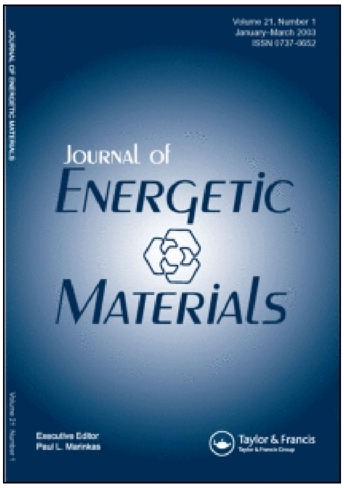

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Ramaswamy, Alba L. , Glass, John , Renn, Phil and Sturgill, Phil(2004) 'The Conversion of a Boron-Containing Pyrotechnic Mix to a "Ceramic-Like" Material by Electron Beam Interaction', Journal of Energetic Materials, 22: 4, 231 — 250

To link to this Article: DOI: 10.1080/07370650490893117

URL: http://dx.doi.org/10.1080/07370650490893117

Energetic Materials, 22: 231–250, 2004

ISSN: 0737-0652 print
DOI: 10.1080/07370650490893117

The Conversion of a Boron-Containing Pyrotechnic Mix to a “Ceramic-Like” Material by Electron Beam Interaction

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The transformation of a boron-containing pyrotechnic mix to a “ceramic” vitreous-like material by the impingement of an electron beam on a boron-barium chromate pyrotechnic, in a scanning electron microscope, is reported. The thickness of the “ceramic”-like material is ×250 the penetration depth for the electron beam and indicates that a self-sustaining chemical reaction was induced by interaction of the energetic material with the electron beam at temperatures well below the mix's ignition temperature of over 1000°C. This links with earlier observations on the low-temperature liquefaction of boron to boron suboxides in an electron microscope.

Keywords: pyrotechnics

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Introduction

Boron-barium chromate pyrotechnic mixes are typically utilized as pyrotechnic delay compositions because of their stable burning characteristics. A range of burn rates is obtained by varying the percentage compositions of the boron fuel. The composition studied in this paper consists of 10% by weight of the boron fuel with 90% barium chromate oxidizer and was manufactured/prepared at McCormick Selph (Pacific Scientific). Boron–barium chromate pyrotechnic delay compositions have good aging characteristics and are generally used for the faster burning or shorter delay times.

In a pyrotechnic delay composition the combustion is often termed as a ''solid-solid'' reaction where the solid fuel is oxidized from the oxygen in the solid oxidizer at the higher temperatures. In fact, as can be seen from the physical properties of boron and barium chromate, provided in Table 1, an igniting flame will first tend to trigger the decomposition of the barium chromate, which occurs at ~1400°C (though some of the amorphous boron can flame up at ~800°C with the initial atmospheric oxygen available). The decomposition of barium chromate generates high temperatures and oxygen gas, which rapidly oxidizes the boron fuel to boron oxide, releasing more heat and accelerating the reaction until a stable self-sustaining condition is rapidly

Table 1
Physical data for boron and barium chromate [1, 2]

Property	Boron (amorphous) (B)	Barium chromate ($BaCrO_c$)
Appearance	Dark-gray powder	Light yellow powder
Density	2.33 g/cm^3	4.498 g/cm^3
Melting point (temperature)	2300°C	Decomposes at 1380°C
Boiling point (temperature)	Sublimes at 2550°C	N/A

created, and a burning front proceeds at a steady rate through the mix.

Boron exists in two forms: crystalline and amorphous. Crystalline boron, although relatively brittle compared to diamond, is second only to diamond in hardness. There are three known crystalline forms of boron showing clear crystal facets under the microscope. One crystalline form of boron is jet-black to silvery-gray in color with a metallic luster, and the other one is of a bright red color [3].

The amorphous form of boron is less dense than the crystalline form and is dark-brown to dark-gray in color. The brown form of amorphous boron is most likely a mix of red ''nano-crystalline'' grains with dark-gray grains giving its brown appearance. Amorphous boron is the more reactive form of boron and is the one used in energetic mixes. In fact, coarse boron crystals are more stable and are difficult to ignite [4]. Amorphous boron oxidizes slowly in air at room temperature and is spontaneously flammable at around 800°C.

The transformation of boron during heating in an environmental scanning electron microscope (ESEM) in an oxygen atmosphere was studied in some detail and is reported in the literature [5,6]. In summary, when amorphous boron is heated, a liquid layer forms because of the melting of boron at around 940°C. This contrasts with the actual high melting point or temperature of boron, which is ~2300°C. To understand this anomalous low melting temperature, boron oxide was melted in the ESEM and was found to undergo the solid-to-liquid transformation at the known melting temperature for the boron oxide. The apparent anomaly for the melting point of boron in the microscope was thus explained in the literature by the dissolution of the boron in liquid boron oxide, which melts at ~450°C and forms on the surface of the boron in contact with oxygen, a model first proposed in an earlier paper by Glassman et al. [7]. The combustion of boron was described in this latter paper as occurring in two separate phases. In the initial phase during the heating, the boron particle is covered by a layer of liquid boron oxide, followed by the second phase where the boron dissolves in the liquid oxide and diffuses through it to reach the surface where ignition can take place. On removal of the liquefied sample from the ESEM, the cooling and air intake transforms the liquid into a solid vitreous residue with a brown color [5,6]. The residue was identified as a $(BO)_n$ polymer using the following characterization scheme: an amorphous X-ray diffraction pattern, brown coloration, insolubility in water and methanol, and a hard, brittle behavior.

In this paper we report the transformation of a boron-containing pyrotechnic mix to a ‘‘ceramic’’ vitreous-like material by the impingement of an electron beam on the boron-barium chromate pyrotechnic in a scanning electron microscope (SEM). The transformation was instantaneous to the eye and converted all of the pyrotechnic, in the field of view of the electron beam, an area of $0.785\,\mathrm{mm}^2$ up to a depth of $\sim 500\,\mu\mathrm{m}$ of the mix, to a globule of hard jet-black ‘‘ceramic’’-like material, which was vitreous in nature and not brittle. The thickness of the ‘‘ceramic’’-like material is ×250 the penetration depth for the electron beam and indicates that a self-sustaining chemical reaction was induced by the interaction of the energetic material with the electron beam at temperatures well below the mix's ignition temperature of over 1000°C, possibly through the catalytic action of impurities. This is linked with earlier observations reported in the literature of low-temperature liquefaction of boron to boron suboxides in an ESEM.

The jet-black vitreous residue thus was produced without any external heating in the microscope or any oxidizing environment since the transformation practically took place in a vacuum. The material was very hard and not brittle. An X-ray diffraction pattern revealed the overlap of a clear crystalline component superposed on an amorphous phase with an additional amorphous band, which were initially identified from the lattice constants. Comparison with an infrared spectrum for the material demonstrated the unequivocal presence of barium tetraborate in an amorphous form possibly with some short-order crystalline range. The crystalline phase evidenced by X-ray diffraction agrees with the lattice constants for cubic barium boride, a very hard ‘‘ceramic’’-like material (though there is an overlap with the borate structure, if there were some short-range crystalline order in the borate, which, however, is highly unlikely). Typically glassy borates give an amorphous X-ray diffraction spectrum, but when recrystallized over 70 or more hours they can give rise to clear X-ray diffraction peaks. The amorphous phase agrees with the lattice constant for nanocrystals of crystalline α-boron. The crystalline component appears to superpose on an amorphous band for the borate structure. The black coloration was in agreement with the presence of cubic barium boride and/or nanocrystals of boron, which are both black in coloration.

As described in this paper, we have evidence to suggest that the transformation was in fact triggered by the electron-beam interaction in the SEM with the boron-containing pyrotechnic mix possibly catalyzed by impurities. We thus believe that the observation made in the earlier literature—that the anomalous low melting point for boron in an ESEM is due to the dissolution of boron in liquid boron oxide—did not take into account the possibility of interaction of the electron beam with the boron, which can cause transformations and reactions at lower than expected temperatures.

Observations and Results

Observation of the Transformation

The boron (10% by weight) barium chromate pyrotechnic mix under study is used as a pyrotechnic delay composition in delay column configurations. The specific configuration investigated was one for a small column insulated delay (SCID) element consisting of an external steel tubing fit concentric to an inner tin sheath with the delay composition packed/consolidated inside. About 14 SCID unit ends were analyzed with the electron microscope microprobe using wavelength dispersion spectroscopy (WDS) in the SEM to determine the elemental composition and distribution in the mixes at the ignition end of each SCID length. WDS was performed using a JEOL electron microscope Model JXA8900R WD microprobe analyzer. A total of 73 WDS scans were obtained. None of the unit ends required surface sputtering of a conductive coating for visualization or imaging in the electron microscope since the metallic elements in the mix, including pure boron, were found to be sufficiently conductive. Figure 1 shows a typical WDS surface compositional map for a SCID unit end.

Table 2 gives the quantitative WDS microprobe analysis data for a typical area. The diameter of the area sampled is 30 µm and is constant for all examined areas. The electron beam penetration depth is of the order of 2 µm for a material such as barium chromate and 1 µm for a heavier element such as lead.

The mix consists of 10% by weight boron, in agreement with the measurements, and the rest barium chromate. The carbon comes from an organic residue used in the mixing process of the boron with the barium chromate. Magnesium is a typical impurity, which is found in the boron and originates as a residue from the manufacturing process of boron, namely, the Moissan process where boron oxide is reduced to boron using magnesium.

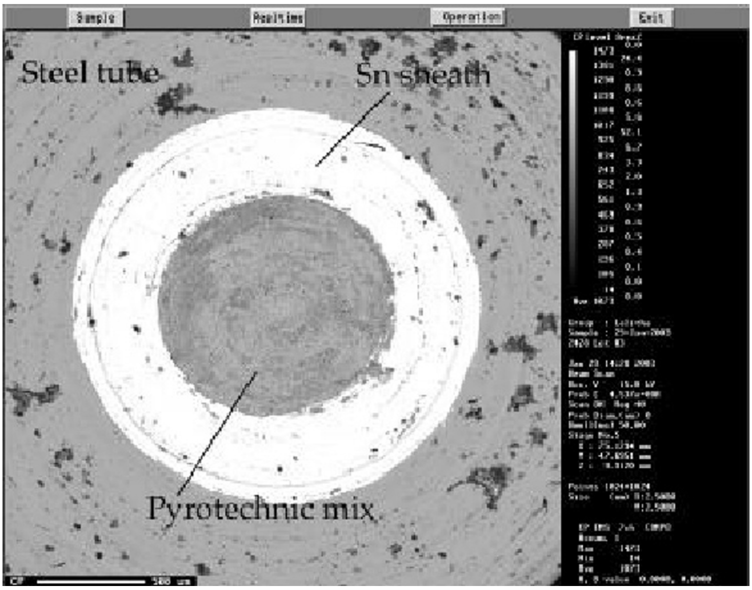

Figure 1. Compositional image of typical SCID end in an SEM.

Table 2
WDS microprobe data for pyrotechnic mix

Element	Weight (%)	Atom (%)
B	10.4064	28.4636
C	1.0774	2.6524
O	26.7021	49.3448
Cr	16.6644	9.4755
Ba	44.8063	9.6462
Mg	0.3433	0.4176

Two SCID units, which formed part of a baseline batch, were cut transversely down the middle of their lengths to examine the typical elemental distribution at the center or bulk of the SCID length. The units were cut by clamping each individually in the chuck of a lathe and rotating it while a clean thin jewelers saw blade was pressed manually on the outer tubing wall. Air was blown on the unit to remove any metallic dust formed from the cutting process and to keep the unit cool. Care was taken to ensure that no contact came between the saw blade and the pyrotechnic mix. The two units were successfully sectioned, and the four fresh areas of exposed pyrotechnic mix were examined in the SEM by WDS. The SEM conditions of electron beam voltage were identical to those used for all other units. The conditions are summarized in Table 3.

The surface of the pyrotechnic mix was examined prior to insertion in the electron microscope and appeared normal for all units, though the cut was not uniformly smooth. All unit

Table 3
SEM accelerating voltage and probe current conditions

	SEM conditions
Accelerating voltage	15.0 kV
Probe/filament emission current	(4.537–0.3) × 10^{-8}A

ends were imaged. For one unit end, as the electron beam in the SEM was focused onto the pyrotechnic mix surface, a large structure of white incandescent material was observed to suddenly form and cover the surface of the pyrotechnic mix. The transformation was followed on the electron microscope video screen and was seen to be almost instantaneous. The incandescence was due to the fact that the material formed was not electrically conductive.

The unit was immediately removed from the SEM, and a large globule of vitrified jet-black “ceramic”-like material was found to have formed and fused to the surface of the mix. By prodding with the end of a very fine metallic tip, the “ceramic” -like material was removed. Figure 2 is a secondary electron image of the sample obtained by sputtering the surface with a coating of conductive carbon.

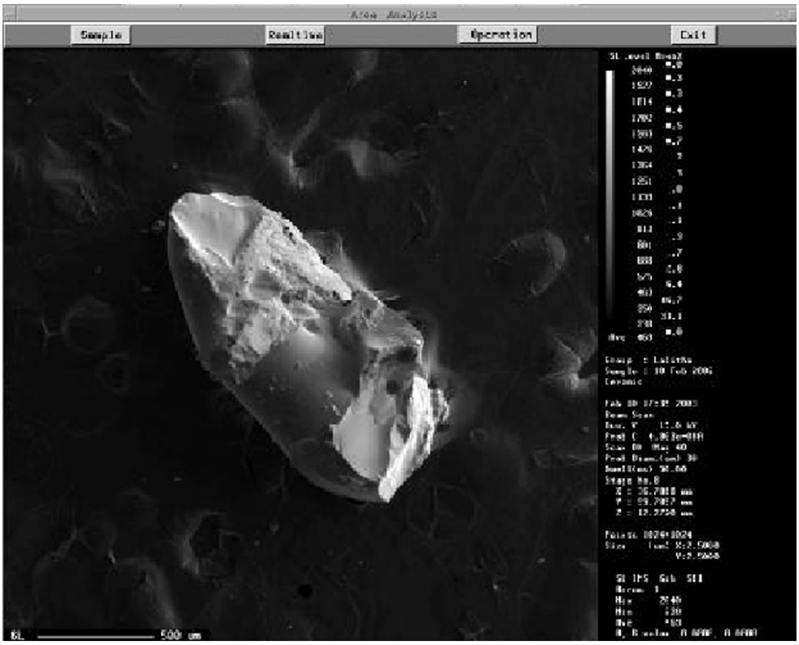

Figure 2. Secondary electron image of “ceramic”-like material.

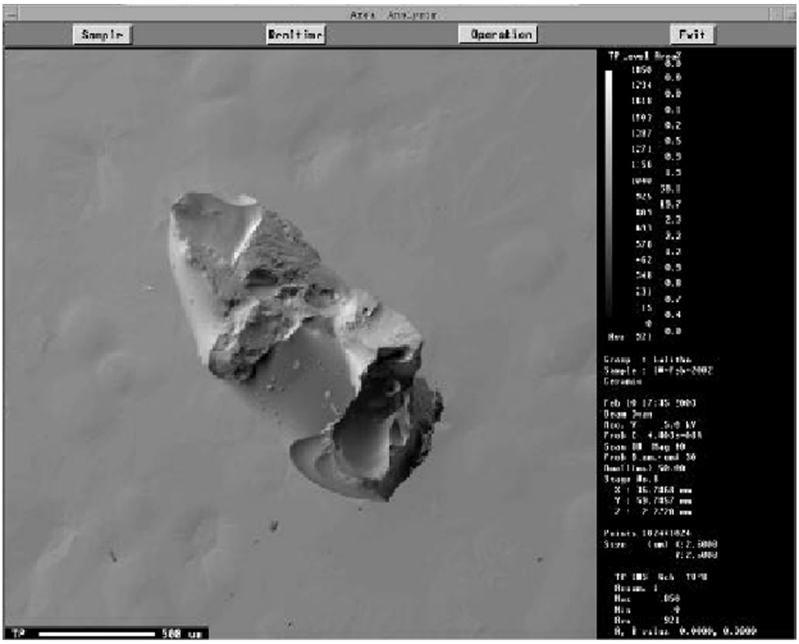

Figure 3. Topographical image of the “ceramic”-like sample.

Figure 3 is a topographical image of the sample. Figure 4 shows how it was located with reference to the SCID end surface. A bottom surface was in contact with or fused to the mix. The top surface, on the other hand, was smooth and curved. Figure 5 shows the secondary electron micrograph image of the residue of the surface of the SCID, once the “ceramic”-like structure was removed. As can be seen, a large hole or crevice was created in the place where the globule of the “ceramic”-like material had formed.

Optical Examination

The sample was examined by optical microscopy. It looked jet-black in appearance, and the vitreous nature was evident by the reflection of light from the surface, as exemplified in the optical image of Figure 6. The sample is viewed from the smooth curved top surface side.

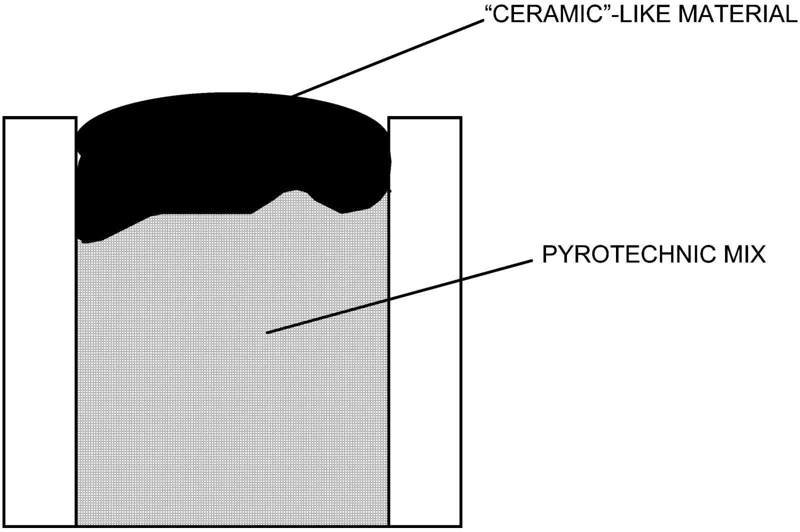

Figure 4. Location of "ceramic"-like material with reference to pyrotechnic mix.

The sample's "vitreous" appearance indicates that it consisted of some form of fused boron oxide forming a "glassy" matrix. Since the sample was imaged under vacuum, the oxygen for the oxidation of the boron must have originated from the barium chromate. It could not have been purely liquid boron, since the temperatures needed for the liquefaction are very high and no heating was performed. The incandescence evidenced an insulating material such as boron oxide. This means that the pyrotechnic reaction appeared to have been triggered in the electron microscope. However, it usually requires a temperature of over 1000°C to induce the pyrotechnic ignition reaction.

The heat generated by the impingement of the electron beam on the pyrotechnic surface was estimated and found to be several 100°C at a maximum, which is well below the ignition temperature. The temperature rise by the electron beam can be estimated from the following equation derived by Potts [8], where the temperature rise ΔT(°C) is from an electron beam

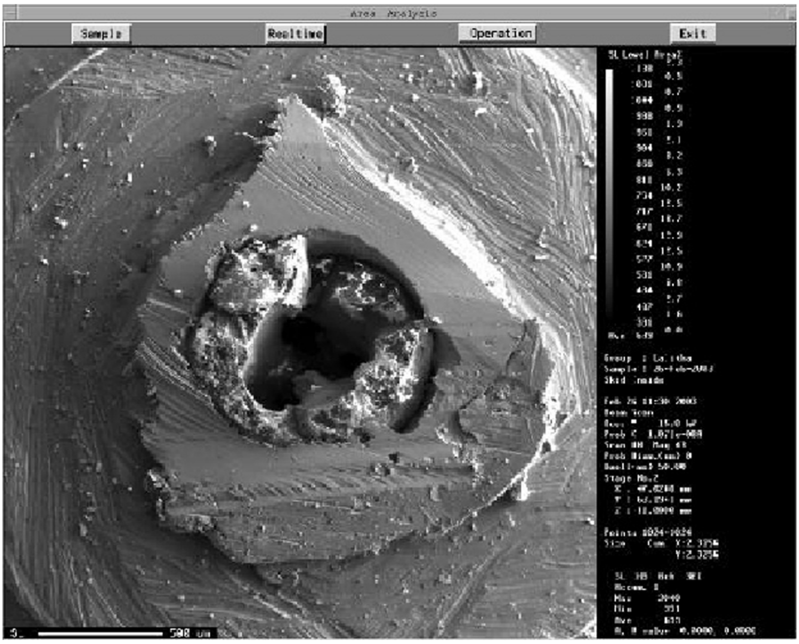

Figure 5. Secondary electron image of scid surface after removal of “ceramic”-like structure.

of diameter d (μm) impinging on a sample of thermal conductivity k ($\mathrm{Wcm^{-1}K^{-1}}$):

$$\Delta T = 4.8\frac{Ei}{kd},$$

where E is the incident energy of the electron beam (in KeV) of current i (μA).

Furthermore the thickness of the “ceramic”-like material was found to be ~500 μm, which is ×250 the penetration depth of the electron beam. This shows that the reaction progressed from the surface inwards in a self-sustained manner, that is, sustained from the heat of the pyrotechnic reaction. The fused boron oxide was apparently formed in the liquid state, as evidenced from the smooth curved surface of the “ceramic”-like material, which is indicative of surface tension on a

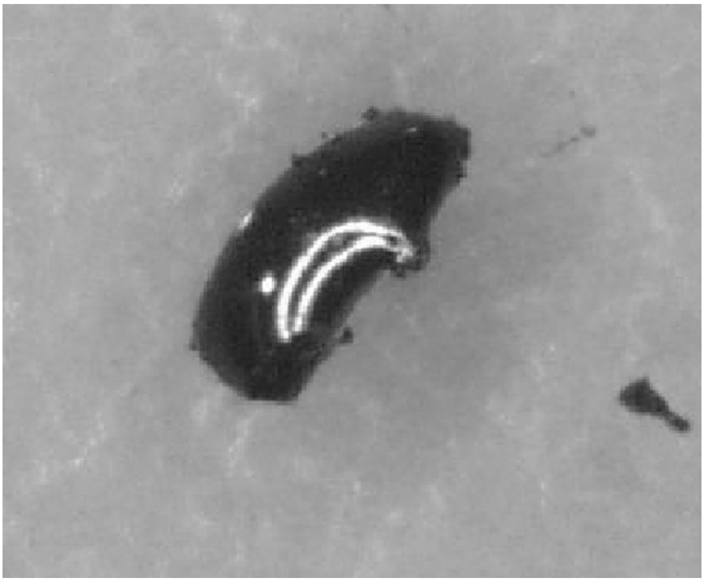

Figure 6. Optical image of sample showing the reflection of the light from the curved smooth top surface.

liquid surface. Boron oxide fuses at 450°C. Solidification or cooling occurred when the SEM was shut down prior to removal of the unit.

The jet-black metallic lustrous appearance is distinctive and can originate from two possible sources, that is, through the formation of areas of crystalline boron intermixed in the glassy boron oxide matrix and/or of an intermetallic compound such as barium boride BaB_6, which has a black coloration. The material appears very hard; this could be due to the contribution of either crystalline boron and/or the boron intermetallics. The sample was clearly very hard and not brittle. This indicated to us that although a boron oxide glassy matrix had formed, it was possibly interspersed or held together by very hard crystalline components such as boron or intermetallic boride formed as a product of the pyrotechnic reaction and rendering the material harder than the glassy matrix. This is why we have termed it "ceramic"-like.

Wavelength and Electron Dispersion Spectroscopies

The sample was analyzed using electron dispersion spectroscopy (EDS) since it had a curved surface and WDS could not be applied. The EDS technique utilized was not sensitive to boron. Figure 7 shows a typical compositional map of the sample.

Figure 8 shows a typical EDS spectrum for the sample. It evidences a large oxygen peak as well as distinctive peaks for Ba and Cr. The B present cannot be detected by EDS. A white spot on the sample was also found to contain some W (tungsten), which is probably a surface impurity picked up from the microscope filament, made of tungsten, possibly on the sample preparation bench prior to insertion in the microscope.

The SCID surface where the sample was formed was analyzed by WDS to determine whether some impurities could have come into contact with the surface to catalyze the observed reaction. When the SCID unit was placed in the electron

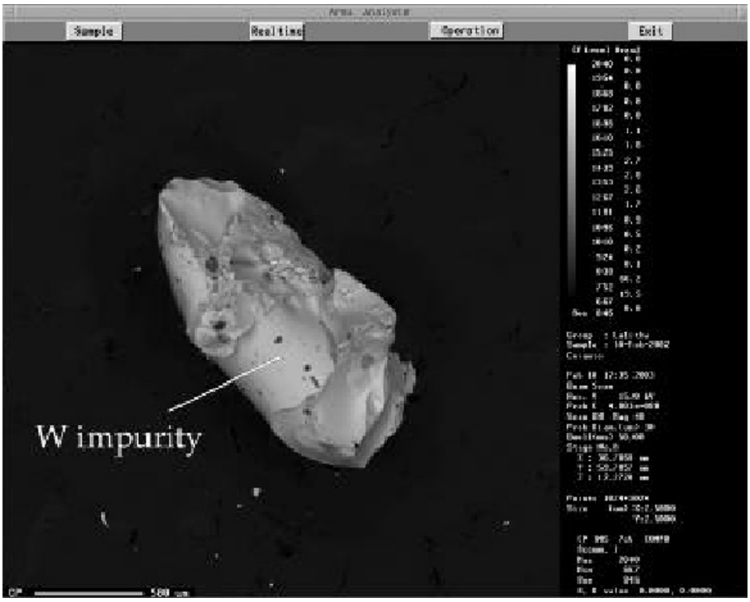

Figure 7. Compositional map of "ceramic"-like sample.

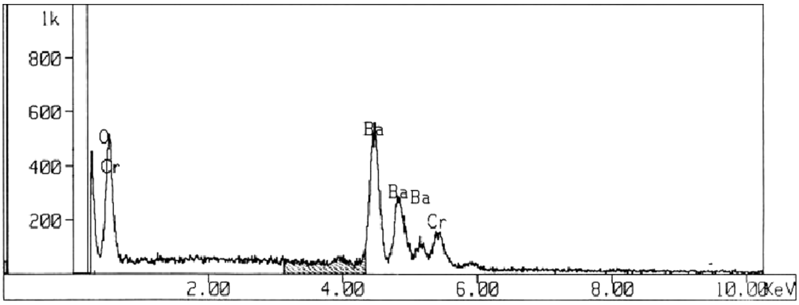

Figure 8. EDS spectrum of "ceramic"-like sample.

microscope, the surface end was found to locally charge and react on focusing of the beam down to a 30µm beam spot diameter. Thus the residual reaction was still in action. The compositional analysis thus could not be performed in those areas. However, the residual reaction occurred on the flat surfaces of the SCID where no transformation had taken place yet. This was indicative of some surface impurity, which could have reached the surface during the cutting process.

Fourier Transform Infrared Spectroscopy

The sample was analyzed using a Fourier Transform Infrared Spectroscope with a Nicolet infrared spectrometer. It was viewed in the microscopy mode where the sample was placed on a clear blank microscope slide and focused in different areas with the infrared beam. The average spectrum is shown in Figure 9.

The infrared bands between 1200 and 1500 cm^{-1} are due to the B-O stretching from the BO_3 group, and the B-O stretching bands of the BO_4 group are in the region from 800 cm^{-1} to 1100 cm^{-1} [9,10]. The infrared bands between 600 and 800 cm^{-1} are mainly due to B-O bending [11]. A comparison with the infrared spectrum for lithium borate ($Li_2B_4O_7$) was obtained, and a very good match for the two spectra in the B-O bond areas was noted, as depicted in Figure 9. This demonstrates that the "glassy" component of the sample consists of BaB_4O_7.

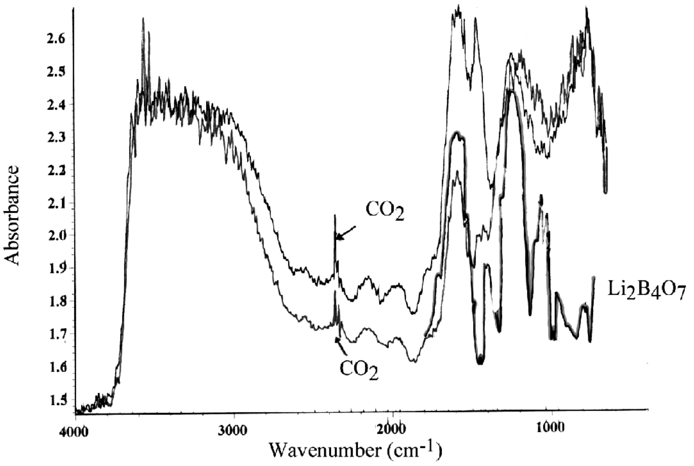

Figure 9. Infrared spectrum of ‘‘ceramic’’-like material.

X-ray Diffraction

The sample was glued to the end of a fiberglass and inserted in a Debye-Scherrer Philips X-ray diffraction (XRD) powder photographic camera. A photographic film was mounted in the camera, and the sample irradiated with the collimated X-ray beam. The sample and film in the camera were exposed for a total of 7 hr, and the resultant film analyzed. A photograph of the film is shown in Figure 10.

It clearly shows two broad bands due to some amorphous phases as well as a distinct sharp line with a fainter one indicative of a crystalline component. From the location of the line, the 2θ diffraction angle could be evaluated, and the corresponding d Å interatomic lattice spacing determined. Table 4 summarizes the d Å measurements obtained from the photographic film. Comparing with the Hanawalt XRD database from the International Center for Diffraction Data, the closest correspondence for the two lines was obtained for cubic barium boride. Table 5 gives the cubic barium boride reported data compared with the observed measurements.

As can be seen from the table, the observed diffraction lines are given in order of intensity with the corresponding (hkl)

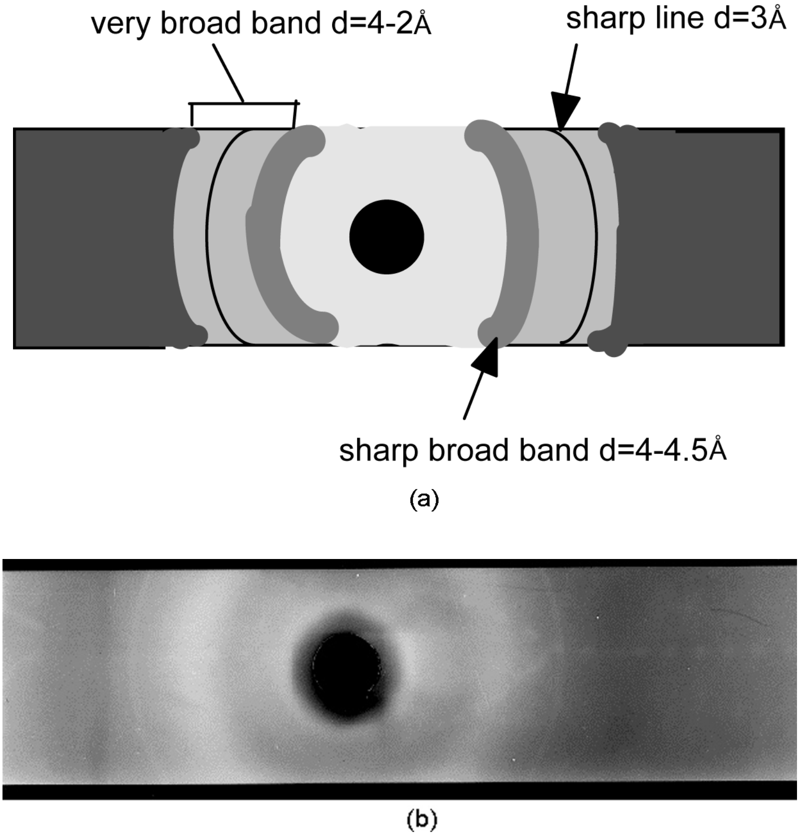

Figure 10. Image of photographic film from Debye-Scherrer XRD camera.

Table 4
d Å interatomic lattice spacing extrapolated from photographic film in Debye-Scherrer XRD camera

Features on photographic film	*d* **(Å)**
Sharp line	3
Faint line	1.9
Broad band	4–4.5
Weak broad band	4–2

Table 5
Reported and measured XRD data (for BaB_6 for first three diffraction peaks) showing very good correspondence

Ba B_6: d (Å)	Int.	h	k	l	Measured d (Å)
3.014	100	1	1	0	3.0
4.261	54	1	0	0	4–4.5
1.9069	48	2	1	0	1.9

Miller indices and the reported d interatomic lattice spacing for the plane in Å. The measured d (Å) is recorded in the last column of the table. There is a very good agreement, with the second most intense peak overlapping on the broad band from the amorphous structure. The database was scanned for the possibility of other structures, but this was the only one that agreed with the data. Furthermore it explains the black coloration of the sample since cubic barium boride is black, as well as its hardness and nonbrittle nature, which may come from a contribution of the boride. With regards to the two broad bands, the one at 4–4.5 Å corresponds most closely to that observed for nanocrystals of crystalline α-boron, and the weak broader band corresponds with the borate.

Thus the crystalline component evidenced by the XRD appears to be barium boride superposed on a gray background on the photographic film from amorphous barium tetraborate with an additional α-boron amorphous phase dispersed in the glass.

Discussion

The pyrotechnic reaction and transformation reported in this paper was obtained without heating in an SEM possibly induced by the action of an electron beam catalyzed by the presence of impurities. This links with earlier observations of liquefaction of boron at lower than expected temperatures in an electron microscope. Thus lower than expected melting temperatures were found for boron when heated in an ESEM under an oxidizing atmosphere [5,6]. This was linked with Glassman et al.'s criterion [7] for the ignition of boron, which occurs in two steps, the first one consisting of an oxidation of the surface of the boron to form boron oxide, and the second a dissolution and diffusion of the boron in the liquid boron oxide to ignite once it reached the surface. As described in this paper, the low temperature melting of boron in an oxidizing atmosphere in an ESEM may also be due to an electron beam interaction component, which was not taken into account in the literature.

The transformation reported herewith consists of an oxidation of the boron to form liquid boron oxide, which on cooling gives a barium tetraborate structure. By examining the atomic percentages of the elements present in the pyrotechnic mix as shown in Table 2, it can be seen that there is an exact stoichiometric proportion of elements to form the barium tetraborate structure. Thus taking 100 atoms as reference (see Table 2), there are 49 atoms of oxygen, 28 of boron, 9 of barium, and 9 of chromium. This gives exactly seven molecules of BaB_4O_7, where 49 atoms of oxygen are used up with 28 atoms of boron, leaving two atoms of elemental barium and nine atoms of chromium:

$$16B + 7BaCrO_4 \rightarrow 4BaB_4O_7 + 3Ba + 7Cr.$$

The XRD data show that either crystalline boron or barium boride was formed and is found embedded in the amorphous part of the tetraborate structure. Thus some of the unreacted boron lying beneath the boron oxide must have dissolved into the liquid boron oxide to recrystallize and form nanocrystalline areas of boron and/or combined with the barium to form barium boride. This would be in agreement with Glassman's criterion. However, the oxidation of the boron from the barium chromate requires very high temperatures, which were not created in the electron microscope. From this observation we infer that the electron beam must have triggered the reaction, possibly catalyzed by some impurities.

That electron beams can be used to trigger chemical reactions is not new, especially to the electron microscopist. Thus during the early development stages of electron microscopes the reaction of contaminating pump oil and sealing grease from the vacuum pumps, triggered by the electron beam interaction, caused polymerization to a carbonaceous deposit [12] and needed to be resolved. Christy [13] studied the polymerization of silicone oil under the action of an electron beam. The polymerization of various organic materials under the action of an electron beam is nowadays used as part of the standard electron fabrication techniques in the semiconductor industry. However, the electron-beam–induced reaction reported in this paper is the first of its kind, especially because the transformation was obtained from a pyrotechnic material, which causes the reaction to become self-supporting, because of the heat release from the energetic material itself once the initial reaction has been triggered.

Acknowledgements

The authors wish to thank Dr. Phil Piccoli (Microanalysis Facility, University of Maryland) for the WDS and EDS spectra. The CAD/PAD Department of NSWC-IH is especially thanked for support of the work and McCormick Selph (Pacific Scientific) and Cambridge University for the collaboration.

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