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312/225-9630

January 30, 1967

Office of Research Grants and Contracts
Code BG
National Aeronautics and Space Administration
Washington, D.C. 20546

Subject: IITRI G6003-2
Quarterly Report No. 2
"Metal Carbide-Graphite Composites"
Contract No. NASr-65(09)

Gentlemen:

Nov. 1, 1966 - Jan 31, 1967

I. INTRODUCTION

This program is concerned with the fabrication of metal carbide-graphite composites by hot pressing at temperatures up to 3200°C, and the 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, using no binders, by additions of as little as six volume per cent of the carbides of the Group IVA, VA, or VIA metals. 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 10 volume per cent or higher, all of the carbide-graphite systems studied exhibit room-temperature flexural strengths of over 10,000 psi. At 2000°C these strength levels are retained or show an increase. At 2500°C, plastic behavior is displayed to varying degrees by different compositions. Composites incorporating TaC or NbC have been found to exhibit highest strengths and resistance to plastic deformation at high temperatures.

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-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. The strength-to-weight ratios of ZrC-C compositions are superior to those for TaC-C and NbC-C. Hafnium systems would be preferable to those of tantalum or niobium in a high-temperature oxygen environment since hafnia is much more refractory than Ta_2O_5 or Nb_2O_5. The molybdenum carbide-graphite system is also being investigated to determine the mechanism by which increased orientation of graphite is obtained through formation and migration of the Mo_2C-C eutectic.

During the present period, studies have been conducted within the TaC-C and NbC-C systems to determine the effect of raw materials and various fabrication parameters on properties. Composites have been prepared for tensile and compressive tests, and preliminary tensile data have been obtained. The relationship between electrical properties and strength has received additional study with the gathering of more data. The effect of heat treatment on composites subsequent to fabrication has been investigated. In addition, three billets in the NbC-C system and two in the TaC-C system have been fabricated for evaluation by LASL.

II. DISCUSSION

A. Compositional Studies

During this period work was continued on characterizing the NbC-C and TaC-C systems with respect to physical and mechanical properties and microstructure. The effect of variations in carbide content upon flexural and tensile strengths were determined. Some experimentation was also conducted on the effect of carbide particle size upon composite properties. Fabrication

parameter studies involved processing at different temperatures and maintaining such temperatures for periods of up to 1 hr. Mixing laws for multiphase materials were applied to the flexural strength data to evaluate the relationship between experimental and calculated strength for the composites.

1. NbC-C Composites

Effect of Processing Temperature on Properties - As reported in the first quarterly report,[3] processing of low metal carbide content compositions at an indicated temperature of 3150°C resulted in loss of material through extrusion and reaction with the mold. Composites displayed nonuniformity of density which was visually observed as a coning effect within the billet. The data in Table I show these variations in carbide content for compositions C-50Nb, 60Nb, and C-60Nb.

In order to eliminate such loss of material, processing of 50 wt% Nb composites were conducted at a lower (3000°C) temperature with a 1/2 hr soak (see 50Nb-C and 50Nb-E in Table I). It is well known that diffusion and sintering rates are affected by both temperature and time. Thus, with a lowering of the processing temperature, soaking at temperature was introduced as a compensatory method for obtaining high density and bonding. Previous work[2] involving temperature soaks was concerned with molybdenum compositions processed in the liquidus range of molybdenum carbide. Loss of molybdenum carbide due to extrusion and reaction with the mold occurred to varying degrees, depending on the processing conditions, and little or no improvement was observed in extent of bonding. The present studies with the NbC-C system are being conducted in the solidus range to minimize such metal loss.

In the case of materials processed at the lower temperatures for longer times, billets could be easily removed with little sticking to the plungers or the mold. In contrast, composites fabricated at 3150°C formed a tenacious bond with

Table I

FABRICATION DATA ON NbC-C COMPOSITES

Compositional Designation	Form of Metal Addition	Pressing Temp., °C	Wt% Nb As Mixed	Wt% Nb Actual	Vol% NbC	Density, g/cc	% Theoretical Density
C-50Nb	NbC	3150	50	32.7 (a)	14.5	2.88	94.1
				47.9 (b)	25.5	3.51	95.6
60Nb	Nb	3150	60	41.1 (a)	20.1	3.07	91.1
				57.1 (b)	34.5	4.01	96.2
C-60Nb	NbC	3150	60	52.5 (a)	29.7	3.75	96.2
				60.2 (b)	38.1	4.27	97.7
50Nb-C	Nb	3000 (c)	50	50.4	27.7	3.58	94.2
50Nb-E	Nb	3000 (c)	50	49.3	26.7	3.55	94.9
C-65Nb	NbC	2850 (d)	65	65.2	44.7	4.60	97.3
65Nb-A	Nb	2850 (d)	65	65.4	45.1	4.58	96.2
80Nb-C	Nb	3000	80	80.5	74.4	6.20	97.2
85Nb-A	Nb	3000	85	84.6	86.0	6.79	96.7

(a) Upper portion of billet

(b) Lower portion of billet

(c) 30 minute soak at temperature

(d) 1 hour soak at temperature

both the plungers and the mold. This behavior is depicted in Fig. 1; portions of the mold wall are shown bonded to the billet after removal.

Metal analysis data for 50Nb-C and 50Nb-E (Table I) indicate very little if any loss of metal. Densities were quite high and uniform throughout these two billets. However, the strengths (Table II: 9,500 and 11,300 psi) are significantly lower than those for an identical composition fabricated at 3100°C which exhibited strength of 14,500 psi (see 50Nb-31, Reference 2). A comparison of density values shows that densification was slightly greater for 50Nb-C and 50Nb-E (94%) than for 50Nb-31 (92%). Thus greater bonding which can occur at higher temperatures is responsible for the higher strengths observed previously for 50Nb-31.

Effect of Carbide Particle Size on Properties - Composition C-50Nb processed at 3150°C (Tables I and II) also displayed higher strengths than 50Nb-C and 50Nb-E. In addition to the bonding resulting from greater diffusion of solid and/or liquid eutectic at the higher processing temperature, the higher strength of C-50Nb may also be partially attributed to the carbide particle size. Microstructures of C-50Nb and 50Nb-C appear in Fig. 2. The more uniform distribution of the carbide phase realized by using a finer (3.6 μ Fisher average particle size) carbide source can be observed for C-50Nb. The use of coarser (9.8 μ Fisher average particle size) niobium metal as the carbide source results in poorer uniformity as seen for 50Nb-C. In the C-50Nb, a greater number of carbide sites which can act as crack stoppers are available. Also, more surface area is available for interfacial bonding between the carbide and graphite phase. Comparison of strength data between 60Nb and C-60Nb, and between 65Nb-A and C-65Nb also show the higher strengths realized by use of the finer particle size carbide source. Soaking studies will have to be repeated using similar particle size in order to obtain the actual soaking effect.

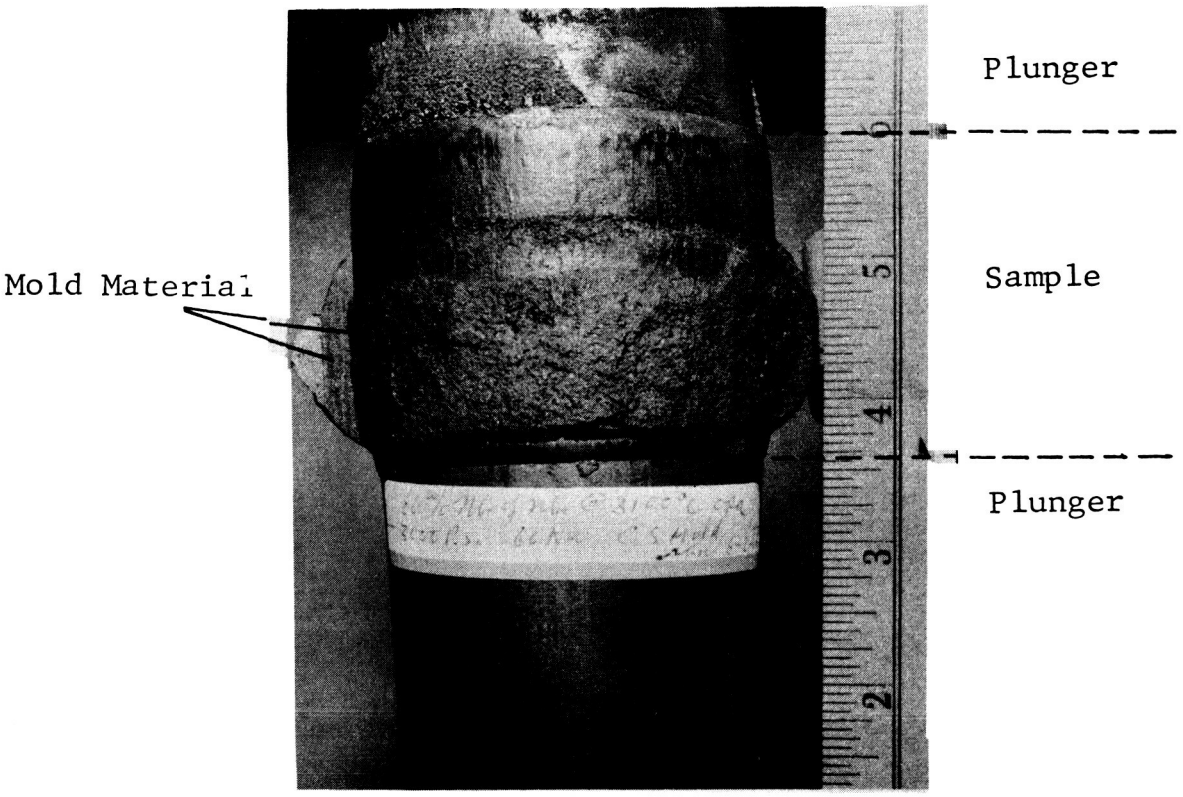


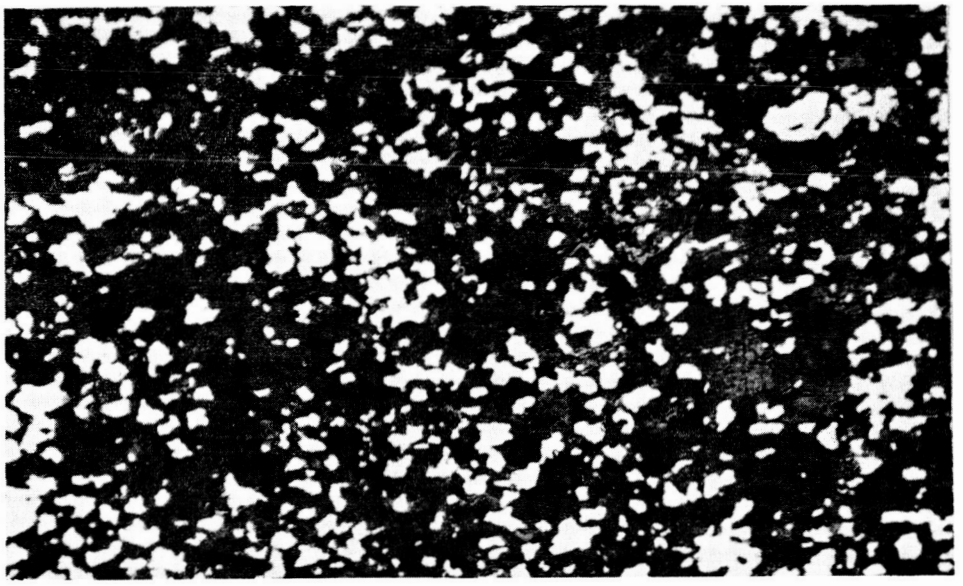
Fig. 1 - COMPOSITE C 60 Nb SHOWING MATERIAL EXTRUSION AND REACTION WITH MOLD

Table II

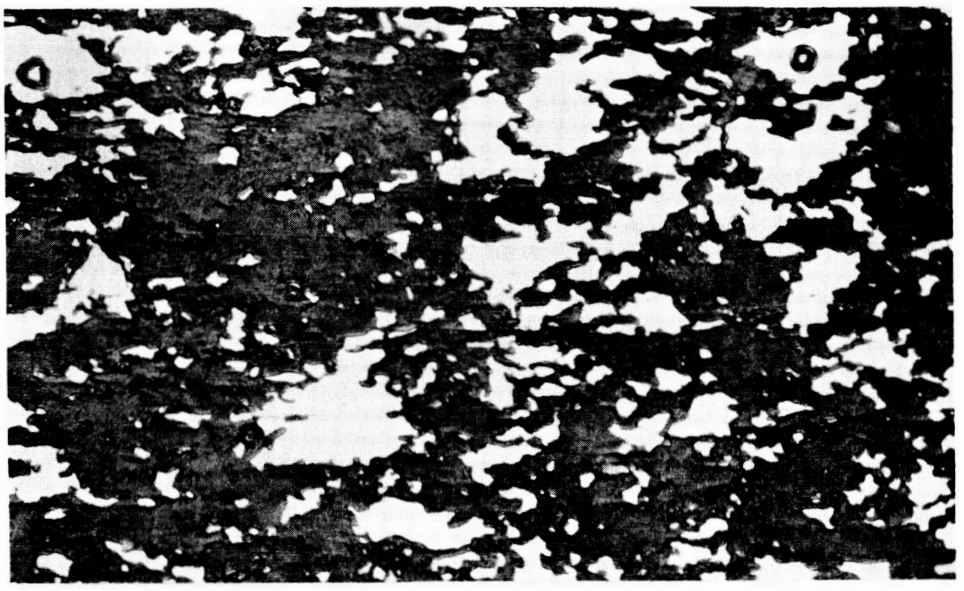
FLEXURAL DATA ON NbC-C COMPOSITES

Compositional Designation	Grain Direction	Flexural Strength, psi R.T	2000°C	2500°C	Flexural Modulus, x 10^6 psi
C-50Nb	W/G	14,960	17,280	14,470	5.16
	A/G	3,590	4,230	3,300	1.03
60Nb	W/G	12,800	13,550	16,520	5.50
	A/G	3,350	5,530	4,660	1.42
C-60Nb	W/G	17,090	15,310	15,430	8.14
	A/G	5,080	5,510	5,530	1.90
50Nb-C	W/G	9,490	10,090	11,030	4.27
	A/G	3,060	3,760	5,230	1.01
50Nb-E	W/G	11,340	11,350	10,070	3.74
	A/G	4,700	3,420	5,040	1.63
C-65Nb	W/G	15,810	6,450	7,010	8.71
	A/G	6,570	3,790	5,390	4.21
65Nb-A	W/G	12,690	10,960	10,800	7.45
	A/G	6,330	5,990	6,080	3.45
80Nb-C	W/G	16,960	20,770	15,010	
	A/G	9,820	15,120	11,540	
85Nb-A	W/G	25,380	>27,000	Creep	
	A/G	18,160	>24,000	Creep	

50 μ



C 50 Nb (3.6μ)



50 Nb-C (9.8μ)

Fig. 2 - MICROSTRUCTURE OF 50 WT% Nb COMPOSITES SHOWING EFFECT OF INCORPORATING CARBIDES OF DIFFERENT PARTICLE SIZE, (320x)

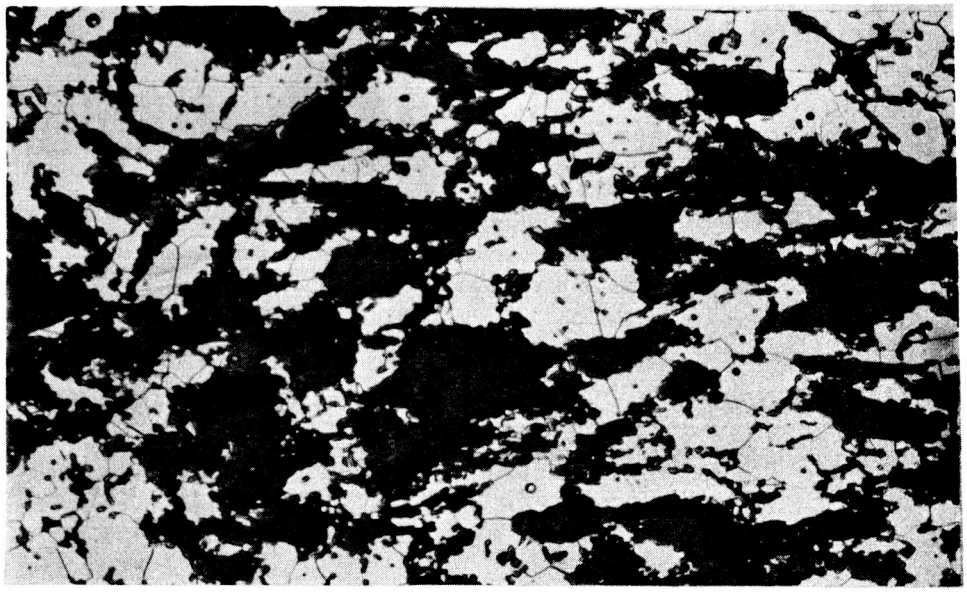
The 65 wt% Nb composites (65Nb-A and C-65Nb, Table I) were processed at 2850°C with a 1 hr soak. The beneficial effect of soaking at temperature during processing as a means of increasing diffusion bonding and sintering is observed in that previous processing of similar compositions[2] at 3000°C with no soak yielded composites having strengths about 35% lower (8,000 psi vs 12,700 psi). Microstructures of the present compositions appear in Fig. 3. The difference in carbide particle size is quite evident in these photomicrographs.

Effect of Processing Temperature on High Temperature Strength - All NbC-C composites to date have shown increases in strength at 2000°C. The strength data obtained in the high-temperature tests for the 65 wt% Nb composites, particularly C-65Nb, were surprisingly low, (6,500 psi at 2000°C vs 16,000 psi at room temperature). The recalibration of test equipment and the testing of additional samples have eliminated instrumental errors as possible causes of this anomaly. It would appear that some de-bonding effect occurs at the 2000°C and 2500°C test temperatures. As will be described in a later section on heat treatment, C-65Nb samples heated at 2500°C for 1 hr and cooled exhibited room-temperature strengths of about 17,000 psi, which is about the same as the values for unheated samples. Therefore, if a weakening effect does indeed occur due to temperature, it no longer exists when the sample is cooled to ambient conditions.

One of the experiments which will be conducted to explain this anomaly will be testing of heat-treated samples at the elevated (2000°C and 2500°C) temperatures. The microstructures of materials tested at these temperatures will be examined. Also, each composition will be fabricated again using the same conditions to determine if the lower processing temperature does indeed produce a composite having the strength-temperature relationship observed.

50 μ

C 65 Nb (3.6μ)



65 Nb-A (9.8μ)

Fig. 3 - MICROSTRUCTURE OF 65 WT% Nb COMPOSITES SHOWING EFFECT OF INCORPORATING CARBIDES OF DIFFERENT PARTICLE SIZE, (320x)

The present experiments with low metal content (less than 50 volume per cent) composites have confirmed the following to be desirable for obtaining composites having optimum properties:

(1) The use of a finer particle size NbC source

(2) Higher processing temperatures and/or soaking at temperature

The second item must of course take into account the detrimental effect of extrusion and reaction with the mold.

Effect of Carbide Content on Anisotropic Behavior - Composites in which NbC is the major phase have been pressed at 3000°C in preparation for sectioning into tensile and compressive test specimens. Two of these pressings (80Nb-C and 85Nb-A) are summarized in Tables I and II.

With the compositions having higher carbide contents, the present studies have involved characterization of across-grain properties. All samples showed an increase in strength at 2000°C and lower values at 2500°C. The susceptibility of 85Nb-A samples to plastic deformation at 2500°C tends to confirm the trend seen in compressive deformation studies[3]--i.e., a direct relationship between creep behavior and carbide content.

As shown in Table II, a trend toward non-directional properties is realized with increasing carbide content due to the dominating influence of the isotropic carbide. As is the case with TaC-C composites, less anisotropy is observed in high-temperature strength tests. For 80Nb-C (Table II), the ratios of W/G to A/G strength are 1.7, 1.4, and 1.3 at room temperature, 2000°C, and 2500°C, respectively. It would appear that greater stress relief occurs in the A/G direction than in the W/G direction at the higher temperatures. This is logical in that during processing, the applied stress is parallel to the A/G or c-axis direction so that higher stresses can be expected to exist in this direction.

Tensile Strength Measurements - Room-temperature tensile tests have been conducted with NbC-C composites containing 73 volume per cent NbC. A pin-type tension specimen is shown in Fig. 4.

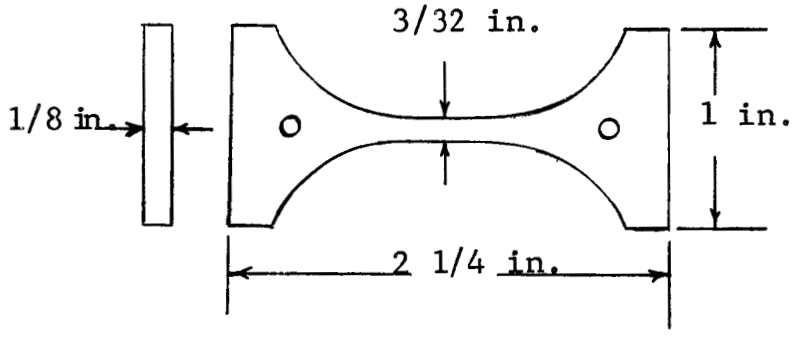


Fig. 4 - PIN-TYPE TENSION SPECIMEN

Modifications in configuration were necessary to obviate failures at the pins in early designs. Samples were machined by EDM; however, it has also been shown that standard methods of machining could be used. The determining factor has been that fabrication by electrical discharge is somewhat less expensive. No difference in strengths due to possible inducement of flaws by the two machining methods has been observed.

A tensile strength of 18,150 psi was determined for 80Nb-E in the W/G direction. Flexural strengths for this particular billet have not been determined. The flexural strengths of other 80 wt% Nb composites have generally been in the range of 17,000 to 19,000 psi. The ratio of flexural to tensile strength appears rather low (about 1) in comparison to that seen for other materials. Ratios of 1.4 to 2 are reported for graphite[4]; higher values of about 2 have been observed for carbides such as TiC and ZrC.[5] It may be that the present 80Nb-E is actually stronger than other 80 wt% Nb composites, and may exhibit a flexural strength of about 25,000 psi. Further

measurements will be made to see if the indicated tensile-flexural relationship is indeed as close to 1:1.

With the establishment of specimen dimensions and test procedure, work is now under way to prepare tensile samples of other compositions. Also, equipment for high-temperature sonic modulus and compression tests are now in final check-out.

2. TaC-C Composites

Effect of Carbide Particle Size on Properties of Low Carbide Content Composites - In addition to preparation of composites to be used for mechanical tests other than flexural, studies were conducted to investigate the effect of raw materials on properties. As detailed in Table III, two composites having about 27 volume per cent TaC (65Ta-B and M-65Ta-A) and a high carbide (M-90Ta, 80 volume per cent TaC) composite were evaluated. The compositions designated with the prefix M were fabricated using Ta metal as the carbide source and 65Ta-B incorporated the finer particle size TaC. From microscopic investigation, the average particle sizes were about 20 μ for the metal and about 5 μ for the carbide.

The data show that no metal loss occurred for any of the billets. The TaC-C eutectic temperature of 3450°C is much higher than the 3200°C processing temperature, and there is no formation of a highly mobile, reactive liquid phase as is the case for NbC-C. Each of the billets exhibited good uniformity in density, and high per cent theoretical densities were attained for 65Ta-B and M-90Ta.

Photomicrographs of the graphite matrix composites in Fig. 5 show the difference in carbide particle size. Carbide grain orientation and a somewhat porous graphite structure are evident in both compositions. A similar structure was seen for 65Ta-A which was reported upon in the Final Report for the previous year's work.[2]

Table III

FABRICATION DATA ON TaC-C COMPOSITES

Compositional Designation	Form of Metal Addition	Pressing Temp., °C	Wt% Ta		Vol% TaC	Density, g/cc	% Theoretical Density
			As Mixed	Actual			
65Ta-B	TaC	3200	65	65.6	26.6	5.32	96.6
M-65Ta-A	Ta	3200	65	65.6	26.6	5.12	92.8
M-90Ta	Ta	3200	90	90.4	80.6	11.73	96.9

Table IV

FLEXURAL DATA ON TaC-C COMPOSITES

Compositional Designation	Grain Direction	Flexural Strength, psi				Flexural Modulus, x 10^6 psi
		R.T.	2000°C	2500°C	2800°C	
65Ta-B	W/G	7,090	10,590	7,710	-----	4.52
	A/G	3,340	3,530	4,120	-----	1.35
M-65Ta-A	W/G	3,740	4,500	------	-----	2.10
	A/G	1,010	1,810	------	-----	0.45
M-90Ta	W/G	25,740	31,000	20,220	15,930	20.7
	A/G	14,260	23,500	15,640	10,900	17.3

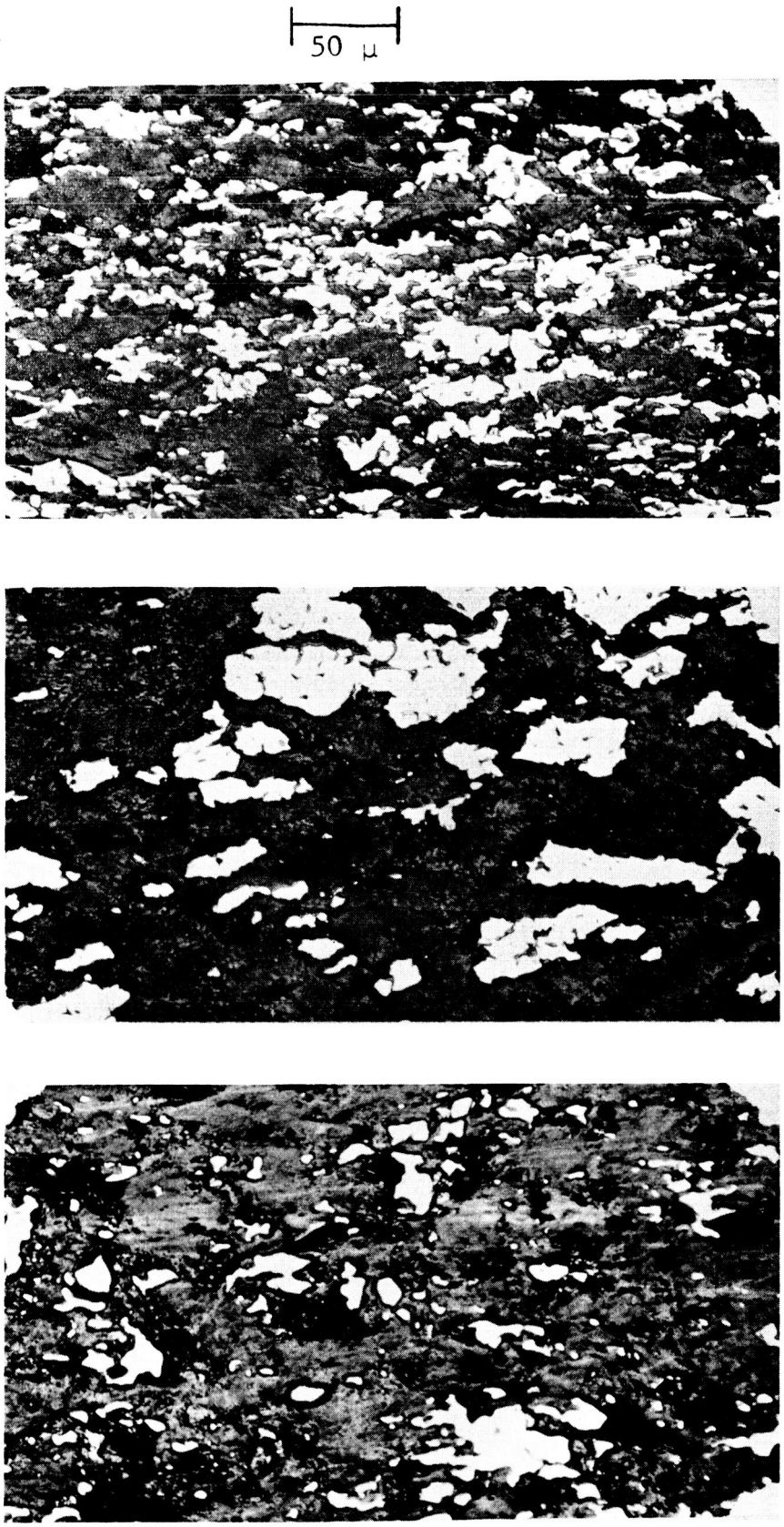


Fig. 5 - MICROSTRUCTURES OF 65 Wt% Ta COMPOSITES SHOWING EFFECT OF INCORPORATING CARBIDES OF DIFFERENT PARTICLE SIZE, (320x)

The flexural strength data for 65Ta-B and M-65Ta-A (Table IV) show that the system having the finer particle size carbide structure was significantly stronger. The composite incorporating the coarser carbide grains was very poorly bonded. The density values (96.6% vs 92.8%) as well as the relative hardness of the composites indicate that more sintering had occurred with the use of the finer particle carbide. It is felt that with these composites, little if any diffusion bonding has occurred and the difference may be attributed to the relative strengths of the graphite phase. As indicated by the density values, the graphite in 65Ta-B is denser than that in M-65Ta-A; thus, 65Ta-B may be expected to exhibit higher strength than M-65Ta-A.

In contrast, 65Ta-A prepared earlier in the program had exhibited strengths of about 19,000 psi, compared to the present values of less than 8,000 psi. This particular billet (65Ta-A) was probably subjected to temperatures higher than 3200°C during fabrication, as suggested by its reaction with the mold and its varying density. The high strengths also indicated that diffusion bonding had occurred. Thus, for low carbide composites in the TaC-C system, it would appear that very high temperatures are necessary to achieve their full potential.

Effect of Carbide Particle Size on Properties of High Carbide Content Composites - The high carbide (M-90Ta, 80 volume per cent TaC) composite incorporating coarser Ta metal was prepared as a comparison to compositions of similar carbide content but containing the finer TaC particles. The results show that, with composites in which the carbide is the major phase, good densification is attained using the coarser particle size carbide source. This is unlike the results obtained for graphite matrix materials as detailed above. In carbide matrix composites, densification and bonding occurs for the carbide phase and the graphite takes on a secondary role. It appears

that this dominant influence of the carbide minimizes the particle size effect seen for the low carbide composites.

A comparison of microstructures between M-90Ta (coarse carbide) and 90Ta-A (finer carbide) appears in Fig. 6. A greater uniformity in dispersion can be seen for the latter. The use of the coarser carbide source for M-90Ta results in some larger islands of graphite. The room-temperature and 2000°C strength values for M-90Ta were similar to those for the finer grain material (see 90Ta-A in Quarterly Report No. 1).[3] Measurements at 2500°C and 2800°C show that composites containing smaller carbide grains have somewhat higher strengths at these temperatures. At present the data are too limited to indicate whether these variations are significant.

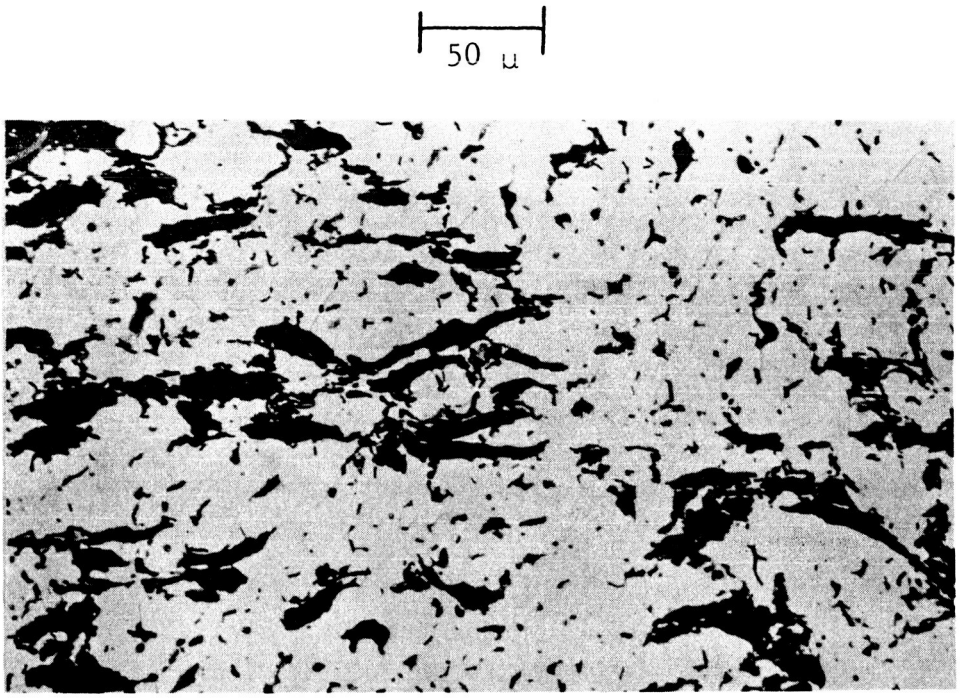
Compressive test specimens of M-90Ta have been fabricated and will be tested for high-temperature deformation. A large grain size dependence of creep has been found in polycrystalline oxides.[6] It will be interesting to see if a similar effect exists for composites incorporating different sizes of carbide particles.

3. Application of Mixing Laws

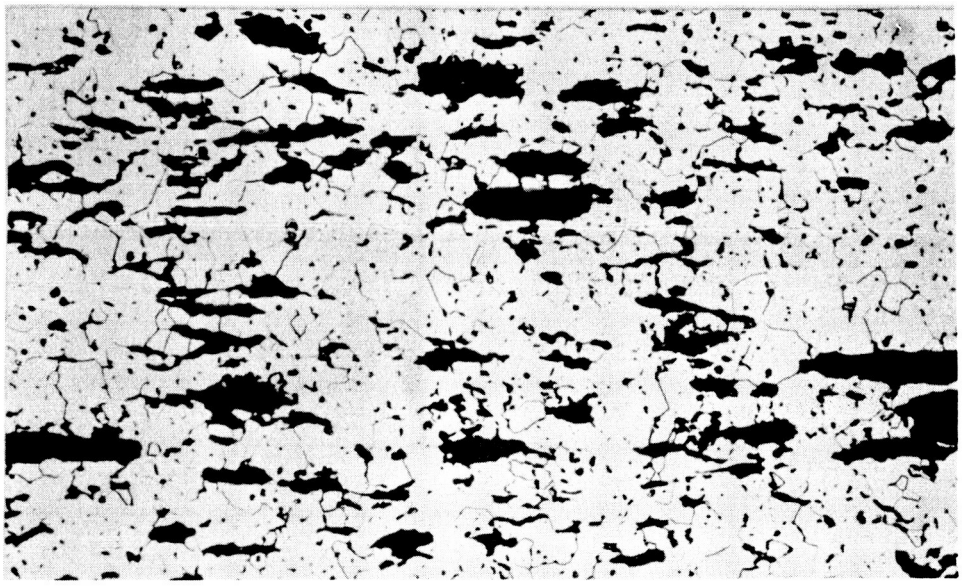
Various theories of multiphase materials and laws of mixture have been proposed to establish upper and lower bounds for the effective elastic constants of heterophase materials.[7] These bounds are determined from acceptable displacement or stress fields within the multiphase material. In a two-phase system the upper bound can be interpreted as uniform strains on the phases and is represented as

$$E_s = E_1 V_1 + E_2 V_2 \qquad (1)$$

The lower bound is a uniform stress model in which the strain on the individual phases is different. The relationship here is



M 90 Ta (20μ)



90 Ta-A (5μ)

Fig. 6 - MICROSTRUCTURES OF 90 WT% Ta COMPOSITES SHOWING EFFECT OF INCORPORATING CARBIDES OF DIFFERENT PARTICLE SIZE, (320x)

$$E_s = \frac{V_1}{E_1} + \frac{V_2}{E_2} \qquad (2)$$

Models for these relationships appear in Fig. 7.

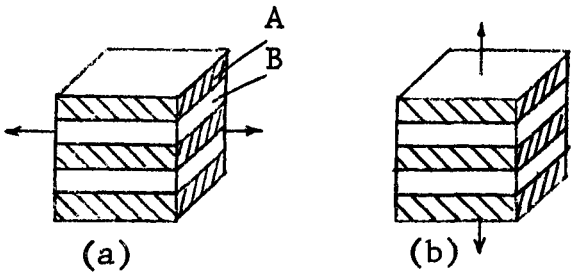


Fig. 7 - MODELS OF PARALLEL AND SERIES SYSTEMS. (a), PARALLEL OR CONSTANT STRAIN MODEL OF TWO PHASES A AND B: (b), SERIES OR CONSTANT STRESS MODEL OF TWO PHASES A AND B.

The aim of this study has been to apply these mixing laws to the metal carbide-graphite systems. It was felt that in considering the relationship between experimental data and predicted mechanical behavior, a better evaluation could be made as to whether the full potential of these systems is being realized.

NbC-C System - The curves presented in Fig. 8 show the caluclated upper and lower bounds as a function of composition for the NbC-C system along with experimental data. Flexural strength has been substituted for elastic modulus in establishing the curves, using values of 10,000 psi for graphite and 35,600 psi[5] for NbC. Upper and lower bound curves based on a value of 53,000 psi for NbC (as determined by LASL[8]) are also presented in Fig. 8.

The graph suggests that the NbC-C composites which have been fabricated on this program are well below potential strengths, especially at the higher carbide contents. The experimental curve itself appears to be linear, indicating an upper bound or uniform strain type of relationship. The assumption of linearity was examined using the statistical

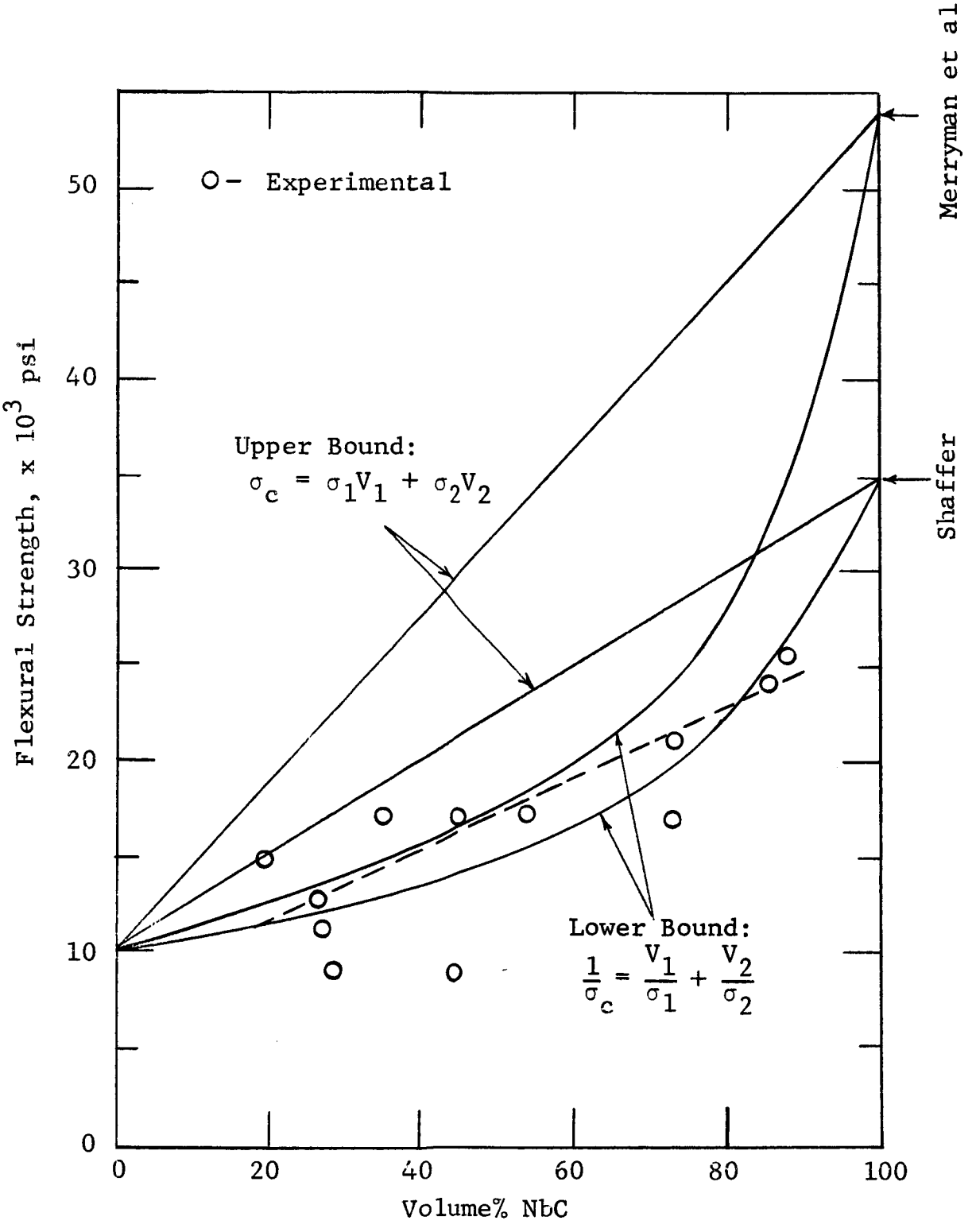


Fig. 8 - APPLICATION OF MIXING LAWS TO FLEXURAL STRENGTH IN NbC-C SYSTEM

method of regression analysis. A value of 0.83 for the correlation coefficient suggests that this assumption is valid. No data are available for compositions of greater than 90 volume per cent NbC to indicate whether a continued linearity or a sharp upturn exists. It may be that our NbC source material would indeed have a strength of only about 30,000 psi as 100% NbC. This would correspond to a strength value of 35,000 psi reported by Shaffer.[5]

Thus the assumptions of 10,000 psi and/or 54,000 psi values for the end members may be somewhat erroneous. However, this analysis is being employed as a guide and should not be considered a rigorous evaluation. It would appear, however, that the full strength potential of NbC-C composites has not as yet been realized.

Higher strength composites in the NbC-C system may be obtainable by using different raw materials and/or changing fabrication parameters. For example, it appears likely that the use of a higher purity finer particle size NbC (and possibly a different graphite source) and processing at higher temperatures for longer times would result in greater densification and diffusion bonding. The practical limitations such as material costs involved in obtaining such NbC and high quality graphite molds would, of course, govern the extent to which this potential is realized.

TaC-C System - The same type of evaluation has also been applied to the TaC-C system; this is illustrated in Fig. 9. The value used for TaC (31,000 psi) was reported by Shaffer.[5] The TaC-C system, similar to the NbC-C, exhibits experimental data which appear to fall on a linear plot. Although the approach of the experimental curve to the upper bounds suggests that optimum composites have been prepared to date, the value of 31,000 psi for TaC may be somewhat low. A recent paper[9] reports values of 56,000 psi, 20,000 psi and 43,000 psi for

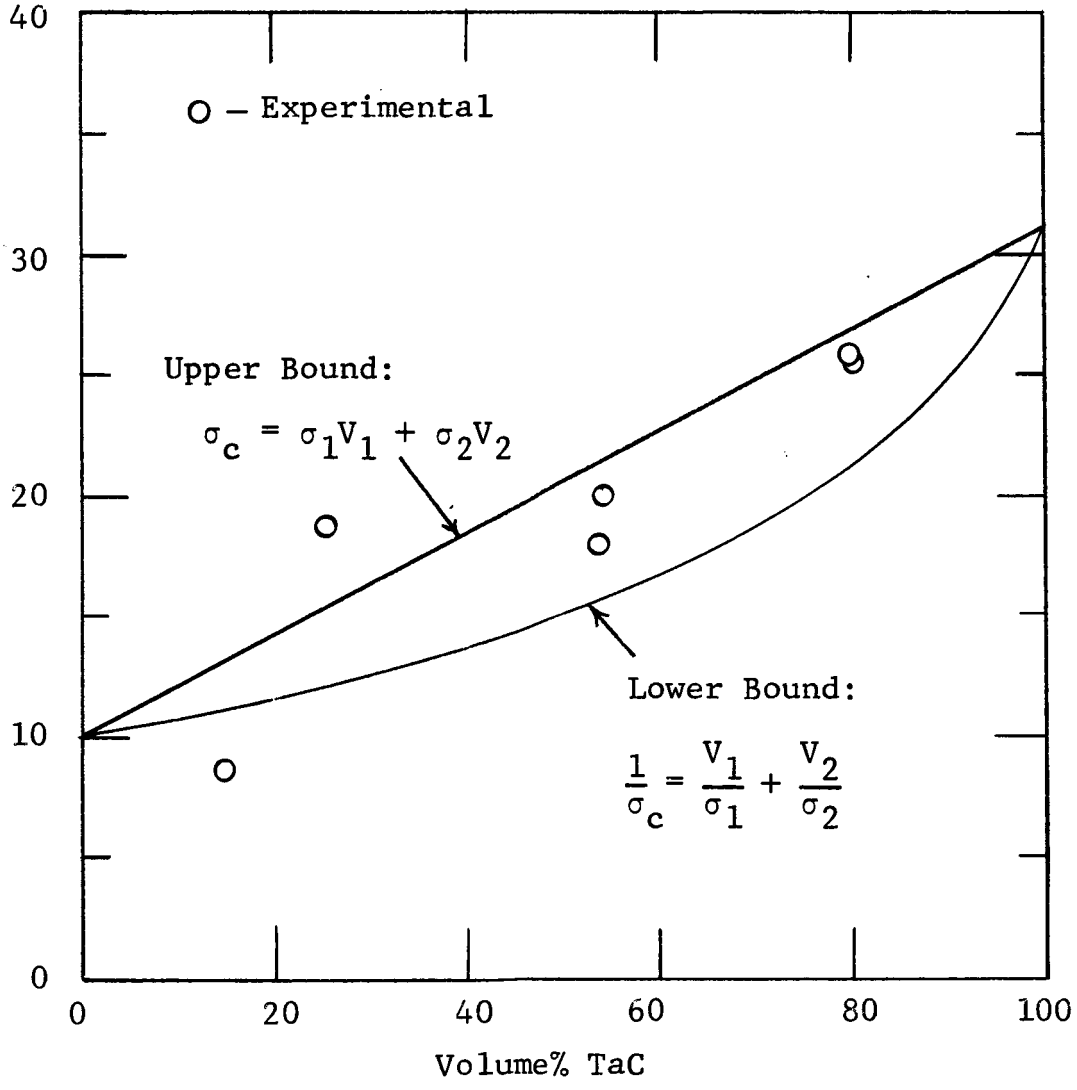


Fig. 9 - APPLICATION OF MIXING LAWS TO FLEXURAL STRENGTHS IN TaC-C SYSTEM

$TaC_{.073}$, $TaC_{0.98}$, and $TaC_{1.26}$ (free carbon), respectively.

B. Electrical Properties

Previous work on the measurement of electrical properties of metal carbide-graphite has revealed that a direct relationship exists between conductivity and flexural strength. With low carbide content composites in which graphite is the matrix, this relationship has been found to be linear.[2] A deviation from this linearity was indicated with composites in which carbide was the dominant phase.[3] Clear establishment of this conductivity-strength relationship appears desirable in that it can constitute a nondestructive method for determining both degree of bonding and homogeneity. In addition, other properties such as thermal conductivity would be closely related to electrical conductivity since both are governed to a large extent by the fraction and morphology of the dispersed phase in two-phase systems.

1. Application of Mixing Laws to Electrical Conductivity

In order to determine what type of electrical behavior might be expected as a function of composition, upper and lower bounds were calculated based on the series and parallel models which were used to describe mechanical strength in the preceding section. Conductivity values assigned were based on resistivities of 500 μΩ-cm for graphite (about the minimum observed for commercial hot-worked ZT graphite)[4] and 35 μΩ-cm for NbC.[10]

Electrical conductivity vs carbide content in the NbC-C system, along with the upper and lower bounds, is plotted in Fig. 10. All values are in the W/G direction. Classically one might expect the experimental data to follow the lower bounds at low concentrations (<20 volume per cent) of NbC where the graphite would be dominant, and the upper bound at the carbide-rich (>80 volume per cent) compositions. The transition region would be in the 20-80 volume per cent NbC range. In reality,

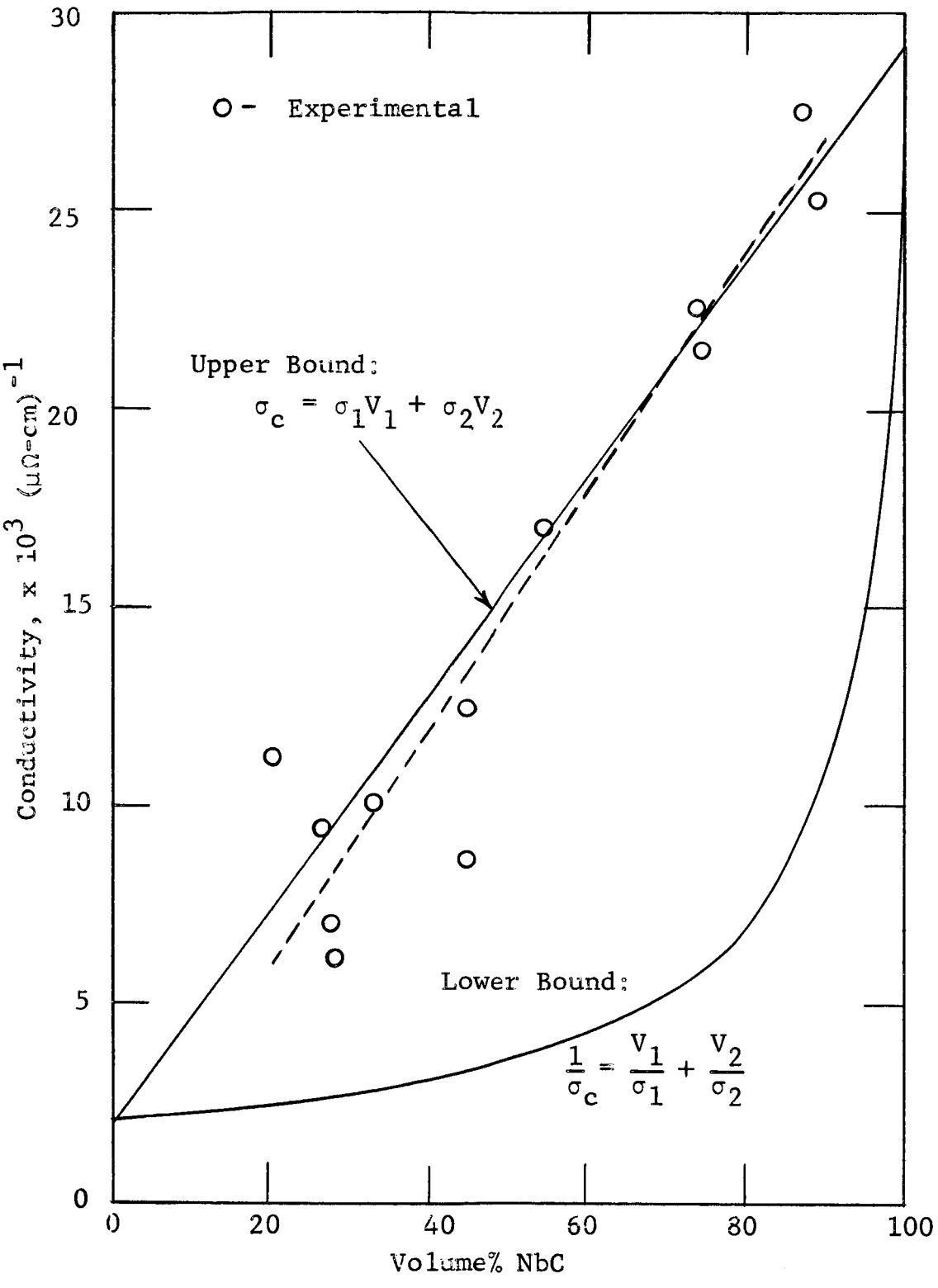


Fig. 10 - APPLICATION OF MIXING LAWS TO ELECTRICAL CONDUCTIVITY IN NbC-C SYSTEM

the data appear to follow a linear upper bound relationship even at the graphite end of the plot. This may be due to a resistivity of graphite which is in fact much lower than the assumed value of 500 μΩ-cm. Calculations based on per cent theoretical densities achieved for the composite show that the graphite phase has a minimum density of about 2.10 g/cc in many cases, and ranges as high as 2.16 g/cc. Such highly ordered graphite would have a resistivity of 300 μΩ-cm based on extrapolation of resistivity-density data for hot-formed graphite.[11] This would, of course, displace the curves for upper and lower bounds to slightly higher values. As more data are obtained, these relationships should become better defined.

2. Electrical Conductivity vs Flexural Strength

Figure 11 presents the relationship between electrical conductivity and flexural strength for NbC-C composites. Earlier work[3] had indicated a deviation from linearity with higher carbide content materials which exhibited low strengths (5000 psi) despite a relatively high conductivity, 15×10^3 $(\mu\Omega\text{-cm})^{-1}$. Additional results obtained during this period show that the previous data were not truly representative of high carbide content samples. The most recent data suggest a linear relationship, extrapolation of which would indicate a strength of about 30,000 psi for NbC.

As mentioned earlier in the discussion of flexural strength vs carbide content, data for composites containing more than 90 volume per cent NbC may cause a change in the slope of the curve to higher strengths. Compositional studies in this very high carbide content range will be conducted to determine the carbide end point more accurately. In addition, measurement of electrical properties of composites fabricated on this program will be continued, and such data will be correlated with mechanical behavior for better characterization of these materials.

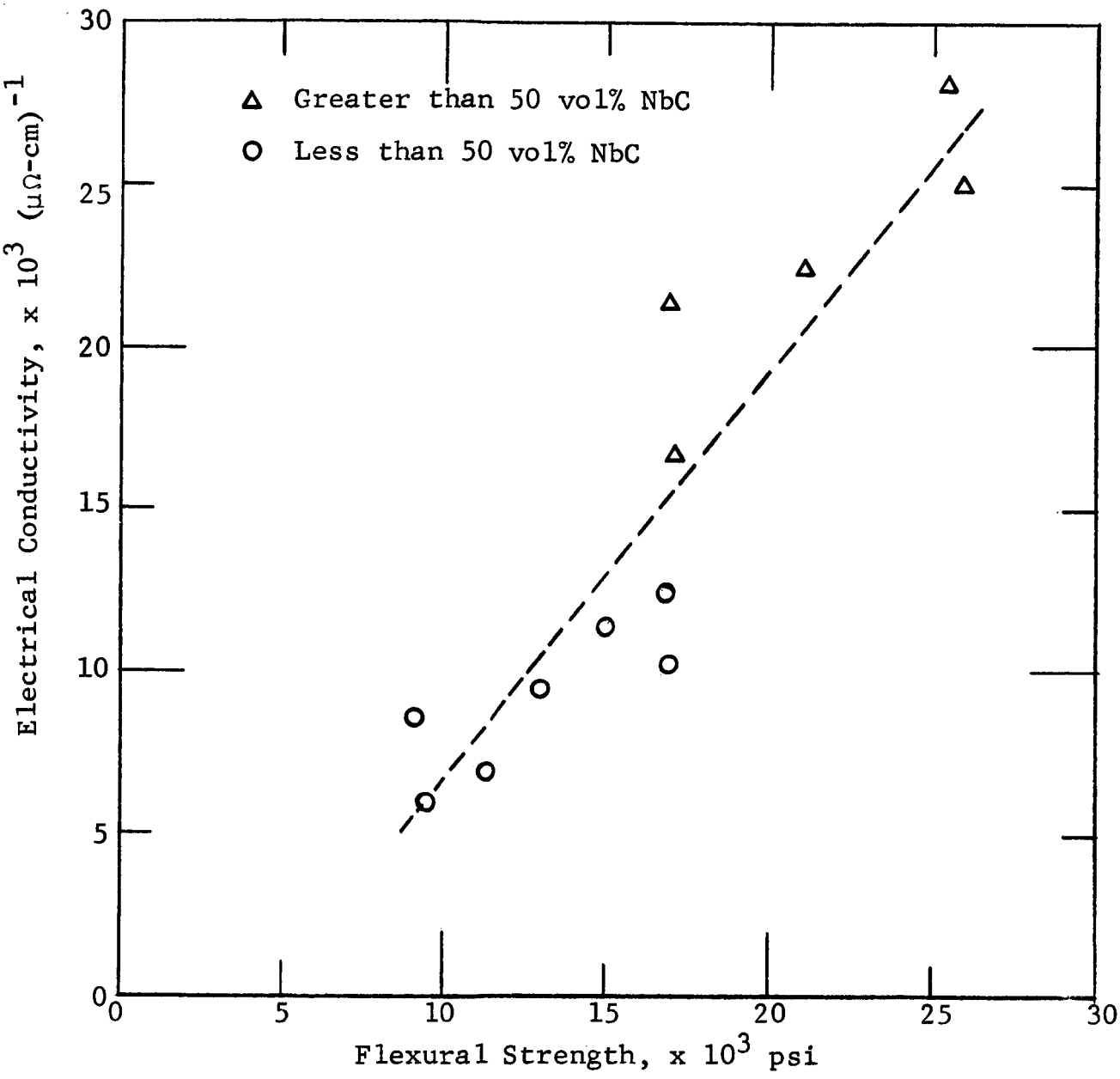


Fig. 11 - ELECTRICAL CONDUCTIVITY-FLEXURAL STRENGTH RELATIONSHIP FOR NbC-C COMPOSITES

C. Heat Treatment Studies

In the determinations of thermal expansion of composites, it was observed that permanent dimensional changes had occurred in the samples due to the heat treatment.[3] These changes were an increase in the A/G or c-axis direction and a decrease in the W/G or ab-plane direction, and were more pronounced with graphite-rich materials. A relaxation of stresses imparted to the composite during hot pressing, may be responsible for such changes. In the cooling process after fabrication, different expansion behavior in the anisotropic graphite crystallites builds up residual stresses which would be relieved on subsequent heat treatment.

1. Heat Treatment Effects on Dimensions

Experiments were conducted during this period on the effect of heat treatment on flexural strength and electrical resistivity as well as dimensional changes. Composites in both the NbC-C and TaC-C systems were subjected to a heat treatment of 2500°C for 1 hr in an argon atmosphere. The resulting changes in dimensions of these materials are summarized in Table V. These compositions exhibited behavior similar to that observed previously, i.e. expansion in the A/G direction and contraction in the W/G direction. Again, the changes diminish with increasing carbide content. This is logical in that as the carbide becomes the dominant phase, stress relief of the minor graphite phase is further restricted by the isotropic cubic carbide. It is felt that the changes are not due to an ordering effect for the graphite crystallites. Such ordering would produce the opposite effect--i.e., increase in the W/G and decrease in the A/G direction--as shown by other investigators.[12]

2. Heat Treatment Effects on Electrical and Mechanical Properties

Most of the samples exhibited little change in electrical

Table V

EFFECT OF HEAT TREATMENT ON PHYSICAL PROPERTIES
OF METAL CARBIDE-GRAPHITE COMPOSITES
(2500°C/1 HOUR)

Compositional Designation	Vol% Carbide	Percent Change*		
		Dimension, W/G	Dimension, A/G	Density
C-50Nb	19	-0.4	+1.5	-0.8
50Nb-C	27	-0.7	+0.5	+0.7
50Nb-E	27	-0.7	+0.3	+1.2
65Nb-S	44	-0.6	+0.7	-0.1
65Nb-C	45	-0.5	-0.5	+1.5
C3-80Nb	73	-0.4	+0.1	+0.5
80Nb-B	73	-0.1	0	+0.3
80Nb-C	73	-0.1	+0.1	0
M-65Ta-A	26	-0.7	+0.3	+0.7
65Ta-B	26	-1.0	+0.5	+0.9
82.5Ta-A	52	-0.4	+0.1	+1.3
M-90Ta	80	-0.3	-0.3	+0.5

* Represents averages of four or more specimens

resistivity or flexural strength due to heat treatment. Exceptions were two materials of high carbide content in the NbC-C system (C3-80Nb and 80Nb-B) which had displayed low strengths (6,600 and 13,000 psi, respectively) in earlier tests. Normally composites containing 80 wt% metal (73 volume per cent NbC) exhibit strengths of about 17,000 to 20,000 psi.

Changes in resistivity and flexural strength are presented in Table VI. Since electrical resistivity involves nondestructive testing, samples could be measured individually before and after heat treatment. On the other hand, flexural strength is a destructive test, so averages for other samples are given as "before" data. The highest values in flexural strengths observed prior to heat treatment were within 10% of the averages: 80Nb-B, W/G - 13,800 psi; 80Nb-B, A/G - 7,950 psi; C3-80Nb, W/G - 8,310 psi; and C3-80Nb, A/G - 4,600 psi.

Permanent decreases in resistivity occurred for all samples; they were particularly pronounced for some of the C3-80Nb specimens. The flexural strengths of the heat-treated samples confirm the improved bonding suggested by the changes in electrical conductivity. In two of the samples (C3-80Nb, samples 1C and 4A) macroscopic cracks were evident both before and after heat treatment. The significant drop in resistivity and increase in flexural strength indicate that some sintering had occurred in these flaws.

3. Heat Treatment Effects on Microstructure

Typical microstructures of C3-80Nb before and after heat treatment appear in Fig. 12. The "before" structure is rather porous in comparison to the "after" structure, indicating that densification had occurred. This was reflected to a small degree in bulk density measurements in which a change of about 0.5% was observed. The photomicrographs also show that carbide grain growth was quite limited. Although increased bonding

Table VI

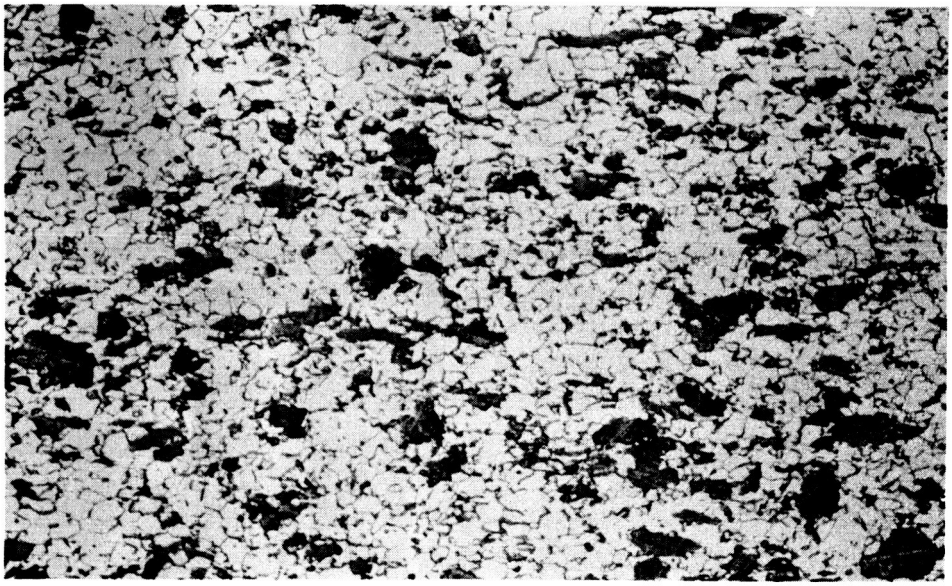
EFFECT OF HEAT TREATMENT ON MECHANICAL AND ELECTRICAL PROPERTIES OF SELECTED NbC-C COMPOSITES

Compositional Designation	Sample No.	Grain Direction	As Pressed		2500°C/1 Hour	
			Flexural Strength, psi	Electrical Resistivity, μΩ-cm	Flexural Strength, psi	Electrical Resistivity, μΩ-cm
80Nb-B	5C	W/G	13,260*	50.1	18,240	44.0
	5A	W/G		49.8	23,750	44.6
	5B	A/G	5,280*	64.3	10,460	57.2
	7B	A/G		61.1	10,380	57.1
C3-80Nb	5A	W/G	6,660*	52.1	16,530	45.6
	5C	W/G		56.3	16,630	48.2
	1C	W/G		232	12,130	45.5
	1A	A/G	4,010*	82.6	12,830	61.1
	4A	A/G		284	7,950	63.0
	2B	A/G		160	10,260	53.1

*Averages for 4 or more samples

50 μ

(a) Before Heat Treatment



(b) After Heat Treatment

Fig. 12 - MICROSTRUCTURE OF C 3-80 Nb COMPOSITE BEFORE AND AFTER 2500°C/1 HR HEAT TREATMENT (200x)

indicates some sintering the heat treatment conditions apparently were insufficient to cause grain growth.

Heat treatment of composites at 2500°C appears to be extremely beneficial in upgrading mechanical properties of high carbide content composites which are poorly bonded. These particular annealing conditions failed to change the properties of graphite matrix composites and TaC-C samples. Thus it would appear that improvement in strength occurs due to improved bonding by sintering rather than by relief of stresses. Furthermore, materials which have been processed to relatively high strengths are also unaffected. It is possible that a higher temperature treatment may be beneficial for TaC-C in which sintering of TaC could occur.

These experiments show that an annealing step subsequent to hot pressing of composites can be quite important in obtaining sound materials. Equally important is the dimensional stability which would be achieved prior to actual use at elevated temperatures. The present studies suggest that dimensional changes observed in compressive deformation tests may in reality be partially attributed to the heat treatment effect, i.e., the changes would have occurred without application of load. Thus for more realistic plastic deformation data, samples will be annealed prior to testing.

III. CONCLUSION AND FUTURE WORK

During this period fabrication studies have considered the effects of raw material particle size and processing temperature on the properties of metal carbide-graphite composites. The relationship between electrical conductivity and flexural strength has been evaluated. Mixing laws for multiphase systems have been employed to analyze electrical and mechanical properties. Heat treatment studies were conducted to examine annealing effects on physical and mechanical properties. The most significant findings in the present work are as follows:

1. In low carbide content composites in which graphite is the matrix, the use of a finer particle size (about 3 μ) carbide, as opposed to coarse (10 μ) metal powders, produces composites of higher strength.

2. Achievement of high strengths is directly related to soaking of composites at processing temperature as well as to the use of higher temperatures. The limiting factor in fabrication temperature is sample extrusion and reaction with the mold.

3. Application of mixing laws which predict upper and lower bounds in properties as a function of composition suggests that higher strength NbC-C composites than those prepared to date may be obtainable. This is especially true for compositions in which NbC is the dominant phase.

4. There appears to be a linear relationship between electrical conductivity and flexural strength for the NbC-C system in the compositional range, 20-88 volume per cent NbC.

5. Heat treatment of high NbC content composites subsequent to hot pressing can result in significant improvement in strength due to sintering and diffusion bonding. The annealing process also produces dimensional changes due to relief of stresses which are imparted to billets on cooling after processing. Thus, for greater reliability, these permanent changes which occur should be induced by an annealing process prior to actual hardware use.

Future work will involve determination of tensile and compressive strength and sonic modulus at elevated temperatures. Further compressive deformation studies will be conducted. Complementary investigations of electrical properties and the use of mixing laws will be continued so that a clearer analysis may be made of carbide-graphite systems.

IV. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

In addition to the writer, the following personnel are participating in this research program: S. A. Bortz, R. Baker,

and J. L. Sievert. Data are contained in Logbooks Nos. C16974, C16986, C16989, C17303, and C17308.

Respectfully submitted,
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