

and contribute to the increase in the mean grain size viewed from the periphery to the centre of the spot.

On the basis of the experimental results obtained by investigation of the Wehner spot in the (1 1 0) direction obtained by bombarding the Cu monocrystal (1 0 0) plane, the following conclusions can be made.

(1) Profilometric investigations show that the thickness distribution of the material deposited on the spot is inhomogeneous. For an energy of 18 keV and a dose of 1.6×10^{18} ions cm^{-2} the thickness in the central part of the spot is about 2000 Å. This thickness is several (2 to 3) times higher than that on the periphery.

It is rather difficult to determine precisely the periphery and the edge of the spot. Because of the defocussing effects in the crystal lattice and surface diffusion of deposited material on the substrate, the spot is spread over a larger area.

(2) The crystal structure in the Wehner spot changes viewed in the direction from the periphery to the centre of the spot. Some of the reasons are probably the different deposition rate of the thin film which forms the spot and the distribution of kinetic energy of the sputtered atoms in the beam forming the spot. Although the fraction with the small grain size structure in the spot can be found, in the central part of the spot the crystallization of the deposited material is almost complete.

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Melting behaviour of $\text{Li}_2\text{TiSiO}_5$

$\text{Li}_2\text{TiSiO}_5$ is reported to be in that rare class of compounds which melts directly to a mixture of two liquids [1]. During a study of phase relations in the system $\text{Li}_2\text{O}-\text{TiO}_2-\text{SiO}_2$, the melting of $\text{Li}_2\text{TiSiO}_5$ was reinvestigated. It does not melt to two liquids but instead, melts incongruently to the high temperature polymorph of Li_2TiO_3 and liquid. This is shown in the diagram of the pseudo-binary join $\text{Li}_2\text{TiO}_3-\text{SiO}_2$, Fig. 1, in which $\text{Li}_2\text{TiSiO}_5$ melts incongruently at $1213 \pm 8^\circ\text{C}$. The diagram was determined by heating samples in a furnace, quenching them into Hg and analysing the products by optical microscopy and X-ray powder diffraction. Full details of the experimental methods used and the results for the

ternary system $\text{Li}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ are given elsewhere [2, 3].

The join $\text{Li}_2\text{TiO}_3-\text{SiO}_2$ is not a true binary join because TiO_2 appears on the diagram over a small range of temperatures between ~ 1139 and 1180°C : since the composition TiO_2 does not belong on this join, as shown in the inset, Fig. 1, the join cannot be a true binary join. Li_2TiO_3 undergoes an order-disorder phase transition at 1213°C [4] and the high temperature polymorph has a disordered rock-salt structure with a very simple X-ray powder pattern, Table I. In stoichiometric Li_2TiO_3 , it is apparently not possible to quench the high temperature polymorph to room temperature [4, 5]. On heating $\text{Li}_2\text{TiSiO}_5$ above $\sim 1220^\circ\text{C}$, however, the high Li_2TiO_3 polymorph which resulted could be quenched to room tem-

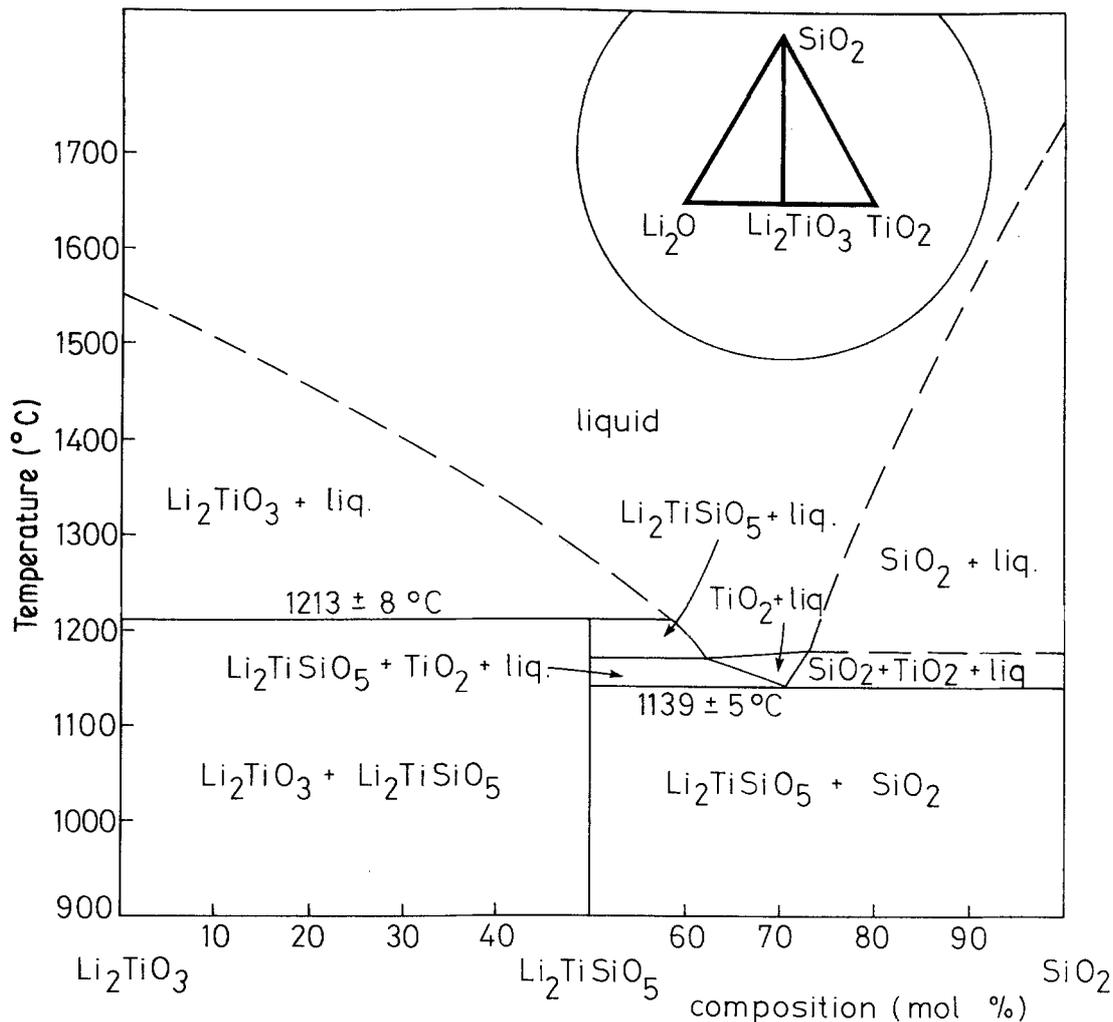


Figure 1 Phase diagram of the pseudobinary join $\text{Li}_2\text{TiO}_3\text{-SiO}_2$ showing the incongruent behaviour of $\text{Li}_2\text{TiSiO}_5$. The location of the join $\text{Li}_2\text{TiO}_3\text{-SiO}_2$ in the ternary system $\text{Li}_2\text{O-TiO}_2\text{-SiO}_2$ is shown as an inset.

perature. Possibly Li_2TiO_3 may dissolve a small amount of SiO_2 at high temperatures and this gives kinetic stability to the disordered polymorph on quenching. A similar effect is known to occur with small amounts of Li_2O dissolved in Li_2TiO_3 [5].

TABLE I Powder X-ray diffraction data for high Li_2TiO_3

$d_{\text{obs}}(\text{\AA})^*$	$d_{\text{calc}}(\text{\AA})^\dagger$	I	hkl
2.0729	2.0722	100	002
1.4654	1.4652	46	022
1.1962	1.1964	13	222

*KCl was added as an internal standard.

†From least squares refinement, $a = 4.144 \pm 0.001 \text{ \AA}$.

There was no evidence for a region of stable liquid immiscibility on the join $\text{Li}_2\text{TiO}_3\text{-SiO}_2$. Although there is a region of liquid immiscibility in the ternary system $\text{Li}_2\text{O-TiO}_2\text{-SiO}_2$ [3], it is restricted to compositions which lie close to and include the $\text{TiO}_2\text{-SiO}_2$ edge. In the partial phase diagram of Kim and Hummel [1] for the system $\text{Li}_2\text{O-TiO}_2\text{-SiO}_2$, a more extensive region of liquid immiscibility is shown which covers much of the join $\text{Li}_2\text{TiO}_3\text{-SiO}_2$, including $\text{Li}_2\text{TiSiO}_5$.

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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 undergone 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 β II-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

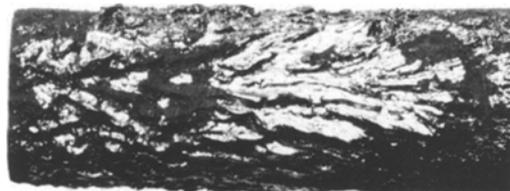


Figure 1 Side surface of the boron electrode treated in N_2 .