IIT Research Institute
10 West 35 Street, Chicago, Illinois 60616
312/225-9630

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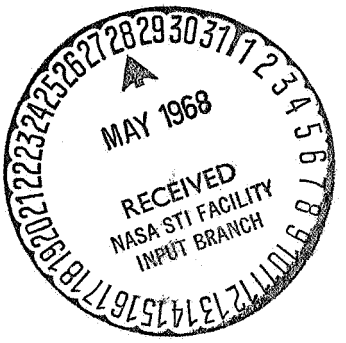

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Subject: IITRI G6003-Q7 (Letter Report)
"Metal Carbide-Graphite Composites"
Contract No. NASr-65(09)

Gentlemen:

I. INTRODUCTION

The purpose of this year's work is to build on the broad base of information which has been established during past research and to obtain a better insight into control of properties. The studies to date have shown how this may be done by raw material choice, e.g., incorporating carbons which have different processing histories, particle size and shape, and purity levels. Less anisotropy and greater creep resistance are two of the properties being developed for the NbC-C composites. The specific studies which are being conducted are as follows:

1. Carbon Source - Variations in carbon source which contrast with the needle coke used in earlier studies[1] are being evaluated.

2. Particle Size and Shape - These parameters are being varied so as to obtain different size relationships between the graphite and carbide phases, in an attempt to control composite properties.

3. Use of Sintering Aids - Small amounts of additives have been incorporated in the TaC-C system to obtain liquification at temperatures lower than the 3450°C eutectic temperature. This permits exploitation of the densification and improved bonding obtainable in liquid phase sintering at processing temperatures of 3200°C or lower.

4. Properties Evaluation - The effects of the above mentioned variables upon physical and mechanical properties of composites in both grain directions are being determined. Particular attention is being paid to creep behavior of these materials at temperatures of 2500°C and higher. Attempts will be made to develop properties conducive to good thermal shock resistance, i.e., increased strength and thermal conductivity, and decreased elastic modulus and coefficient of expansion.

During this period, the study of NbC-C composites using different carbon sources has been continued, and the effect of densification aids for TaC-C composites are being evaluated; particular emphasis has been placed on flexural creep experiments at 2500°C. Additional information obtained includes flexural strength and modulus, thermal expansion, and compressive creep at elevated temperatures.

II. NbC-C SYSTEM

The work for this year in the NbC-C system has involved incorporation of carbon powders of differing size, shape and processing histories into composites of 47vol% NbC. The variations in carbon source have been introduced in an attempt to control properties such as strength, thermal expansion, high temperature deformation resistance, and degree of anisotropy. Evaluation of the various composites has shown that although room temperature data were quite similar, high temperature measurements revealed significant differences in behavior.

The present studies include further determinations of creep behavior as a function of carbon source. In addition, additional composites have been fabricated and characterized. Description of the results are presented in the following sections.

A. Raw Materials

Eight carbons have been considered in these studies. Brief backgrounds on these materials are as follows:

1. Varcum (V) - A glassy resin coke prepared by the CMB-6 Section at Los Alamos Scientific Laboratory (LASL). Particle size range - 44 to 100μ.
2. M-2 (M2) - A graphite flour, also from CMB-6: LASL. Particle size range 44 to 100μ.
3. Calcined petroleum coke (CPC) - A needle coke with average particle size of 3.1μ.
4. Ceylon graphite (Cy) - A fine natural graphite, 1 to 5μ.
5. Gilsonite (G) - A somewhat harder coke than CPC. Used in a particle size of less that 74μ.
6. Thermax (Th) - A fine carbon black with average particle size of about 0.4μ.
7. Sterling 10R (S10R) - A very fine carbon black with particle diameter of less than 0.1μ. Obtained from Cabot Corporation.
8. High expansion graphite (Hex) - A high thermal expansion isotropic graphite powder of less than 44μ. This material was milled from rod stock by Union Carbide at Lawrenceburg, Tennessee.

Both Varcum and M-2 graphite flour have received considerable study by the CMB-6 Section of LASL and were included in our studies for comparative evaluation. Gilsonite coke, Thermax and S10R carbon black were chosen to obtain more isotropic properties, since these particles can be termed "spherical" as opposed to the petroleum coke (CPC) or the platy Ceylon graphite. The latter carbons have been shown to increase anisotropic behavior. The choice of carbon blacks was also dictated by the reported low creep behavior of lampblack-base graphite (CEP: Union Carbide). The high expansion coke was used in an effort to influence expansion properties of the resulting composite.

The studies[2] with the various carbon sources have shown that incorporation of carbon black (Sterling S10R) yields NbC-C composites of low anisotropy and good resistance to high temperature deformation. Work with this particular carbon source has been continued with fabrication and evaluation of 46.5NbC-C-2S10R. In this billet the carbide source was a very fine powder with an average particle size of about 0.16μ (Blend Nb-2 supplied by N-1:LASL). Mixing of this NbC with the 0.1μ S10R black was accomplished easily by dry blending. This contrasts with the more elaborate wet mixing methods used previously when 3.1μ NbC powder was used in 46.5NbC-1S10R.

Another carbon source which is now under evaluation is M-3 graphite obtained from LASL. This material is the successor to M-2 which was evaluated in earlier studies.[2] Billet 46.5NbC-M3 was fabricated using M-3 in the as-received unscreened form. Screen analysis shows the particle size to be as follows:

Mesh	Size (μ)	Wt%
+ 100	≥149	1.5
-100 + 140	149 - 105	11.9
-140 + 200	105 - 74	23.0
-200 + 325	74 - 44	23.7
+ 325	<44	33.9

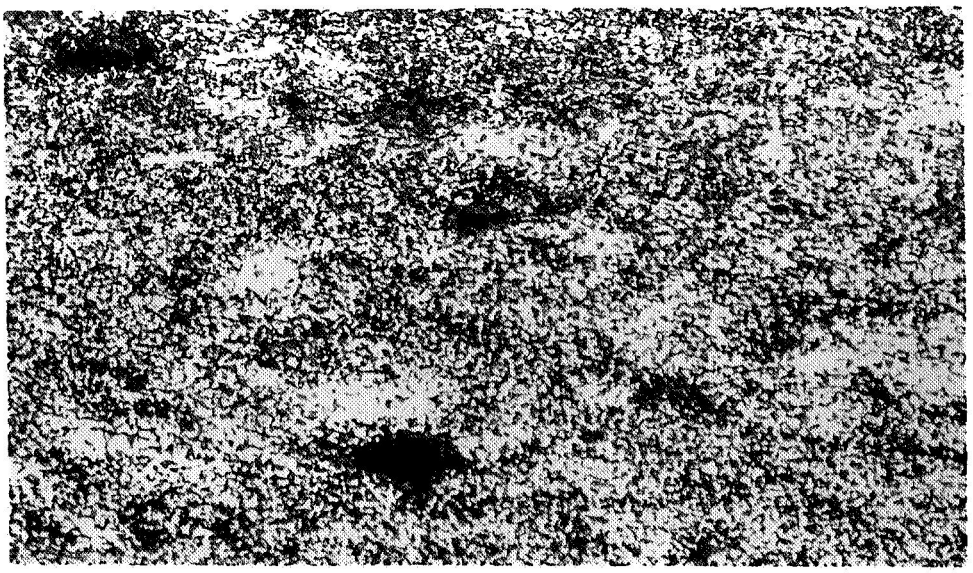
B. Processing

In keeping with the constant parameter for the other NbC-C composites in the carbon source study, the hot pressing time-temperature-pressure cycle for the present composites was maintained at: 1.5 hr to 3150°C, 15 min soak under 3000 psi. The composite incorporating the very fine S10R and Blend Nb-2 was cold pressed in a steel die at 10,000 psi prior to hot pressing.

C. Microstructure

Metallographic examination of the 2S10R composite revealed a very fine dispersion of carbide (Fig. 1) with some tendency toward clustering. As pointed out in our most recent report[2] such aggregation exists for this extremely fine NbC even prior to mixing. Nevertheless, the use of the fine carbide (.16μ) with an equally fine carbon source, i.e., S10R carbon black (0.1μ) yielded a much more uniform dispersion than with the use of the coarser CPC (3.1μ). The 46.5NbC-3CPC composite[2] exhibited a skeletal carbide phase surrounding the relatively coarse graphite particles.

Some fairly large pores can be observed in the microstructure of 2S10R in the W/G direction (Fig. 1). Apparently the standard pressing conditions were not sufficiently rigorous enough to eliminate entrapped gasses. This incomplete removal of porosity has been a general condition whenever one or both



a) Sample 2C-T (W/G)

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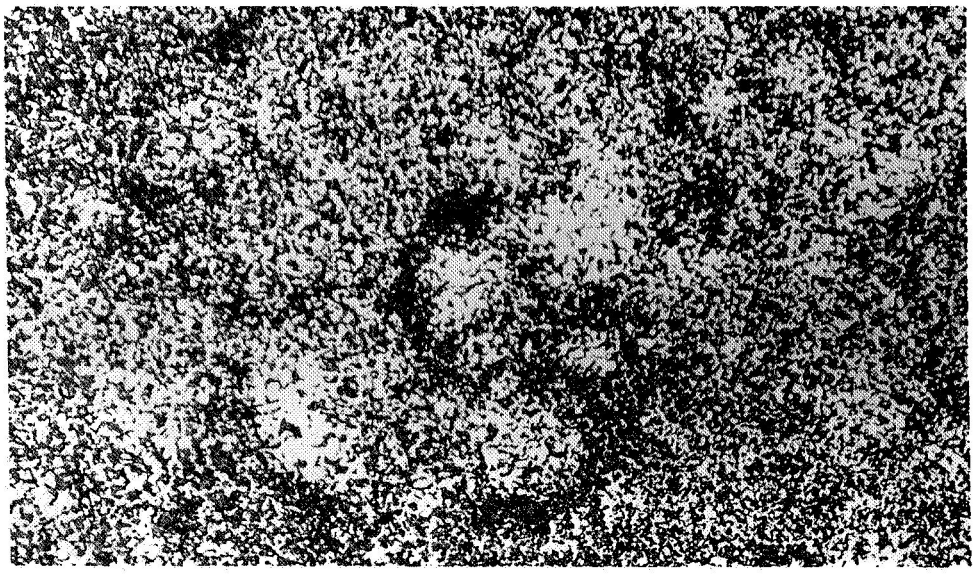

b) Sample 2C-Th (A/G)

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Fig. 1 - MICROSTRUCTURE OF NbC-C COMPOSITE INCORPORATING FINE NbC (0.2μ) AND S10R CARBON BLACK

of the phases was a very fine particle size material. The only exception was the 1S10R composite[2] which went thru two hot pressing operations. It may be possible to attain the relatively pore-free condition by increasing the pressure to 4000 psi or by holding at the processing temperature for longer times. This will be conducted in the near future.

The composite incorporating M-3 graphite (46.5NbC-M3) had a somewhat heterogeneous microstructure as seen in Fig. 2. More than 36% by weight of the M-3 is of a particle size greater than 74μ. The finer NbC (3μ) particles formed a network around these coarse graphite grains, similar to the condition previously observed for the M-2 and Varcum coke containing composites.

D. Room Temperature Properties

It was believed that a carbide "skeleton" might result in higher strength, modulus and electrical conductivity. However, the data for M-3 show that this does not occur. The composite having the highest modulus and electrical conductivity was the CPC body in which the matrix or continuous phase was graphite. Evidently the graphite is the dominant species at this carbide level of 47vol%. The densities achieved with the 2S10R and M-3 are listed in Table I. The values of 95.5 and 96.0% theoretical density fall within the range of 94 to 97% shown by previously fabricated composites using other carbon sources.

The W/G strengths (Table II) of 16,290 psi for the 2S10R composite compare favorably to those for composites using other carbon sources (14,000 to 18,000 psi). However, the A/G strength was rather low, and the anisotropy ratio of 2.57 placed 2S10R among the highly directional composites such as the Ceylon (3.28) and needle coke (CPC) bodies (2.09). The anisotropy for the latter materials can be attributed to pronounced orientation of the carbide and graphite phases.

50μ

a) Sample 4A-T (W/G)

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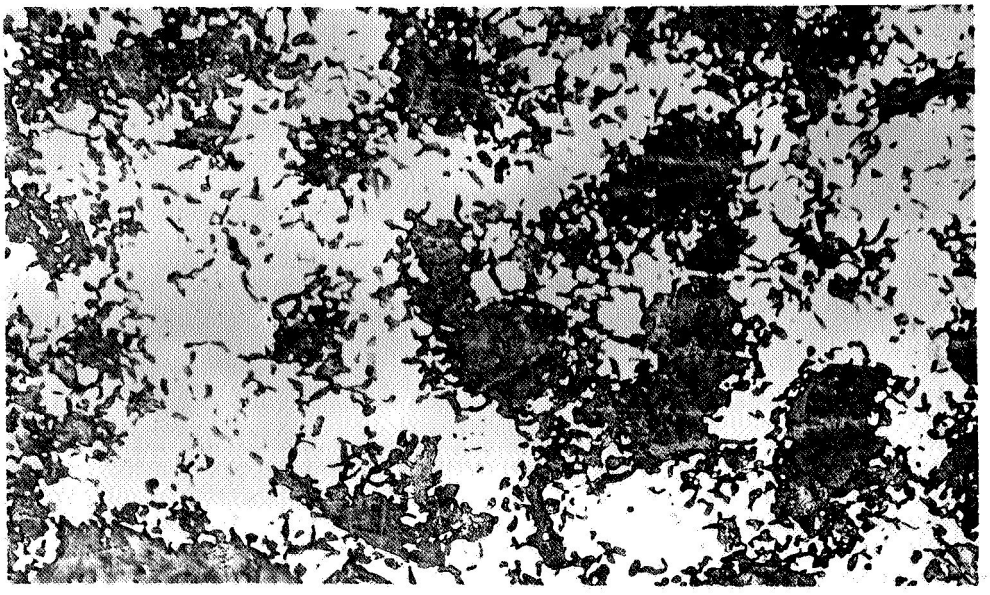

b) Sample 4B-L (A/G)

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Fig. 2 - MICROSTRUCTURE OF NbC-C COMPOSITE INCORPORATING M-3 GRAPHITE

Table I

FABRICATION SUMMARY FOR NbC-C COMPOSITES

Compositional Designation	Starting Materials		Carbide Content		% Theoretical Density
	Carbon	NbC	wt%	vol%	
46.5NbC-2S10R	Sterling 10R	Blend Nb-2	73.3	44.3	95.5
46.5NbC-1M3	M3	SP11678A	75.3	46.8	96.0

Table II

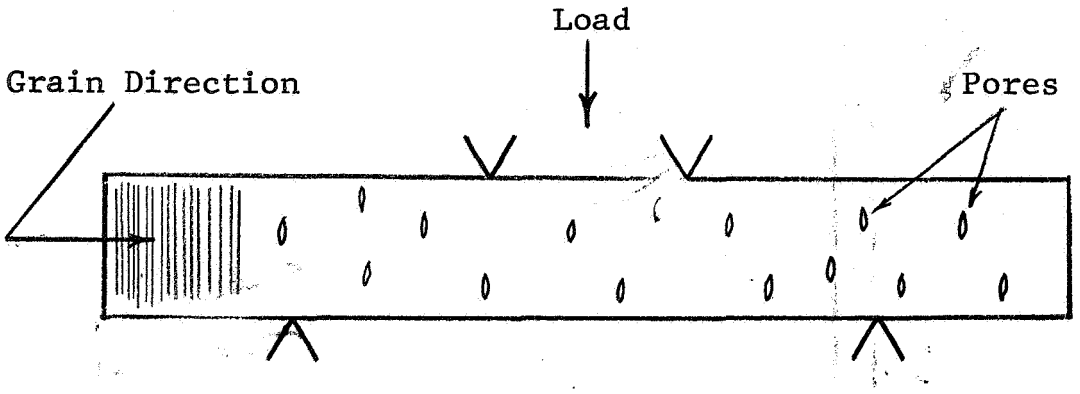
PROPERTIES SUMMARY FOR NbC-C COMPOSITES

Compositional Designation	Grain Direction	Flexural Strength, psi RT	2000°C	2500°C	Elastic Modulus x10^6 psi	Electrical Condcutivity$_1$ x10^{-4}(Ω-cm)
46.5NbC-2S10R	W/G	16,290	18,920	11,160**	8.5	0.93
	A/G	6,330	9,250	5,450**	4.1	0.56
	(A.R.)*	2.57	2.05	2.05	2.07	1.66
46.5NbC-1M3	W/G	18,190	15,470	10,600	8.2	1.40
	A/G	7,970	8,870	6,600	4.6	0.99
	(A.R.)*	2.28	1.74	1.61	1.78	1.41

*(A.R.) = Anisotropy Ratio

**Highest stress which could be applied prior to plastic deformation.

For the 2S10R, such strong orientation of phases is not evident in the microstructure (Fig. 1). However, the elliptical pores which are aligned perpendicular to the pressing direction may be the cause of the low strength and modulus in the A/G direction. The ends of these pores may be considered as points of stress concentration. Thus when the sample is stressed in the A/G.direction, the pores can act as crack propagators. Furthermore, the low modulus may be attributed to the high strain fields around the pores and the development and opening of microcrackes.



Flexural Loading of Sample in A/G Direction

The low electrical conductivity may also be a function of this porosity. The pores are perpendicular to the electrical path and present relatively large areas of insulation. The conductivities of the W/G orientation would not change radically because of the relatively small area presented by the pores in this direction.

The room temperature properties of 46.5NbC-M3 are also tabulated in Table II. The A/G flexural strength and modulus are somewhat low in comparison to values determined previously for other carbon source composites, but may be considered within the variability for these materials.

E. High Temperature Flexural Strength

The flexural strengths of 2S10R and M3 are tabulated in Table II and illustrated in Fig. 3. The 2S10R exhibited the usual increase in both grain directions at 2000°C. At 2500°C the specimens displayed a large amount of plastic deformation and could not be stressed to failure. The M3 composite displayed a decrease in W/G strength at 2000° and 2500°C.

Other investigators[3] have observed increasing flexural strength with temperature for NbC-C composites. They have found that the peak in strength occurs at about 1700° to 1800°C, with decreasing strengths at higher temperatures. It is quite probable that a similar peak exists at a similar temperature for this M3 composite. However, the low strength at 2000°C suggests a rapid deterioration in properties at temperatures above that for peak strength. This may be brought about by activation of various creep mechanisms in the NbC and/or graphite. It has been reported that the brittle to ductile transition temperature for NbC is 1750°C.[4] The drop in strength beyond this temperature may be due to microcracks developed along the grain boundaries or at the triple point during grain boundary sliding which occurs beyond this temperature range. At this time no speculations can be given for the variability of behavior between certain of the NbC-C components where different raw materials are being used.

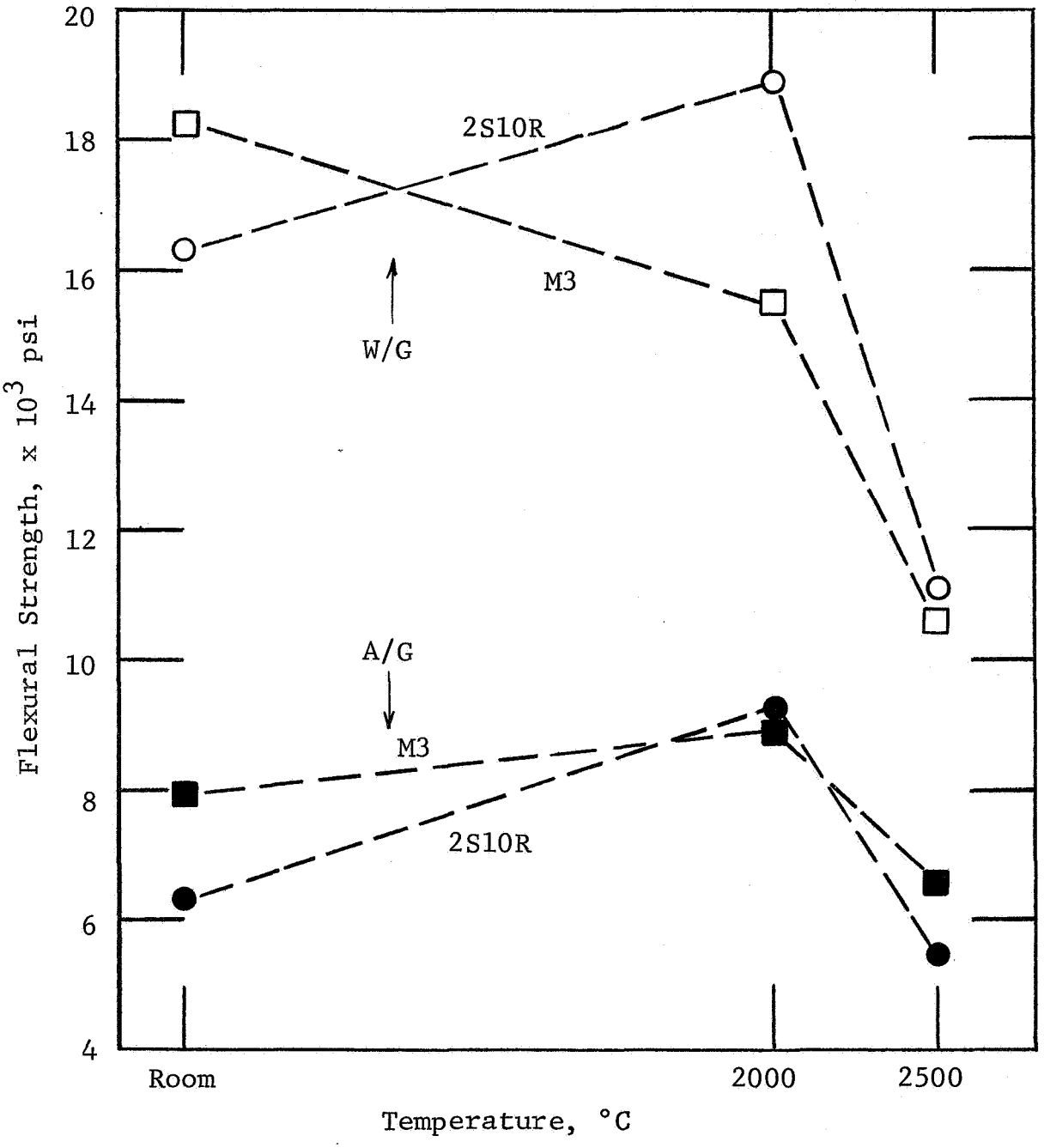


Fig. 3 - FLEXURAL STRENGTH VS TEMPERATURE FOR NbC-C COMPOSITES

Selected compositions will be tested in flexure at various temperatures between 1000° and 2500°C in order to locate the peak in strength for our composites.

F. Flexural Creep

In the work to date, creep behavior appears to be influenced by the graphite phase. This is inferred from the anisotropy in creep properties, and also from variations in creep resistance as a function of carbon source. Creep in graphite is diffusion controlled; movement of vacancies and dislocations must be minimized if good deformation is to be realized. At the same time, creep behavior in the NbC phase and creep resulting from interaction between the two phases must be considered.

One of the possible reasons for differences in creep behavior is degree of graphitization. X-ray studies show that all of the composites, including the difficult to graphitize Varcum coke and the carbon black, display lattice parameters virtually identical to that for graphite. Thus degree of graphitization appears to play a minor role in deformation resistance of these composites, since all of the materials are well graphitized.

Studies of high temperature flexural deformation have been continued during this period. During the last report period, preliminary work had indicated that the 1S10R (carbon black) composite had creep resistance superior to that for composites using other carbon sources. The more recent studies, however, show that composites incorporating M2 graphite flour or Varcum resin coke are equally creep resistant.

Deformations observed in flexural creep tests at 2500°C under 5000 psi for one hour are depicted in Fig. 4. Included in this figure are data for samples heat treated for one hour at 2500°C prior to testing. Seldin[5] has shown that for molded carbons, the magnitude of creep and also the creep rate decrease when the sample is heat treated prior to testing. He attributes this to increased degree of graphitization.

Comparison of deformations between heat treated and non-heat treated samples show no significant differences (Fig. 4). Unlike the molded carbons, the carbon phase in those NbC-C composites is fairly well graphitized, and additional graphitization and ordering at 2500°C/1 hr, if any, does not materially affect creep resistance.

Among these four composites, the best W/G creep resistance was shown by M2 and Varcum, and the best A/G resistance by M2 and S10R. Thus the best composite creep behavior under these particular conditions can be said to be that for the M2 body. The creep rates for the samples which were not heat treated appear in Fig. 5.

We are now attempting to increase our understanding of creep mechanisms by other studies. Impurities as a source of high creep behavior will be examined by evaluation of a recently fabricated NbC-C composite doped with 1% iron. In addition, our raw materials are now being chemically analyzed for purity levels.

We are also attempting to analyze creep behavior by determinations of activation energies. This is given by the slope of creep rate vs reciprocal absolute temperature. We now have two points, one at 2000° and the other at 2500°C. Obviously more data at other temperatures are needed to determine possible changes in the slope, and correlation of these energies to known values such as that for carbon diffusion in graphite.

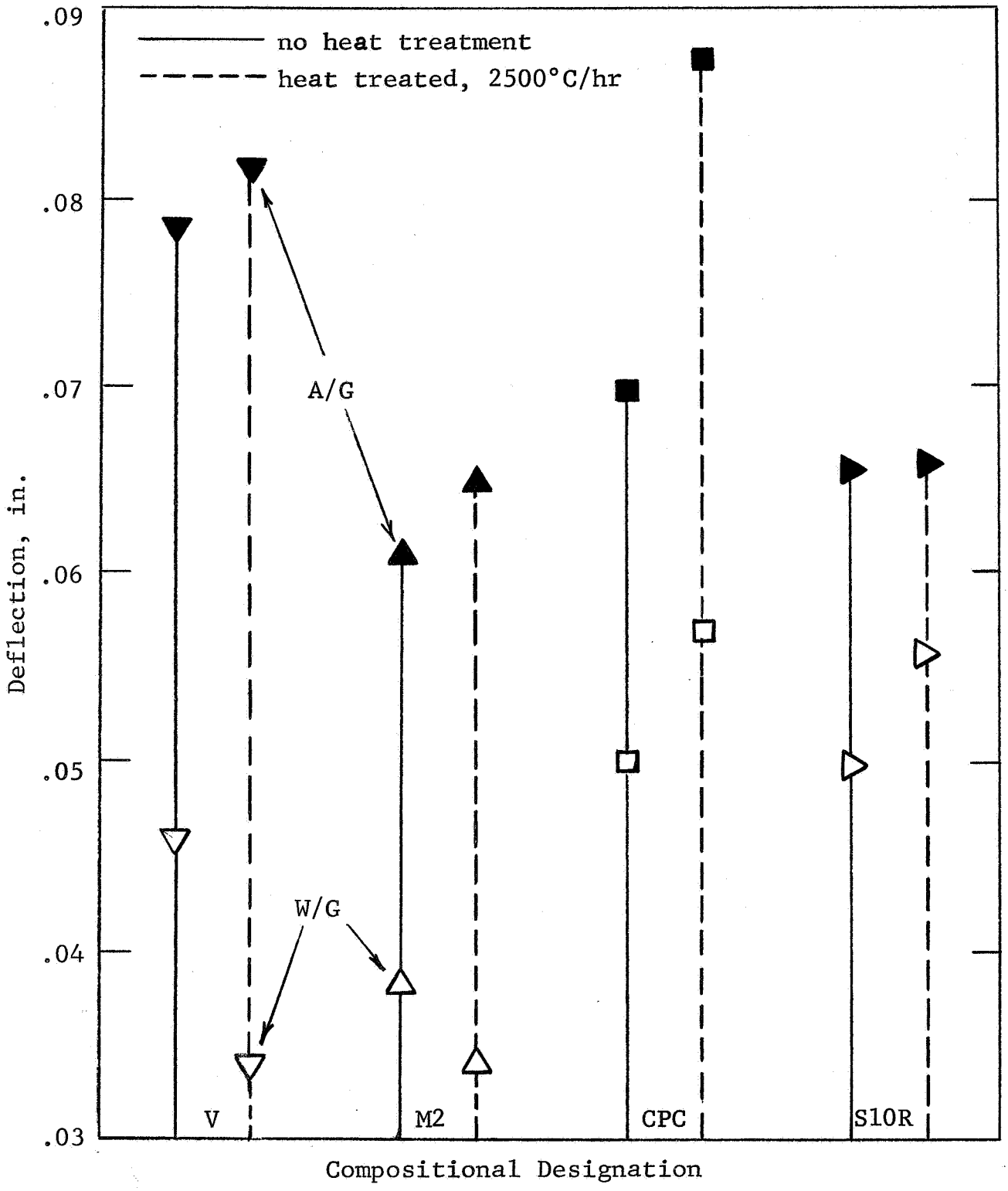


Fig. 4 - FLEXURAL DEFORMATION FOR NbC-C COMPOSITES (2500°C, 5000 psi, 1 hr)

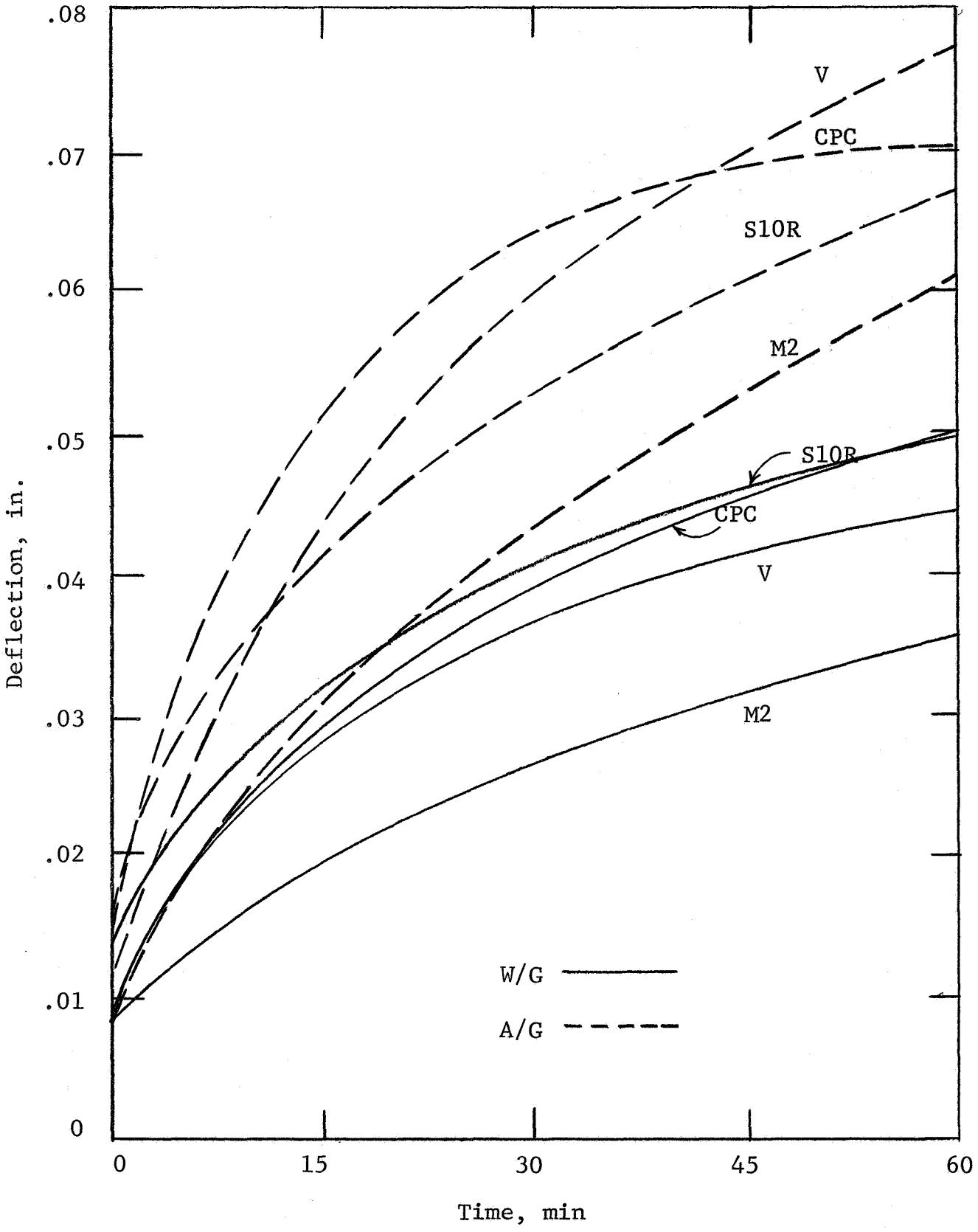


Fig. 5 - FLEXURAL CREEP RATES FOR NbC-C COMPOSITES (2500°C, 5000 psi, 1 hr)

The creep rates for the more recently fabricated 2S10R and M3 composites are presented in Fig. 6. These materials show a higher W/G deformation than for composites incorporating other carbon sources (Fig. 5). In the A/G direction, a very high creep rate was observed for M3. The 2S10R composite would not sustain the test load of 5000 psi.

Included in Fig. 6 are creep rates in both "grain directions" for pure NbC. An understanding of the behavior of the carbide phase is needed for a good analysis of composite behavior. The W/G direction refers to test bars with their long axis perpendicular to the hot pressing direction, and the A/G, to samples with their long axis parallel to the pressing direction. The observed creep rate is somewhat higher than reported in the last quarterly report[2]; however, the deformations are significantly lower than those for the NbC-C composites incorporating 46.5vol% NbC.

G. Compressive Creep

Flexural creep tests at the fairly high stress level of 5000 psi are being used to exaggerate differences among the various composites. Compressive creep tests under conditions corresponding to those used at other institutions were also conducted during this period with composites incorporating various carbon sources.

The compressive creep tests were conducted on specimens ¼ in. in diameter and 3/4 in. high under the conditions: 2700°C, 2000 psi, 30 minutes. The total deformation diametrally as well as in length are presented in Table III. These data reflect differences observed in flexural creep tests as a function of carbon source i.e. the M2, V, and S10R composites displayed the best resistance to plastic deformation. Less than 1% change in length can be expected in either grain direction for these composites.

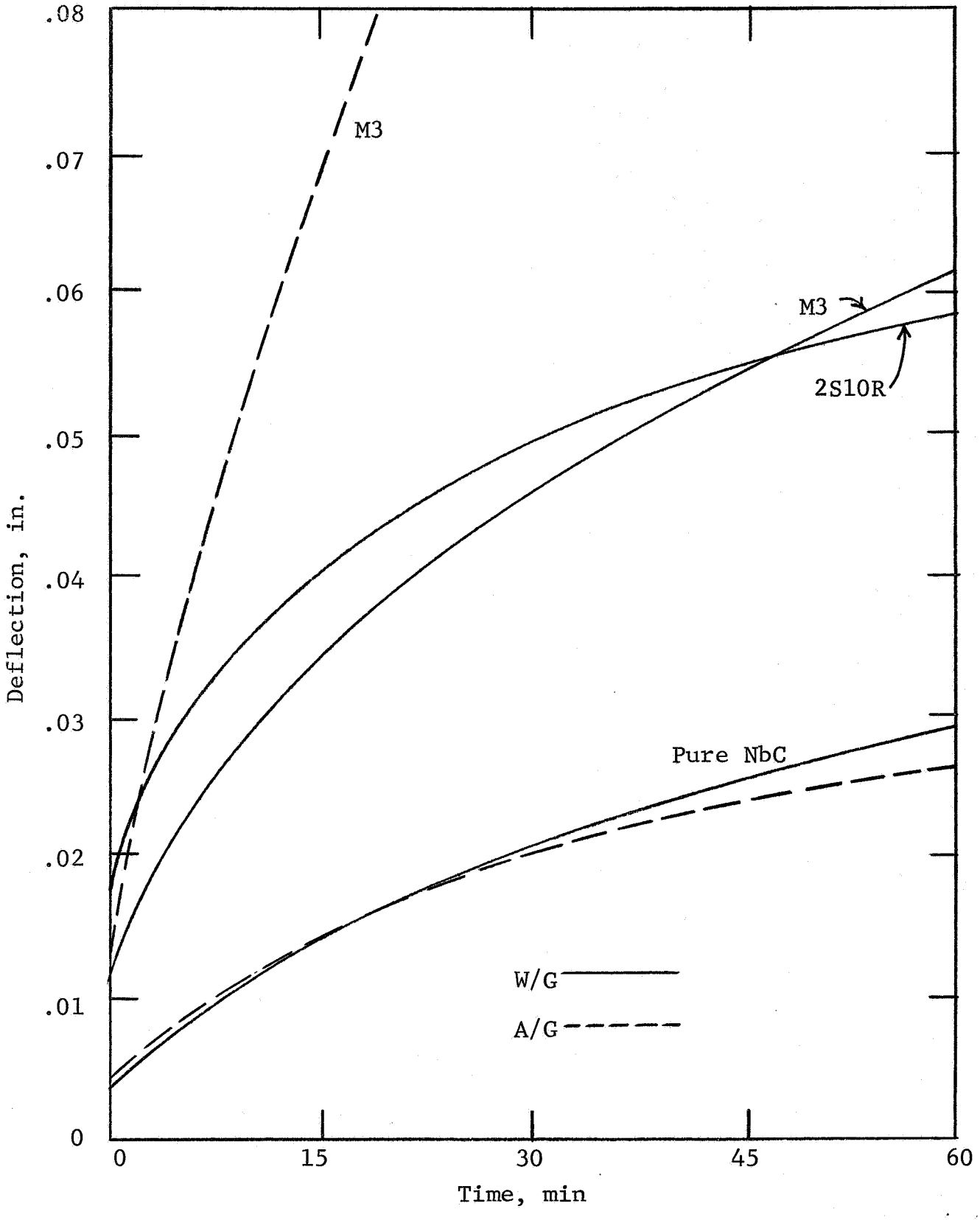


Fig. 6 - FLEXURAL CREEP RATES FOR NbC-C COMPOSITES AND PURE NbC (2500°C, 5000 psi, 1 hr)

Table III

COMPRESSIVE CREEP DATA FOR NbC-C COMPOSITES
FABRICATED USING DIFFERENT CARBON SOURCES

Compositional Designation	Carbon Source	Grain Direction	2700°C/2000psi/30 min. Δlength,%	Δdiameter,%*
46.5NbC-M2	M2 graphite flour	W/G	-0.5	+0.8
		A/G	0	0
46.5NbC-V	Varcum coke	W/G	-0.4	+0.8
		A/G	-0.3	0
46.5NbC-CPC	Calcined petroleum coke	W/G	-2.3	+2.9
		A/G	-1.1	+2.0
46.5NbC-Th	Thermax carbon black	W/G	-2.7	+3.0
		A/G	-3.1	+2.0
46.5NbC-G	Gilsonite coke	W/G	-1.1	+0.2
		A/G	-1.1	+0.2
46.5NbC-Cy	Ceylon graphite	W/G	-2.7	+3.0
		A/G	-0.7	0
46.5NbC-1S10R	S10R carbon black	W/G	-0.8	+0.8
		A/G	-0.4	+0.6

*ΔDiameter taken at point of greatest change.

The percent changes in length are presented graphically in Fig. 7. The Gilsonite composite exhibited remarkably good creep resistance in view of its flexural behavior at high temperatures. The anisotropic behavior of the CPC and Cy composites are again observed in these compressive creep tests.

III. TaC-C SYSTEM

In earlier work[1] with TaC-C composites containing less than 50vol% carbide, temperatures in excess of 3250°C appeared necessary for obtaining dense, well-bonded composites. This is probably due to the limited carbide diffusion at about 3250°C which is still some 200°C below the TaC-C eutectic of 3450°C.[6] It is obvious that hot pressing at temperatures closer to this solidus is hampered by rapid deterioration of the graphite mold at these temperatures.

The present work involved the use of Mo, W and NbC as densification aids. It has been established at IITRI[1] that amounts as small as 10vol% of either Mo or W yielded strong (~15,000 psi) Mo_2C-C or WC-C composites with dense graphite matrices. This was accomplished at the relatively low temperature of 2800°C and can be attributed to exsolution of a dense graphite from the molten Mo_2C or WC on cooling. NbC in amounts of less than 10vol% has also been shown to produce dense graphite matrices by a similar mechanism.

A. Raw Materials

The composites were prepared using small amounts of these additives (about 5vol%) in TaC-C composites. The carbon source for all of the pressings was the above described unscreened M-3 graphite. The TaC was obtained as -325 mesh powder from Wah Chang as SP11679A. Both Mo and W powders were extremely fine, exhibiting particle size of less than 5μ. The NbC powder has also been described above.

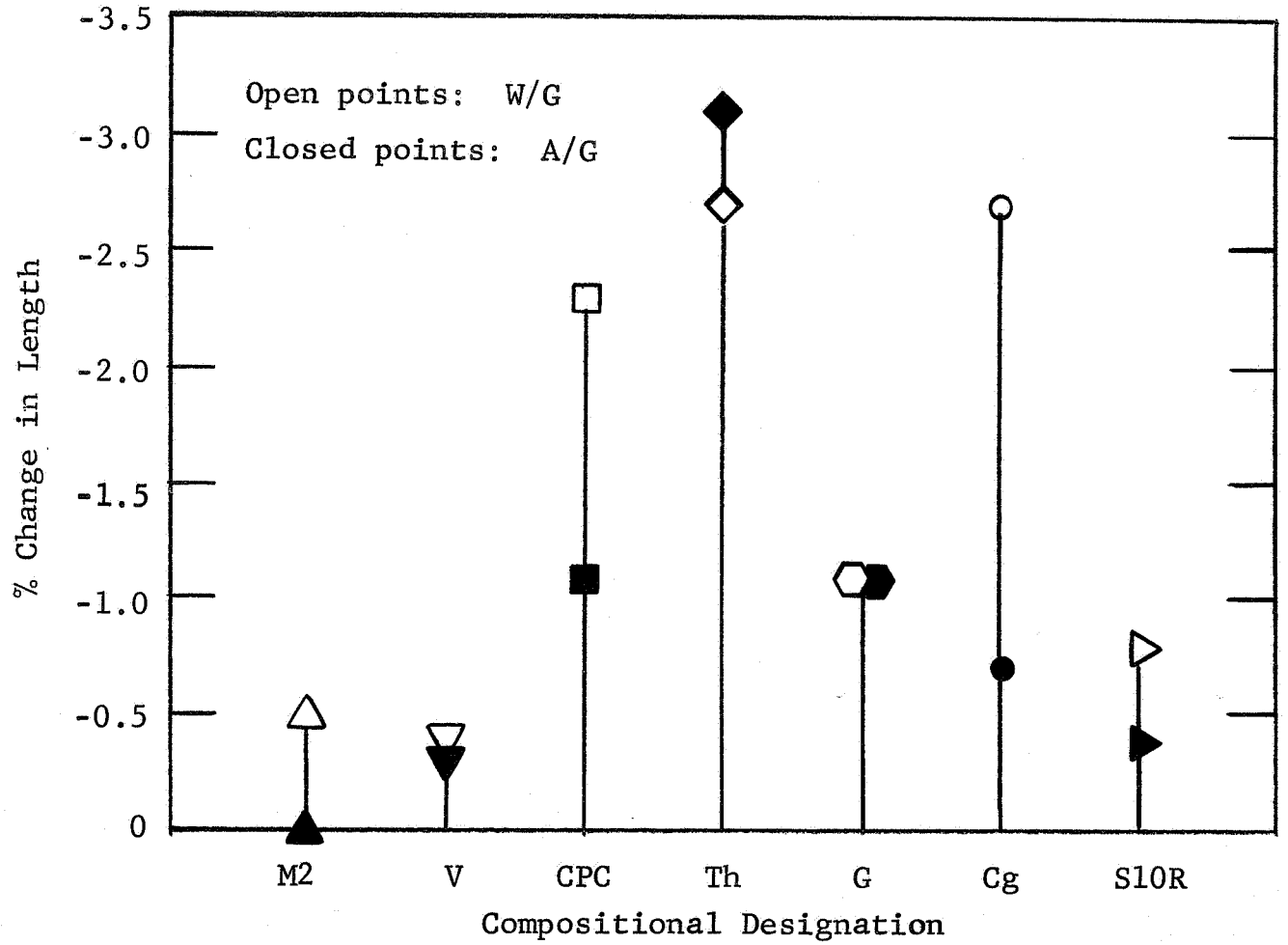


Fig. 7 - COMPRESSIVE DEFORMATION FOR NbC-C COMPOSITES FABRICATED USING DIFFERENT CARBON SOURCES (2700°C, 2000 psi, 30 min)

B. Processing

The TaC-C and TaC-C-additive mixtures were blended by dry tumbling with rubber stoppers for 16 hours. After cold pressing at 1000 psi, the various bodies were hot pressed at 3200°C. This is well above the melting points of Mo_2C (2600°C)[7] and WC (2775°C)[8] and quite close to the solidus for NbC-C, (3220°C)[9].

The use of densification aids in TaC-C composites resulted in dense, well-bonded materials at 3200°C. Temperatures closer to 3300°C appeared necessary for non-additive TaC-C composites in earlier work. As the data in Table IV show, the wt% of the TaC phase was maintained at 80. With the addition of the third phases, i.e., Mo, W, and NbC, the volume ratios of the components were varied. Thus the total carbide content was: 38.4TaC-1Mo, 49.6vol%; 38.4TaC-1W, 54.4vol%; and 38.4TaC-1NbC, 50.3vol%.

In earlier work, it had been shown that for Mo_2C-C composites, as much as 40% of the Mo_2C was squeezed out during hot pressing. Thus it was not surprising that the composite incorporating Mo (46.5NbC-1Mo) lost 2.4% by weight during pressing. If this loss can be assumed to be exclusively Mo_2C, the level was lowered from 5.7 to 3.6vol% or by about 37%. The other composites showed no such weight change due to fabrication. Although WC can be expected to be liquid at this temperature (3200°C), apparently none of it was lost. It would appear that under these conditions, the W is not as mobile as the Mo.

C. Microstructure

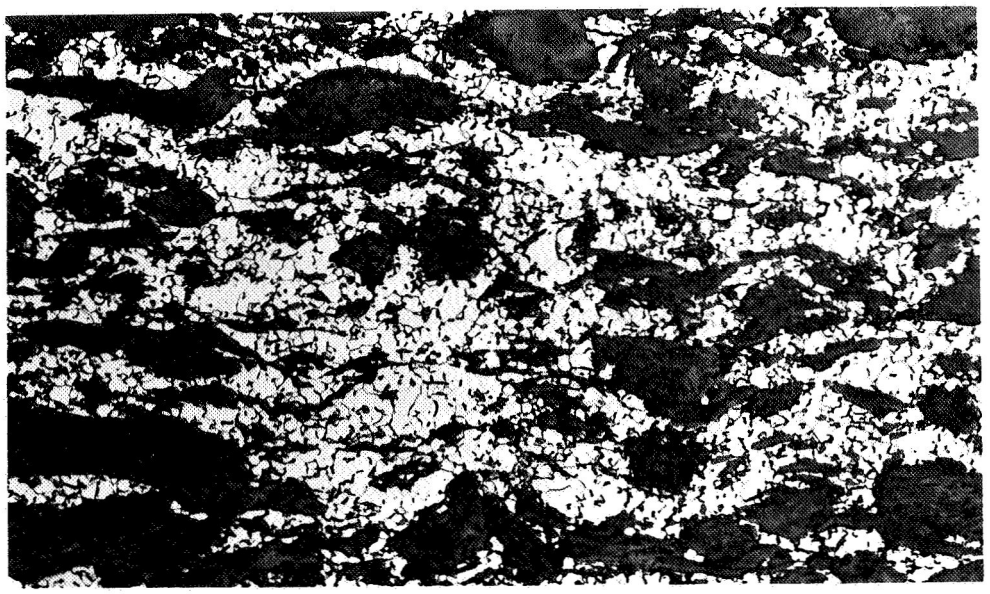
The microstructures of the four TaC-C composites are shown in Figs. 8 thru 11. The influence of the larger particles of M-3 is quite evident in that the finer particle carbide phase appears to be almost forced into a skeletal network around

Table IV

FABRICATION SUMMARY FOR TaC-C COMPOSITES

Compositional Designation	TaC*		Carbon**		Additive***		Density g/cc	%Theoretical Density
	wt%	vol%	wt%	vol%	wt%	vol%		
38.4TaC	80.0	38.4	20.0	61.6	-	-	6.54	94.0
38.4TaC-1Mo	81.5	46.0	14.4	50.4	Mo_2C:4.1	3.6	7.77	95.7
38.4TaC-1W	80.0	49.6	11.5	45.5	WC:8.5	4.9	8.59	95.6
38.4TaC-1NbC	80.0	44.2	14.0	49.7	NbC:6.0	6.1	7.66	95.8

*SP11678A TaC, Wah Chang. Average particle size :3-4μ.
**M-3 graphite, LASL:CMB-6.
***Additives added as Mo, W, and NbC.



a) Sample 1A-T (W/G)

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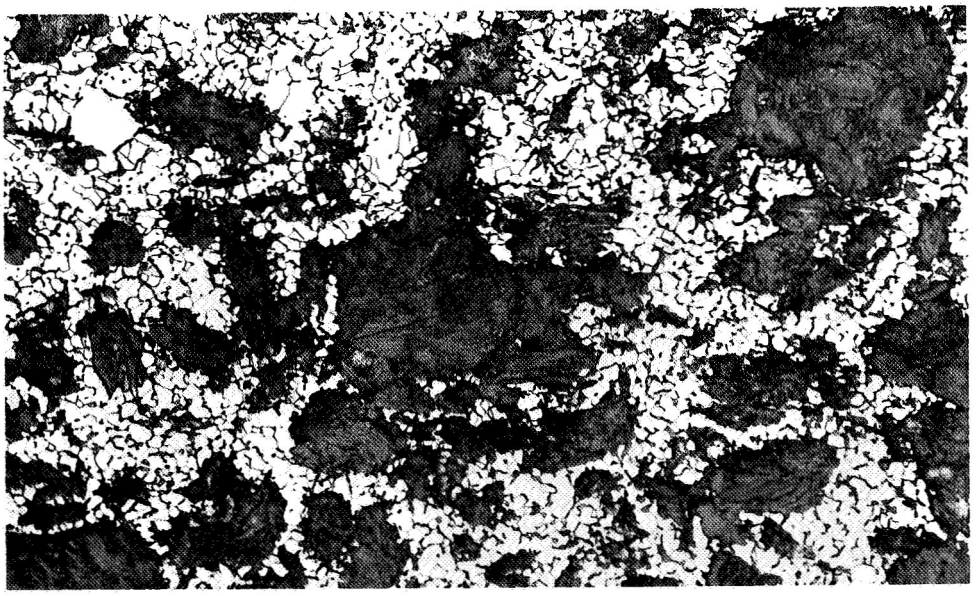

b) Sample 1A-TL (A/G)

Neg. 34885 Mag. X200

Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 8 - MICROSTRUCTURE OF TaC-C COMPOSITE CONTAINING 38.4 vol% TaC

50u

a) Sample 1A-T (W/G)

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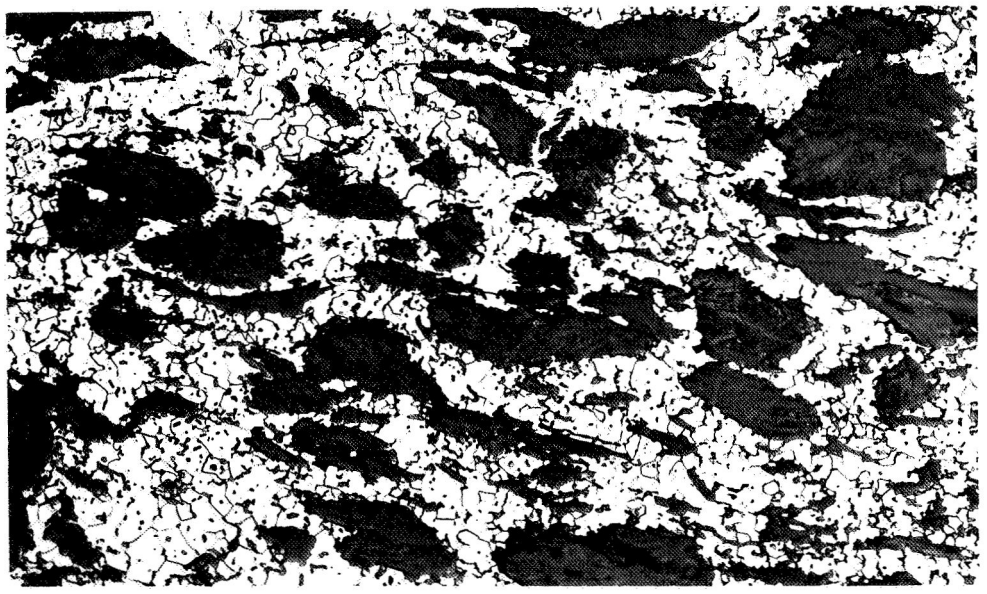
b) Sample 1A-Th (A/G)

Neg. 34891 Mag. X200

Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 9 - MICROSTRUCTURE OF TaC-C COMPOSITE INCORPORATING 4 vol% Mo_2C AS DENSIFICATION AID



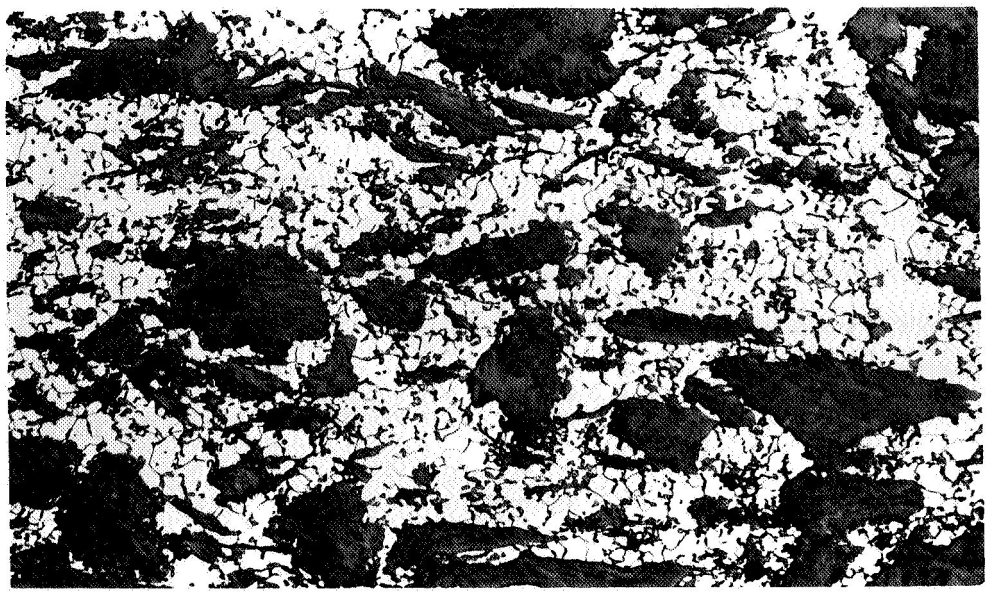
Sample 3C-T
(W/G)

Neg. 34886

Mag. X200

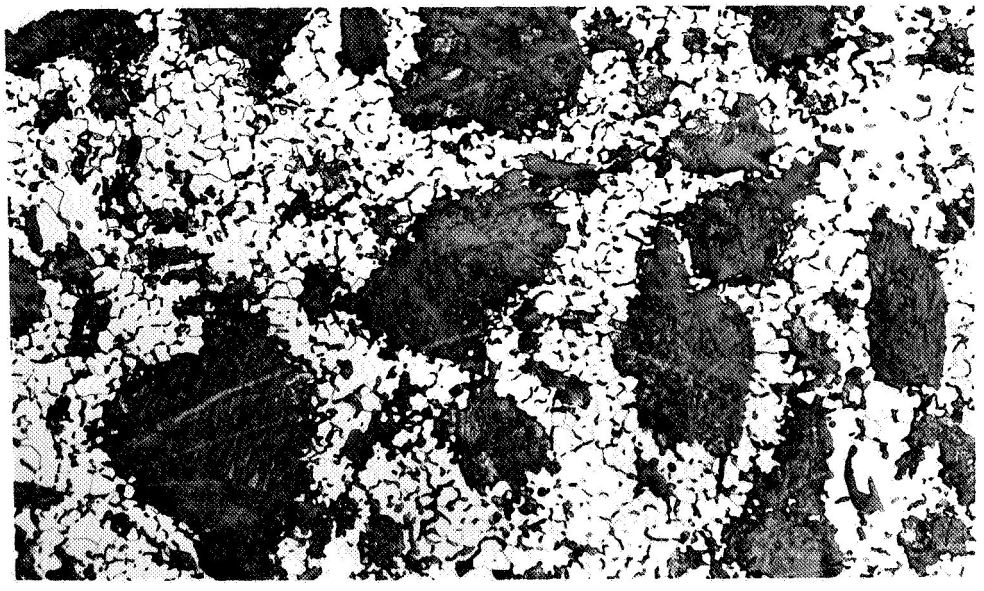
Etchant:
$K_3Fe_2(CN)_6$-NaOH

Fig. 10 - MICROSTRUCTURE OF TaC-C COMPOSITE INCORPORATING 5 vol% WC AS DENSIFICATION AID



a) Sample 3C-T (W/G)

Neg. 34888 Mag. X200



b) Sample 3C-TL (A/G)

Neg. 34889 Mag. X200

Etchant: $K_3Fe_2(CN)_6$-NaOH

Fig. 11 - MICROSTRUCTURE OF TaC-C COMPOSITE INCORPORATING 6 vol% NbC AS DENSIFICATION AID

these larger graphite grains. Strong grain directionality was observed in the W/G direction for 38.4TaC (Fig. 8) 38.4Ta-1W (Fig. 10) and 38.4TaC-1NbC (Fig. 11). The Mo_2C containing composite (Fig. 9) did not appear to be as highly oriented as the others. Furthermore the carbide grains in this composite appeared somewhat larger and more rounded than in the others. The latter condition of grain size and shape suggests that sintering and grain growth may have occurred.

Further microstructural examination will involve the use of microprobe analysis to determine if solid solutions may have been formed. Solid solutions can probably be expected to give different properties from discrete carbide phases. It has been reported that a continuous mutual solubility exists for TaC-NbC and that carbides of the sixth group, Mo_2C and WC, can be dissolved in TaC up to 70%.[10] Determination of lattice constants using x-ray techniques will also be employed.

D. Flexural Strength and Modulus (Room Temp.)

Relationships between carbide content and strength in the TaC-C system incorporating needle coke (CPC) was established in earlier work.[1] Those relationships show that at a carbide level of 38vol%, the W/G and A/G strengths were 13,000 psi and 4500 psi respectively. The present values of 12,010 psi (W/G) and 5710 (A/G) for 38.4TaC shows that less anisotropy exists when M-3 graphite is substituted for the CPC.

These earlier studies[1] also revealed strengths of 17,800 psi (W/G) and 6800 psi (A/G) for composites incorporating 54vol% TaC. The total carbide content in each of the present TaC-C-additive composites is about 50vol%, and the strengths for these composites in Table V are comparable to those for the earlier CPC-containing composites. Anisotropy ratios are somewhat lower for the additive bodies (1.85 to 2.22) as compared to the 2.63 volue using CPC, reflecting the influence of M-3 graphite.

Table V

PROPERTIES SUMMARY FOR TaC-C COMPOSITES

Compositional Designation	Grain Direction	Flexural Strength, psi RT	2000°C	2500°C	Elastic Modulus x10^{6}psi	Electrical Conductivity^{-1} x10^{-4} (Ω-cm)
38.4TaC	W/G	12,010	16,900	12,400	6.4	1.43
	A/G	5,710	7,850	6,450	2.6	0.74
	(A.R.)*	2.10	2.15	1.92	2.47	1.93
38.4TaC-1Mo	W/G	16,430	22,620	16,650	10.3	0.97
	A/G	8,890	11,450	10,850	7.0	0.57
	(A.R.)	1.85	1.98	1.53	1.48	1.70
38.4TaC-1W	W/G	16,970	26,620	19,420	10.9	1.32
	A/G	7,730	12,070	12,450	6.9	0.85
	(A.R.)	2.20	2.21	1.56	1.60	1.55
38.4TaC-1NbC	W/G	17,800	27,250	17,250	12.0	1.89
	A/G	8,030	13,200	10,250	6.2	1.24
	(A.R)	2.22	2.06	1.68	1.94	1.52

*(A.R.) = Anisotropy Ratio

The departure from strongly directional behavior is also observed for moduli values. The present aniostropy ratios of 1.48, 1.60 and 1.93 are considerably lower than the previously determined 2.40 for TaC-C using CPC.

The more isotropic behavior of the TaC-C additive composites can be attributed to the use of M-3 graphite. It is doubtful that any of the additives contributed to this isotropy; actually greater anisotropy might be expected from the highly oriented graphite exsolved during solidification of the carbides of molybdenum or tungsten. Apparently this latter condition is quite limited due to the very small amounts of additives.

E. Electrical Properties

When we again refer to the earlier work in the TaC-C system incorporating CPC, we find that the electrical conductivities were: 1.6 (W/G) and 0.6 (A/G) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$ for 38vol% TaC, and 2.3 (W/G) and 1.4 (A/G) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$ for 53vol% TaC. The conductivity values for 38.4 TaC in Table V, 1.43 (W/G) and 0.74 (A/G) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$, reflect the more isotropic behavior when M-3 is the carbon source.

The conductivity values for the composites incorporating the additives Mo or W were surprisingly low. As shown in Table V, the W/G data, 0.97 (Mo) or 1.32 (W) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$, were lower than that for the 38.4 TaC, 1.43 x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$. The TaC contents for 38.4 TaC-1Mo and 38.4 TaC-1W are 46.0 and 49.6 vol% as compared to 38.4vol% TaC for 38.4 TaC. Although the resistivity values for Mo_2C ($71\mu\Omega$-cm)[11] or WC ($25\mu\Omega$-cm)[11] are higher than that for TaC ($22\mu\Omega$-cm), it is unlikely that these additives have a higher resistivity than the graphite phase. A possible reason for this lower conductivity may be the formation of solid solutions which may be of lower conductivity. As pointed out earlier in this report, x-ray and microprobe analyses will be used to establish such interaction between TaC and the additives.

The composite incorporating NbC (38.4TaC-1NbC) exhibited higher conductivities of 1.89 (W/G) and 1.24 (A/G) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$. However, these values are significantly lower than the 2.3 (W/G) and 1.4 (A/G) x 10^{-2} $(\mu\Omega\text{-cm})^{-1}$ for 53vol% TaC-47vol% CPC (needle coke). This may be due to lower conductivity for M3 graphite, and also to the somewhat lower conductivity for NbC. (The low conductivity values are probably not due to lower degrees of bonding, since the flexural strength values for the TaC-C composites containing additives are all quite high.

F. Flexural Strength (High Temp.)

The flexural strength of these composites were all higher at 2000°C and lower at 2500°C as shown in Fig. 12. As seen previously[1], the TaC-C composites (even with the low melting additives) showed better retention of strength than NbC-C composites. In general, TaC-C bodies exhibit 2500°C strengths somewhat higher than those at room temperature, whereas the NbC-C composites have 2500°C strengths which are 10 to 20% lower than at room temperature.

The improved high temperature properties resulting when TaC is incorporated instead of NbC can be clearly seen by referring back to the data for 46.5NbC-1M3 in Table II. The W/G strength at 2500°C for M3 represents a 40% dropoff from the room temperature value. The TaC-C-additive composites incorporating the same carbon source, M-3, all showed excellent strengths at 2500°C.

Based on the aforementioned work by Speck[8], it is likely that the peak strength in the TaC-C system exists at a temperature other than 2000°C, but at a temperature higher than the 1700 to 1800°C peak for NbC-C. Additional tests will be conducted at temperatures other than 2000° or 2500°C to determine this peak.

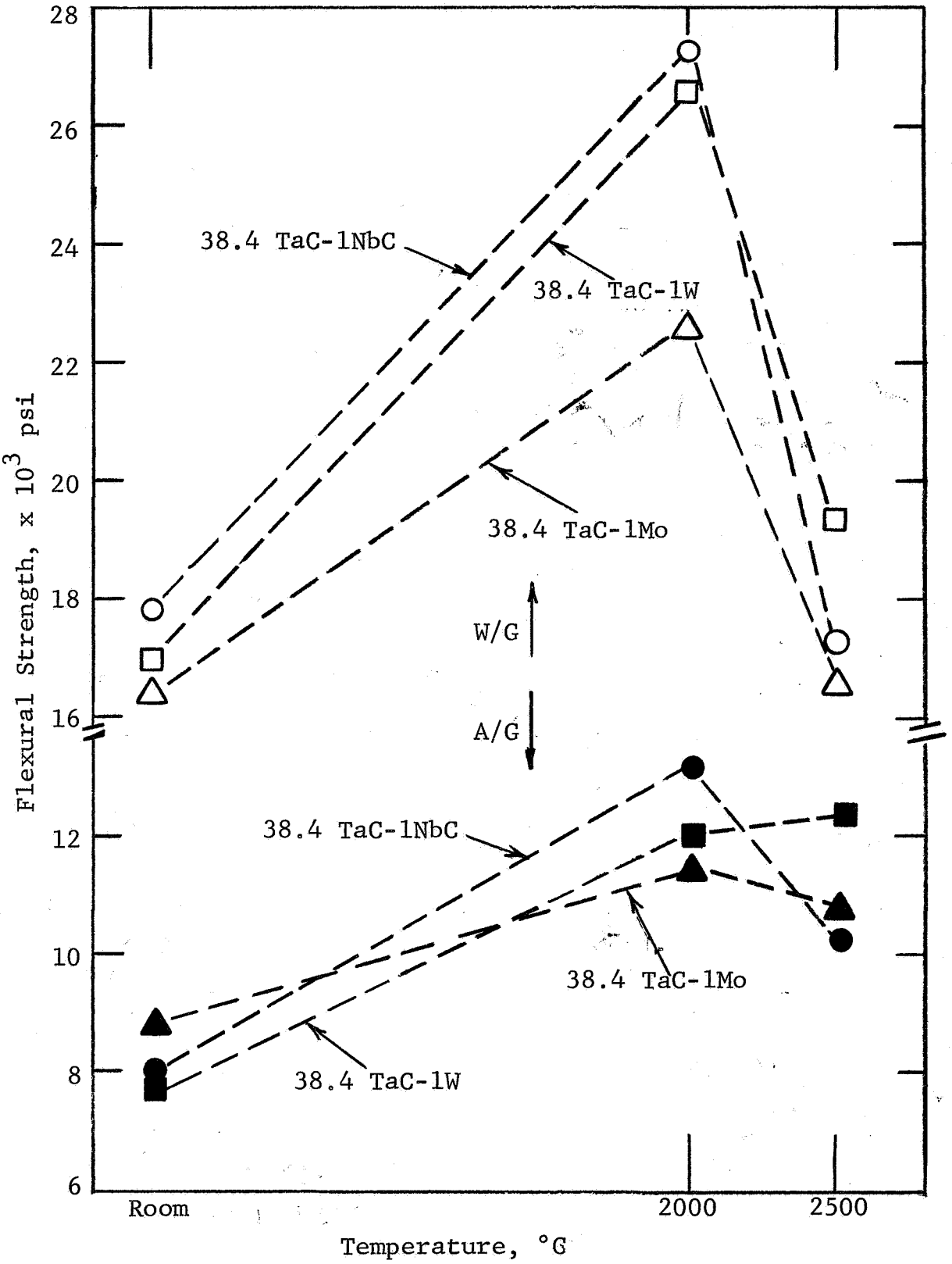


Fig. 12 - FLEXURAL STRENGTH VS TEMPERATURE FOR TaC-C COMPOSITES INCORPORATING ADDITIVES

G. Flexural Creep

High temperature deformation resistance of the TaC-C-additive composites is significantly superior to that for NbC-C composites. The TaC-C composites incorporating additives were tested in flexure at 2500°C under a load of 5000 psi for 1 hr. The observed deflections are presented in Fig. 13; creep rates are shown in Fig. 14.

As shown earlier in Fig. 6, the NbC-C composite incorporating M-3 exhibited a deflection of over .06 in. in the W/G direction. The data in Fig. 13 show that the W/G deflections for the TaC-M3-additive composites were less than .025 in., and the A/G deflections were less than .05 in. Included in Fig. 14 is the creep rate for a 53vol% TaC composite using CPC as a carbon source (compositional designation: 82.5 Ta-A). The additive composites are somewhat more creep resistant than the body without a third phase.

These tests show that incorporation of a lower melting additive in these amounts (about 5vol%) does not degrade creep resistance. A tentative argument would be that an actual improvement is realized, possibly thru improved sintering and bonding. This suggests that TaC-C composites may be fabricated at a lower temperature of 3000°C into equally creep resistant materials. For a realistic comparison, a TaC-C composite of 50vol% TaC using M3 as a carbon source and incorporating no additives, will be fabricated for evaluation.

Furthermore, these results opens an avenue into preparation of NbC-C composites of good high temperature properties by using small amounts of Mo or W. It has been well established in past work[1] that a fabrication temperature close to the solidus is necessary for obtaining NbC-C composites of high strength. However, temperatures in the range 3150° to 3200°C are difficult to control, and exceeding the eutectic temperature

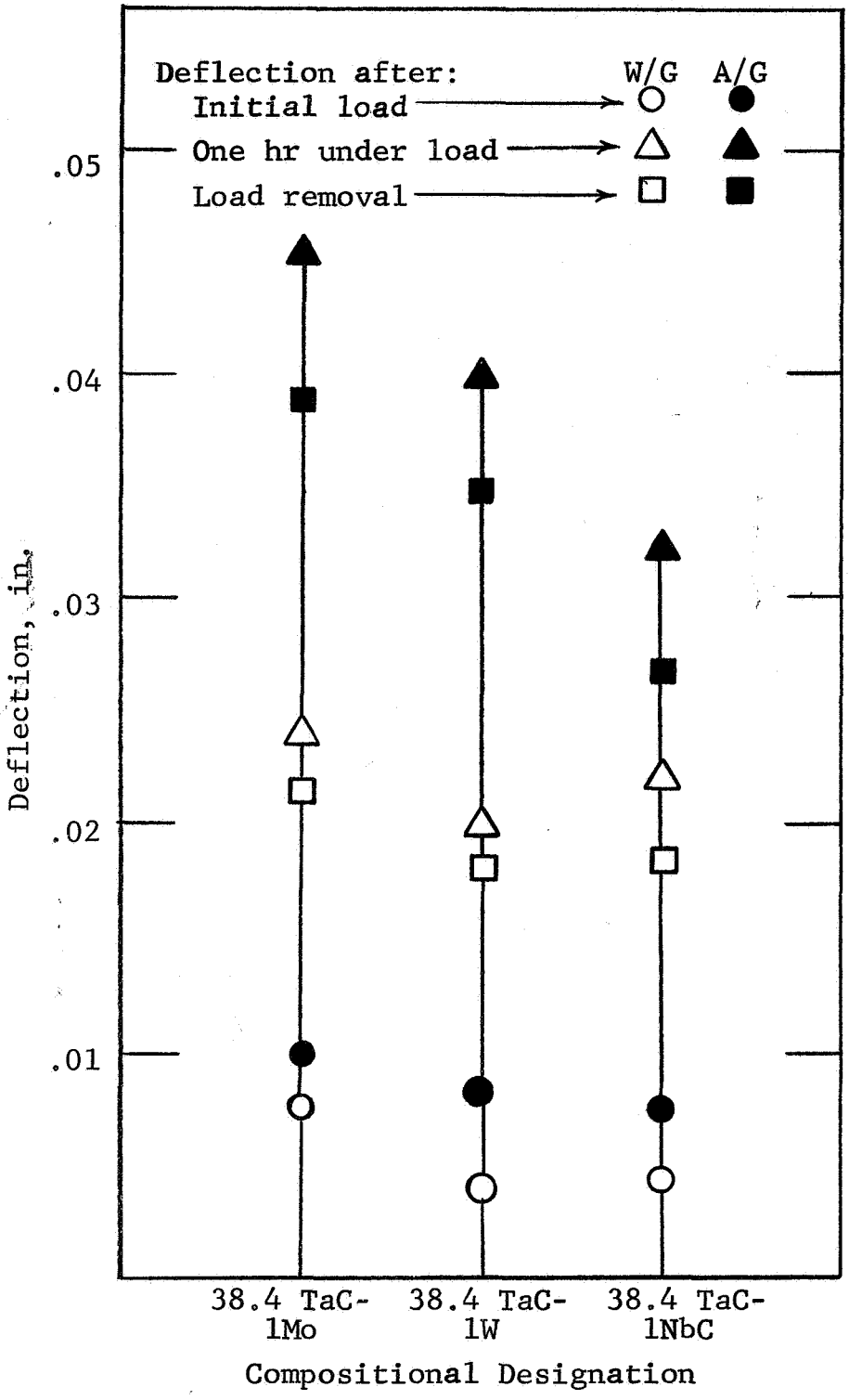


Fig. 13 - FLEXURAL DEFORMATION FOR TaC-C COMPOSITES INCORPORATING ADDITIVES (2500°C, 5000 psi, 1 hr)

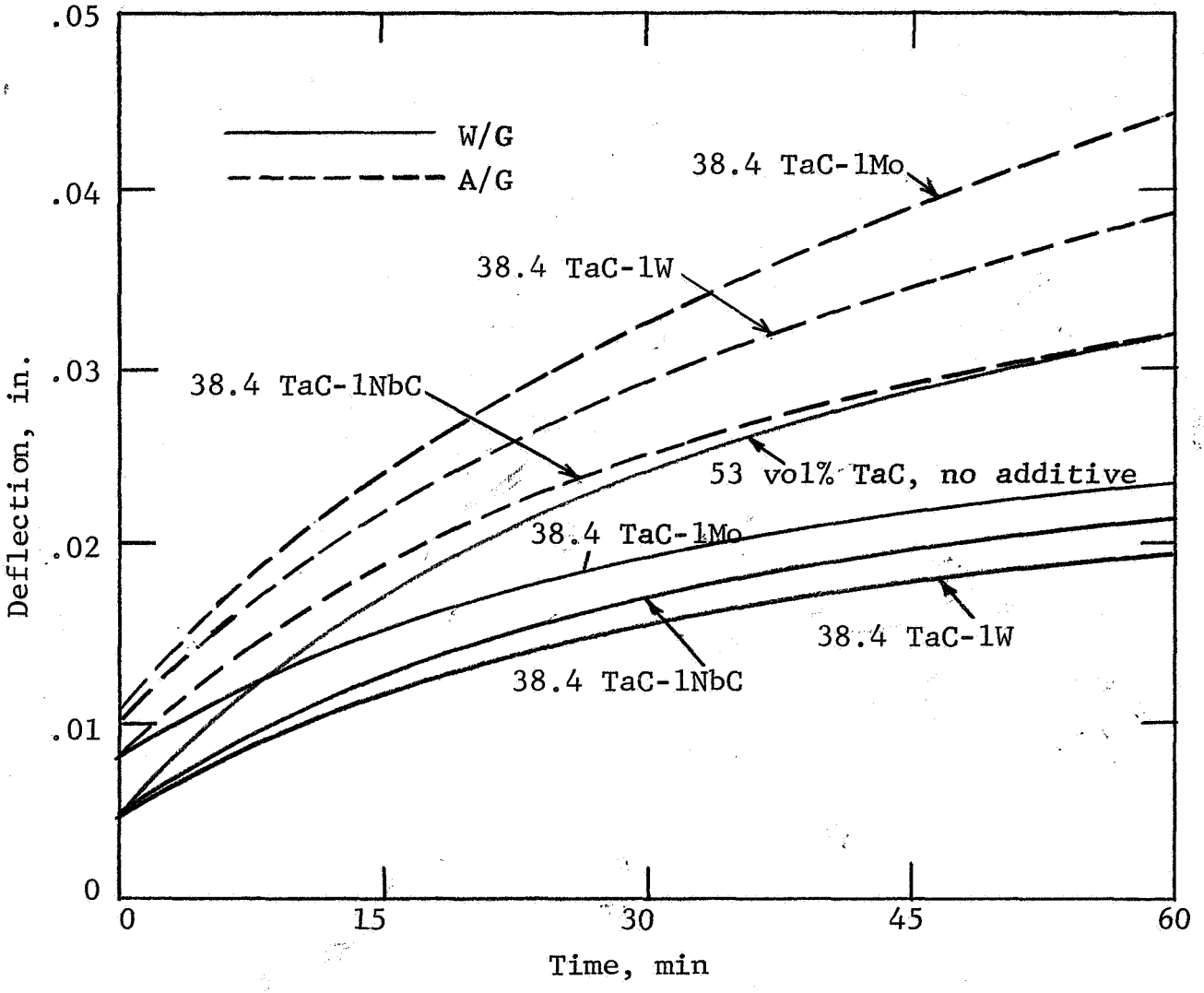


Fig. 14 - FLEXURAL CREEP RATES FOR TaC-C COMPOSITES INCORPORATING ADDITIVES (2500°C, 5000 psi, 1 hr)

of 3220°C can result in gross loss of material. Thus if the fabrication temperature can be lowered to about 3000°C, quality control can be effected much more readily.

Studies of the effect of carbide content upon creep resistance of TaC-C composites have also been conducted during this period. The observed deflections are shown in Fig. 15, and the creep rates in Fig. 16.

A trend as a function of carbide content is seen for the TaC-C system which is similar to that for the NbC-C system, i.e., a trend toward isotropic behavior at higher carbide levels. The NbC-C system had also shown a peak in the deformation vs carbide content curve at about 70vol% NbC. The data gathered for the TaC-C system to date is not sufficient to establish any similar peak.

At the 80vol% TaC level, two composites were evaluated: "90Ta-A" with 3 to 4μ particle size TaC, and "M90Ta" with particle size of about 10 to 15μ. As the data show, the coarser material was more creep resistant than the finer material. This is in keeping with particle size - creep resistance relationships established by other investigators. Where deformation is mainly at grain boundaries, the lower surface contact area with coarser grains does not allow for as many diffusional activation centers as with smaller grains.

IV. CONCLUSIONS AND FUTURE WORK

High temperature evaluations of 47vol% NbC - 53vol%C composites fabricated with different carbon sources have revealed certain composites to have superior properties. From the creep tests conducted at high temperatures, the following findings are the most significant:

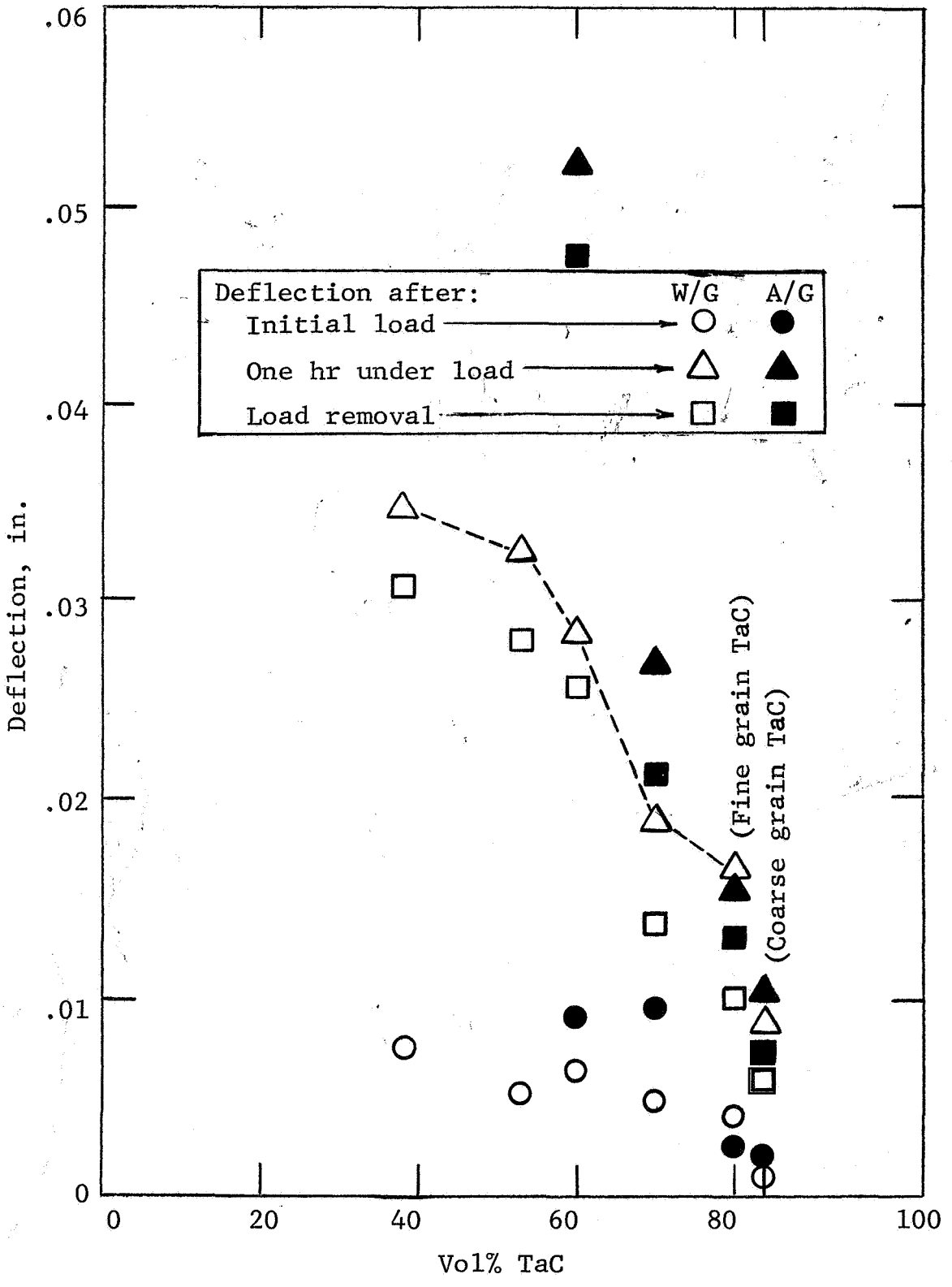


Fig. 15 - FLEXURAL CREEP VS CARBIDE CONTENT FOR TaC-C COMPOSITES (2500°C, 5000 psi, 1 hr)

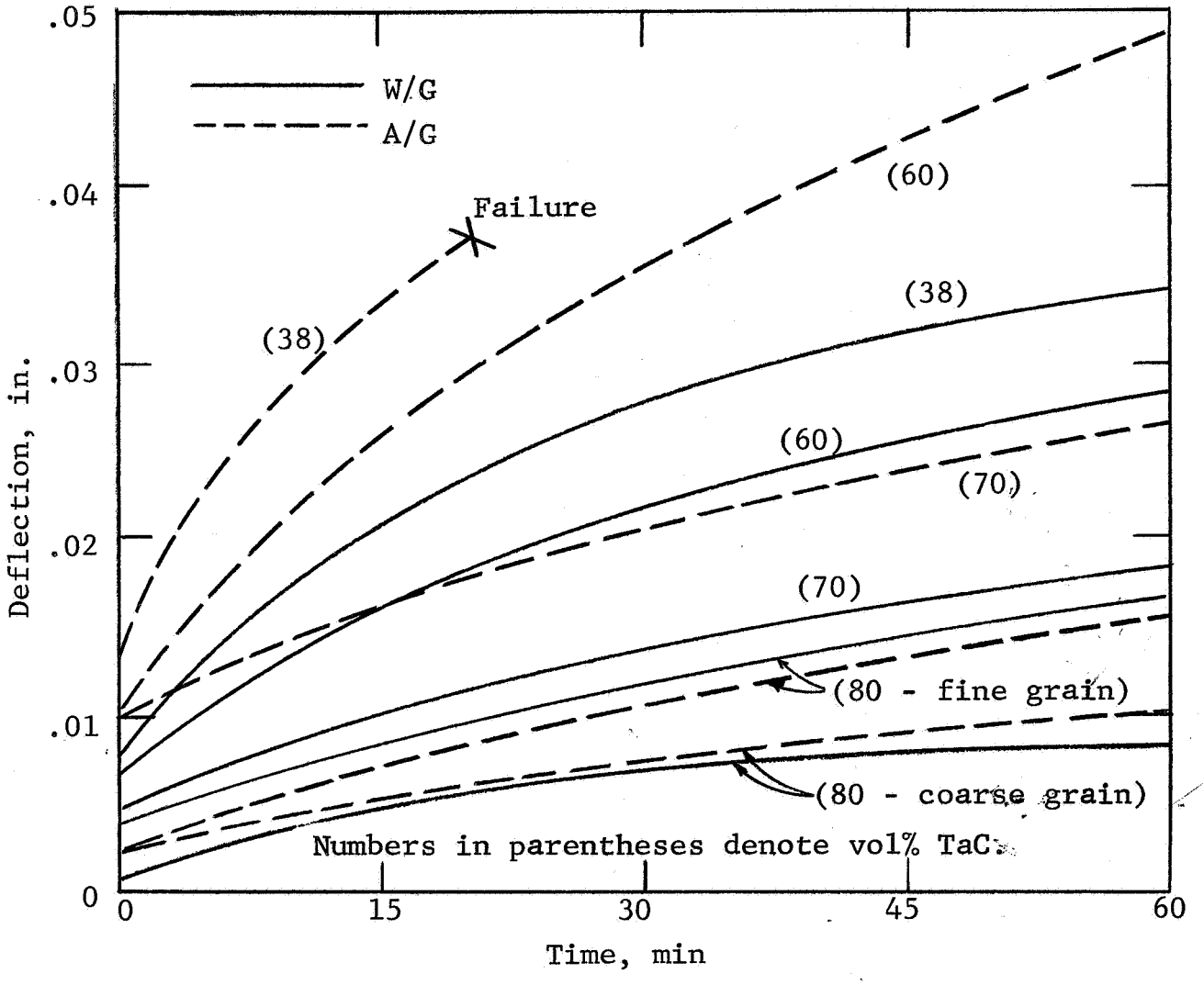


Fig. 16 - FLEXURAL CREEP RATES FOR TaC-C COMPOSITES OF DIFFERENT CARBIDE CONTENT (2500°C, 5000 psi, 1 hr)

1. The best creep resistance in both grain directions is exhibited by composites incorporating M2 graphite. Slightly higher deformations were observed for bodies incorporating Varcum coke, S10R carbon black, or CPC (needle coke).
2. A heat treatment of 1 hr at 2500°C does not materially change the creep behavior of NbC-C composites. Evidently any annealing or further graphitization is too limited to be of benefit.
3. Examination of compressive creep behavior at 2700°C, 2000 psi for 30 minutes, for these various NbC-C composites show that changes in length of less than 1% in either grain direction can be expected for composites incorporating M2 graphite, Varcum resin coke, or S10R carbon black.

The TaC-C system studies have shown that the use of densification aids in amounts of 5vol% such as Mo, W or NbC in composites containing about 45vol% TaC yield dense, well-bonded composites which have excellent high temperature properties. The preliminary studies show that the additive-incorporating composites of a total carbide content of about 50vol% exhibit better creep resistance than equivalent TaC-C composites without additives. Two areas of great potential for the NbC-C system are suggested by these findings:

1. Use of additives in the NbC-C system to obtain improved high temperature properties.
2. Use of lower fabrication temperature which would be easier to control, and also preclude possible loss of material in liquification.

Future work will consider the use of densification aids in the NbC-C system. Work now in progress involves evaluation of a series of composites which have been prepared with different particle size ranges of the carbon source, keeping the NbC a constant. Concurrently, the studies designed to gain an understanding of creep mechanisms will be continued. These studies include investigation of the effect of impurities, determination of activation energies, and correlation of these activation energies to known values for different creep mechanisms.

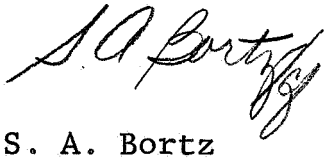
V. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

In addition to the writer the following personnel have been involved in this research program: S. A. Bortz, J. L. Sievert and C. J. Levesque. Records are detailed in Logbook Nos. 18069, 18443, 18450, 18451, 18455, 18457, 18596, 18602, 18605 and 18610.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Y. Harada
Associate Ceramist
Ceramics Research

APPROVED:



S. A. Bortz
Senior Engineer
Ceramics Research

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