

IMPROVEMENT IN BORON NITRIDE CERAMICS PREPARED BY ELECTROCONSOLIDATION

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The contribution brings an analytical assessment of thermal expansion for ceramic parts on boron nitride base prepared by a new pressure-sintering method registered by Superior Graphite Company, USA known as Electroconsolidation®. The prepared samples were compared with common hot pressed ceramics. Together with usual starting BN powder two additionally modified powders were prepared: a special type purified by deoxidative chlorination and a mixture with B,C in order to prove the changes in BN sinterability. Further noteworthy properties of these products are discussed. Thermal expansion of electroconsolidated samples has an average value of $4.56 \times 10^{-6} \text{ K}^{-1}$ and its course is linear up to 1470 K. Above this temperature the course is influenced by oxygen traces and/or B,C addition. Measurement of flexural strength using the four-point bending method showed a 30 % increase for electroconsolidated samples compared to values of samples prepared by conventional hot pressing in graphite dies. Young modulus values were higher as well, but they are strongly dependent on structural anisotropy. The compressive strength measurement indicated the priority of electroconsolidation too.

INTRODUCTION

The proportion of continuously casted steel increases rapidly worldwide. At the same time grows the importance of ceramic materials used for crystallizers and other thermally loaded components of metallurgical equipments eg. for filtration of slag inclusions. An important position in this family of nonoxidic ceramic materials occupies the hexagonal boron nitride. Therefore the main consumer of boron nitride ceramics is the steel industry.

From the three structural modifications of boron nitride: hexagonal, cubic and wurtzitic which are analogous to the carbon modifications graphite, diamond and lonsdaleite, only the hexagonal lattice comes into consideration for high-temperature ceramics production. The attractive forces between individual planes represented by van der Waals bonds are significantly weaker than bonding forces between neighboring atoms in the same plane of this hexagonal lattice.

Hexagonal boron nitride was described for the first time in mid-19th century and for more than a hundred years it was believed that it has the same structure as

graphite. It was only in 1952 when Pease [1] demonstrated different arrangement of hybrid sp^2 bonds and determined the interplanar spacing in BN ($d = 0.3306 \text{ nm}$). Thirty years later this value was corrected to $d = 0.33281 \text{ nm}$, but because of the extreme difficulty to synthesize a perfectly crystalline and pure h-BN one can expect lower interplanar spacing to be found in the future.

The common hot-pressed h-BN ceramics has a random arrangement of layers because the powdered precursors are prepared at temperatures as low as possible to prevent the unwanted crystallisation. The "classic" reductive nitridation of boron oxide does not yield the necessary free arrangement at temperatures under 1773 K. When ammonia is used as reaction agent, the temperature about 1273 K is sufficient especially when a precursor with an organic precursor is elected. Urea, thiourea or melamine turned out to be the best starting compounds. Due to mutual rotation of plane-parallel layers during chemical reaction expanded interplanar spacings of freely arranged BN cells are formed. This low-temperature form of h-BN with structural distortions is called turbostratic again in analogy to the graphitic modification of carbon.

In contrast to perfectly crystalline h-BN obtained only at quite high temperatures, powders prepared at lower temperature exhibit, owing to imperfect crystalline structure, a good sinterability, leading during subsequent thermal treatment to fully dense ceramics. An important feature is the influence of remaining oxygen bonded in the lattice. Such imperfections cause surprisingly higher sinterability which again leads to better mechanical properties of final bodies.

The h-BN crystallinity expressed by the hexagonalization coefficient

$$J = (I_{100} + I_{101}) / I_{102} \quad (1)$$

correlates with the change of mechanical properties, such as hardness. The measurements revealed that the samples with higher content of turbostratic phase were about 50 % harder than the samples where the well-defined hexagonal structure prevailed.

Further the phonon mobility value in the ceramic skeleton can be used for Young modulus determination. It has been stated that the higher the starting crystallinity, the softer but stronger is the ceramics.

Comparison of production equipments

For the production of BN ceramics hot pressing at 8-15 MPa of turbostratic powder form in graphite dies is usually applied. In the table 1 there are compared the advantages and drawbacks of other methods which may alternatively be used, EC, HIP, CERACON and ROC.

A specific feature of the EC method is the use of special graphite microgranules with excellent electrical conductivity. They act not only as the pressure-transferring medium but also as the direct heating medium on the principle of resistance heating. Thus, no protective medium is necessary. A successful application requires only a good compatibility of the hot-pressed material with carbon. This sintering method registered by Superior Graphite Company, USA, is known as Electroconsolidation® (EC), see figure 1 [2,3].

During hot isostatic pressing (HIP) developed by the Swedish ASEA Company, metallic or nonmetallic powders and their mixtures are subjected to heat treatment at temperatures up to 2270 K under pressure up to

300 MPa exerted by protective gas, mostly argon, in a closed vessel up to 1.5 m diameter. The disadvantage of this method is the necessity to cover near-net shape pre-forms by a hermetic (eg. glass-like) coating or to encapsulate the powders into a hermetic thin-walled container and to evacuate and seal it before the heat treatment starts. The weight of such a container may represent several tons and require further finishing operation after sintering. If the gas damages the coating or the container walls during contraction, it penetrates into pores of the treated product which is unable to shrink in a prescribed manner.



Figure 1. EC®-equipment of Superior Graphite Co., (Chicago, USA).

Table 1. Comparison of technological parameters of different hot pressing methods.

method	maximal temperature (°C)	maximal pressure (MPa)	maximal diameter of product (m)	sintering of more pieces	necessity of casing	necessary time for operation (min)
EC	2500	70	0.2	possible	No	30 - 90
HIP	2000	300	1.25	possible	Yes	150 - 500
CERACON	1500	400	0.4	difficult	No	60 - 150
ROC	1500	900	0.4	difficult	Yes	20 - 60 + 5

The Ceracon method is based on patents of the CERACON Company dating back to 1967. Preheated preforms are inserted in the die which is subsequently filled with special granules from non-oxidic ceramics and pseudo-isostatic pressure up to 400 MPa is exerted by aid of these granules. The necessity to preheat the preform outside the die and the ceramics partial oxidation restricts the temperature to 1273-1473 K maximum. In exceptional circumstances the temperature may reach 1773 K.

The last method, repeated omnidirectional compaction (ROC), developed by the Dow Chemical Company, uses a different kind of ceramic grain filling, which melts at prescribed temperature in the heated die with preforms. After the quick transfer to the press, the incompressible medium exerts a pressure up to 900 MPa.

EXPERIMENTAL

Preparation of samples A, B, C

Conventionally hot-pressed h-BN samples with relatively high oxygen content (A) were compared with modified samples with low oxygen content, obtained by chlorine deoxidation of BN powder (B). A third series of samples (C) was prepared using electroconsolidation.

Preparation of A-type samples

The starting BN powder was prepared according to a Czechoslovak patent [4]. Its structure and other properties are described in our reports [5,6]. For current experiments, the lot with the highest bonded oxygen content (14 %) was chosen. Compact cylindrical samples with a diameter of 200 mm were manufactured by hot pressing in graphite dies under a pressure of 8 MPa and a temperature of 1615°C, measured on the outer wall of the die. This temperature was held for 60 min.

Preparation of B-type samples

The starting BN powder with 14 % bonded oxygen content was subjected to deoxidation by reductive chlorination in a quartz tube furnace, using a procedure described in [7,8]. Chlorination by carbon tetrachloride vapor was done at 1000°C. The oxygen content was reduced by this treatment to 5.6-6.0 %. Sintering proceeded under the same conditions as in the case of A-type samples.

Preparation of C-type samples

The starting BN powder with 14% bonded oxygen content was mixed with 4 % B₄C (its particle size was 5 μm) and cold pressed under 14 MPa pressure to pre-

forms of 60 mm diameter and 10 mm height. These preforms were further processed by electroconsolidation. For the sintering of BN ceramic (C-type samples, deoxidized by boron carbide) by the EC method, temperature of 1600°C, pressure of 14.3 MPa and time of 30 min were selected. The applied EC-equipment can be seen on figure 1. Chemical and structural analysis of these samples are presented in the discussion.

Mechanical properties measurement

Samples were tested for flexural strength and flexural modulus in four-point bending and for compressive strength. All tests were carried out at ambient temperature. Dilatometric analysis contributed to the assessment of macroscopic anisotropy.

Flexural strength and Young modulus

The dimensions of samples for four point bending tests were 60 × 10 × 3.5 mm. The distance of deflection gauge rollers was 23.5 mm and of the lower rollers was 46.9 mm. A 1.0 kN load cell was used. Samples were loaded with a displacement rate of 6 × 10⁻⁴ m/min. Certain loading steps were followed by partial unloading, to determine the flexural modulus. The test was terminated by sample fracture.

Compressive strength

From a compact BN ceramic, cube-shaped samples with dimensions 5 × 5 × 5 mm were made and placed in a self-regulating 100 kN loading unit. Samples were loaded with a displacement rate of 10⁻⁴ m/min. The test was finished in the moment when the sample were crushed.

Dilatometric measurements

Linear thermal expansion was measured on samples oriented parallel or perpendicular to the compacting pressure, using a Setaram Setsys TMA-18 dilatometer with temperatures up to 1600°C.

RESULTS AND DISCUSSION

The samples prepared by the common HP and EC methods described above were cut into test pieces according to the schematics in figures 2a, 2b. The degree of anisotropy and arrangement of the crystallites are documented on the fracture surface image on figure 3. X-ray analysis was used to determine the hexagonality coefficient J , defined by the intensity ratio. For the A-type samples, its value was $J_A = 2.7$, for the B-type

samples it was $J_B = 2.1$. The C-type samples, due to shorter heating time during the synthesis, exhibited a higher value $J_C = 3.3 - 4.6$. Characterization of the samples was completed by porosimetry (Mercury porosimeter Micromeritics Auto Pore 9200), yielding the pore size distribution and skeletal density, see figure 4. The values of total intrusion volumes, pore areas, median pore radii and skeletal densities are listed in table 2.

Table 2. Mean values of mercury porosimetry characteristics.

measured values	sample		
	A	B	C
total intrusion volume (cm ³ /g)	0.0242	0.0352	0.0314
total pore area (m ² /g)	18.55	25.23	17.81
median pore radius (nm)	1.9	2.1	2.1
skeletal density (g/cm ³)	2.10	2.12	2.14

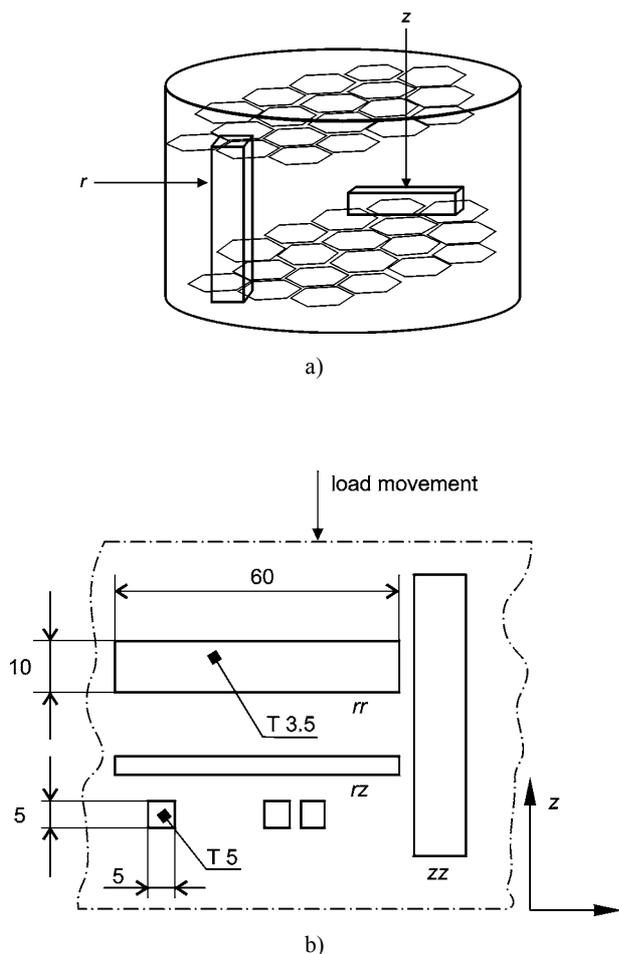


Figure 2. a) Schematic demonstration of sample cutting in the radial (r) and axial (z) direction of preferred orientation of BN crystallites; b) Alternatives of test piece orientations with respect to original (as-pressed) sample.

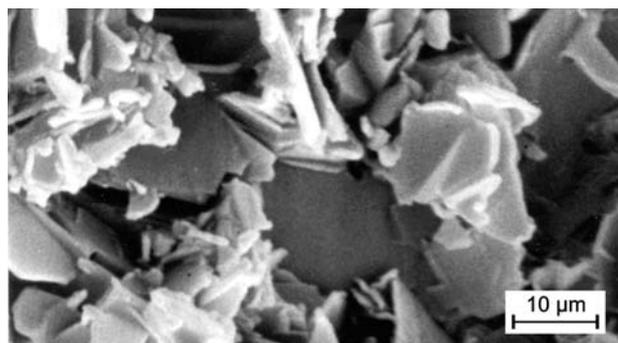


Figure 3. Microstructure of a fracture of A-type h-BN sample (magnification 5000×).

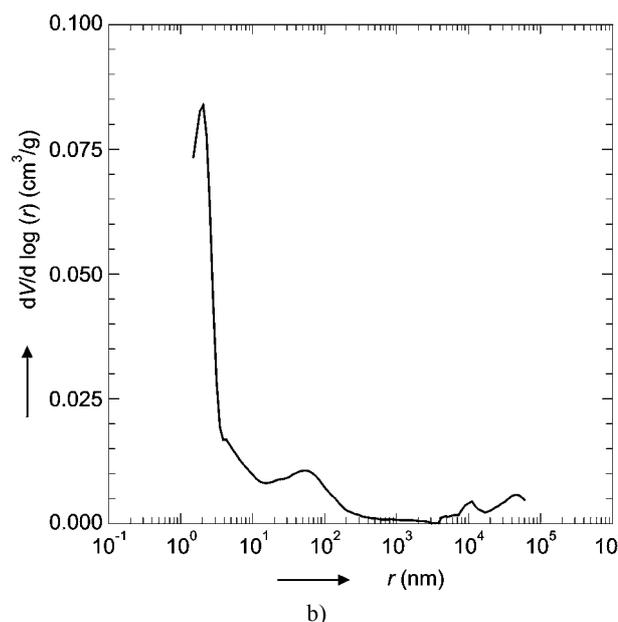
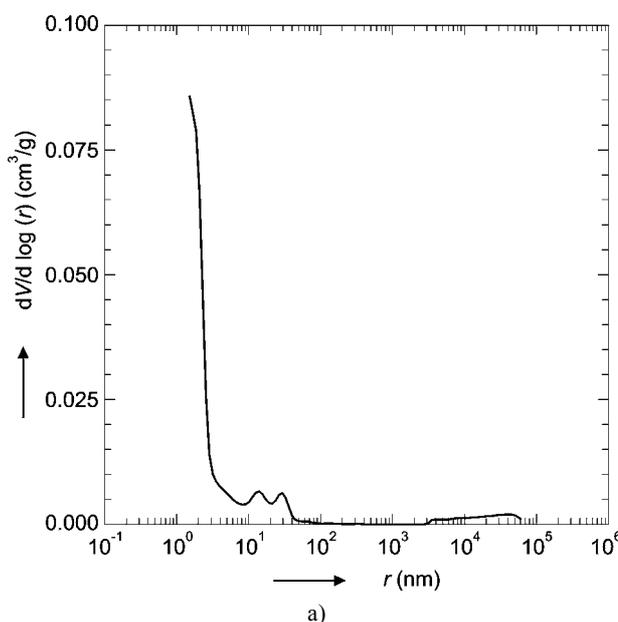


Figure 4. Differential distribution of pore size in samples A (a), B (b).

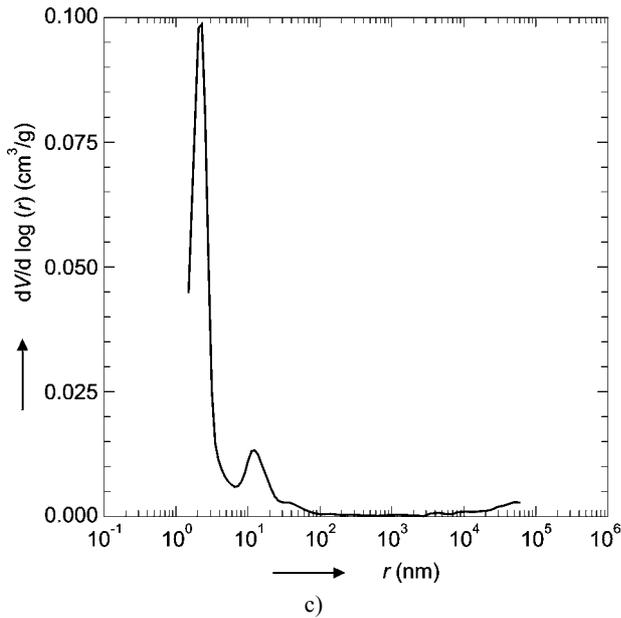


Figure 4. Differential distribution of pore size in samples C (c).

Results of the flexural strength and Young modulus measurements are presented in table 3. From these values it follows that Young modulus varies quite significantly due to the anisotropy, while the variation of flexural strength is relatively small. Our results are close to those obtained by Allen et al. [9]. A typical loading-unloading curve for Young modulus measurement is shown in figure 5. Correlation of flexural strength and Young modulus in both orientations of loading is documented in figure 6.

The compressive strength values, presented in table 4, show the difference in compressive behavior of the studied materials. The differences between values for different directions cannot be attributed solely to changing sample orientation. One has to consider the possibility of some parasitic effects caused by difficult centering of the sample, friction of the supporting body (cf. figure 3) and the degree of anisotropy in a given direction.

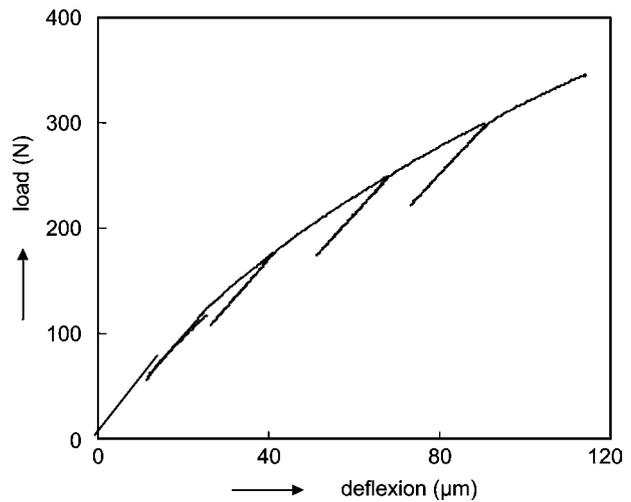


Figure 5. Typical loading-unloading curve for Young modulus measurement, C-type sample.

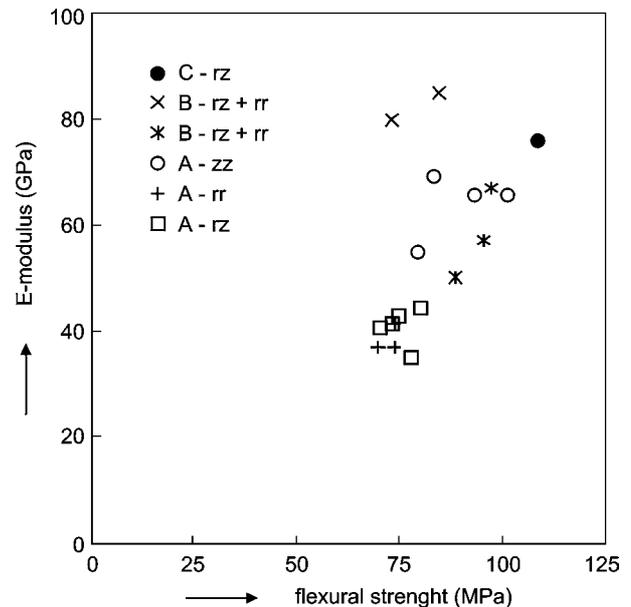


Figure 6. Correlation between flexural strength and Young modulus of BN samples A, B, C.

Table 3. Mean values of flexural strength and Young modulus for samples A,B,C.

sample	A	A	A	B	C	ref. [9]
orientation: cutting direction vs. load	zz	rr	rz & rr	rz & rr	rz	
flexural strength (MPa)	89	72	94	79	109	81
E-modulus (GPa)	64	38	58	82	76	65

Table 4. Mean compressive strength values.

sample	A	A	B	B	C	C
orientation	z	r	z	r	z	r
compressive strength (MPa)	138	131	182	136	211 ± 14	202 ± 24

The effect of anisotropy is apparent from comparison of the compressive strength when the loading was parallel with the preferred orientation of boron nitride macromolecular layers (in the 002 plane) and perpendicular to it. Reduction in compressive strength in the radial direction is significant in all series of samples.

Thermal expansion coefficient $\alpha = 4.57 \times 10^{-6} \text{ K}^{-1}$ was determined from the data in figure 7. The curve is approximately linear in the temperature range 200-1200°C; there is a steeper increase in the 1200-1600°C region, which exhibits some hysteresis during cooling. The anisotropic nature of the structure manifests itself in these measurements, too, but the amount of data is not sufficient for definitive conclusions.

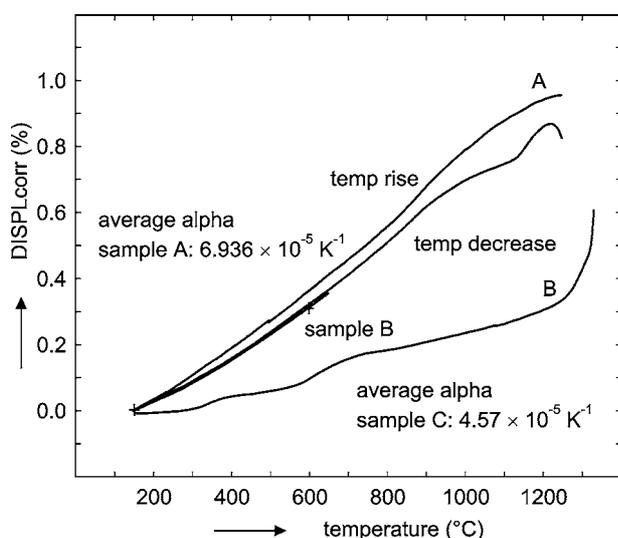


Figure 7. Dilatometric curve for BN samples.

CONCLUSION

During the startup of BN brake rings production which were necessary for the introduction of horizontal continuous casting of steel it has been necessary to state their properties. The crystallizers equipped with boron nitride ceramics with gradually changing content of residual oxygen from 6 to 8 %, prepared by hot pressing in graphite dies under 8 MPa pressure, were verified in service. In this work, we studied and compared the properties of BN ceramics prepared by common reduction method with a concurrent deoxidation by boron carbide additive. By regulating the deoxidation additive, the amount of residual oxygen was reduced from original 14 % to a level of products (6-8 %) already approved in service. This reaction sintering by electroconsolidation leads to an increase of Young modulus and flexural strength by about 20 % and to reduction of degree of anisotropy, characterized by the mean value of hexagonality coefficient $J = 4$, which gives us a basis for broadening the field of applications of mechanically loaded boron-nitride-based ceramics.

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ZLEPŠENÍ VLASTNOSTÍ BORNITRIDOVÉ KERAMIKY PŘIPRAVENÉ METODOU ELECTROCONSOLIDATION

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Článek přináší analytické ocenění teplotní roztažnosti keramických součástí na bázi hexagonálního nitridu boritého, připravených novou metodou žárového lisování, registrovanou u firmy Superior Graphite Company, USA, pod ochrannou značkou *Electroconsolidation*[®]. Touto EC metodou lze obecně zvýšit teplotu žárového lisování a dosáhnout rovnoměrného rozložení tlaku v lisovacím nástroji. Připravené vzorky byly porovnávány s běžnou žárově lisovanou bornitridovou keramikou. Vedle komerčního práškového nitridu boritého byly za účelem sledování změn slinovatelnosti vyrobeny dva nové modifikované prášky, a to BN deoxidovaný reduktivní chlorací a dále BN s přísadou karbidu boru.

Teplotní roztažnost elektrokonsolidovaných vzorků lze charakterizovat průměrnou hodnotou dilatačního koeficientu $\alpha = 4.56 \times 10^{-6} \text{ K}^{-1}$ s lineárním průběhem až do 1470 K. Nad touto teplotou je průběh ovlivněn zbytkovými stopami vázaného kyslíku, případně přísadou karbidu boru. Měření pevnosti v ohybu čtyřbodovou metodou ukázalo 30% vzrůst u elektrokonsolidovaných produktů v porovnání s hodnotami běžných produktů žárově lisovaných v grafitových pouzdrech. Vyšší byly také hodnoty Youngova modulu, ty jsou však silně ovlivněny anizotropií struktury. Měření pevnosti v tlaku rovněž prokázala přednost elektrokonsolidační metody. Další předností EC metody je zvýšení hustoty, dosažené snížením pórovitosti produktu o 2 až 5 %.