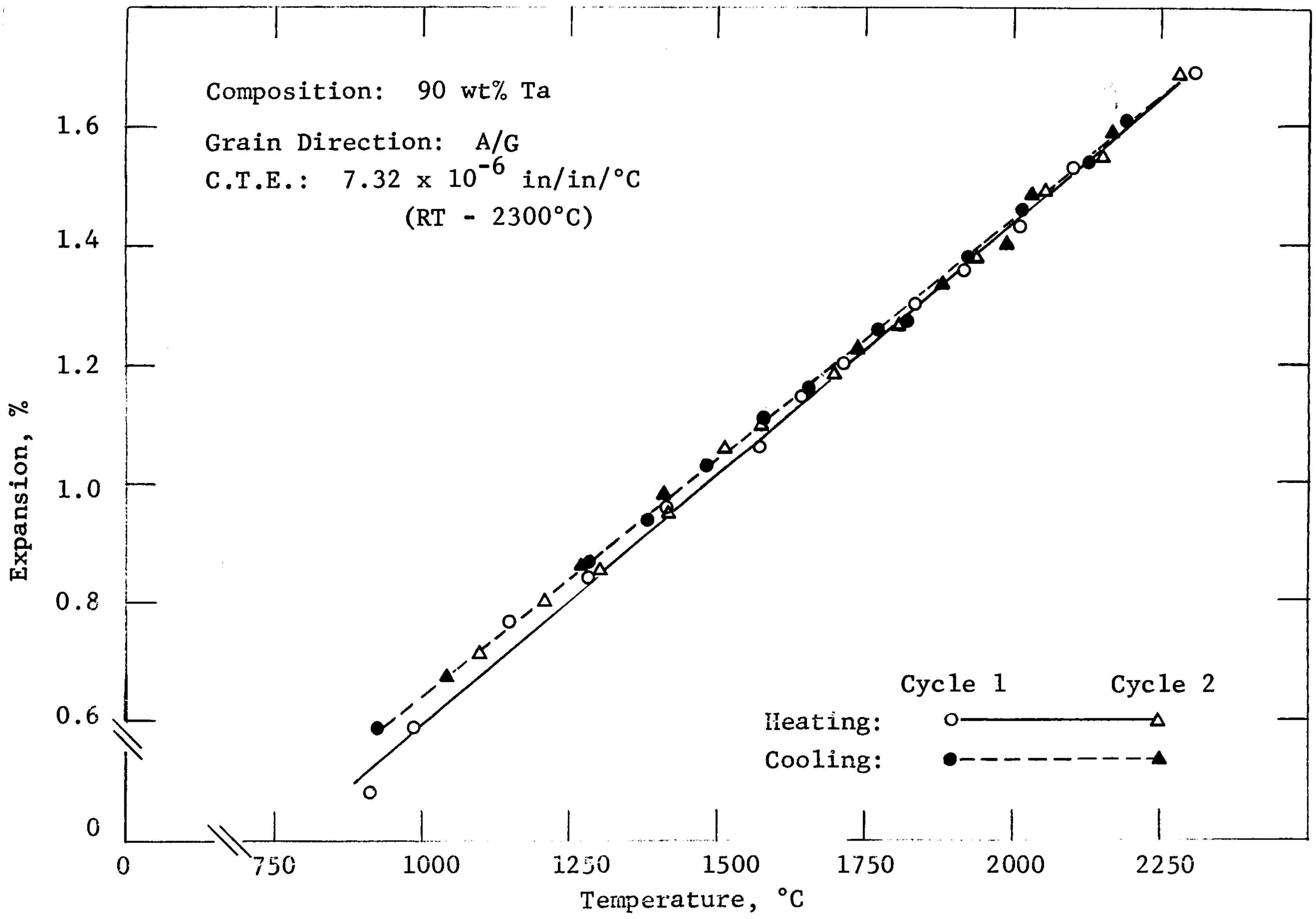


Fig. 6 - THERMAL EXPANSION OF TaC-C (90 WT% Ta, A/G)

C. Compressive Deformation

Additional information has been gathered this quarter on the resistance to high-temperature compressive deformation. Compositions in the NbC-C and TaC-C systems were subjected to test conditions of 2000 psi at 2700°C for 30 min. A ZrC-C composite was also included in these studies. The results are presented in Table IV.

In general, all of the materials tested, with the striking exception of 80.7 Zr, exhibited little change. Certain trends which are indicated by the present data are:

1. TaC-C composites are more resistant to deformation than are those in the NbC-C system. This is probably related to the respective eutectic temperatures of 3450° and 3250°C. Since the TaC-C system liquifies at a higher temperature, its mobility may be expected to be correspondingly smaller than that for NbC-C at the same temperature.
2. No correlation was observed between metal carbide content and compressive deformation. The test load of 2000 psi is probably too low to induce changes significant enough for our instrumentation. Under more severe conditions such as higher temperature and/or load, a trend may be observable.
3. Samples tested in the W/G direction showed greater lateral expansion than those tested in the A/G direction. As shown in Figure 7, these lateral deformations may be considered as A/G for the former, and W/G for the latter.

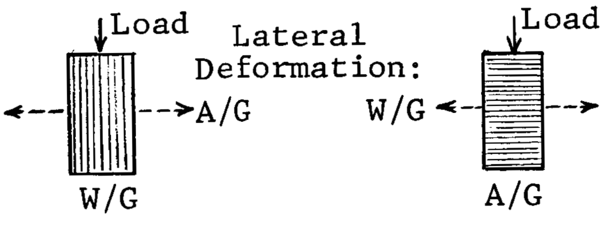


Fig. 7 - GRAIN ORIENTATION IN COMPRESSIVE DEFORMATION TEST SPECIMENS

Table IV

COMPRESSIVE DEFORMATION OF METAL CARBIDE-GRAPHITE COMPOSITES

(2700°C, 2000 psi, 30 min)

Compositional Designation	Composition, Wt% Metal	Sample No.	Density, g/cc	% Theoretical Density	Grain Direction	Δ Length %	Δ Diameter %
50 Nb-31	48Nb	C4-T	3.43	93	W/G	-0.9	+2.4
70 Nb	71Nb	4A1-T	5.12	97	W/G	-1.4	+1.3
C 70 Nb	70Nb	2C2-T	5.05	96	W/G	-2.2	+1.2
80 Nb-S	80Nb	T2X-T	6.00	95	W/G	-2.5	+0.9
81.3 Nb	81Nb	B1-T	6.77	97	W/G	-1.6	+0.8
84 Nb*	84Nb	T3-T	6.62	95	W/G	-0.3	0
65 Ta-A	65Ta	3A2-T	5.40	98	W/G	-0.4	+1.9
		2B-L	5.36	98	A/G	-0.5	+0.6
82.5 Ta-A	83Ta	3B2-T	8.64	98	W/G	-1.1	+1.3
		3A2-L	8.54	97	A/G	-0.1	+0.3
90 Ta	90Ta	3A3-T	11.64	97	W/G	-0.7	+0.4
80.7 Zr	80Zr	B3Y-T	5.56	99	W/G	-24.4	+39.5

* 10 minutes

In the CTE evaluations, permanent positive deformations were observed in the A/G direction and permanent negative deformations in the W/G direction. Thus under compressive load, lateral deformation in the A/G orientation may be expected to be greater than that in W/G deformation. These lateral changes appear to decrease with increasing carbide content. This also relates to the CTE measurements in which permanent deformations in testing decreased with increasing carbide content.

The gross deformation which occurred for the sample incorporating ZrC would seem to preclude its utility at these temperatures and loads. The clear superiority of tantalum and niobium systems as high-temperature materials is seen from the present experiments.

D. Electrical Resistivity

In previous work on this program[2] a linear relationship had been shown to hold between flexural strength and conductivity for low carbide content materials. This relationship appeared to hold for any particular system regardless of density or wt% metal. The linearity indicated that the strength was directly proportional to particle-to-particle contact of the carbide or eutectic which is the strength-providing phase.

In continuation of these studies, electrical resistivity measurements were conducted on a number of metal carbide-graphite composites, including carbide matrix materials. A change was made in the method in that 2 amps were passed through the sample instead of the previously used 10 milliamps. This was done so as to obtain a greater potential drop and, hence, assure greater accuracy in instrumental measurements. The potential drop was measured with a Keithley Electrometer.

Listed in Table V are the results obtained for NbC-C materials. A plot of these data along with previously obtained values appears in Figure 8. The values obtained for the lower carbide content composites appear to fit the curve fairly well.

Table V

ELECTRICAL RESISTIVITY OF METAL CARBIDE-GRAPHITE COMPOSITES

Compositional Designation	Composition Wt% Metal	Composition Vol% Carbide	% Theoretical Density	Grain Direction	ρ, microhm-cm	$(\rho)^{-1}\times10^3$	Flexural Strength, psi
C 50 Nb	50	27	92	W/G	115	8.7	14,960
				A/G	510	2.0	3590
60 Nb	60	38	92	W/G	105	9.5	12,800
				A/G	325	3.1	3350
C 60 Nb	60	38	92	W/G	100	10.0	17,090
				A/G	230	4.3	5080
70 Nb	71	54	97	W/G	77	13.0	17,050
80 Nb-B	80	73	97	W/G	47	21.2	13,750
				A/G	64	15.6	3980
C 3-80 Nb	80	73	98	W/G	225	4.4	3750
				W/G	85	11.8	8310
				A/G	260	3.8	4010
85 Nb	85	88	98	W/G	40	25.0	26,040

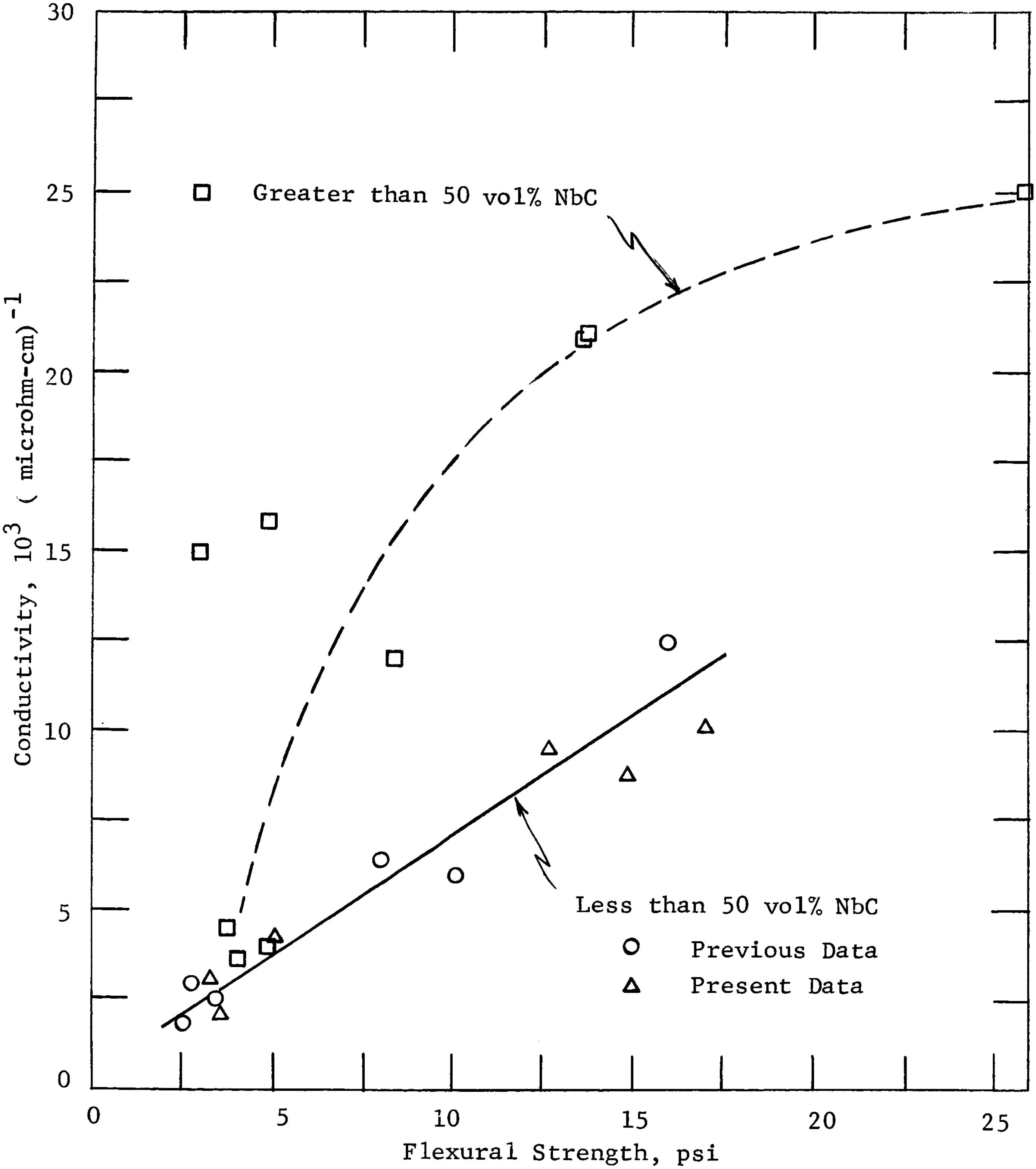


Fig. 8 - ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FLEXURAL STRENGTH FOR NbC-C COMPOSITES

However, in compositions where the carbide is the dominant phase, the values no longer obey the linearity shown by graphite matrix materials. This may be explained by the fact that we actually have two types of structure: one in which the dispersed phase is the carbide, and the second in which graphite is the dispersed phase. Thus different conductivity behavior may be expected as the matrix material changes. A more rigorous analysis of this relationship will be conducted with the accumulation of more data.

Interesting behavior was exhibited by C3-80 Nb samples. Despite a high carbide content (73 vol%), this particular pressing was quite poorly bonded. This was probably due to a low fabrication temperature (2950°C) and, hence, limited diffusion bonding. Although density variations were exceedingly small (about 1%), a variation in flexural strengths existed depending on location in the billet. This heterogeneity was reflected in the electrical measurements in that a weaker (3750 psi) sample had a resistivity of 225 microhm-cm, whereas a stronger (8310 psi) specimen displayed a much lower resistivity of 85 microhm-cm. The densities of these samples were 6.09 and 6.08 g/cc, respectively. Furthermore, probing of a longitudinal (A/G) sample from the same C3-80 Nb billet showed a range in resistivity, again reflecting the difference in bonding. Thus, it would appear that electrical measurement is a sensitive method of determining both degree of bonding and homogeneity. More experimentation and data gathering are necessary to sophisticate this method so as to obtain absolute numbers.

III. CONCLUSIONS AND FUTURE WORK

During this period, property determinations of carbide-graphite composites have included flexure strengths, high temperature compressive deformation, thermal expansion, and electrical resistivity. The most significant findings in the present work are as follows:

1. Heterogeneity in carbide content within a single billet can occur if the fabrication temperature is high enough

to cause extensive loss of material through extrusion and reaction with the mold. However, strength differences are limited (10-15%) despite density variations (caused by differing carbide contents) of as much as 30%.

2. In high carbide content composites such as 90 wt% Ta and 80 wt% Zr, the anisotropy ratio in flexural strength diminishes to 1.5. Graphite matrix composites in these systems can have ratios as high as 5 to 6. There appears to be a trend toward even more isotropic behavior for 90 Ta at high temperatures.

3. Anisotropy in thermal expansion behavior diminishes with increasing carbide content. At vol% levels of 73 for NbC and 80 for TaC, isotropic behavior may be expected since the carbide becomes the controlling structural factor. The absolute CTE values for these composites are similar to those for the pure carbides reported in the literature.

4. Resistance to compressive deformation at high temperatures is greater for the TaC-C as compared to the NbC-C system. There is no significant correlation between carbide content and compressive deformation under the test conditions to date.

5. The linearity between electrical conductivity and flexural strength observed for low carbide content (<50 vol%) has been shown to hold in additional tests. A different type of relationship appears to exist for carbide matrix materials in which graphite is the dispersed phase. Nevertheless, a definite direct correlation exists between electrical and mechanical properties, and this relationship may be exploited as a method for determining degree and homogeneity of bonding.

Future work will involve continued characterization of physical and mechanical properties in the TaC-C and NbC-C systems. Limited fabrication studies will be conducted to determine processing conditions for obtaining optimum properties in composites. The electrical measurement studies will be broadened to characterize behavior of carbide matrix composites.

IV. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

The following personnel have participated in this research program: S. A. Bortz, R. Baker, D. L. Berent, and J. L. Sievert. Data are contained in Logbook Nos. C16816, C16973, C16974, C16986, and C16989.

Respectfully submitted,
IIT RESEARCH INSTITUTE

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