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MASTER

THE SINTERING KINETICS OF PURE AND DOPED BORON CARBIDE

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ABSTRACT

The sintering of pure and doped boron carbide was investigated over the temperature range 1898° - 2380°K and at additive levels ranging from 0.75 to 10.0 wt%. The addition of 0.75 and 3.8 wt% of AlF_3, Ni, Fe, and Cu resulted in a deactivation in the sintering of boron carbide at all temperatures. In contrast, the addition of 10.0 wt% of these dopants resulted in enhanced shrinkage in B_4C for the temperatures 1898° and 2133°K. At the highest temperature, 2380°K, the addition of AlF_3 at the 10.0 wt% level was the only case where enhanced shrinkage was observed. X-ray analysis showed the formation of a $B_{12}C_2Al$ compound and the total release of the fluorine. These results are interpreted in terms of a grain-boundary diffusion process for pure and doped boron carbide.

I. Introduction

Interest in the utilization of covalently bonded solids in a variety of high temperature applications has refocused attention on their sintering behavior. Materials such as silicon carbide, silicon nitride, and boron carbide have been considered for application as high stress components in gas turbines, as Lysholm expander blades in topping cycles, and as materials in the nuclear reactor technology.[1,2] In contrast to metallic substances, covalent solids are not easily sintered. This has led to various proposals explaining this phenomenon and to numerous attempts to activate the sintering of these materials through alterations of their chemical and physical characteristics.

Proposals for explaining the low densification associated with the sintering of covalent solids have included the role of grain boundary energy[3] and point defect formation and migration[4,6]. The latter consideration is explained in terms of high activation energy for self diffusion in the highly directional bond structures of covalent solids.

Relatively little work has been done on the sintering of boron carbide. Stibbs, et al.[7], showed that additions of up to 10 wt% Al, Mg, or a metal boride (e.g., TiB_2) produced B_4C bodies of 99+% of theoretical density when sintered at temperatures between 2423°-2533°K. Dzhenclinskii, et al.[8], on the other hand, sintered B_4C by adding up to 10 wt% Ti and produced densities of 97+% of theoretical. Dzhenclinskii's results also showed a desirable decrease in the brittleness of the sintered boron carbide as a result of this addition. Grabchuk and Kislyi[9,10] demonstrated that pure boron carbide can be sintered to densities of 85-95% of theoretical if powders of less than 3μm are sintered at temperatures near the melting point. These authors believe that at high temperatures, isovalent replacement of one element by the other can take place and would facilitate the material transport processes. Although Boron is usually trivalent it may also become tetravalent if it can capture an electron from another element in the compound or an impurity atom. It then produces an electron configuration similar to carbon as B^-, i.e. $1s^2 2s^1 2p^3$. Since carbon and boron have similar atomic radii some of the carbon atoms in boron carbide can be replaced by boron atoms[11].

The latest and most extensive research on the sintering of boron carbide is that of Borchert and Kerler[12]. They studied the kinetics of the sintering of boron carbide by shrinkage measurements as a function of temperature, particle size, and green density. Their results showed that the sintering process for boron carbide consists of two early stages, a middle stage, and a late stage. For the first stage of early sintering they identified the dominant transport mechanism to be plastic flow with an activation energy of 89 kcal/mole. It was also believed that surface diffusion makes a small contribution in the transport process, specifically at low temperatures for very fine powders. The second stage of early sintering was believed to be viscous flow with an activation energy of 398 kJ/mol. In the middle stage the dominant mechanism was determined to be grain-boundary diffusion, and for the late stage volume diffusion was found to be the operative mechanism with activation energies of 184 and 422 kj/mol, respectively.

II. Experimental Materials and Methods

A. Materials. High purity powders produced by the Ceradyne and Callery Chemical Companies were used to determine the sintering kinetics of boron carbide. Powders with particle sizes of 2-5μm (High Purity Ceradyne Powder) and approximately 0.03μm (Callery powder) were used in a mixture of 25 to 75 wt%, respectively. Mixing of these two powders was made so as to provide optimum sintering conditions by using submicron powders and to establish a range of particle sizes so that the integrity of the pressed powder compacts could be maintained. Other typical properties of the powders are listed in Table 1. A typical impurity analysis showed them to contain Fe, Ti and Zn in the 150-200 ppm range and others (Ca, Al, Si) at considerably lower concentration (50 ppm).

The effect of activators on the sintering kinetics of boron carbide was investigated by mixing different percentages of various additives into the base material. The additives and percentages mixed in the boron carbide are listed in Table 2.

Table 1

Powder Properties

Vendor	Particle Size, μm	Surface Area, m^2/gm	Composition
Ceredyne	2-5	2.14	78.1 wt% B
Callery Chemical Company	0.03	50	74.1 wt% B 25.9 wt% C

Table 2

Sintering Additives

Additive	Vendor	Purity	Size, Mesh	wt% Additive
AlF_3	Cerac/Pure	99.5%	100	0.751 3.850 10.000
Ni	General Chemical	99.5%	325	0.757 3.810 10.000
Fe	J. T. Baker Chemical	99.5%	325	0.764 3.800 10.000
Cu	Electronic Space Products, Inc.	99.95%	325	0.771 3.800 10.000

B. Sample Preparation. A mixture of 25 wt% High Purity Ceradyne powder and 75 wt% Callery powder were blended in plastic bottles with approximately 2.7 wt% polyethylene glycol (carbo-wax 6000) in toluene at a volume ratio of 1:3, respectively. The glycol was used as a binder to help in the pressing of the powder compacts. The required weight percent of each additive was added to this mixture and allowed to mix for 24 hr on a ball mill. After mixing, the powders were filtered and then allowed to dry in a fume hood for 24 hours. The dry powders were then ground with a marble pestle in a pyrex petri dish to break up agglomerated pieces. The dry ground powders were then further mixed in glass bottles for 2 hr to assure that the additives were uniformly distributed. The powder mixtures were stored in plastic bottles for further use.

Sintering pellets were pressed in a tool steel dye employing a double piston action to apply a static load of 26.7 kN (6000 lbs) across a 0.6502 cm (0.2560 in) diameter piston. The walls of the dye were treated with stearic acid to make easy the separation of the pellets from the dye. Compacting was accomplished with a pressure of 800 MPa (116,570 psi). This pressure resulted in pellets with initial green densities in the range 42-46% of the theoretical value depending on the amount of additive present in the powder mixture. Each pellet required two pressings. After the first compaction the pellets were broken up and then repressed. This produced crack free pellets which were then measured with a micrometer with an accuracy of $\pm 2.5 \times 10^{-3}$ mm and weighed with an accuracy of $\pm 1 \times 10^{-5}$ gm. After making the initial measurements the pellets were stored in graphite crucibles for further use. Specimens were prepared in groups of three for each sintering run.

C. Equipment and Procedure. The system used for all sintering runs consisted of a top loading vacuum chamber with a tungsten mesh heating element capable of attaining a maximum temperature of approximately 3000°K. The specimens were arranged in graphite crucibles and placed on a molybdenum pedestal which was situated in the previously determined constant-temperature region of the furnace. The temperature of the samples was monitored through a calibrated optical pyrometer.

The boron carbide pellets were arranged in their respective graphite crucibles and then placed on the molybdenum pedestal. The system was then evacuated to a minimum pressure of 13.3 mPa. Once this vacuum was obtained the diffusion pump was turned off and the system was flooded with argon to approximately 50.5 kPa and then re-evacuated with sorption pumps to a pressure of 66.5 Pa. The argon atmosphere was maintained at this level throughout the sintering run by use of the sorbtion pumps whenever needed. A heating rate of 20°K/min was used to obtain a temperature of 1373°K. At this temperature the pellets were allowed to outgas for 30 min to drive off any remaining volatiles. After outgasing, the heating rate was increased to 40°K/min until the isothermal sintering temperature was obtained. Three sintering temperatures, 1898°, 2133°, and 2380°K, were selected. These corresponded to 0.66, 0.76, and 0.86, respectively, of the melting point of pure boron carbide. The selected sintering times were 60, 120, and 240 min. Ground powders, fractured surfaces, and pellet surfaces of sintered specimens were carefully selected and prepared to be examined by x-ray diffraction, scanning electron microscope, and electron microprobe, respectively, to determine surface morphollogy and the effects of additives on the sintering of boron carbide.

III. Results

The change in the linear shrinkage of sintered boron carbide pellets with the isothermal sintering time is shown as a log-log plot in Figure 1 for three sintering temperatures. From the slopes of these lines, the mechanism characteristic exponent, N, was calculated to be 6.4, 6.3, and 6.2 for the temperatures 1898°, 2133°, and 2380°K, respectively. The change in the linear shrinkage versus the inverse of the sintering temperature is shown in Figure 2 for three sintering times. The experimentally obtained values for the activation energy for the sintering of boron carbide compacts for 60, 120, 240 min sintering times are 162.0, 160.7, and 164.9 kJ/mol, respectively, with an average value of 162.4 ± 2.1 kJ/mol.

Scanning electron micrographs (SEM) of the as-pressed and sintered boron carbide compacts are shown in Figures 3(a) and (b). Figure 3(a) shows the unsintered pellet while Figure 3(b) shows the microstructure of a pellet sintered at 1898°K for 60 min. Figures 4 and 5 show the variation in linear shrinkage with sintering time for B_4C with AlF_3, Ni, Fe, and Cu additives sintered in argon at 1898°K. Similar plots for B_4C with these additives for the sintering temperatures 2133°K and 2380°K are shown in Figures 6-7 and 8-9, respectively. Also shown in each figure is a plot of the change in linear shrinkage versus sintering time for pure boron carbide powders sintered under the same conditions. The experimentally obtained values for the mechanism characteristic exponents have been calculated, and the average values along with their standard deviations are listed in Table 3 for the different powder compositions. Figures 10 and 11 show the variation in linear shrinkage with the inverse of the sintering temperature for doped boron carbide powders sintered in argon for 60 min. Again each figure includes a plot of the temperature dependence of the linear shrinkage for pure boron carbide powders sintered under the same conditions. Calculated activation energies with their standard deviations are listed in Table 3 for these different powder compositions.

Table 3

Calculated Average Values of N and Q for the Sintering of Boron Carbide Powders in Argon With Additions of AlF_3, Ni, Fe, and Cu

Material	wt% Additive	Average N	Average Q Kj/mol
B_4C	0.00	6.3 ± 0.1	162.4 ± 2.2
$B_4C + AlF_3$	0.751	6.4 ± 0.7	180 ± 24
	3.850	6.1 ± 0.6	163 ± 12
	10.000	5.97 ± 0.01	105.0 ± 1.2
B_4C + Ni	0.757	6.5 ± 0.1	188 ± 4
	3.810	6.2 ± 0.3	159 ± 12
	10.000	6.02 ± 0.04	105.1 ± 0.8
B_4C + Fe	0.754	6.6 ± 0.4	163 ± 16
	3.800	6.1 ± 0.4	134 ± 20
	10.000	6.00 ± 0.03	104.2 ± 2.3
B_4C + Cu	0.771	6.1 ± 0.3	167 ± 16
	3.800	6.2 ± 0.3	163 ± 8
	10.000	5.97 ± 0.04	105.5 ± 1.2

The results presented above show the dramatic influence of the impurities on the sintering of boron carbide. It was observed that additions of approximately 0.75 and 3.8 wt% of AlF_3, Ni, Fe, or Cu reduced the linear shrinkage, i.e., deactivated the sintering process of boron carbide for all the temperatures and times under investigation. It was also observed that additions of 10.0 wt% of AlF_3, Ni, Fe, or Cu increased the linear shrinkage or activated the sintering process of boron carbide for the temperatures of 1898° and 2133°K. For the highest temperature (2380°K) the addition of 10.00 wt% AlF_3 was the only case in which the sintering process of boron carbide was activated. These results are summarized in Figures 12 through 19. In Figures 12-15 the degree of activation, defined as the percent difference between the linear shrinkage of doped and pure boron carbide, was plotted versus the weight percent of AlF_3, Ni, Fe, and Cu, respectively. Figures 16-19 show the variation of the degree of activation with sintering temperature for a constant wt% of AlF_3, Ni, Fe, and Cu, respectively. From these figures it is evident that the addition of 10.00 wt% AlF_3 provides the best activator for the sintering of boron carbide. At this concentration of additive the linear shrinkage is increased and the degree of activation is maximized at the lowest sintering temperature 1898°K.

Table 3 provides definite trends for the effect of sintering additives on the activation energy, Q, and the characteristic exponent, N. For the cases where deactivation of the sintering process occurred the values of the activation energies are generally greater than or nearly equal to the activation energy for the sintering of pure boron carbide. For the cases where the sintering process was activated the values of the energies are significantly lower. The generally observed trend for the characteristic exponent was that for increasing amounts of additives the value of N decreased.

Scanning electron micrographs (SEM) of boron carbide pellets with 10.00 wt% AlF_3 sintered at 1898°K are shown in Figures 20(a) and (b) for the sintering times of 60 and 240 min, respectively. Analysis of boron carbide surfaces with additions of AlF_3, Ni, Fe, and Cu were made by means of electron microprobe techniques. These analyses indicated the presence of a significant amount of aluminum and the absence of fluorine in the boron carbide matrix. This suggests that AlF_3 completely dissociates during sintering. Results on boron carbide pellets with additions of 10.0 wt% Ni sintered for 120 minutes at temperatures of 1898° and 2380°K indicated that Ni remains in the boron carbide at the lower sintering temperature, but is totally absent at the higher temperature. Similar results were obtained with 10% Fe additions. In the case of 10% Cu additions, the results of the microprobe analyses indicated the absence of Cu in the samples sintered at 1898° and 2380°K for 120 min.

IV. Discussion

Of major interest in this work is the role of the various additives in the sintering of boron carbide. The elemental scanning conducted with the electron microprobe, and the diffractometer scans of B_4C + 10.0 wt% AlF_3 and pure B_4C specimens, provided an interesting insight into the method by which sintering can be enhanced or activated through the addition of impurities. It was first believed that AlF_3 was added to provide a thin layer on the boron carbide particles which would enhance grain boundary diffusion producing an increase in the sintering rate. It was also thought that the additive would sublime, leaving behind a pure dense compact of boron carbide. From the present study it is apparent that a considerable amount of Al was incorporated into the B_4C matrix while no F was detected. The diffraction scans of samples with AlF_3 indicated a consistent downward shift in the peak locations. These peak shifts provide strong evidence that Al is substitutionaly incorporated into the B_4C lattice, resulting in a slight expansion of the unit cell. It is likely that a limited formation of a $B_{12}C_2Al$ type structure is occurring. In support of these conclusions, it is noted that the strongest new B_4C peaks correspond closely to the strongest peaks of $B_{12}C_2Al$ as reported by Lipp and Roder[13]. These observations also agree with previous work on the hot-pressed boron carbide[14] with additions of AlF_3.

The incorporation of aluminum in the boron carbide lattice provides an explanation for the observed loss of fluorine. Carbon and fluorine can combine to form CF_x gas, most likely CF_3 or CF_4 or a mixture of both. Therefore, it is quite likely that boron carbide reacts with AlF_3 in the following manner:

$$3B_4C(s) + AlF_3(s) = B_{12}C_2Al(s) + CF_3(g).$$

The absence of thermodynamic data for the compound $B_{12}C_2Al$ makes the assessment of the energetics for this reaction impossible. It is concluded that additions of 10.0 wt% AlF_3 in boron carbide will activate the sintering process by lowering the diffusion energy barrier for the dominant transport mechanism of grain boundary diffusion through the alteration of the chemical nature of the grain boundary layer. As stated earlier the calculated activation energy for the sintering of pure boron carbide decreased from 162.4 to 105.1 ± 1.3 kJ/mol as a result of the addition of 10.0 wt% AlF_3.

The other additives which activated the sintering process of boron carbide were Ni, Fe, and Cu at the 10.0 wt% level and the lower two temperatures. The difference between these additions and AlF_3 is that they also deactivated the sintering of boron carbide at 2380°K. Electron microprobe and x-ray diffraction analyses offer interesting contrasts. For the additives of Ni and Fe the electron microprobe analyses showed the presence of Ni and Fe precipitates at 1898°K but not at 2380°K. Whereas the microprobe analyses of samples with copper additives showed no Cu at either temperature. Furthermore, these diffraction scans indicated possible compound formations of Fe with carbon and boron at 1898°K. These results indicate that additions of 10.0 wt% Ni, Fe, and Cu in boron carbide will activate the sintering process at 1898° and 2133°K by possibly the same mechanism as that proposed for AlF_3. The activation energies for the sintering of pure boron carbide decreased from 162.4 to 105.1 ± 1.0, 104.2 ± 2.1 and 105.5 ± 1.2 kJ/mol as a result of the additions of 10.0 wt% Ni, Fe, and Cu, respectively. The apparent deactivation of the sintering of boron carbide in the presence of 10.0 wt% Ni, Fe, and Cu at 2380°K is explained by the relatively high vapor pressures of these elements at this temperature. It is believed that at this temperature the additives sublimate and leave the compacts. Furthermore, the rapid sublimation of these additives at the higher temperature may result in trapped gases in closed pores, and hence reduced shrinkage. This loss of additive is supported by results obtained in the electron microprobe and x-ray diffraction analyses.

The addition of 0.75 wt% and 3.8 wt% AlF_3, Ni, Fe, and Cu is believed to be insufficient to provide the compacts with an evenly distributed layer of the additive on the boron carbide particles. For the compacts with approximately 3.8 wt% additions, a layer of approximately 1.6 Å thick is provided whereas the compacts with approximately 0.75 wt% additions provide a layer of only 0.3 Å thick. Therefore, isolated islands of the additive are likely to occur throughout the powder, with the consequence that they act as either obstacles or sinks for the migration of vacancies along the grain-boundaries. Rapid sublimation of these additives can also produce entrapped gases in closed pores. Since the calculated activation energies for the sintering of boron carbide with approximately 0.75 wt% and 3.8 wt%

additions of AlF_3, Ni, Fe, and Cu are nearly equal to the activation energy for the sintering of pure boron carbide, a contribution from another mechanism, e.g., surface diffusion, is taking place. This would explain the observations that even though the shrinkage was reduced the activation energy for the total overall process did not increase.

V. Acknowledgements

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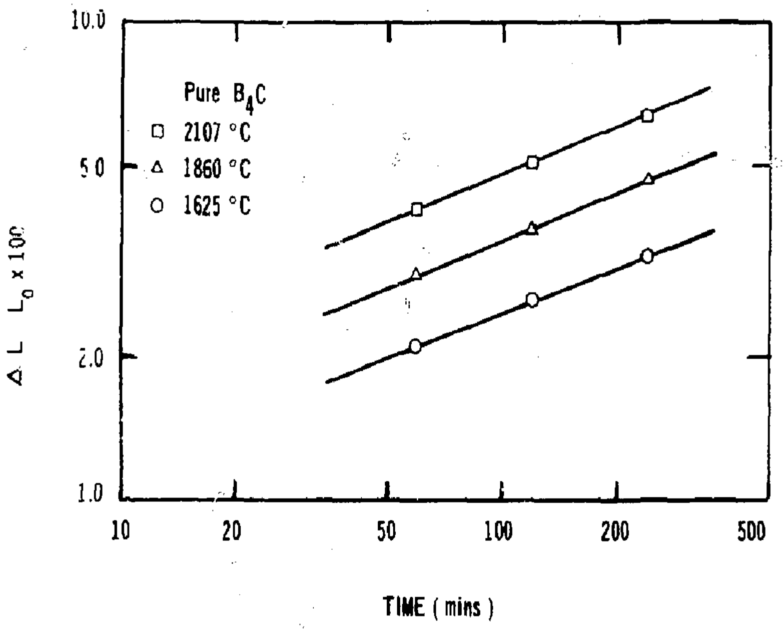

Figure 1. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon for Various Temperatures

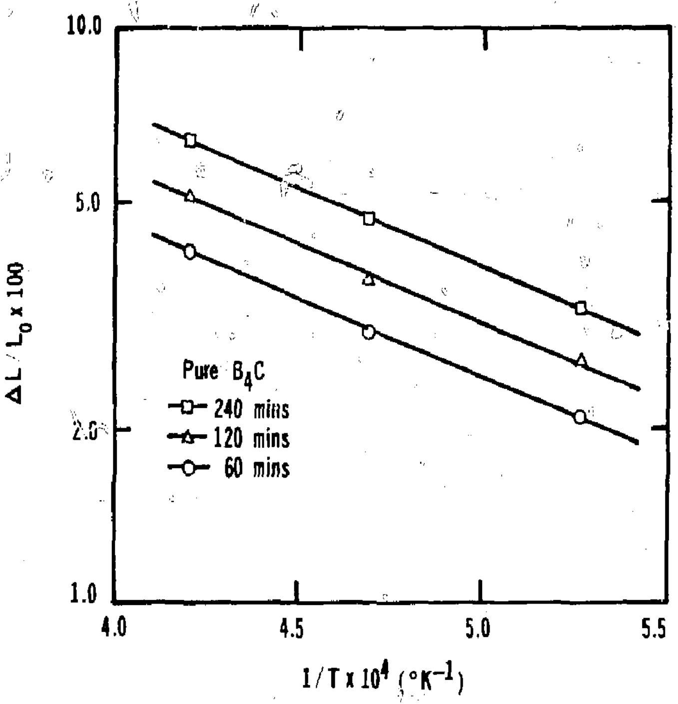

Figure 2. The Temperature Dependence of Linear Shrinkage for Boron Carbide Powders Sintered in Argon for Various Times

Figure 3(a). Unsintered Boron Carbide (SEM 28000X)

Figure 3(b). Boron Carbide Sintered in Argon for 60 min
at 1898°K (SEM 28000X)

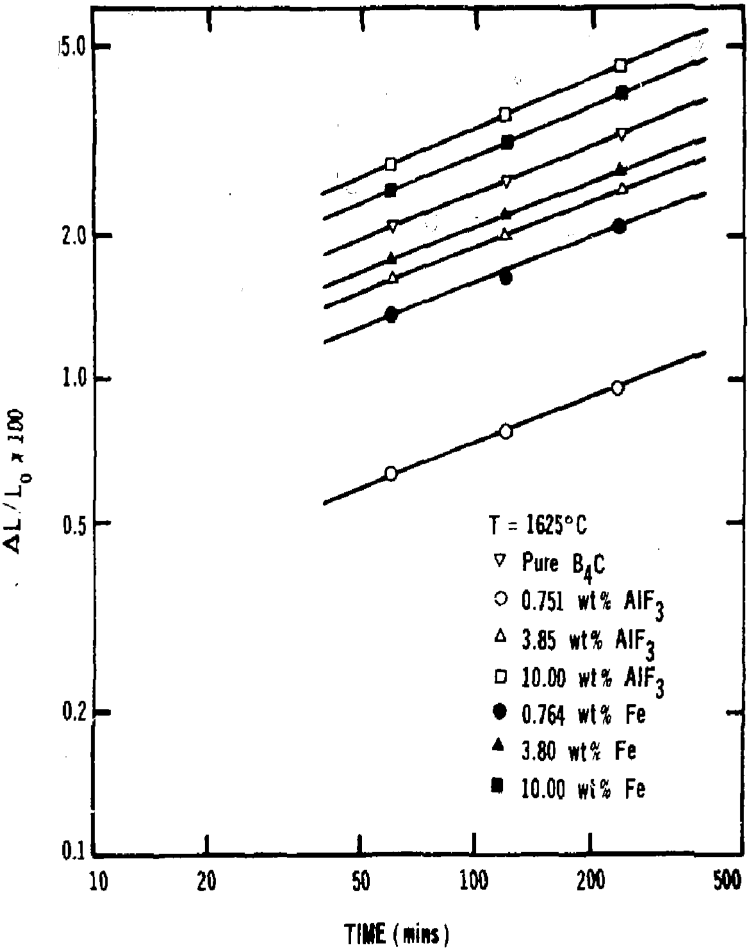

Figure 4. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 1625°C with Different Percentage of AlF_3 and Fe

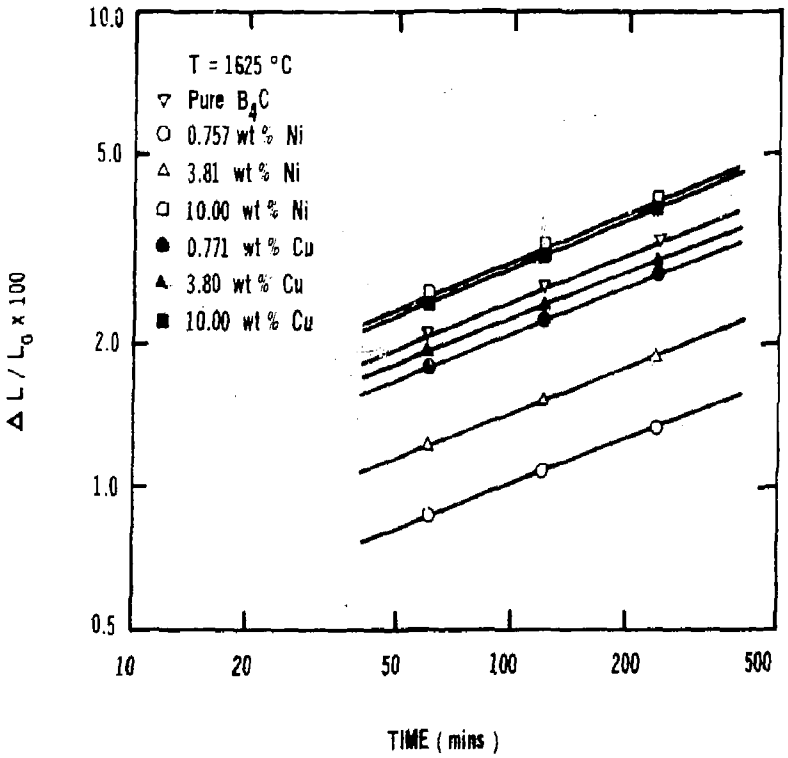

Figure 5. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 1625°C with Different Percentages of Ni and Cu

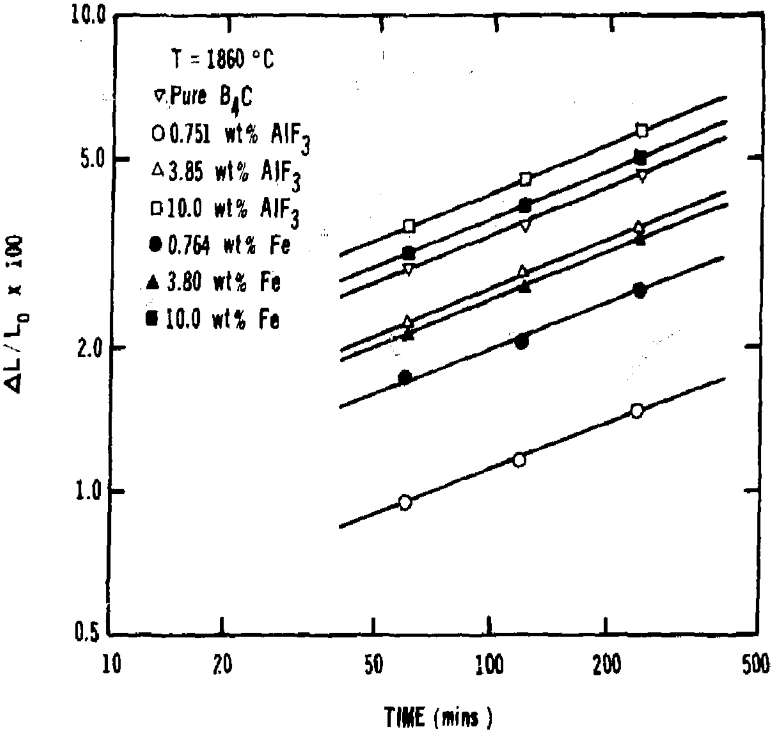

Figure 6. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 1860°C with Different Percentages of AlF_3 and Fe

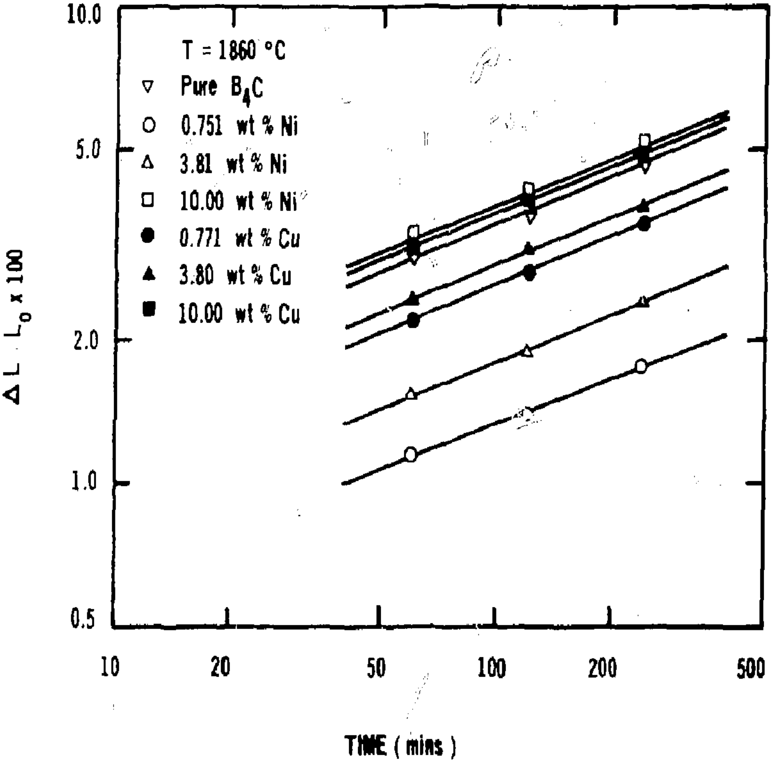

Figure 7. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 1860°C with Different Percentages of Ni and Cu

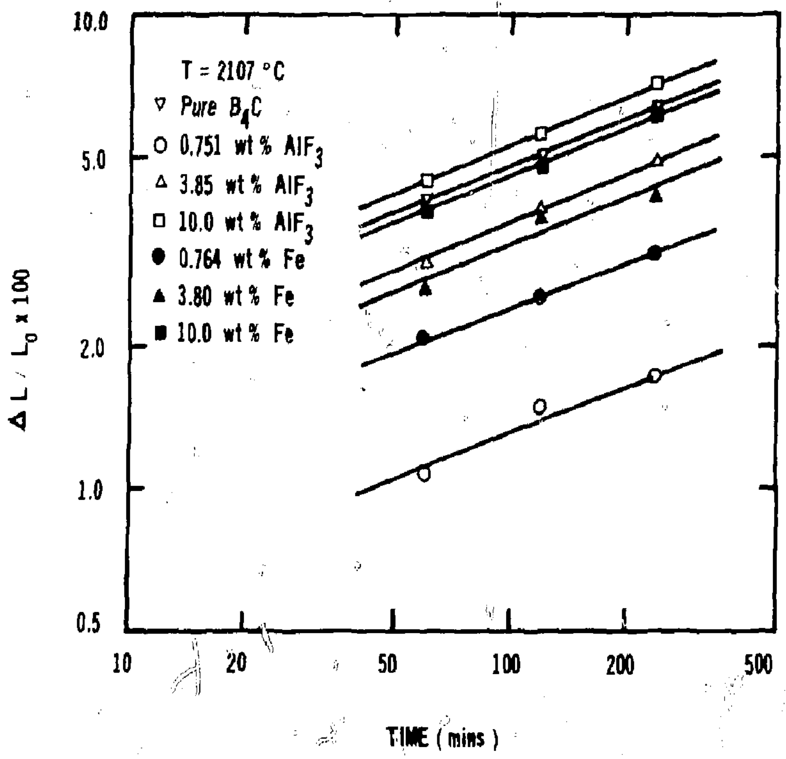

Figure 8. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 2107°C with Different Percentages of AlF_3 and Fe

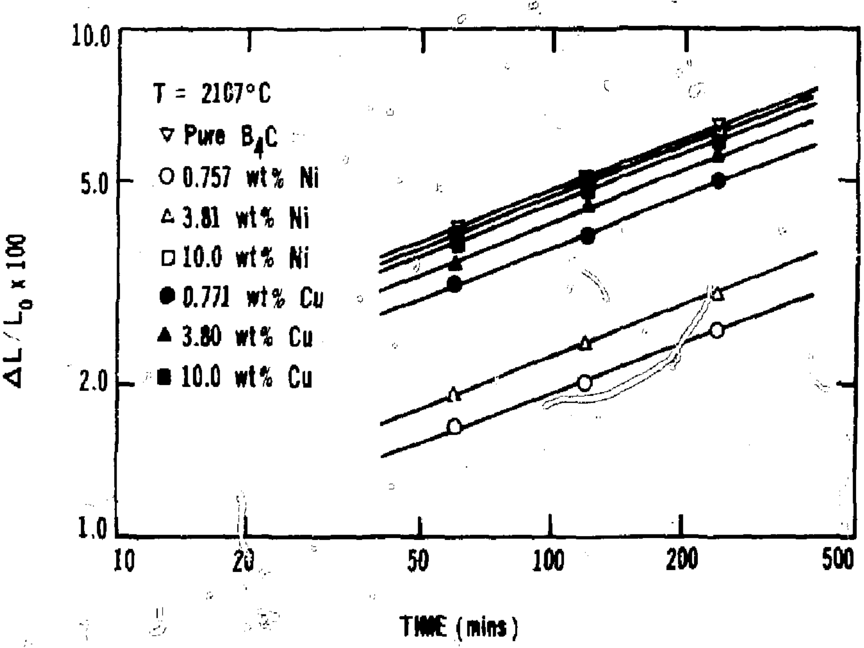

Figure 9. Variation in Linear Shrinkage with Sintering Time for Boron Carbide Powders Sintered in Argon at 2107°C with Different Percentages of Ni and Cu

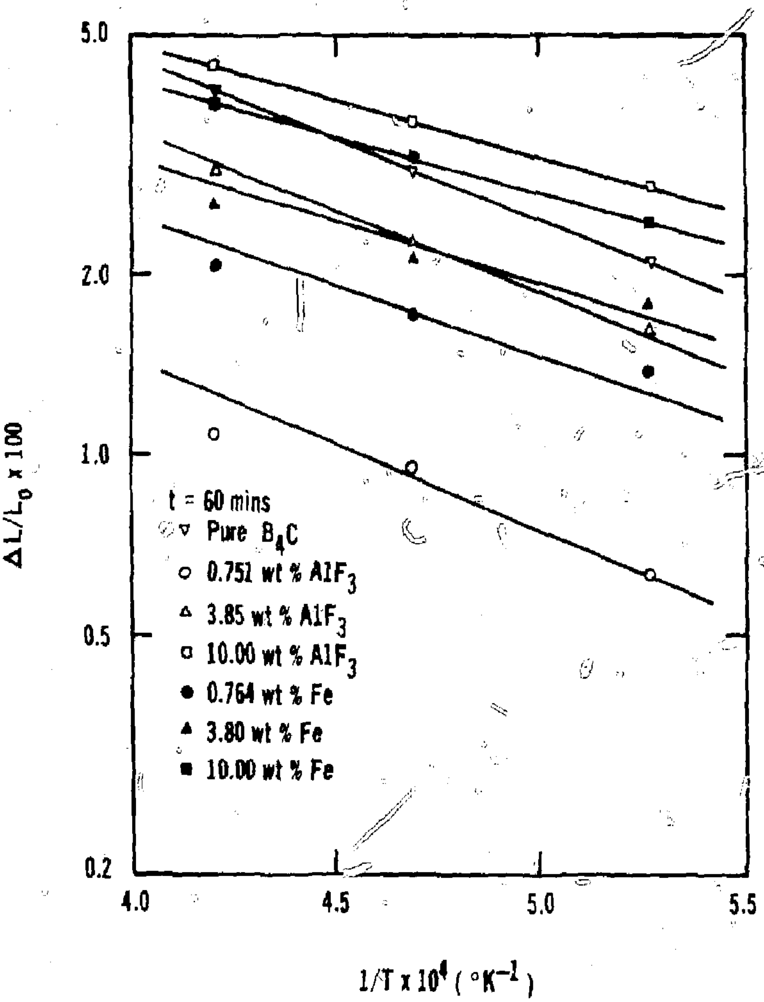

Figure 10. The Temperature Dependence of Linear Shrinkage for Boron Carbide Powders Sintered in Argon for 60 Minutes with Different Percentages of AlF_3 and Fe

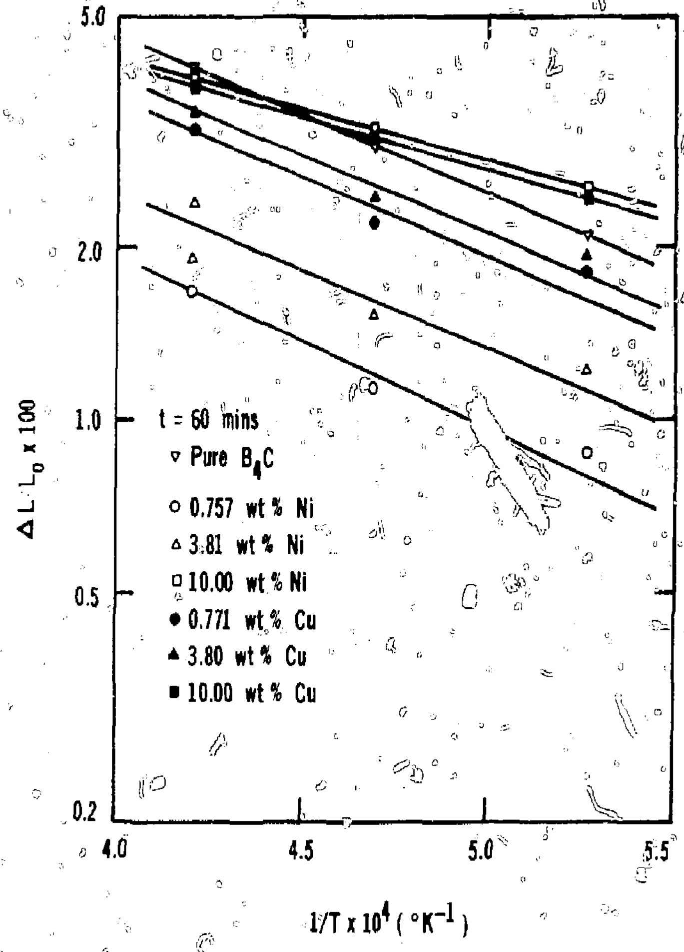

Figure 11. The Temperature Dependence of Linear Shrinkage of Boron Carbide Powders Sintered in Argon for 60 Minutes with Different Percentage of Ni and Cu

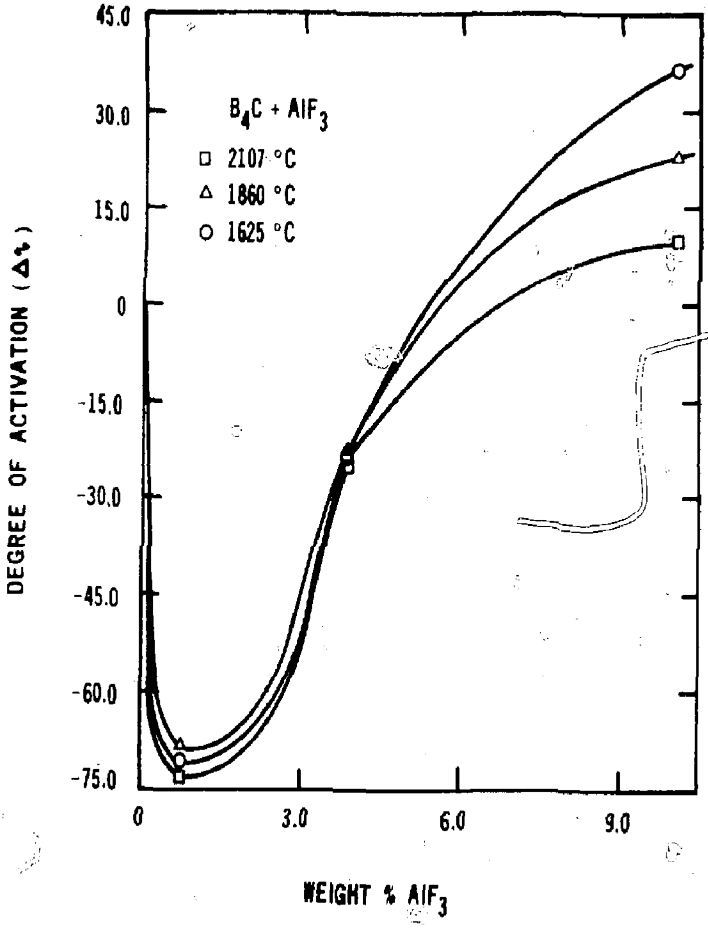

Figure 12. The Degree of Activation Versus Percent Additive for Boron Carbide Powders Sintered in Argon with Addition of AlF$_3$

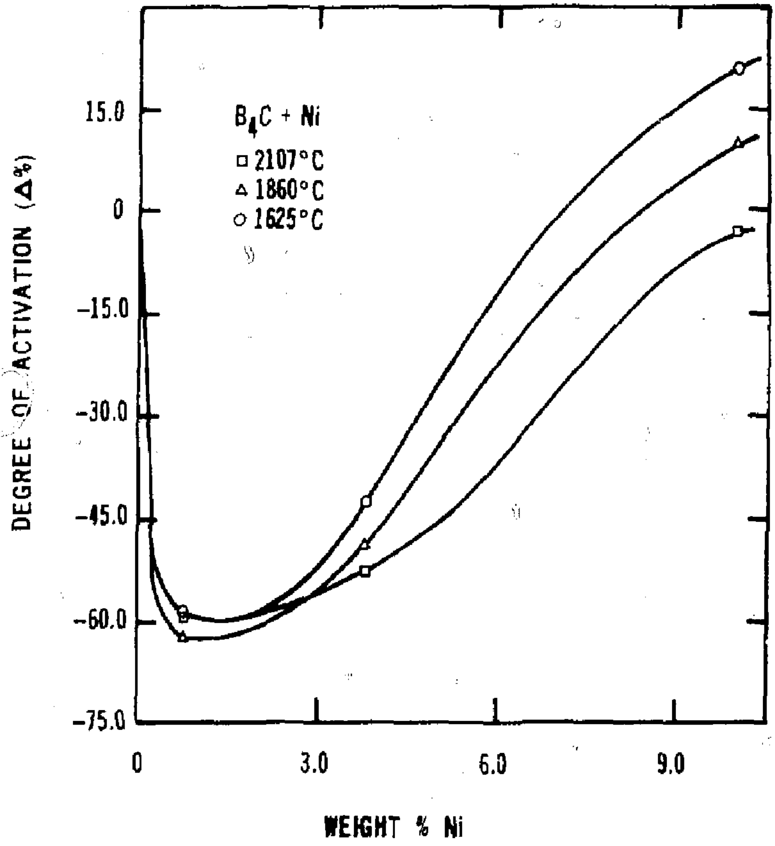

Figure 13. The Degree of Activation Versus Percent Additive for Boron Carbide Powders Sintered in Argon with Additions of Ni

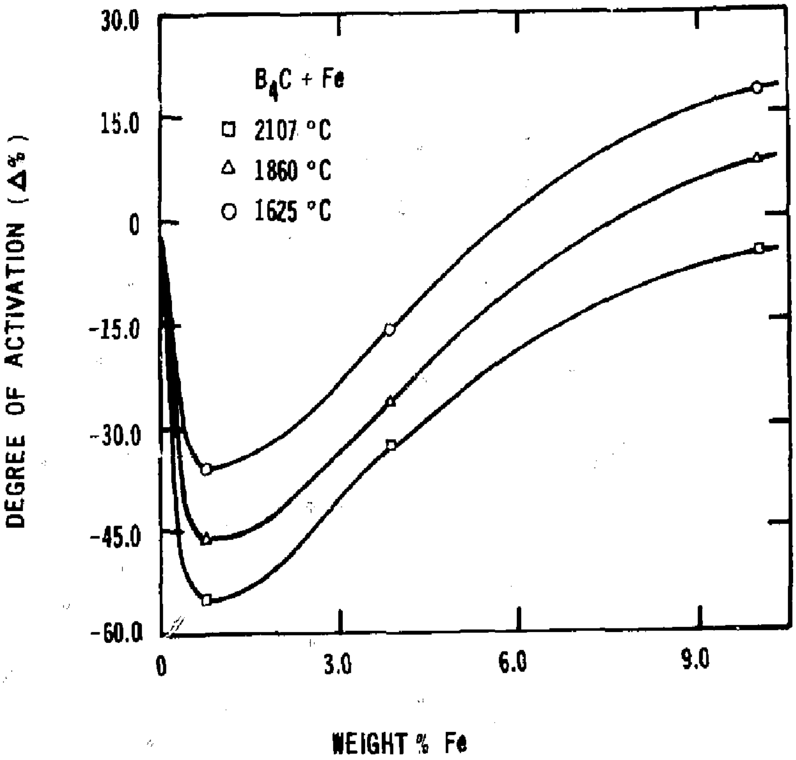

Figure 14. The Degree of Activation Versus Percent Additive for Boron Carbide Powders Sintered in Argon with Additions of Fe

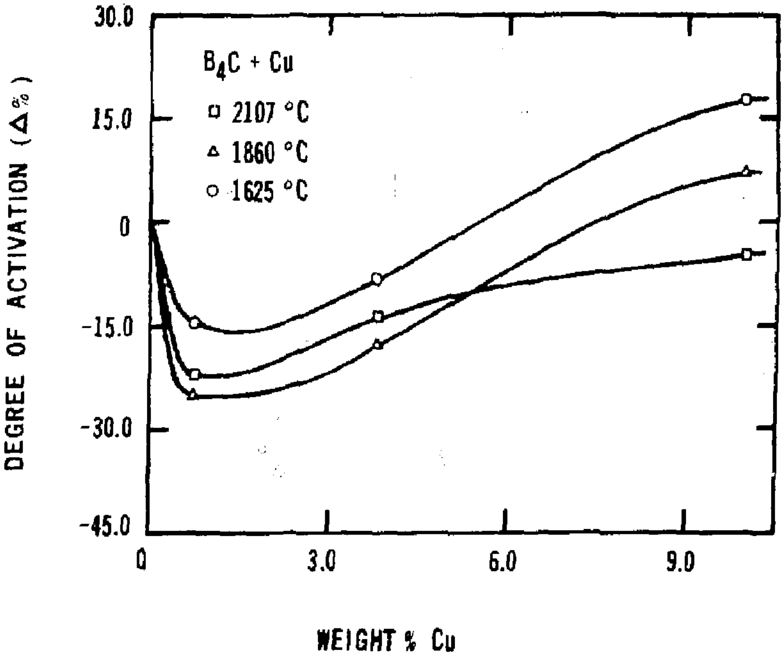

Figure 15. The Degree of Activation Versus Percent Additive for Boron Carbide Powders Sintered in Argon with Additions of Cu

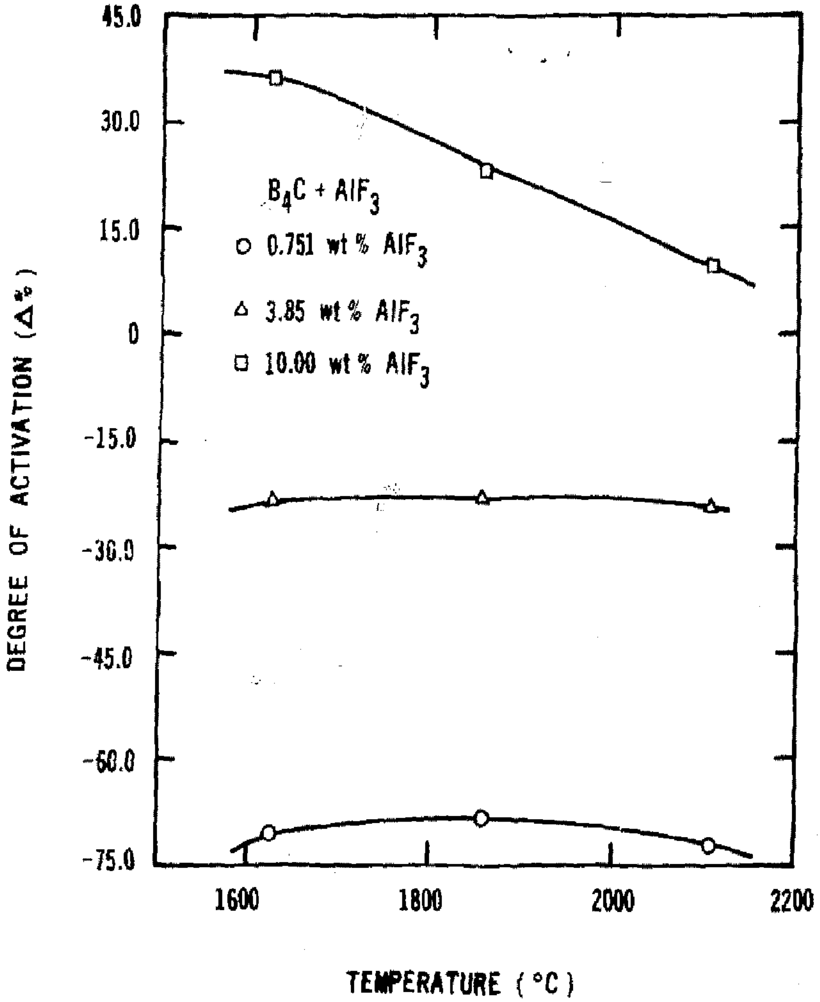

Figure 16. The Degree of Activation Versus Sintering Temperature for Boron Carbide Powders Sintered in Argon with Addition of AlF_3

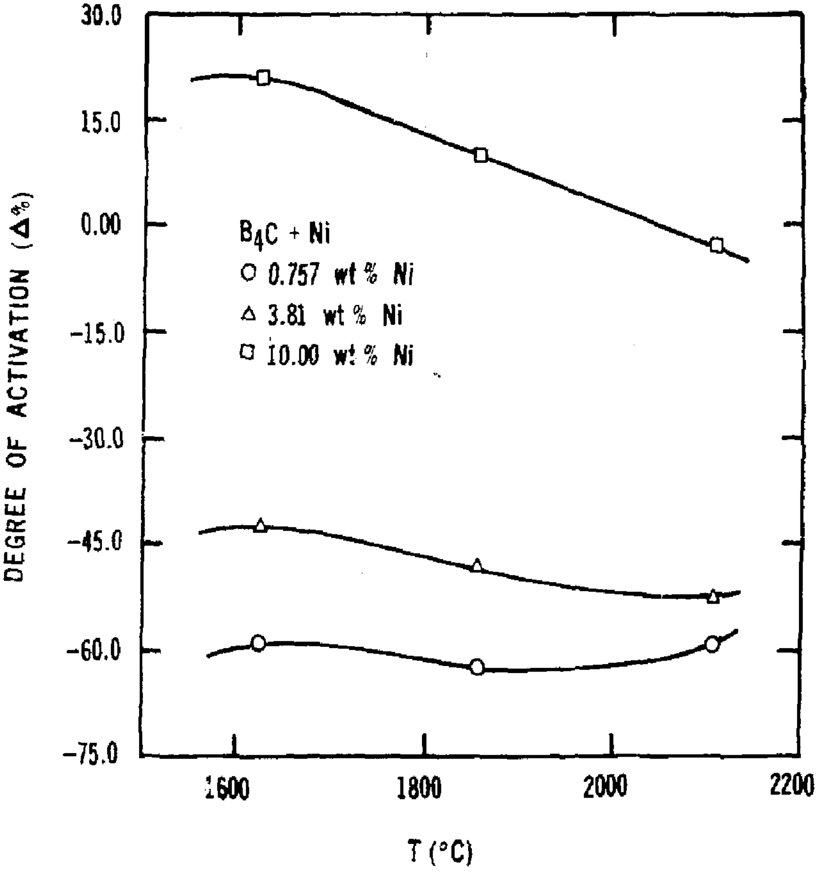

Figure 17. The Degree of Activation Versus Sintering Temperature for Boron Carbide Powders Sintered in Argon with Additions of Ni

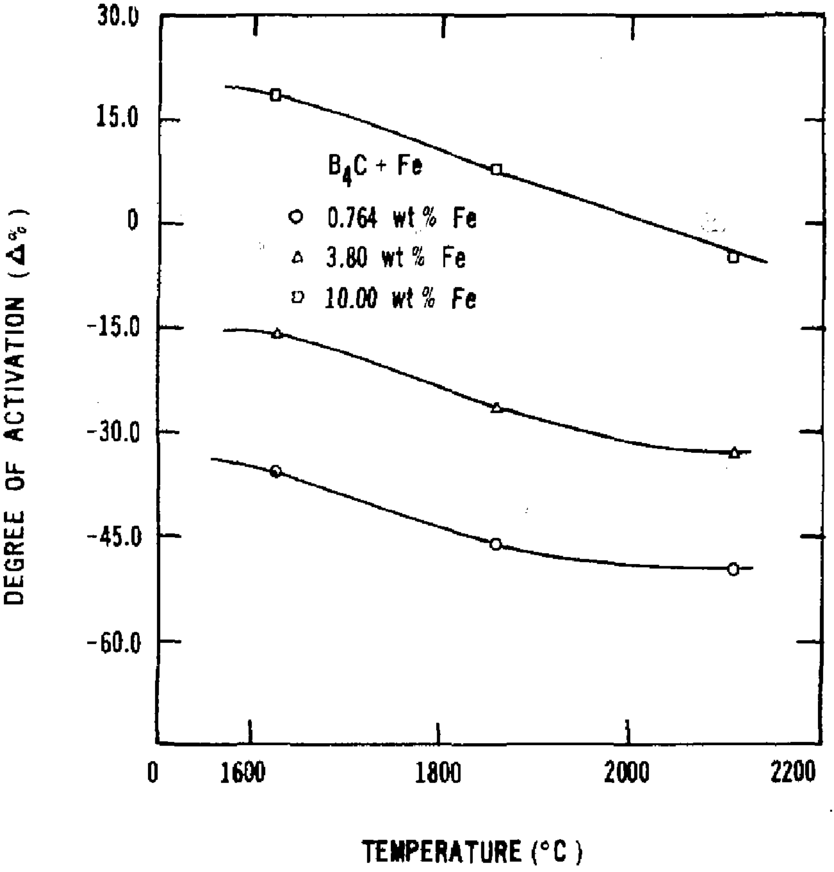

Figure 18. The Degree of Activation Versus Sintering Temperature for Boron Carbide Powders Sintered in Argon with Additions of Fe

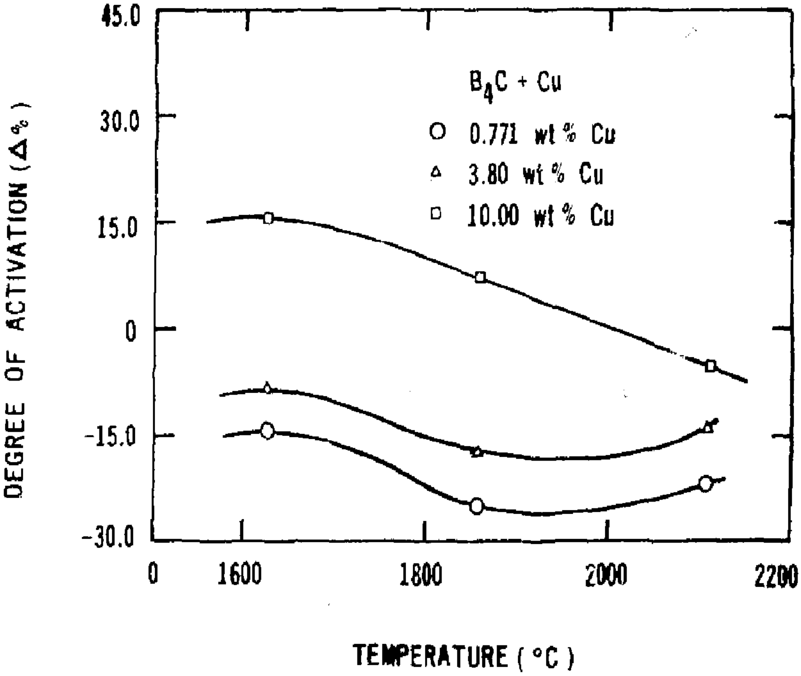

Figure 19. The Degree of Activation Versus Sintering Temperature for Boron Carbide Powders Sintered in Argon with Additions of Cu

(a) 60 min

(b) 240 min

Figure 20. Boron Carbide with 10.0 wt% AlF_3 Sintered at 1898°K (SEM 28000X)