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Westinghouse Astronuclear Laboratory

DEVELOPMENT OF A PROCESS TO LOWER THE THERMAL EXPANSION OF HOT PRESSED NIOBIUM CARBIDE - GRAPHITE COMPOSITES (U)

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DEVELOPMENT OF A PROCESS TO LOWER THE THERMAL EXPANSION OF HOT PRESSED NIOBIUM CARBIDE - GRAPHITE COMPOSITES (U)

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ABSTRACT

(CRD) Recent analysis of the NERVA hot end support system revealed that the high with-grain (WG) thermal expansion and the high creep deformation of NRX-A6 NERVA-type 75 w/o niobium carbide - 25 w/o graphite hot pressed composite material may not be entirely satisfactory in future designs. Design requirements have shown the need for a better match between the normally-high average coefficient of thermal expansion ($\bar{\alpha}$) of the composite material and the fueled graphite. A Manufacturing Engineering program was initiated to investigate methods for reducing the difference in the CTE between the fuel and the carbide composite and, in addition, methods for reducing the creep rate. These objectives were targeted to be accomplished on 75-25 w/o composite material.

(U) The experiment was divided into three basic parts: 1) to evaluate the degree of change in the coefficient of thermal expansion (CTE) with hot pressing time at temperature, 2) to evaluate the effect of a carbon source instead of graphite on the CTE, and 3) to evaluate the effect of a heat treatment while under compression on various properties of the billet.

(CRD) It was demonstrated that the coefficient of thermal expansion can be reduced by about 50 percent of the difference between the coefficient for fueled graphite and that for the NRX-A6 type of composite material without compositional changes. In addition, by a slight modification of the carbide-graphite ratio, the process should permit the matching of the CTE of fueled graphite and composite material.

(CRD) The improvements can be accomplished by a compressive heat treatment process in which the billet is subjected to a laterally unrestrained axial compression at an elevated temperature and can be accelerated by the substitution of calcined-petroleum needle coke in place of the graphite flour. A reduction of approximately 50 percent of the difference between the NRX-A6 and fueled graphite CTEs was accomplished with a compressive heat treatment without a die at 2700°C and 2000 psi for 60 minutes.

(CRD) A further reduction of 10 percent was accomplished when these parameters were changed to 2500°C and 3000 psi for 120 minutes.

(CRD) In addition to the reduction in the CTE that can be accomplished by the inclusion of the compressive heat treatment and the use of coke as a carbon source, the creep rate of the material is significantly reduced from the former 3 to 8 percent to a new range of from

2 to 4 percent; WG flexural strength seems to be more uniform and generally higher than NRX-A6 material properties. It has been further concluded that this combination of process changes and, in particular, the compressive heat treatment also reduces the spread within a billet and from billet to billet.

(CRD) The experiments also predicted that the CTE of the fueled graphite might possibly be matched by changing the carbide/graphite composite composition ratio to 65 - 35 w/o. One process for accomplishing this will consist of a compressive heat treatment cycle of 2500°C and 3000 psi for 120 minutes on the 65 - 35 w/o hot-pressed billet with a 50 - 50 ratio of -100 + 150 mesh and -150 + 320 mesh needle coke as the graphite source.

1.0 INTRODUCTION

(U) The number of structural materials that offer satisfactory performance diminishes rapidly as temperature requirements increase. Metal carbides and graphite have received increasing attention since they are among the most refractory materials known.

(U) Graphite is one of the most widely used high temperature materials. Its physical properties are fairly good, grades can be selected with very good thermal shock resistance, and its machinability is excellent. A major shortcoming is its poor high temperature oxidation and hydrogen corrosion resistance.

(CRD) Refractory metal carbides possess an extremely high melting point, exhibit high strength, and have excellent resistance to hydrogen corrosion. However, they have very poor thermal shock resistance and are extremely difficult to machine by conventional methods into hardware configurations. This led to the development of hot pressed composites which are blends of carbide and graphite powders. The 75-25 w/o billets of niobium carbide and graphite have offered a most attractive means for overcoming the poor corrosion resistance of the graphite, and the poor thermal shock resistance and machinability of the metal carbides.

(CRD) Considerable effort in the Manufacturing Engineering programs has been directed toward developing and characterizing the 75-25 w/o composition of hot pressed carbide-graphite composite material and the manufacturing process for NERVA hot end support application, and has resulted in the utilization of composite protection cups in the NRX-A6 reactor. The corrosion performance of these cups was excellent.

(CRD) These programs have dealt almost entirely with 75-25 w/o niobium carbide-graphite composites produced with graphite flour. The effects of raw material purity, processing parameters, hot pressing temperature, and billet size have been examined and several conclusions have been reached. Billet size properly proportioned as to L/D ratio is not process sensitive as long as temperature gradients are not excessive. Pressing temperature has a pronounced influence on creep behavior, i.e., the higher the temperature of hot pressing, the lower the creep deformation. Carbide powder purity and graphite flour particle size are also of major importance since high residual metallic impurities in the carbide powder or superfine graphite flour can double the observed creep deformation. Room temperature

flexural strength is extremely sensitive to pressing temperature or to thermal gradients throughout the billet; the higher the temperature, the higher the flexural strength.

(U) Increased emphasis on the requirements for the NERVA reactor have dictated that a closer look be taken at certain material characteristics and properties as they relate to future designs.

(CRD) Analysis of the hot end support system revealed that the high WG thermal expansion and the high creep deformation of the NRX-A6 type of composite material will not be entirely satisfactory. Reactor Design requirements have shown a definite need for a better match between the normally high average coefficient of thermal expansion $\bar{\alpha}$ of the composite components and that of the fueled and unfueled graphite. The difference in the expansion of the materials is manifested in shear stress at the braze joint between the fuel elements, central elements, and the composite tips as the temperature is varied from the brazing temperature. Furthermore, the higher CTE of the tips requires an undesirable cold clearance to eliminate interference at elevated temperatures. Another factor is the relative expansion of the support pedestal to the tips of the cluster. A lockup due to welding in the expanded condition, or a cold friction lockup and resulting spreading and bending of the ends of the elements during heatup and cooldown can result in high stresses and possible breakage of the fuel elements. Therefore, considerable engineering emphasis was placed on lowering the thermal expansion of hot pressed composites, particularly the 75-25 w/o composition as used in the NRX-A6 reactor.

(CRD) The program described in this report was established to investigate the CTE range that could be covered by practical process and manufacturing changes, and to define a process that would effectively reduce and control the with-grain CTE. This effort included both analytical studies of the literature and planned experimentation. In addition, another major objective of the investigation was to be the reduction and control of the spread of the AG compressive creep rate.

(CRD) The objectives were targeted to investigate processes that would reduce the difference in the coefficient of thermal expansion between the fuel and the carbide composite as much as possible, and reduce the maximum creep rate to a nominal 4 percent under present test conditions. These improvements were to be accomplished without degrading the corrosion resistance or the mechanical properties of the material.

2.0 THEORETICAL ANALYSIS OF PROBLEM (U)

(U) There was no prior art in controlling the CTE of hot pressed carbide-graphite composite materials by process variations. This property was considered to be dependent primarily upon the composition ratio of the carbide to the carbon phases.

(CRD) The 75-25 w/o composition is approximately a 50/50 volume ratio of the carbide and graphite phases, and the hot pressed structure usually consists of two random, intermingled and continuous networks of the carbide and the graphite. Due to the axial pressure during hot pressing, these networks are flattened in the direction of pressing to form elongated "grains" 90 degrees to the direction of pressing. The properties of strength, creep, thermal expansion, conductivity, etc., are therefore markedly different in the with-grain (WG) direction, perpendicular to the direction of pressing, and across-grain (AG) direction, parallel to the direction of pressing.

(U) A method of analysis in which composite materials are treated as a structure rather than a material, led to a disclosure[1] on a process to control the thermal expansion characteristics of hot pressed carbide-carbon composite material. The analysis and theory leading to the disclosure are discussed in the following paragraphs.

(U) The coefficient of thermal expansion of the hot pressed carbide-graphite composite material is controlled at the lower portion of the temperature range by the carbide network because the strength and modulus of elasticity of the carbide is many times that of the graphite. At the upper third of the temperature range, where the coefficient of expansion becomes very important, the modulus and strength of the graphite approach or exceed that of the carbide; therefore, the coefficient of expansion is largely controlled by the expansion characteristics of the graphite.

(CRD) Conventional composite materials have a substantially different characteristic of the carbide network in the WG and AG directions, which is primarily caused by the pressing operation. The strongest carbide network is in a plane perpendicular to the pressing, the WG direction. Upon heating, the carbide network tends to expand faster than the graphite; therefore, at elevated temperatures the graphite tends to restrain the carbide from expanding, thus lowering the expansion of the composite to an intermediate value. Unless the hot pressing

was done isostatically (not conventionally), the graphite portion of the composite will become anisotropic due to the pressure distribution in the die. This anisotropy of the expansion characteristics of the graphite will cause a larger restraint to the carbide in the WG direction and, therefore, lower its CTE. Conversely, it will raise the CTE in the AG direction which is also the weakest direction of the carbide network.

(CRD) Theoretically, the expansion characteristics of a composite material can be changed by varying the composition (the relative amounts of carbide to graphite), and/or by making the graphite portion more anisotropic. Since our composition ratio range is restricted, and our interest is primarily in the expansion characteristics in the WG direction, it appears most practical to determine the range of expansion control possible by making the graphite component of the composite more anisotropic. This might be accomplished in several ways. First, a longer pressing cycle in the conventional hot pressing process should achieve more anisotropy of the graphite, though it does not appear that this change will result in the greatest reduction of the CTE because of the restraining effect of the die in decreasing the anisotropy of the graphite. Second, a post-pressing compressive heat treat can be used in which the hot pressed billet is re-pressed without a die. In this manner, an unrestrained axial compression should more effectively reorient the graphite phase to a more anisotropic material, thus reducing the CTE in the direction perpendicular to the axis. The magnitude of this reduction in the CTE should be controllable and predicted by the temperature, pressure, and time and would probably be limited only by the amount of deformation or slumping acceptable. This treatment also should be beneficial in densifying the billet and improving the resistance to creep. Third, the substitution of a carbon or coke for the graphite flour would permit graphitization in situ in a highly oriented manner due to the axial pressure distribution and should, therefore, be a more rapid means of lowering the WG expansion characteristics.

3.0 EXPERIMENTAL PROCEDURE AND RESULTS (U)

(CRD) A purchase order was placed to investigate the effect of hot pressing dwell time, post pressing hot compressive heat treatment, and the use of needle coke on the WG thermal expansion properties. This hot pressing and thermal expansion measurement was conducted at the Carborundum Company's New Products Division, primarily because of their large billet hot pressing facilities capability and their thermal expansion capability (optical tracking) to 2500°C. The thermal expansion test procedure and apparatus are described in the appendix.

3.1 BASIC EXPERIMENT (U)

(CRD) Five billets, 3-1/8 inch OD x 3-1/2 inches long, consisting of two halves of different compositions of NbC and graphite (Figure 3-1), were hot pressed at 3100°C and 3000 psi. This procedure gave the advantage of moderately large billet manufacturing procedures and abundant material of two compositions manufactured under identical pressing conditions for the determination of a single variable of the properties of two compositions.

(CRD) A 50/50 w/o ratio of the carbide and graphite was selected as the low composition for four of the billets, the high-composition half being the conventional WANL 75-25 composition. This 50/50 weight ratio was selected to obtain an end point that permitted interpolation for intermediate compositions if they appeared acceptable from a corrosion point of view. One dual billet with 65/35 and 60/40 compositions was included in this initial evaluation. The combinations and pertinent process information are shown in Table 3-1.

(CRD) TABLE 3-1

SPLIT BILLET FABRICATION DATA (U)

Billet Ident.	Composition L	Composition H	Carbon Source (-60 +150 Mesh)	Hot Press Time (min.)	Heat Treatment Temp. (°C)	Heat Treatment Press (psi)	Heat Treatment Time (min.)
1	50/50	75/25	WANL Flour	90	2500	None	60
2	50/50	75/25	Needle Coke	90	2500	None	60
3	50/50	75/25	Needle Coke	15	2500	None	60
4	50/50	75/25	Needle Coke	15	2700	2000	60
5	60/40	65/35	Needle Coke	90	2500	None	60

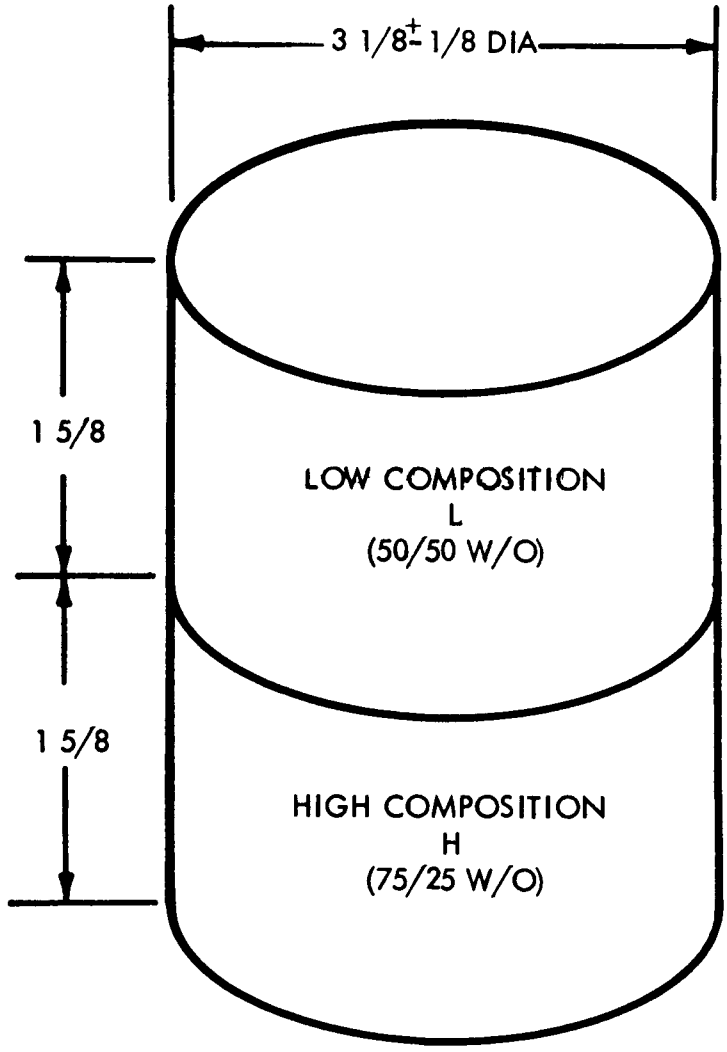


Figure 3-1. (CRD) Billet Configuration (U)

(CRD) The ten materials in Table 3-1 were evaluated for thermal expansion behavior to 2500°C, AG compressive creep resistance at 2500°C, 4000 psi for 60 minutes, and room temperature WG four-point loading flexural strength and density. Results are shown in Table 3-2. Included are the properties of a similar size billet manufactured under NRX-A6 process conditions, evaluated on the same thermal expansion apparatus (see Appendix A).

(CRD) TABLE 3-2

SUMMARY OF SPLIT BILLET PROPERTY DATA (U)

Billet Identity	CTE ($\bar{\alpha}$)	Billet Density (% TD)	Creep Data (%)	Flexural Strength (psi)
1 H	7.59	94.2	1.9	16,050
2 H	7.35	94.6	4.1	14,800
3 H	7.50	94.7		
4 H	7.00	97.5	3.8	17,000
5 H	6.05	93.5		
1 L	6.58	87.0	2.1	8,450
2 L	5.16	91.8	2.7	11,850
3 L		82.5		
4 L	4.87	92.6	3.0	10,350
5 L	5.29	88.2		
5 1*	8.25	93.5	6.0	10,500

* NRX-A6 Prototype 75/25 billet.

3.2 OPTIMIZATION OF THE COMPRESSIVE HEAT TREATMENT (U)

(U) This phase of the program was undertaken to fully exploit the potential of the second compressive heat treatment operation in reducing the thermal expansion as illustrated by the evaluation of Billet No. 4.

(CRD) For this series of experiments, billet size was scaled up to production size and the following conditions were maintained identical for all billets hot pressed:

Carbon Phase	-60 +150 mesh needle coke
Composition	75 w/o carbide and 25 w/o carbon
Hot Press Temperature	3100°C
Hot Press Pressure	3000 psi
Dwell Time	15 minutes
Billet Size	3-1/2 inch diameter x 4-3/4 inches long

(CRD) A billet (No. 6) was pressed for reference purposes only, followed by the conventional stress relieving heat treatment of 2500°C for 1 hour. Then, four billets were hot pressed and the compressive heat treatment was varied. Process information is shown in Table 3-3.

(CRD) TABLE 3-3

THE COMPRESSIVE HEAT TREATMENT CYCLE (U)

Billet Ident.	Hot Press Time at 3100°C (min.)	HEAT TREATMENT Temp. (°C)	Pressure (psi)	Time (min.)
6	90	2500	None	60
7	15	2700	2000	60
8	15	2700	3000	6
			1500	90
9	15	2700	2500	20
			1000	70
10	15	2500	3000	120

(U) Evaluation of the effect of variations in the compressive heat treat cycle on pertinent properties is shown in Table 3-4.

(CRD) TABLE 3-4

SUMMARY OF PROPERTY DATA OF SECOND PRESSING CYCLE OPTIMIZATION (U)

Billet No.	CTE ($\bar{\alpha}$)	Creep Deform. (%)	WG Flex.	% TD
6 (Ref.)	7.40	not tested	13,400	97.0
7	7.00	3.3	15,000	96.0
8	6.85	4.1	14,300	96.3
9	6.70	3.5	13,800	95.3
10	6.10	3.9	13,900	95.4

3.3 SENSITIVITY OF PROCESS TO CARBIDE AND CARBON LOTS (U)

(U) After the experiment on the compressive heat treatment cycle optimization was accomplished, an evaluation was made of the effect of various lots of carbide and carbon powders on the room temperature flexural strength of hot pressed billets. A 3-1/2 inch x 4-1/2 inch "Dagwood" was made, consisting of four wafers or layers, to determine the variations that might be introduced by various combinations of old and new carbide powder and new and old calcined-petroleum-coke lots. No significant change was noted in the billet properties of the four combinations of powder lots as shown in Table 3-5.

(CRD) TABLE 3-5

EFFECT OF POWDER LOTS ON FLEXURAL STRENGTH (U)

Wafer No.	Material Combination	Percent Change in Flexural Strength
1	Carbide - new WANL Flour - old	13,400 psi (Ref.)
2	Carbide - new CPC - new	+ 10.5%
3	Carbide - new CPC - old	+ 5.9%
4	Carbide - old WANL Flour - old	+ 6.5%

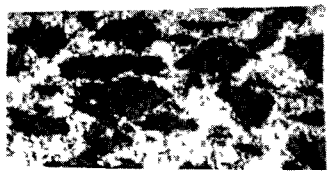
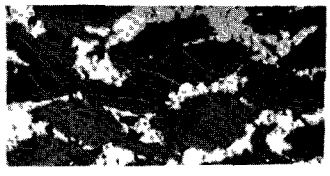
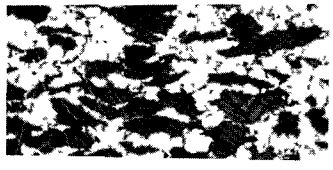
3.4 SENSITIVITY OF PROCESS TO CARBON PARTICLE SIZE (U)

(CRD) Another large 75/25 "Dagwood" was made from material and four layers again had the carbon phase mesh size as illustrated in Table 3-6.

(CRD) The results and wafer microstructure of this experiment are also shown in Table 3-6. It was concluded from this experiment that a 50-50 mixture of both screen sizes as shown in Figure 3-2 should be specified in order to ensure improved process control and thereby better mechanical property control. Obviously, more work should be done on optimizing the selective screening and blending of the materials.

(CRD) TABLE 3-6

EFFECT OF CPC MESH SIZE ON BILLET PROPERTIES (U)

Wafer No.	Carbon Phase	Flexural Strength Average of 3 Tests (psi)	Creep Rate (%)	Microstructure
1	-150 +325 Mesh Graphite Flour	13,000	2.5	
2	-60 +150 CPC	16,300	1.8	
3	-100 +200 CPC	17,200	2.8	
4	-150 +325 CPC	17,500	3.4	

Notes:

1) Manufactured per PDS 30106-2, except carbon phase as noted.
2) Flexural Test - Span 3/4 inch outer, 3/8 inch inner on 0.250 x 0.200 inch specimen.

4.0 DISCUSSION OF RESULTS (U)

4.1 GENERAL (U)

(U) As development time was limited due to reactor schedules, a minimum number of tests were planned and arranged in a sequence such that the following experiments could take advantage of the results of the preceding ones. The main purpose of the experiments was to determine trends rather than absolute values; therefore emphasis was placed on relative changes. To eliminate the majority of the variables, when possible the comparative test billets contained two compositions and were made from the same batch of carbide powder and carbon source, which added confidence to the validity of the experiments. Furthermore, the repeatability of the relative CTE measurements was previously established to be of the order of ± 1 percent. Appendix A presents representative thermal expansion curves and discusses the methods of measurement.

(U) These analyses will be made first on the individual experiments, and the overall analyses and conclusions will be presented separately.

4.2 THERMAL EXPANSION (U)

4.2.1 Effect of Pressing Cycle Time on CTE (U)

(CRD) The composites made of nuclear-grade graphite for reactor use are normally held at maximum pressures and temperatures for 15 to 45 minutes. Heatup times have varied from 10 minutes to 3 hours, depending on furnace type, size, billet size, and method of heating. The heatup time of the furnaces used in these experiments was approximately 3 hours, as shown in Figure 4-1, since this process was developed for large billet sizes. During a normal pressing cycle, some degree of anisotropy in the graphite component is obtained which will be reflected in a difference in CTE in the WG and AG directions. The WG (perpendicular to the pressing direction) expansion characteristics are of prime interest, because with this orientation the composite material is in direct contact with the graphite at the brazed joint of the tips. The pedestals are also oriented in machining from the billets such that the WG direction becomes the important factor.

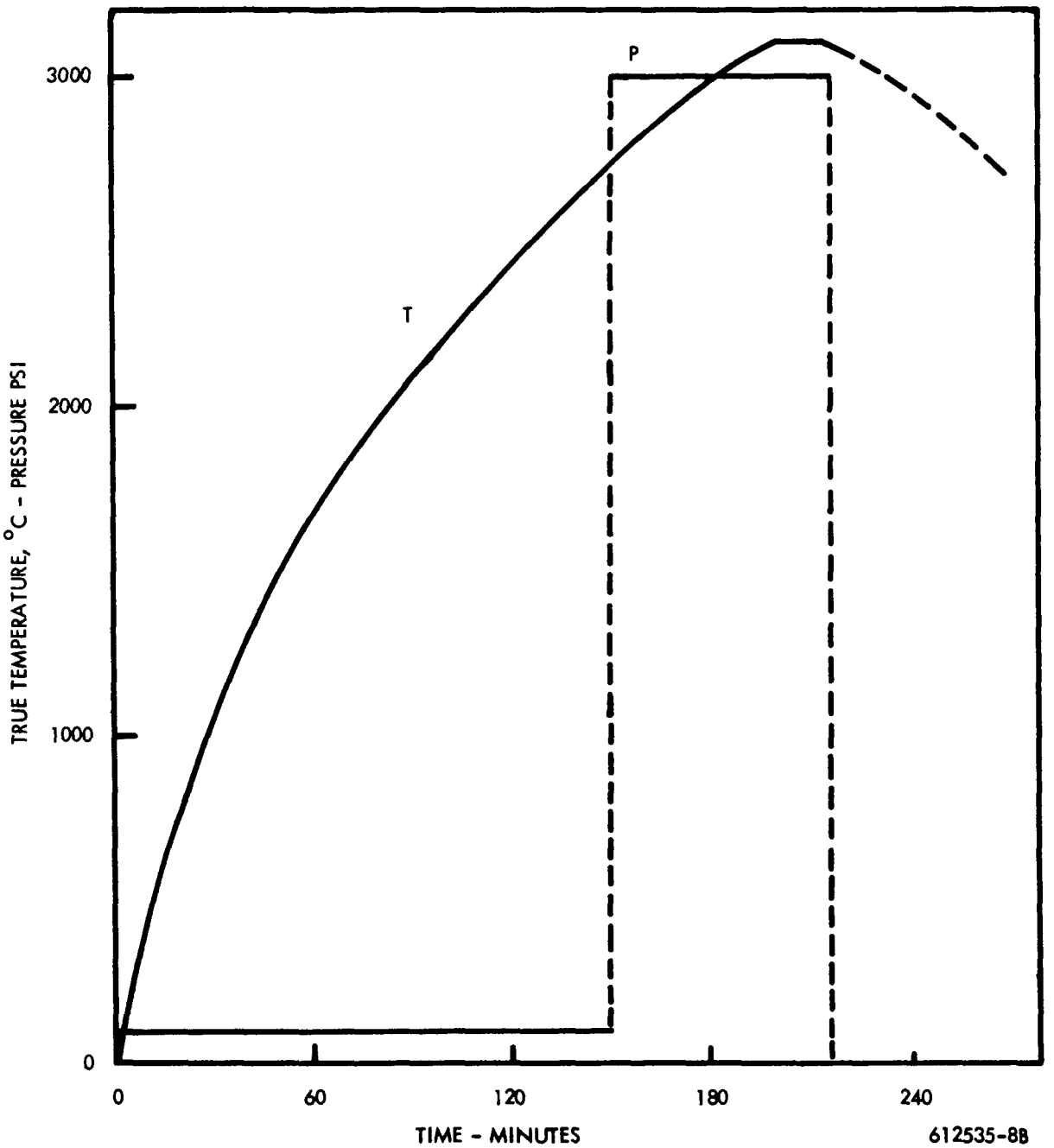


Figure 4-1. (CRD) Typical Large Billet Time, Temperature, Pressure Hot Pressing Cycle (U)

(CRD) Previous standards of the expansion characteristics of composite materials were based on the NRX-A6 production type in which the normal pressing cycle was approximately 30 minutes. To explore the effect of longer pressing times, billet 1H was pressed for 90 minutes, utilizing the same type of nuclear grade graphite carbon source and carbide powder as used in the previous composites. It was also given the standard 1 hour at 2500°C unrestrained heat treatment to ensure dimensional stability. The thermal expansion of this billet was reduced from the previous normal by approximately 8 percent, and as shown in Figure 4-2 the difference in the CTE of A6 composite and fueled graphite was reduced by 20 percent.

4.2.2 Alternate Carbon Source (U)

(CRD) An alternate carbon source was selected for the second phase of this portion of the experiment. Calcined-petroleum-coke (CPC), a high-purity, partially-graphitized petroleum product normally used for high-quality graphites, was chosen in view of the wide use of this type material by other experimenters (Carborundum, IITRI). These experimenters indicated a slight reduction in the reported values of the thermal expansion compared to that of normal nuclear grade graphite made using an identical process. Therefore, Billets 2 and 3 were made with 90-minute and 15-minute pressing cycles, respectively, to establish the trend of reduction with time for this carbon source. The 15-minute pressing cycle showed approximately a 9 percent reduction in the CTE from the previous standard nuclear grade flour NRX-A6 billets. The 90-minute cycle indicated a further reduction, the difference between NRX-A6 material and fueled graphite CTE's having been reduced by about 25%. It was concluded from this portion of the experiment that increased pressing times could significantly lower the CTE of the composite, and in conjunction with needle coke as the carbon source could significantly reduce the difference of the CTE between NRX-A6 material and fueled graphite. However, even with a different carbon source the rate of reduction was enough to warrant investigation of the compressive heat treat cycle. Furthermore, the CPC appeared to offer the lowest expansion with the minimum amount of pressure, temperature, and time.

(U) In addition, starting with a carbon source instead of a graphite source should improve the density. Carbon has been shown to have a creep deformation rate much larger than graphite, and a greater compaction of the irregularly shaped particles of graphite and carbide was to be expected.

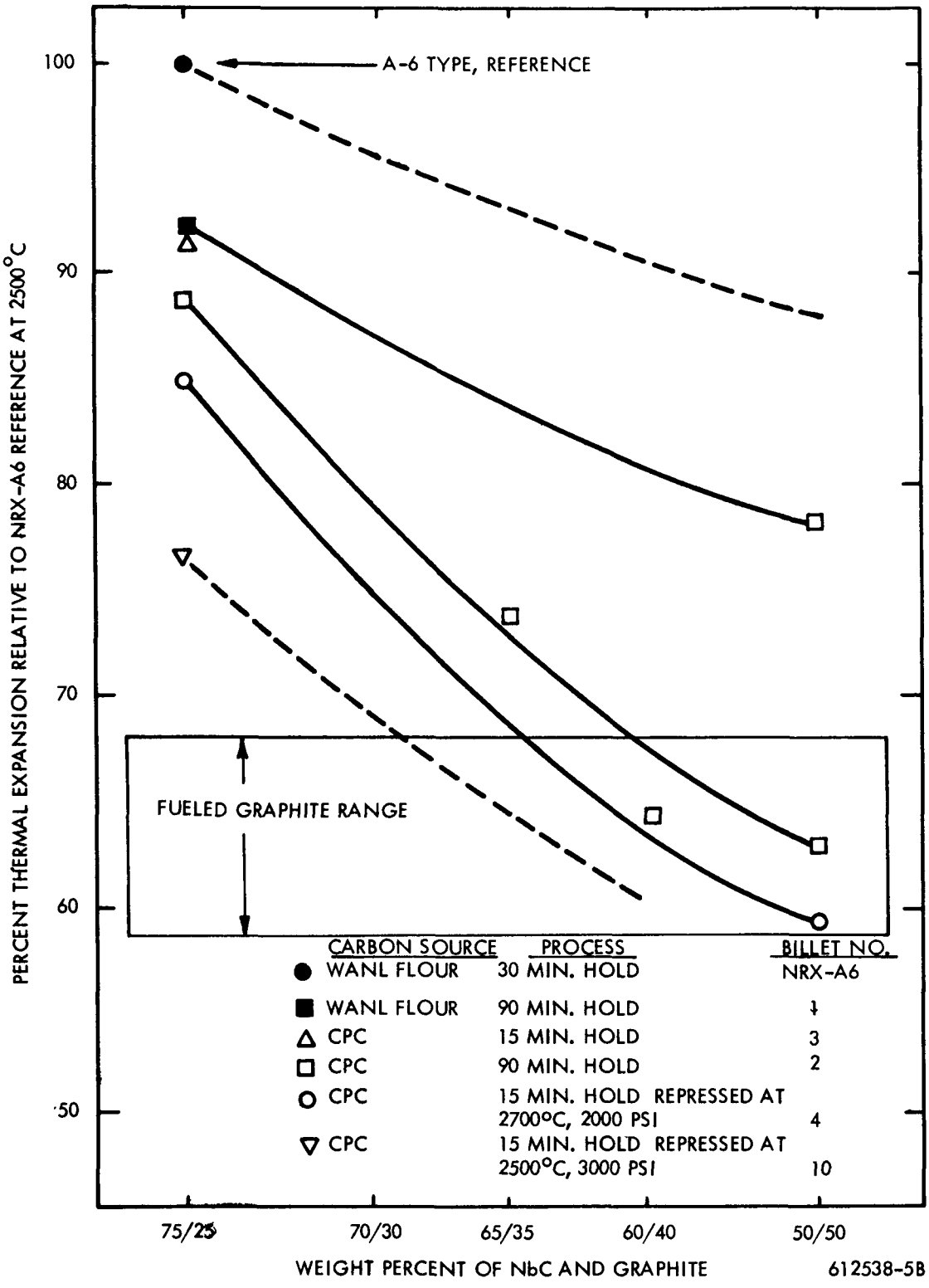


Figure 4-2. (CRD) The Effect of Hold Time and Second Pressing Cycles on the CTE for Various Carbon Sources (U)

(U) This increase in density amounted to 3 to 6 percent over that measured for NRX-A6 and PeWee I billets made from nuclear grade graphite.

4.2.3 Effect of Compressive Heat Treatment (U)

(CRD) Billet 4 was pressed at the normal hot pressing temperature for 15 minutes, using CPC as the carbon source. It was then repressed without a die for 1 hour at 2700° and a 2000 psi axial pressure for 60 minutes. This resulted (as illustrated in Figure 4-2) in a reduction in expansion of 16 percent, an effective decrease of 50 percent in the difference for the NRX-A6 composite material and fueled graphite. This verified the basic analysis[1] that this compressive heat treatment would be the most effective way of reducing the CTE without a change in the basic 75-25 composition. It appeared that this operation warranted further exploration to determine the basic trends of the effect of pressure, time, and temperature with CPC as the carbon source.

(CRD) No experiments were run on a repressing cycle with the standard nuclear grade flour, since it was concluded from the results of the first test that considerably more time would be required to reorient this highly graphitized material than would be required to orient the calcined-petroleum-coke during graphitization in the pressing operations. There is no apparent reason, however, given sufficient time, temperature, and pressure, that this could not be accomplished to the same degree as with the coke source.

4.2.4 The Effect of Composition Changes (U)

(CRD) Each of the billets described above was made with one-half of a 50-50 w/o composition, designated L in Table 3-2. In Figure 4-2, the top dashed line is from previously reported data on the expansion characteristics of various compositions and shows the normal trend of expansion, with composition following the normal manufacturing cycle. These data were reported by Carborundum, where this experiment was conducted; therefore, the dotted line is considered valid within the experimental accuracy.

(CRD) In the case of the 90-minute hold time (second line from the top in Figure 4-2), the reduction from reported values was approximately 15 percent with the 50-50 composition, or almost twice as much as in the case of the 75-25 composition. This is to be expected since,

as previously mentioned, the graphite is the controlling factor and there is a substantially greater graphite-to-carbon ratio in the lower composition and the reduction in expansion should be greater. In the case of the new carbon source (CPC) (line 3 from the top, Figure 4-2), a substantially larger reduction was also obtained on the lower composition. The compressive heat treated material utilizing CPC (line 4 from the top) also followed the expected trend with the lower composition.

4.2.5 Effects of Varying Parameters for the Compressive Heat Treat Cycle (U)

(CRD) There was no previous art on the effect of compressive heat treatment on the properties of a composite, particularly for the expansion characteristics. The first experiment utilized 2700°C, 2000 psi, and 60 minutes, based on an estimated 5 percent deformation of the billet during this cycle. It was considered undesirable to permit excessive deformation, and yet it was necessary to determine the general effects of the three variables, temperature, time, and pressure, on the WG expansion characteristics of these materials. Other factors considered desirable were a practical maximum of approximately 2 hours of furnace time and a minimum of 2500° temperature. These were considered the optimum from a thermal stability standpoint as related to expected reactor temperature limits. The lower curve of Figure 4-2 shows the expected trend of the CTE versus composition for this maximized cycle.

(CRD) Figure 4-3 shows the general trend of the CTE control over the limited range of parameters investigated. The four billets in the experiment are compared on this figure to the CTE obtained with composites made with CPC as-pressed for 15 minutes without any further heat treatment, i.e., zero time, zero degrees, and zero pressure. The top solid line shows the expected trend at 2700° and 60 minutes, pressed at 2000 psi. The dashed portion of this line indicates the extrapolated values that would be unacceptable from a deformation standpoint. The second solid line indicates the trend at 2700° for a longer period of time or 90 minutes. In order to maintain the maximum acceptable deformation, the pressure will have to be limited to around 1800 psi. Again, the dashed portion indicates the region unacceptable from a deformation standpoint. The trend utilizing a lower temperature, 2500°, for a longer period of time, 120 minutes, at 3000 psi is shown on the lower right of Figure 4-3. This gave the lowest value of CTE and the approximate value of deformation that occurred on the two previous

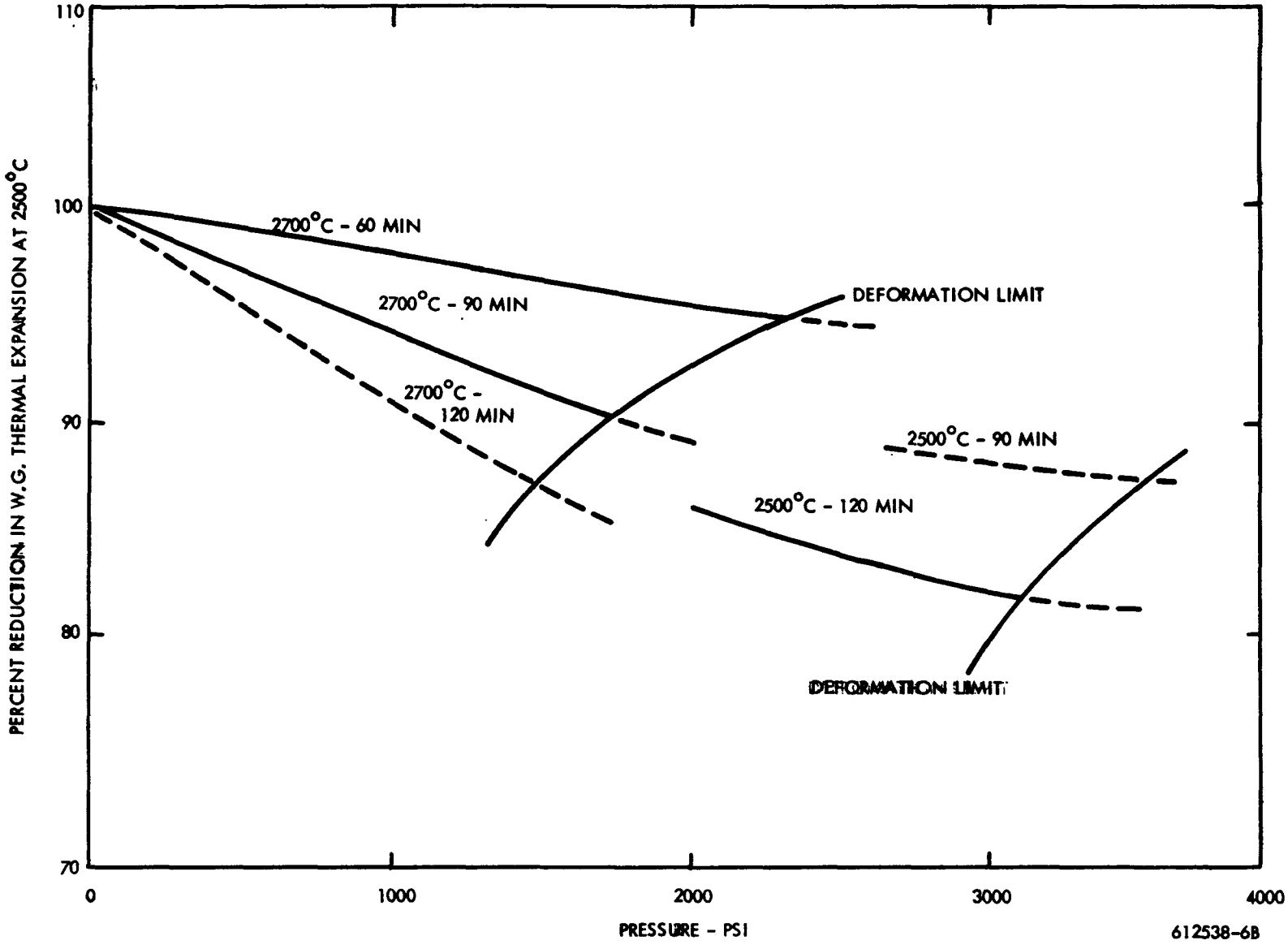


Figure 4-3. (CRD) Projected Parameters for Second Pressing Operation (75-25 CPC) (CRD)

process conditions. The bottom dotted line at the left of the figure is the anticipated trend for 2700° and 120 minutes. Note, however, that the deformation limits expected for this high temperature and longer time would not result in as low a CTE as could be obtained by the lower temperature, longer time, and higher pressure.

(CRD) While the above experiment was based only on a few variations of the basic parameters, it does appear that the 2500°C and 120-minute time at 3000 psi is a practical base line for any further studies, since it resulted in an additional 10 percent reduction of the CTE of material compressively heat treated by the 2700°C, 2000 psi, 60-minute cycle.

4.3 EFFECT OF PROCESS PARAMETERS ON OTHER PROPERTIES (U)

4.3.1 Creep (U)

(CRD) A secondary but also important purpose of the experiments to vary the parameters in the compressive heat treat cycle was to determine its effect on the creep characteristics of the material. The creep characteristics of most interest to the design application of these materials is for a period of operation of 1 hour. Consequently, a standard for determining creep characteristics has been called out in existing specifications to be the percent reduction in length of a cylindrical specimen of a 2/1 L/D ratio when subjected to an axial pressure of 4000 psi at 2500°C for 1 hour.

(CRD) Experiments conducted at WANL indicated that approximately two-thirds of the deformation occurs during the first half-hour of the 60 minute test.[2] It was anticipated that this compressive heat treatment would, therefore, shift the creep characteristics of this material for subsequent cycles to the flatter portion of the creep characteristic curve. No correlation could be found from the limited data generated to indicate that any of the compressive heat treatment cycles would be significantly better, as related to creep rate, than the others. This is believed to be entirely due to the experimental error in determining creep deformation. With reference to the data available (Reference 2), the critical dependence of creep on temperature plus the difficulty of measuring temperature accurately and repeatably indicates that a variance of ± 50°C of temperature for a creep test could produce readings on a material having a nominal creep rate of 3-1/2 percent of values from 2.8 to 5 percent. Thus, until statistical data are available, no conclusions can be drawn regarding

the advantage, as far as creep rate is concerned, of any one compressive heat treat cycle over another. Figure 4-4 compares the data of compressive heat treated material with A6 and PeWee I data.

(CRD) Of significance, however, is the fact that using a carbon powder rather than graphite flour has materially aided in the densification of the basic billet. The reason for the densification may not be apparent; however, when starting with graphite and hot pressing the composite, the graphite has inherently higher resistance to creep and does not densify except under high temperature, pressure, and long times. The calcined-petroleum-coke, however, is basically carbon which has a creep rate possibly an order of magnitude higher than the graphite. It, therefore, allows the quick densification of the composite during the hot pressing operation before complete graphitization has taken place.

(CRD) This densification is further enhanced by the compressive heat treatment, and previous work has indicated that high density billets have inherently low creep characteristics. It is expected, therefore, that this second operation will tend to reduce the spread of the creep from billet to billet, and the maximum values as reported appear to be quite acceptable from a design viewpoint.

(CRD) Experiments with the lower compositions reveal a substantial lowering of the creep, as was to be expected with lowering carbide content materials and with the better bonding and densification obtained by the use of calcined-petroleum-coke.

4.3.2 Flexural Strength (U)

(CRD) The flexural strength of the composites made during this evaluation have indicated generally better properties than had previously been obtained on the NRX-A6 material. Figure 4-5 shows the average values plotted for the various compositions made from CPC. Since the CPC was chosen for the reason of easier CTE control, the values of the reported data of this carbon source are of the most importance. There are two basic reasons why the flexural strength should be improved over the NRX-A6 type composite material. First, the basic pressing temperature has been raised by 100°C and, second, the graphite phase is approaching theoretical density and its strength is increasing rapidly. This increase in graphite strength not only contributes to room temperature flexural strength, but other investigators have reported that the composites made from this carbon source have elevated

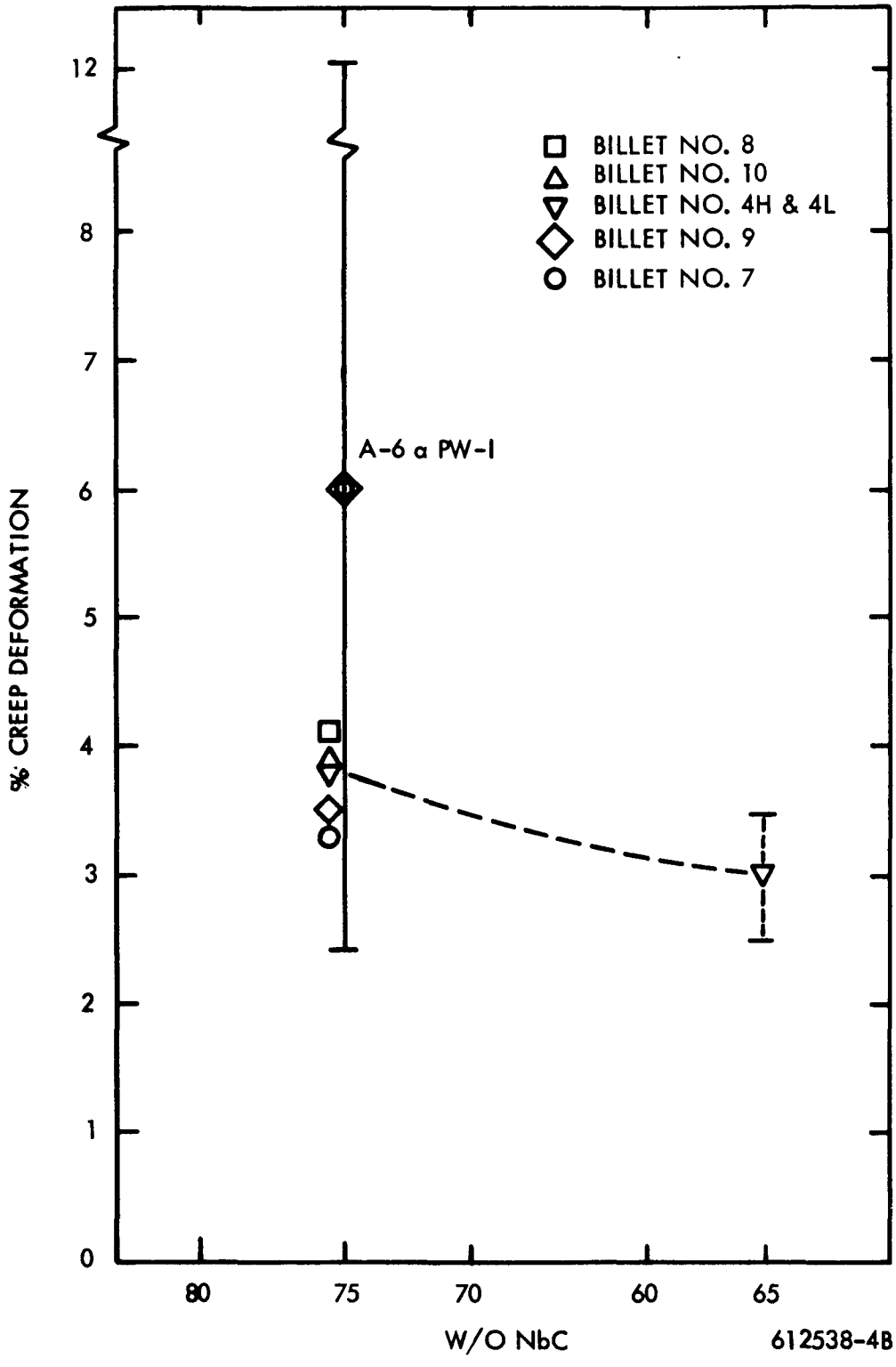


Figure 4-4. (CRD) Comparison of Creep Deformations (U)

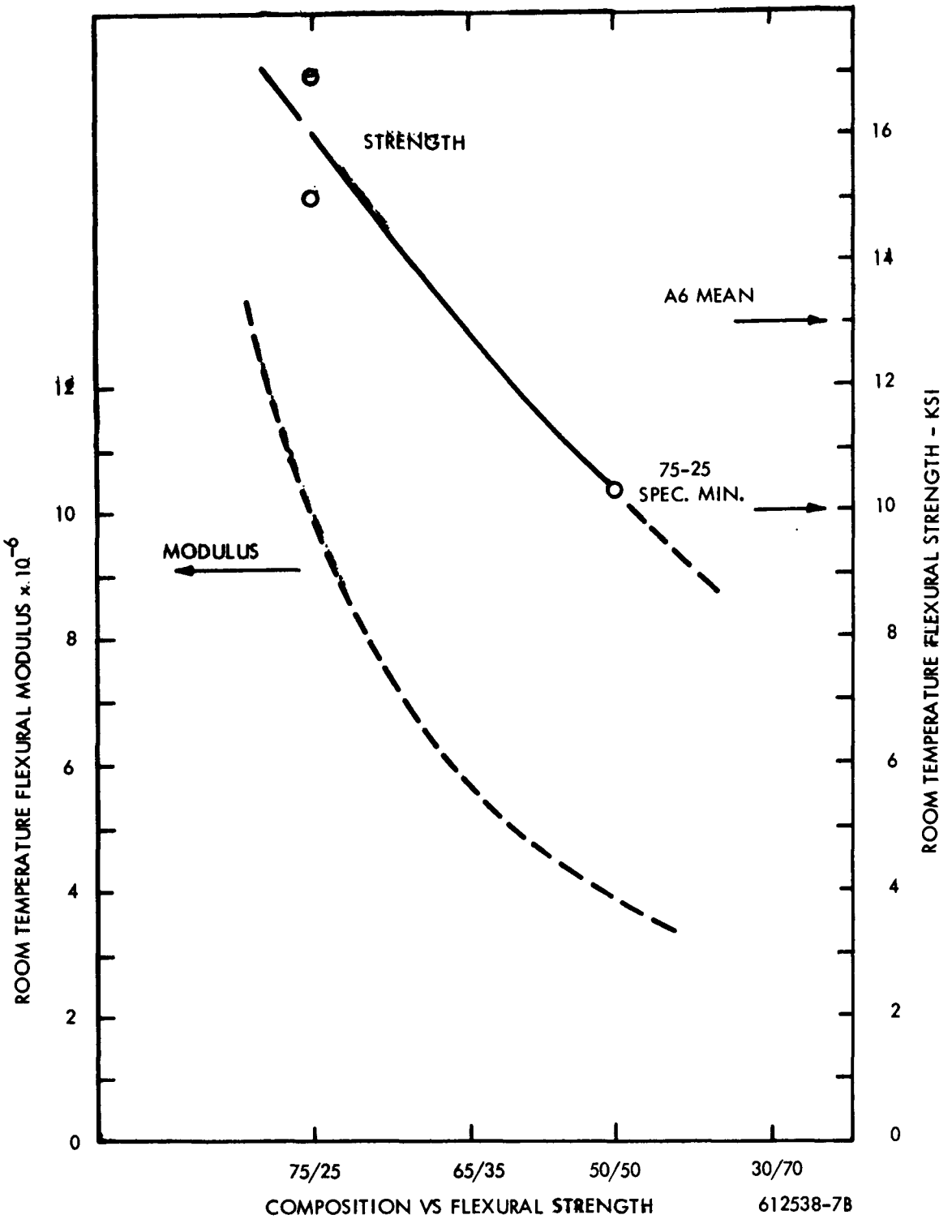


Figure 4-5. (CRD) Composition Versus Flexural Strength (U)

temperature strength much higher than composites made from graphite. This compressive heat treated composite made from CPC material will naturally be somewhat more anisotropic than the previously used composite materials. However, anisotropy, per se, is not harmful in that the with-grain direction is the direction in which the principal stresses occur on all existing designs utilizing these materials. Furthermore, the CTE is the most important design factor.

4.3.3 Carbon Powder Particle Size (U)

(CRD) From the experiments conducted (results shown in Table 4-1), in which a "Dagwood" type of billet composed of four wafers with various carbon particle mesh sizes was hot pressed, it was concluded that the optimum properties, the needle coke powder particle size, should be a 50-50 mixture of -100 +150 and -150 +325 mesh sizes. This is illustrated in Figure 4-6. The effect of the carbon powder sizes on the hot pressed 75-25 billet microstructure of the four wafers is shown on Table 4-1.

4.3.4 Microstructure (U)

(CRD) Figure 4-7 shows the difference in microstructure of the isotropic NRX-A6 graphite flour and the needle-like nature of the calcined petroleum coke used in this program. Also, these photomicrographs graphically illustrate the difference in the size fractions of the -150 +325 mesh flour used in the NRX-A6 billets and the -60 +150 mesh needle coke selected for this program. Other experimenters[3] reported that needle coke results in an increase in the anisotropy of the hot pressed billets, and that a larger carbon particle size tends to further increase this anisotropy. In addition, it was believed that larger graphite particles would decrease the creep rate. Since the total area per unit volume of the carbon powder is decreased by using a larger mesh fraction than used on NRX-A6 billets, a more dominant continuous carbide network should result for any composition with subsequent improved corrosion resistance. Photomicrographs (Figures 4-7, 4-8, etc.) seem to confirm this improved carbide structure.

(CRD) The increase in the directionality of the microstructure resulting from the substitution of needle coke for the isotropic flour is shown in Figure 4-8. Two billets, 1H and 2H, were pressed under identical process conditions and parameters, the only difference in their makeup being the carbon source; 1H is -60 +150 mesh flour and 2H is the same size

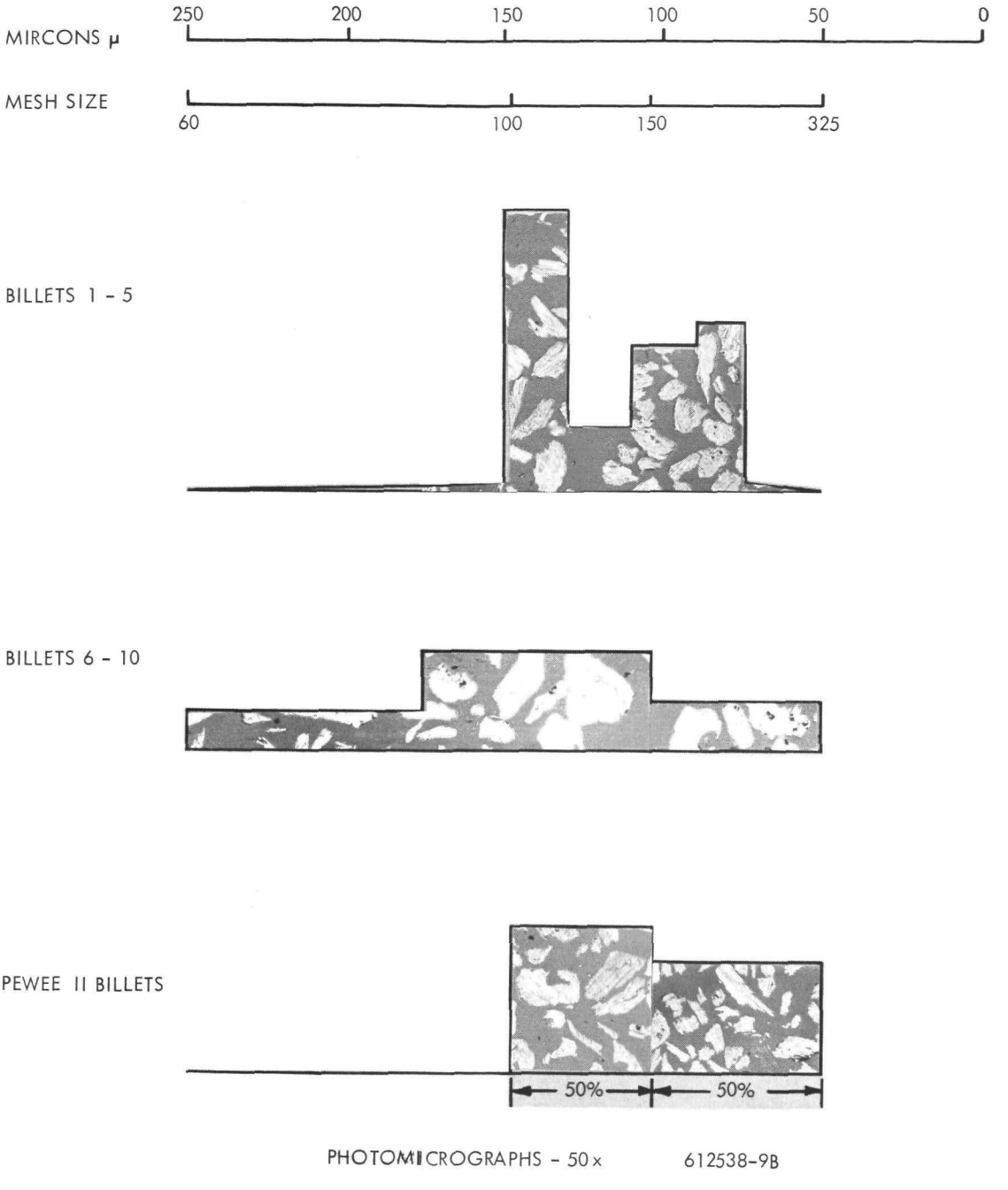
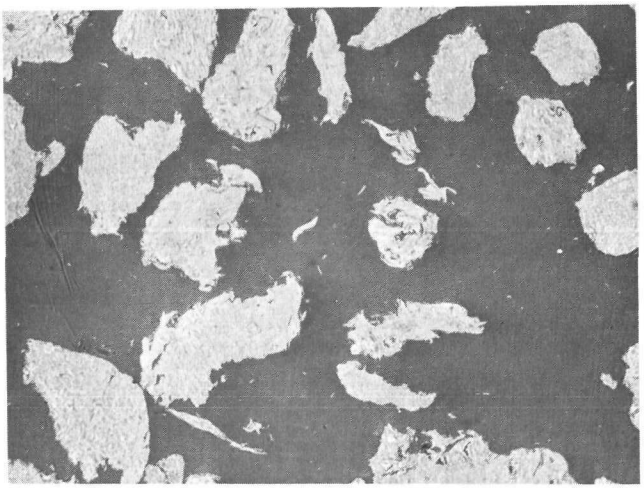


Figure 4-6. (CRD) Calcined Petroleum Coke Characterization - 50X (U)

Nuclear Graphite Flour,
-150 +325 Mesh



Calcined Petroleum Needle
Coke, -60 +150 Mesh

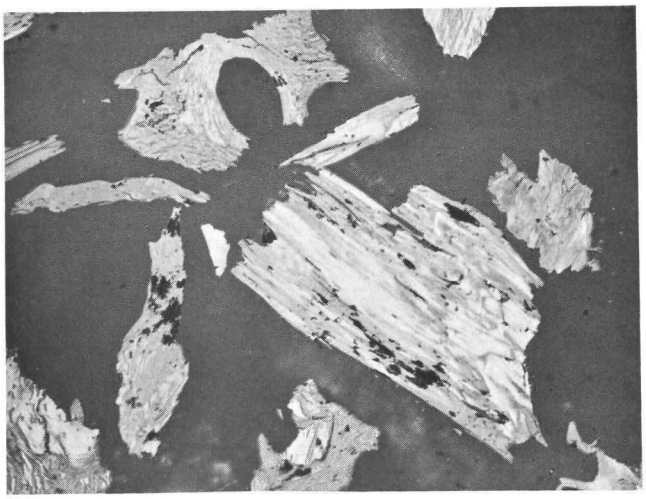
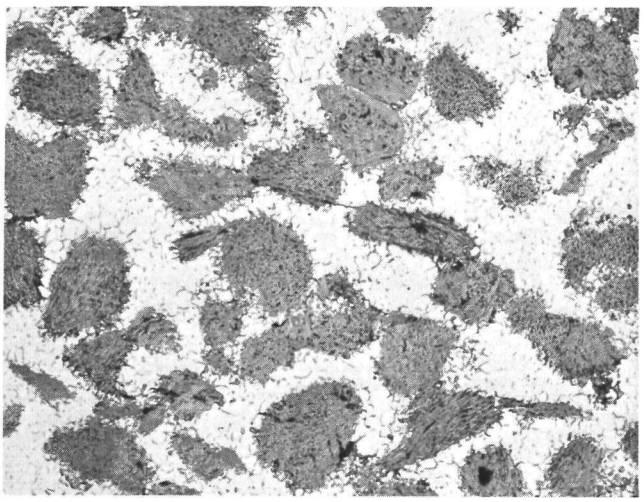


Figure 4-7. (CRD) Particle Size and Shape of Carbon Powders - 250X (U)

BILLET 1H

Hot Pressed 90 Minutes with
-60 +150 Mesh Nuclear Graphite
Flour



BILLET 2H

Hot Pressed 90 Minutes with
-60 +150 Mesh Calcined
Petroleum Coke

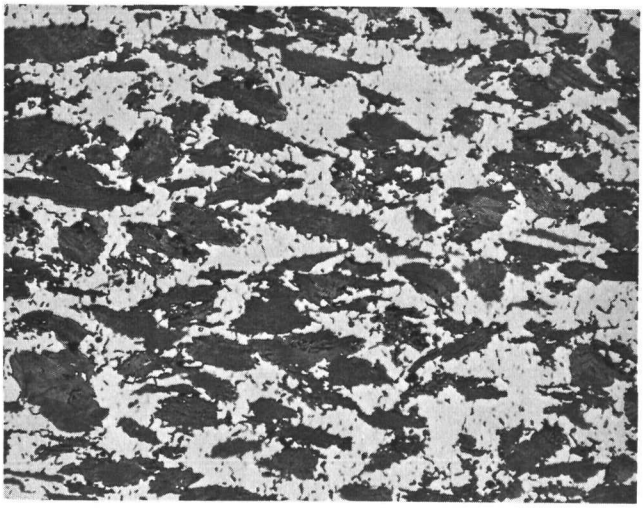


Figure 4-8. (CRD) Effect of Carbon Source on Microstructure - 100X (U)

BILLET 3H

Hot Pressed for 15 Minutes

BILLET 4H

Hot Pressed for 15 Minutes, and Repressed at 2700° for 60 Minutes

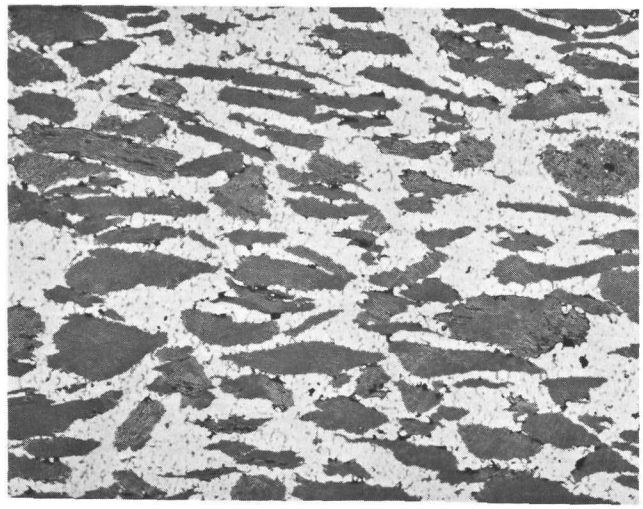
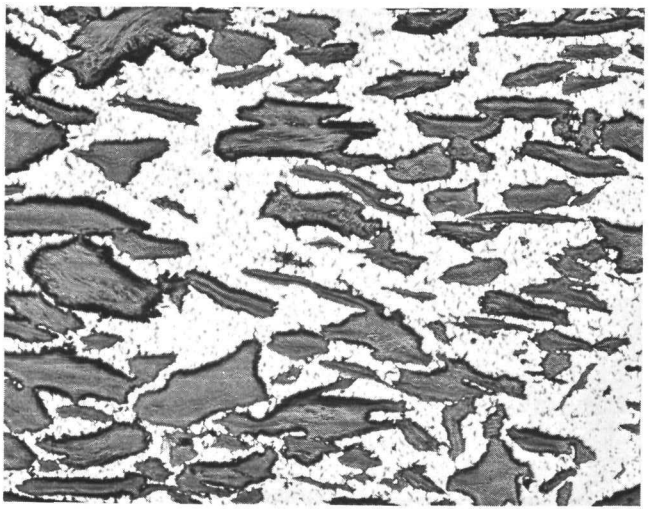


Figure 4-9. (CRD) Process Variation Effects on the CPC Phase Microstructure of Hot Pressed and Repressed Billets - 100X (U)

BILLET 7

Repressed 2700°C,
2000 psi for 60 Minutes



BILLET 10

Repressed at 2500°C,
3000 psi for 120 Minutes

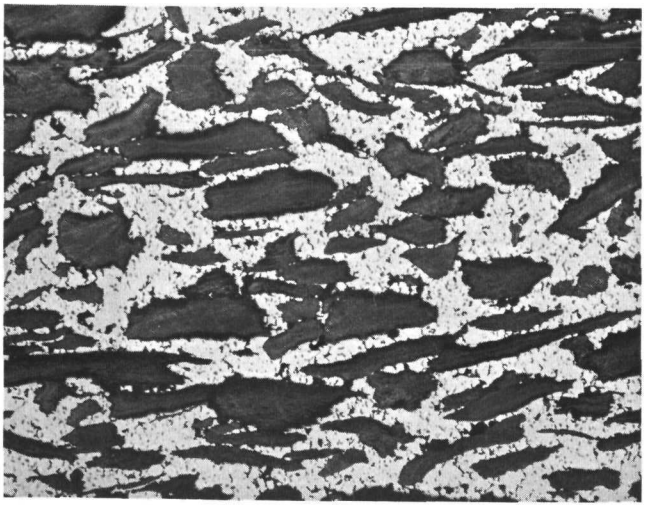
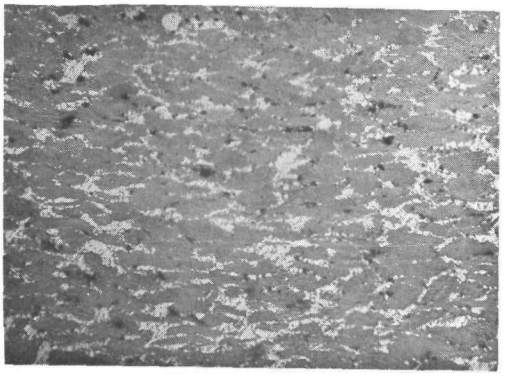
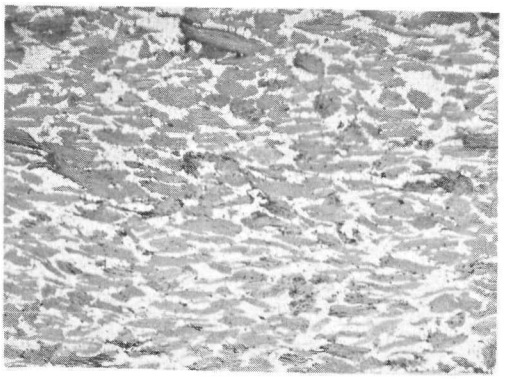


Figure 4-10. (CRD) Microstructure of Billets 7 and 10, Repressed Without a Die - 100X (U)

Double Pressed
50/50 w/o
(32.5/67.5 v/o)



Double Pressed
65/35 w/o
(35/65 v/o)



Double Pressed
75/25 w/o
(47/53 v/o)

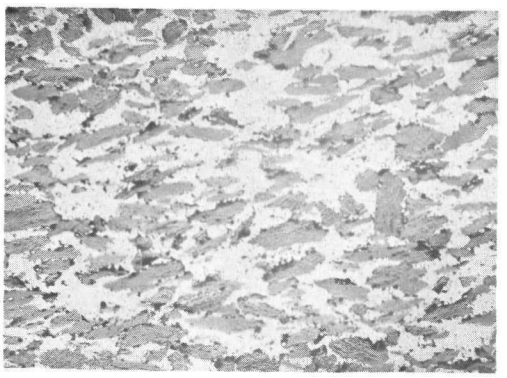


Figure 4-11. (CRD) Microstructure of Three Compositions of Double-Pressed NbC-Calcined Petroleum Coke (-60 + 150 Mesh) Powders - 100X (CRD)

needle coke. This alignment probably accounts for the 7 percent reduction in the CTE of billet 2H from 1H.

(CRD) Figure 4-8 shows the increase in the WG graphite alignment in the microstructure that occurred upon increasing the dwell time at the hot press temperature under pressure for 15 minutes for billet 3H to 90 minutes for billet 2H (Figure 4-9). After 15 minutes, the needle-like graphitized carbon particles are only randomly oriented in the carbide matrix, a few being aligned in the WG direction.

(CRD) At 90 minutes dwell time, a much stronger directionality, 90 degrees to the direction of pressing, occurred, which is revealed in Billet 2, and is reflected in the greater anistropy of the graphite and approximately 5 percent reduction in the WG CTE of 2H from 3H. The microstructure of Billet 4H, shown at the bottom of Figure 4-9, illustrates the additional increase in WG graphite alignment achieved by the compressive heat treatment conducted without a restraining die at 2700°C and with an axial pressure of 2000 psi for 60 minutes. This quantitive increase in the directionality of the graphite alignment is further evidence of the greater anistropy of the graphite and is a primary cause for the further 9 percent reduction in CTE that Billet 4H shows over 3H. These process changes, use of a needle coke, shortening of the dwell time during the hot pressing of the blended powders, and the addition of a compressive heat treatment, evidently increased the WG alignment of the graphite and its anistropy sufficiently to reduce the difference of the CTE between the NRX-A6 composite material and fuel graphite by 50 percent.

(CRD) The highest order of WG graphite alignment was achieved on Billet 10; this microstructure is shown in Figure 4-10. This billet was compressive-heat-treated without a restraining die at 2500°C, and 3000 psi for 120 minutes. This even further increase in the graphite WG directional orientation over that shown for the microstructure of Billet 7, shown in the same figure, lowered the CTE of Billet 10 by 10 percent. This reduction of the difference of NRX-A6 composites and fueled graphite was 65 percent, and the difference in the CTE of the PeWee-1 type of hot pressed material amounts to over 50 percent.

(CRD) Figure 4-11 illustrates the increased dominance of the carbide network as the weight percent of the composition is increased from 50/50 through 65/35 to 75/25 carbide graphite ratio. At 65/35 the carbide skeleton becomes a continuous network and should result in a material with good coating adherence and corrosion resistance.

5.0 CONCLUSIONS (U)

(CRD) The experiments conducted in this program were directed towards systematically and quickly establishing for PeWee-2 design considerations a process for accomplishing a reduction of both the CTE and the compressive creep deformation rate of 75-25 w/o composite material.

(CRD) Conclusions based on the evaluation of the data generated from the process experiments conducted are as follows:

1) The experimental work resulted in the development of a process to lower and control the thermal expansion of hot pressed carbide-graphite composites for hot end support hardware. It has been demonstrated that the coefficient of thermal expansion of 75-25 hot pressed composite material can be decreased to about 50 percent of the difference of NRX-A6 material and fuel material. This is accomplished by the substitution of calcined petroleum needle coke for the nuclear graphite flour and by inclusion of a compressive heat treatment. The first operation is accomplished by hot pressing the blended powders at 3100°C for 15 minutes in place of the former 45 minutes. The second cycle may be accomplished at 2700°C and 2000 psi for 60 minutes without a die. In this manner, the laterally unrestrained axial compression further reorients the now-graphitized carbon to a still more anisotropic material, resulting in the reduced WG CTE. This process has been selected for manufacturing PeWee 2 billet material. Further reduction of the CTE occurs when the second pressing cycle temperature is reduced to 2500°C, but pressure and time are increased to 3000 psi for 2 hours.

2) The experiments also demonstrated that the CTE of the fueled graphite can possibly be matched by slightly altering the composition from a 75-25 w/o composition to a 65-35 w/o composition, and by optimizing the compressive heat treat cycle to 2500°C, 3000 psi, for 120 minutes in order to increase the anisotropy of the material. These data are presented in Figure 4-2. It is believed that the corrosion resistance of this lowered carbide material is not significantly different than prior manufactured 75-25 material since the microstructure appears still to have a continuous carbide network. This was accomplished by decreasing the total area per volume of graphite by increasing the carbon particle size from -150 +325 mesh to 50 percent -100 +150 and 50 percent -150 +325.

3) In addition to the reduction in the CTE that can be accomplished by the coke substitution and the inclusion of the compressive heat treat operation, the creep rate of the material is most significantly reduced from 3 to 8 percent to 2 to 4 percent, and WG flexural strength seems to be more uniform and higher than for NRX-A6 material properties. It was further concluded that this combination of process changes and, in particular, the compressive heat treatment not only significantly improves the nominal values of the properties but also reduces the spread within a billet and from billet to billet.

4) At the conclusion of this program, PDS 30106 was revised to define the processing procedure and Quality Control requirements for purchasing hot pressed 75-25 composite material with a significantly lower CTE. In addition, PDS 30125 was written to define a process and the Quality Control requirements of a slightly modified (65/35) hot pressed material with a CTE matching that of the fueled graphite.

APPENDIX A (U)

APPARATUS (U)

(U) The thermal expansion measurements were performed by directly sighting on the ends of the sample in the furnace and reading the change in length by means of an optical micrometer.

(U) The furnace consisted of a graphite tube approximately 3 inches in diameter and 6 inches in length, clamped in two graphite holders attached to water-cooled electrodes. This assembly is surrounded by a thin graphite shield and is enclosed in a water-cooled metal jacket. The graphite heater is slotted at the top to permit insertion and removal of the sample holder. Holes are provided approximately 3 inches apart in the heater and the shield to permit direct observation of the sample ends. Illumination is provided during the lower temperature portions of the run; when the sample is hot, it provides illumination. Temperature measurements are made by means of an optical pyrometer sighting directly on the sample within the holder.

(U) Changes in length are measured by direct sighting on the sample ends by two Gaertner optical micrometers mounted side-by-side on an Invar frame. The mounting of this frame permits three-dimensional movement of each unit independently and simultaneously to permit accurate focus and control of the field of view. Reported accuracy of measurement is within $\pm$0.02 percent on the 2.8-inch nominal specimen size used.

(U) An argon atmosphere is maintained in the apparatus following evacuation and purging.

DATA TREATMENT (U)

(CRD) For this experiment, approximately seven data points were obtained for temperatures ranging from 900°C to 2500°C; three observations were recorded on the cooldown cycle. These data were corrected for the true temperature and the percentage change in length at each temperature, and the results were plotted. A smooth curve was fitted to these data points, and the average CTE ($\overline{\alpha}$) was calculated from the $\Delta L/L$ at the intercept of this curve at 2500°C. Typical curves are attached for the referenced material: Billet 51; and for compressive heat-treated billets 7 and 10. These curves represent the processes of most interest. (Refer to Figures A-1, A-2, and A-3.)

Figure A-1. (CRD) Thermal Expansion of Billet No. 51 (U)

Figure A-2. (CRD) Thermal Expansion of Billet No. 7 (U)

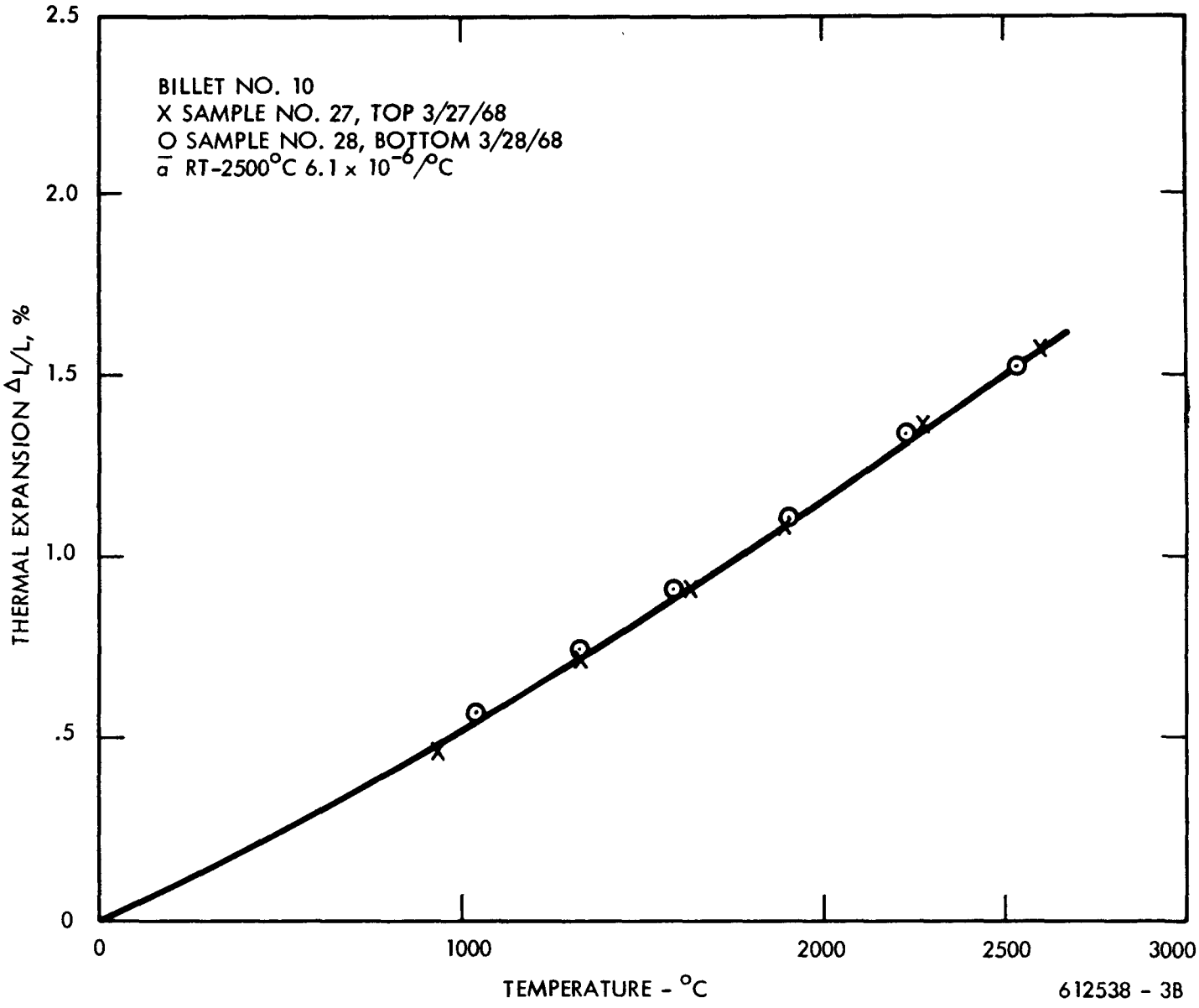


Figure A-3. (CRD) Thermal Expansion of Billet No. 10 (U)

ACCURACY (U)

(CRD) The repeatibility and consistency of the expansion measurements can be observed from the two samples from the top and bottom of Billet 10. The confidence level in the consistency of the measurements can be found from the observation of the scatter of the individual data points of the curve. The absolute values of the CTE reported cannot be established. The ability to repeat measurements on the same sample has been demonstrated to be very good; since all data used for comparison in this report were taken on the same apparatus, the confidence in the relative values of the CTE is very high. The fuel data spread shown in this report is based on data from WANL measurements. Resolutions of the calibration between WANL apparatus and the apparatus used in this report are contingent upon completion of a "round robin" testing program currently underway and sponsored by the Quality Control and Materials Departments at WANL. As an indication of the agreement of the reported values of WANL and LASL, it should be recognized that both of their reported values for CTE have been somewhat lower than values generated for this apparatus for the same type of composite material.

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1) Process to Control Thermal Expansion Characteristics of Composite Materials, AL 67-67, George W. Ellenburg, Westinghouse Astronuclear Laboratory, dated 8/31/67. (U)

2) WANL-TME-1664, "Characterization of Carbide-Graphite Composite Material", dated October 1967. (U)

3) IITRI-G6003, Progress Reports, "Metal Carbide-Graphite Composites," (Contract NAS-r-65109), dated 1965, 1966, and 1967. (U)

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