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Crystallization and densification of plasma H.F synthesized boron powder

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Abstract: Boron powder was synthesized by reducing a boron halide in a microwave plasma:

Synthesized powder is under micro sized, amorphous and contains high chlorine level. It is necessary to inflict a thermal treatment to purify and recrystallize the powder before densification. Direct hot isostatic pressing on this powder conducts to broken samples.

It is realized in a vacuum furnace at temperature between 1500 and 2000 °C on 30 * 30 mm cylinders made using cold isostatic pressing at 400 MPa. Green density is among 1.3.

Boron recrystallizes in β rhomboedral form. Total transformation is obtained at temperatures up to 1900 °C, but density is almost the same the rough material one. No diffusion can be observed between powder grains.

Hot isostatic pressing was used for the densification. Samples are put in titanium can with a carbon diffusion barrier. The pressure applied was 150 MPa and temperature varies between 1250 and 1600 °C.

Theoretical density is obtained at 1600 °C without grain size increase.

Total densification of plasma synthesized boron powder is obtained by hot isostatic pressing, but a thermal recrystallization treatment is necessary before H.I.P.

1) Introduction:

The aim of this paper is the study of crystallization and densification of plasma H.F synthesized boron powder.

There are a lot of methods to synthesize ceramic powders. The reduction of a halide in a microwave plasma is one of them. In the case of boron powder the produced reaction is:

The HCl produced is neutralized.

The obtained powder contains very small particles. The grain size analysis indicates two things:

- * the average grain size is about 0.47 micrometer.
- * the grain size distribution is narrow. 10 % of the grains have a diameter lower than 0.25 μm and 10 % of them have a diameter higher than 0.75 μm . These two characteristics have been confirmed by some microphotographies made by S.E.M.

The X Ray diffraction of this powder indicates that it is amorphous. This density is 3.33.

At last, as we can see in the following figure, the boron powder produced by plasma H.F is very pure. It only shows us the principal impurities:

elements	Mg	Ti	Cr	Fe	Ni	Cu	other	C	H	O	N	S
impurity rate (ppm)	16	31	22	98	13	5	22	4300	6460	2.6 %	20	650
total	207 ppm							3.743 %				

table 1: Principal impurities contained in the boron powder.

The process of high frequency plasma enables us to obtain a very fine and a pure powder which is not crystallized.

II) Experimental procedure:

Before studying the densification and the crystallization of this powder, we have examined the operating sequence to densify it. The first step of the process is the latex encapsulation. A cold isostatic pressing is made on the powder. The pressure applied on the sample is 400 MPa. The compact obtained is sintered in a vacuum furnace to crystallize it. The sample is rough machined. Then the titanium encapsulation is made. 30 * 20 mm titanium cylinders are used. After that, samples are hot isostatic pressed at 150 MPa and at a temperature between 1250 and 1600 °C.

III) Crystallization of high frequency plasma boron:

Direct hot isostatic pressing realised on the boron powder conducts to broken samples and this result is obtained whichever the temperature between 1250 and 1600 °C. Moreover the initial boron powder:

- * is amorphous,
- * contains a high H_3BO_3 rate,
- * and has a high shrinkage coefficient.

For all these reasons, the crystallization by natural sintering is essential.

IV) Natural sintering:

The crystallization of the boron by natural sintering have been realized under vacuum .

Experiments were made between 1500 and 2000 °C to determine precisely the temperature of the plasma boron powder.

By examining figure 2, we can see that the crystallization temperature is about 1915 °C. The curve indicates clearly that the crystallization of the boron begins at 1800 °C.

The crystallization rate is calculating by using the following formula:

$$C.R = ID/(Id+Ip+Ith)$$

where:

- * ID is the intensity diffracted by the crystallized boron,
- * Id " " " the amorphous boron,
- * Ith is the thermal intensity,
- * Ip is the parasite intensity.

Figure 3 shows the evolution of cristallization in fonction of temperature. It confirms this previous result. Moreover, by natural sintering, the density obtained is very low (Fig 2). It's almost the same than the density got after C.I.P. It is about 60 % of the theoretical density. We can also notice, by examining figure 2, that the density decreases against the temperature between 1500 and 1930 °C. This can be

explained by the fact that the amorphous boron has a density of 3.33 whereas the crystallized one has a density of 2.34.

We can easily notice that the plasma H.F synthesized boron doesn't densify by natural sintering. So samples should be hot isostatic pressed in order to obtain a high density.

V) Results obtained after sintering by H.I.P:

In the present study, the thermal cycle used is the following:

- * Pmax = 1500 bars,
- * Tmax = 1250 → 1600 °C,
- * Heating temperature rate: 400 °C/h,
- * Cooling temperature rate: 400 °C/h,
- * Bearing time: 1 hour.

Figure 4 shows the characteristics of the samples after sintering by hot isostatic pressing. If we plot the density in fonction of temperature between 1250 and 1600°C, we can say that the charateristic is almost linear. This is due to the fact that it's only the effect of pressure, and not diffusion, which allows densification.

The comparison of the results obtained by plasma H.F synthesized boron powder and with a natural one (Starck boron) shows that they seem to have the same behaviour opposite to temperature. In both cases, at 1600 °C, we obtain the theoretical density. X-Ray diagrams have been made on samples sintered by H.I.P at 1600 °C. These diagrams are the same as the one obtained after natural sintering at 1930 °C. They indicate that the boron is crystallized in β rhomboedral form.

Some optical micrographies have been made on 1600 °C sintered boron. We can't see any porosity. The second constatation is that the sintering occurs without significant grain size increase.

Use of high frequency synthesized boron powder, allows to get the theoretical density with small grains. To reach this result samples should be sintered at temperatures up to 1915 °C in a vacuum furnace and hot isostatic pressed.

VI) Conclusion:

By using the method of the reducing of a boron halide in a microwave plasma, a powder with the following properties is obtained:

- The powder is amorphous. Recrystallization is necessary.
- It doesn't densify in natural sintering.
- Full density is obtained by H.I.P at 150 MPa and 1600 °C.
- There is no change in grain size.

So we can think that this kind of materials could be interesting for hardness applications.

Figure 2 : Crystallization rate and densification plotted against temperature.

Figure 3 : Evolution of crystallization in fonction of temperature : High temperature XRD diagrams.

Figure 4 :Density of hot isostatic pressed samples