References

1. K. H. KIM and F. A. HUMMEL, *J. Amer. Ceram. Soc.* **42**, (1959) 286.
2. G. IZQUIERDO, Ph.D. thesis, University of Aberdeen, 1980.
3. G. IZQUIERDO and A. R. WEST, unpublished work.
4. M. CASTELLANOS and A. R. WEST, *J. Mater. Sci.* **14** (1979) 450.
5. G. IZQUIERDO and A. R. WEST, *Mater. Res. Bull.* **15** (1980) 1655.

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Formation of E-phase BN layers and shock-wave compressed BN on boron as a result of boron reactive electro-erosion

In previous papers [1, 2], the results have been presented of our investigations on the erosion process taking place on Ti and Al electrodes which have been subjected to a pulse discharge in the atmosphere of a gas capable of entering into stable chemical compounds with the metal examined. In this investigation a new mechanism of erosion has been found: the reactive electro-erosion mechanism. This reactive electro-erosion process differs considerably from the electro-erosion of metals in vacuum or in a neutral gas, and consists of a chemical interaction of the gas with the metal vapours or with the electrode material. It has also been found for Ti electrodes that the electrode material undergoes phase transformations into a metastable form: the α'-martensitic Ti phase.

The aim of the present work was to examine the phase and chemical changes resulting from the electro-erosion of boron which constitutes the electrode in an electric pulse discharge carried out in nitrogen. Nitrogen is a gas which is able to form compounds with boron (BN).

The experimental conditions of the process are given in Table I. The main details of the boron electrode technology and geometry are presented in Table II. The boron electrode was used as the hot central electrode in the co-axial plasma generator described by Sokołowski [3].

TABLE I

Discharge energy (J)	Pressure (Pa)	Shot repetition frequency (Hz)	Process duration (h)
2800	10^{-3}	0.01	8

The side surfaces of the electrode were examined after they had underdone the electro-erosion process. A coarse, crystalline layer of melted material was observed to appear on them (Fig. 1). Table III presents the results of the X-ray phase analysis of the initial material and the material of the surface layer formed during the electro-erosion process. From the X-ray diffraction results it can be stated that boron, initially in the high-pressure B form, has undergone a phase transformation into a βII-B-tetragonal form. This form may also be obtained by heating amorphous boron at 1300 K in an inert atmosphere at 10^{-3} Pa [4]. It was also observed that the boron electrode had been subjected to the reactive electro-erosion process and boron nitride had been produced on the electrode surface as a result of the erosion (Fig. 2).

The most interesting result is that a metastable phase of BN called the E-phase, was formed during this process. The E-BN phase may also be obtained [5, 6] from hexagonal graphite-like α-BN by the use of shock-wave compression at much

Figure 1 Side surface of the boron electrode treated in N_2.

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TABLE II

Two-stage manufacturing process of the boron electrodes by a powder metallurgy technique		Dimensions of the boron electrode	
First-stage	Second-stage	Diameter (mm)	Length (mm)
Hydrostatic pressing at 400 MPa of amorphous B doped with 1 wt % W	Sintering at 1200° C and 10^{-5} Pa for 10 h	5	50

higher temperatures and pressures than those present in a pulse plasma. It seems obvious to us that the observed phase transformation of B may occur under the thermal conditions of a pulse discharge. The formation of the E-phase BN is rather unexpected and can be explained in one of two ways.

(1) The transient values of pressure and electrode temperature on the microscopic areas encountered in our experiments under discharge conditions were similar to those during an explosion.

(2) The physical and chemical state of the electrode during the discharge is conducive in some specific manner to the formation of the metastable phases although they are thermodynamically unstable during the whole process.

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TABLE III

Initial material		B (high-pressure) (ASTM 17-788)*		Eroded surface layer material		E-BN (ASTM 18-251)		B_{tetr}-(βII) (ASTM 11-617)	
d†	I/I_0‡	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
–	–	–	–	5.03	100	–	–	5.03	100
4.41	50	4.40	60	–	–	–	–	–	–
–	–	–	–	4.27	80	4.25	10	4.30	80
–	–	–	–	3.86	30	3.85	50	3.93	30
–	–	–	–	3.56	30	3.54	20	–	–
–	–	–	–	3.20	20	3.22	100	–	–
–	–	–	–	2.97	50	2.98	10	–	–
–	–	–	–	2.64	30	2.68	50	2.86	4
2.52	50	2.53	100	–	–	–	–	–	–
–	–	–	–	2.48	50	–	–	2.52	10
–	–	–	–	2.41	20	2.43	10	2.41	18
2.35	48	2.31	100	2.21	30	2.20	50	2.23	10
2.15	16	2.15	20	2.04	30	2.07	50	–	–
–	–	–	–	1.99	30	1.95	50	–	–
–	–	–	–	1.68	20	1.69	20	–	–
1.69	12	1.68	20	–	–	–	–	–	–
1.61	12	1.60	20	1.55	10	1.54	20	–	–
1.45	16	1.45	60	–	–	–	–	–	–
1.43	18	1.41	80	–	–	–	–	–	–
1.36	33	1.35	60	1.35	8	1.35	10	–	–

*The notation in parentheses refers to the American Society for Testing Metals standard.

†*d* is the crystallographic spacing.

‡I is reflected intensity and I_0 is the beam intensity.

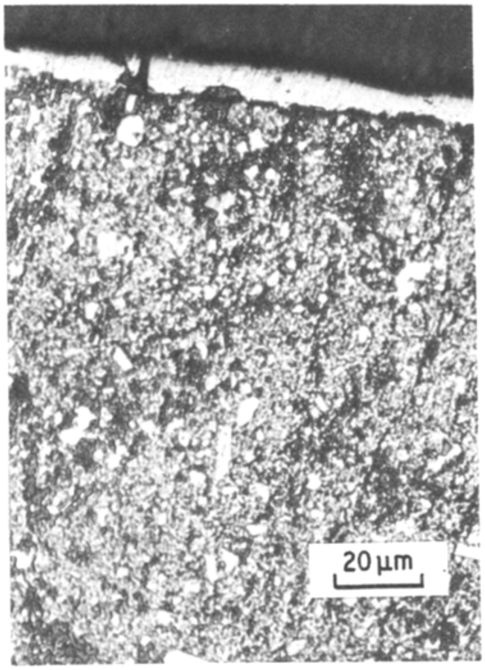

Figure 2 Cross-section of the boron electrode treated in N_2 (unetched).

References

1. M. SOKOŁOWSKI, A. SOKOŁOWSKA, A. RUSEK, A. MICHALSKI and J. GLIJER, *J. Mater. Sci.* **14** (1979) 841.
2. A. RUSEK, M. SOKOŁOWSKI, A. SOKOŁOWSKA, A. MICHALSKI, Z. ROMANOWSKI and B. GOKIELI, IV Krajowa Konferencja Naukowo-Techniczna, Częstochowa, 1979r.
3. M. SOKOŁOWSKI, *J. Cryst. Growth* **46** (1979) 136.
4. J. S. GILLESPIE, Jr, *J. Amer. Chem. Soc.* **88** (1966) 2423.
5. S. S. BACANOV, G. E. BŁOCHINA and A. A. DERIBAS, *Z. Struktur, Chim.* **6** (1965) 227.
6. T. AKASHI, A. SAWOHA, S. SAITO and M. ARAHI, *Jap. J. Appl. Phys.* **15** (1976) 891.

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Formation of Li_2TiO_3 solid solutions by $4Li^+ \rightleftharpoons Ti^{4+}$ substitution

During a study of the phase diagram Li_2O–TiO_2 [1], it was found that at high temperatures Li_2TiO_3 forms a wide range of solid solutions between 44 and 66 mol% TiO_2. These solid solutions have a disordered rock salt structure based on the high temperature polymorph of Li_2TiO_3. Li_2TiO_3 itself undergoes an order–disorder phase transition at 1213° C [2]. Some structural features of these solid solutions are discussed further in this note since they appear to form by an unusual replacement mechanism which involves monovalent and tetravalent cations.

Direct conformation of mechanisms of solid solution formation normally requires accurate measurements of densities over a range of compositions. It was not possible to measure the density of most of the high Li_2TiO_3 solid solutions present because they cannot be stabilized to room temperature; instead; they decompose and/or transform to low Li_2TiO_3, even on rapid quenching from high temperatures. Consideration of the high Li_2TiO_3 structure, however, reveals that there is only one likely solid solution mechanism. Assuming an oxide array (face centred cubic or cubic close packed) that is essentially unchanged with composition, the overall solid solution mechanism may be written as

$$4Li^+ \rightleftharpoons Ti^{4+}. \qquad (1)$$

For the lithia-rich solid solutions, this involves the formation of interstitial lithium ions, probably on tetrahedral sites and for the titania-rich solutions, the formation of cation vacancies on the octahedral sites.

The formula of the lithia-rich solid solutions may be written as

$$Li_{2+x}(\text{oct})\,Li_{3x}(\text{tet})\,Ti_{1-x}(\text{oct})O_3 \qquad 0 < x \leqslant 0.08. \qquad (2)$$

The only sites that are available in the rock salt structure for the extra $3xLi^+$ are tetrahedral sites and at the solid solution limit ($x = 0.08$) 4% of these tetrahedral sites must be occupied by Li^+.