The preparation of TiB_2 powder by carbothermal reaction using a DC electric arc furnance

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Abstract. The method of carbothermal reaction is used to prepare titanium boride (TiB_2) in a DC electric arc furnance by using a powder mixture of TiO_2, H_2BO_3 and C. The initial product is milled and the impurities are removed by pickling and reverse flotation. The final TiB_2 powder with a purity of over 99% can be obtained. The structure and impurities of the products are studied by X-Ray Diffraction, field emission scanning electron microscope (FESEM) , energy dispersive spectrometer (EDS) and inductively coupled plasma (ICP).

Introduction

As a newly-developed inorganic nonmetallic material, titanium boride draws more and more attention of the reseachers, because of its various advantageous properties and the widespread uses .Due to its high melting point (3225˚C)[1] ,good conductivity[2] and the good wettability to melted aluminum,titanium boride could be processed on the anode in the aluminum electrolytic cell. Because of the high hardness (30 GPa)[3] and the low density (4.5 g/cm^3), one of usage of TiB_2 is hard tools material.Titanium boride could be also used to in the manufacture of evaporation boats and PTC materials, because of its good conductivity and the good thermal shock resistance[1, 4]. At present, there are also restrictive factors in its wider applications,such as high price, high producing costs,low producing efficiency.

At present, the industrial methods of titanium boride preparation mainly includes self-propagating high-temperature synthesis, chemical vapor deposition method,and carbothermal reduction method by carbon tube furnance, etc[5]. Self-propagating high-temperature synthesis (SHS) has the advantages of lower reaction temperature, less energy consuming and smaller particle size, but leads to stable oxide impurities,which is difficult to be separated,moreover,maximization and automation of the equipment are also problems[6,7]. The chemical vapor deposition (CVD) is more appropriate to produce a small amount of TiB_2 production or film coating[8,9]. The carbon tube furnance carbothermal reduction method contains a problem of low efficiency, low energy utilization and equipment maximization, because a high temperature of more than 1500^{o}C is needed in the carbothermal reaction[10].

The arc furnance carbothermal reduction method made some progresses in recent years, but there are still some remaining problems, such as the appearance of TiC impurities which is hard to be separated, the existence of C impurities which is hard to isolated[11]. In this paper, a series of process of TiB_2 powder preparation was researched including the arc furnance carbothermal reduction process, milling process and purification process. Because of the advantages like high and centralized temperature supplying that the arc plasma supplys[12], less TiC emerges. After the processes of milling, reverse flotation and pickling, TiB_2 powder with a purity of 99% and particle size of 5μm is obtained.

Experimental

The raw materials and their contents are given in the Table 1, and petroleum coke is used as the carbon source in this experiment:

Table 1 Raw material of arc furnance experiment

raw material	purity/%	Si	Fe	water	ash
H_3BO_3	>99.00	<0.02	<0.01	-	-
TiO_2	>98.00	<0.02	<0.01	<1.50	-
petroleum coke	-	-	-	-	<0.40

According to the thermodynamic calculation and the previous experiments, the ratio of H_3BO_3 should have a 30% overdose,and the ration of C should have a overdose of 10%,so the mass ratio of every raw material is TiO2: H3BO3:C=1:2.015:0.825.

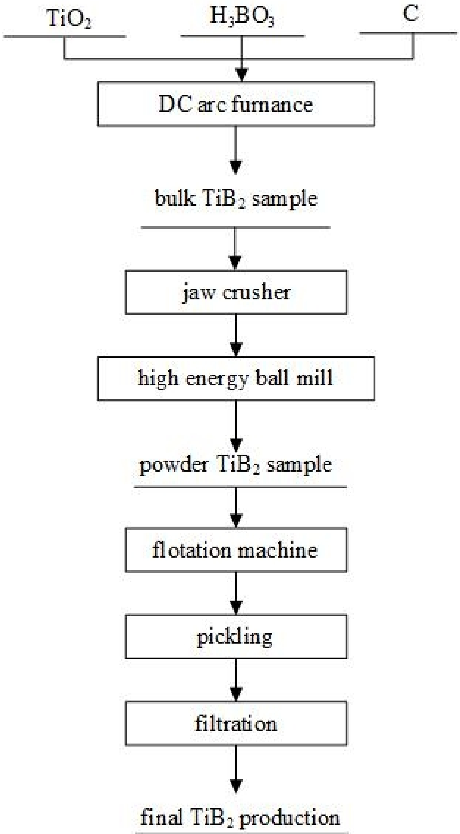

Figure 1 The process chart of TiB_2 powder preparation

The processes of experiment are as follows:1.Mix the raw materials according to the ratio,and put them into the arc furnance to smelt; 2.When the smelting process is done,pull the graphite electrode out,and wait the bulk sample cooling together with the furnance; 3.Crush the bulk sample into little pieces with the jaw crusher,and then mill them into powders in an average size of 5μm; 4.Use reverse flotation method and pickling method to purify the powder production,and finally attain a production with a purity of 99% and a particle size of 5 μm. The process chart is shown in the Figure 1 .

Results and discussion

The results of smelting experiment. Figure 2 is the XRD pattern of bulk TiB_2 sample after the smelting process.As it is shown in the figure,in the method of arc furnance smelting, TiB_2 is prepared,which has a inclusion of C.In the mixing process, an extra 10% in the raw material powders is mixed,which aims to prevent the appearance of TiC.The pattern shows that there is no TiC peaks.The reaction happens in a very rapid way,due to the extremely high temperature of over 2000˚C which is applied by the arc furnance [11].According to the theoretical calculations,if enough or overdosed TiO2 and C are applied,the reaction balance leads to the appearance of TiB_2 .So the overdose of boric acid and petroleum coke helps to prevent the appearance of TiC,and that is proved in the Figure 2.

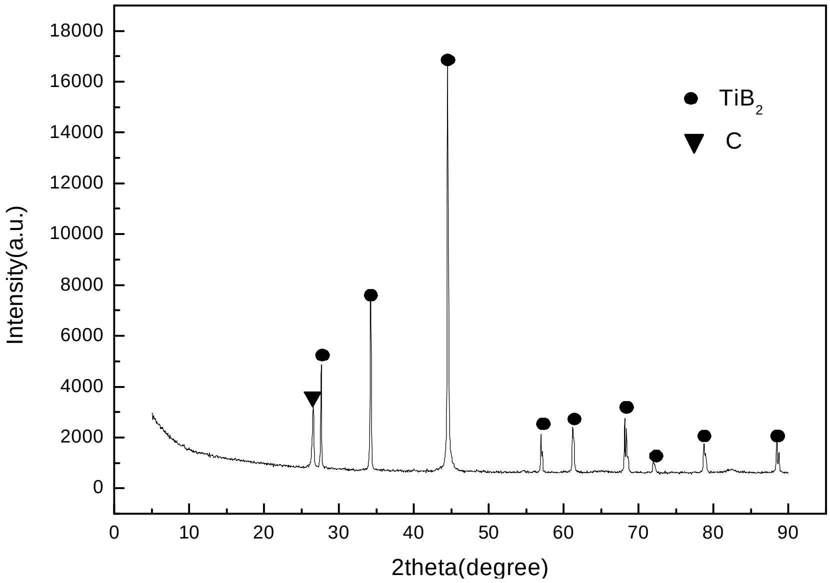

Figure 2 XRD pattern of TiB_2 sample after the carbothermal reaction

The SEM micrographs and EDS result of the smelting-prepared bulk TiB_2 sample are shown in the Figure 3(a) and (b).And as shown in the Figure 3(b),the EDS result of spot 1 proves that the impurity content is carbon.The Figure 3(a) displays that the bulk TiB_2 sample includes an impurity of C inside,which shows a morphology of irregularity and a scale of 10μm.The impurity C is included in the uniform TiB_2 grains,and the grain boundaries between them are clear.Because of the extremely high temperature the arc plasma implies[11],the TiB_2 melts after the carbothermal reaction completes. Moreover,all these processes happen within seconds,which results in the uniform of TiB_2 grains and the singleness of the impurity grains.

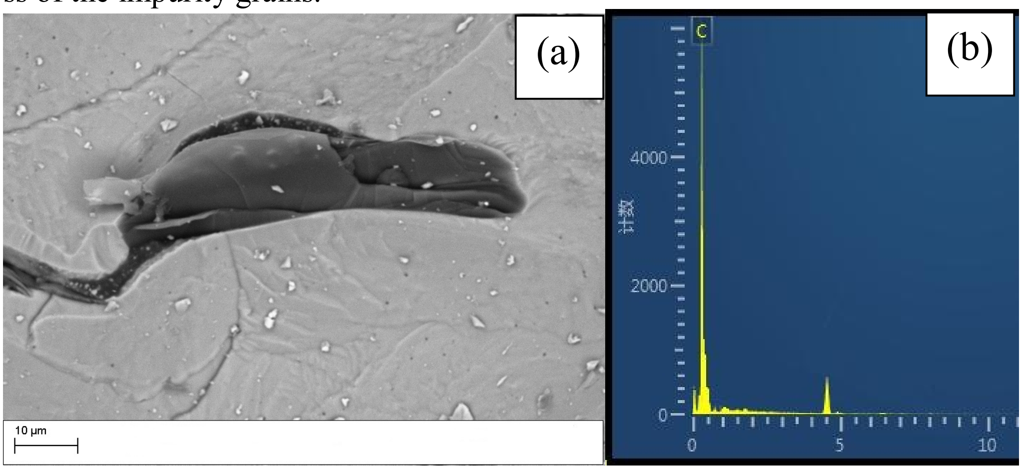

Figure 3 SEM micrograph and the EDS results of TiB_2 bulk sample

The results of reverse flotation. The carbon removal rates and recovery yields during the reverse flotation process are displayed in the Figure 4, in which the percentages of carbon are measured by the ICP method.The original percentage of C impurity is 5.67%, which decreases to 0.86% at the third time and 0.81% at the fourth time using the method of reverse flotation. The carbon removal rate increased greatly in the first reverse flotation process,in which the recovery yield is 76.9%.The carbon removal rate increases steadily but slowly in the 2 to 4 levels of reverse flotation process,however,the recovery yield keeps decreasing.As shown in the chart,the recovery yield decreases faster from the third time to the fourth(from 65.63% to 57.12%),however,it does not lead to a increase of carbon removal rate obviously.So 3 series of reverse flotation is the optimal selection in the practical operation.

XRD patterns of TiB_2 powder shown in the Figure 5 displays that the peak of C vanishes after reverse flotation,which means the reverse flotation method is a proper way of purifying TiB_2 prepared by arc furnance carbothermal reaction.

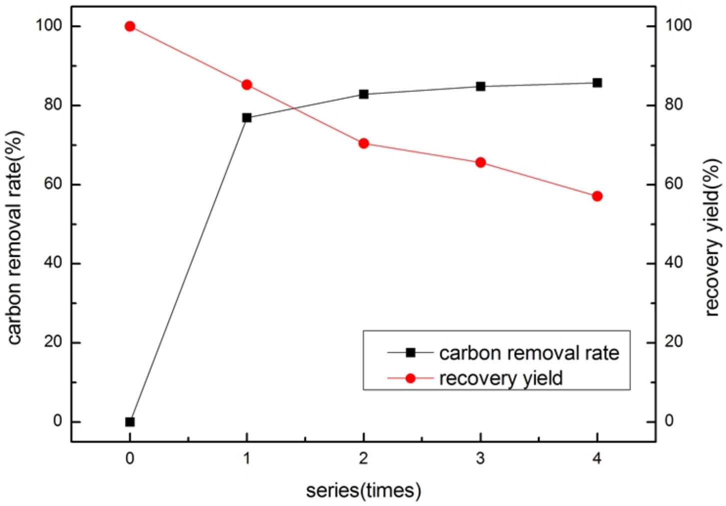

Figure 4 Carbon removal rate and recovery yield of TiB_2 samples at varies series of reverse flotation (a concentration of 30%, 0.075mol/L pine oil, pH=7)

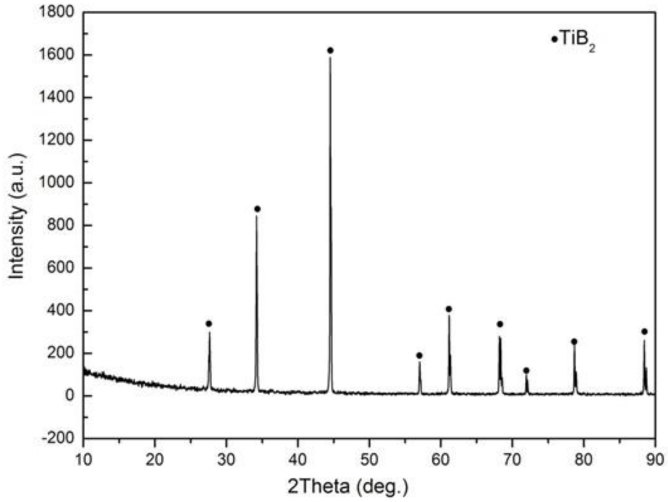

Figure 5 XRD patterns of TiB_2 sample after reverse flotation process

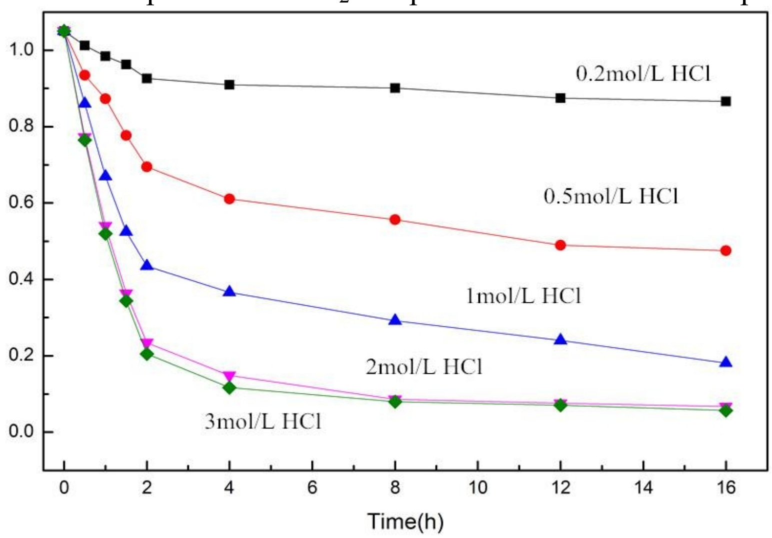

Figure 6 Concentration of Fe in different pickling conditions(various concentration of HCl and pickling time)

The results of pickling. As shown in Figure 6, the percentage of Fe impurity, which emerged during the milling process,decreases from 1.05% to 0.057% at least using the method of HCl pickling.The decreasing tendencies varies when the concentrations of HCl and pickling time change,and the decreasing speed in the first 2 hours goes much faster,than later.3mol/L HCl leads to the most obvious decrease to the minimum of 0.057% in 16 hours, in which the decreasing rate 94.57% attains. 2mol/L has a decreasing tendency barely the same as 3mol/L, reaching a concentration of 0.067% in 16 hours' pickling.

Conclusion

TiB_2 powder with a purity of over 99% can be prepared by the method of arc furnance carbothermal reaction. The TiC impurity is prevented by using a fixed raw material ratio, particle size and the mixing method. The C impurity is reduced from 5.67% to 0.86% after fourth reverse flotation. And then, the Fe impurity decreases from 1.05% to 0.067% by using 2 mol/L hydrochloric acid pickling for 16 hours. The results of ICP and XRD shows that TiB_2 powder with a purity of over 99% is obtained.

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