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Mechanism of reaction synthesis of Li-B alloys

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Abstract A model for reaction synthesis of Li-B alloys has been presented. Results show that the first exothermal reaction can be divided into three stages. The first stage is an instantaneous reaction on the boundary between boron particles and lithium melting, in which the caloric released is inversely proportional to the particle size of the boron powder. The second stage is a reaction between the unreacted boron and the lithium that diffuses through the product LiB_3 on the surface of the boron particle. This process can be described by Johnston model. The third stage is dissolution of the product LiB_3 to Li liquid, which takes place at temperature up to 420℃. At the same time, the second exothermal reaction begins, which consists of nucleation and growth of the last Li-B compound. It can be divided into two substages, i.e. the nucleation pregnant stage and the exploded reaction stage. When the concentration of the particle nucleated is high enough, an exploding reaction takes place. The lower the temperature, the longer the time needed for the exploding reaction. By the model presented, the experimental phenomena in the synthesis are explained.

Keywords: lithium-boron alloy, reaction synthesis, thermal battery.

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Li-B alloy[1] has greater specific capacity, more negative potential and greater specific power than the well-known anode materials of thermal battery[2—4]. As a promising anode material for the thermal battery, the Li-B alloy is in nature a composite that consists of porous and refractory Li-B compound frame and metal Li filled in the porosity. That is why it can be kept in solid state at above 600℃, with the electrochemical properties very similar to those of pure Li. Though its application in themal battery has been studied for a long time, it is only recently that the crystal structure of the Li-B compound in the Li-B alloy is determined [5,6]. As the synthesis process of Li and B involved two exothermal reactions, it is very difficult to get perfect microstructures with usual synthesis process. The basic synthesis method was put forward by Wang[7], and the heat released in the two exothermal reactions was measured by Dallek[8]. The effects of the content and particle size of boron powder on dynamical parameters of the two exothermal reactions were investigated by Ernst[9]. The experiments with a scale up to 400 g/furnace were reported by Szwarc[10]. However, up to now, deep and systematical studies on the synthesis mechanism are still lacking. Because of the lag in basic research, the properties of this synthetic alloy were not stable, thus blocking its application[11]. The present work proposes a physical model for the reaction synthesis of Li-B alloy, and presents an explanation for the experimental phenomenon.

1 Experimental procedure

The raw materials used in experiments were pure lithium (purity 99.95%), crystal boron (purity 99%) and amorphous boron powder (purity 90%, oxygen 6% and a small amount of magnesium). The amorphous boron powder was pretreated, namely first degassed at high temperature in vacuum, then pressed into lump with cold isostatic press (CIP), broken and sieved through 100 mesh, and finally degased again at high temperature in vacuum.

The reaction synthesis was carried out in two ways. One is in small batch synthesis, only about 1 g per batch, used for measuring phase composition and observing experimental phenomenon. The other is relatively large batch synthesis, about 100 g per batch, used for measuring thermal stability, discharge properties and mechanical properties. For the small batch synthesis, a rectangular iron crucible was designed to meet the experimental condition in X-ray diffraction (XRD) measurement. The reaction synthesis was finished under the protection of argon gas in an enclosed furnace. Because there were two exothermal reactions at about 330 and 530℃, a special program for controlling the temperature (fig. 1) was worked out to avoid interference of the two reactions. For the large batch synthesis, a cylinder iron crucible was used, with a thermal couple attached on its outer surface to ensure precise measurement of the temperature. The synthesis was finished in a stainless steel glove box that can be vacuumized. First, metal lithium ingot was melted, and then boron powder was added slowly under strong stirring. Before the second reaction took place, the stirring rod was pulled out. The density of the alloy was measured according to Archimedes principles, with liquid paraffin as medium. All operations on Li-B alloy were completed in a glove box with a relative humidity of $R_{\mathrm{H}} \leqslant 2\%$.

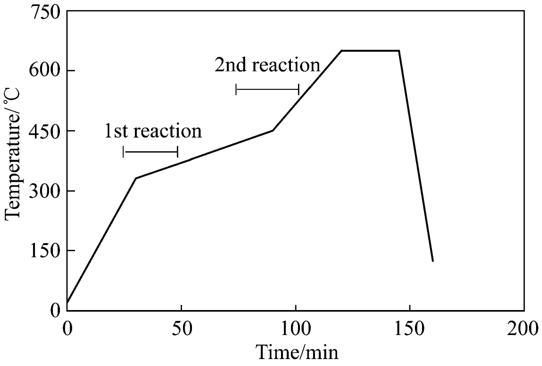

Fig. 1. Temperature control in reaction synthesis of Li-B alloy.

2 Experimental results

2.1 Experimental phenomenon in reaction synthesis

In the large batch reaction synthesis, all experimental phenomena could be observed through the windows on the glove box. First we heated the metal lithium to 330℃ for a few minutes, and then added pretreated amorphous boron powder slowly into it and at the same time stirred fast the mixture. The addition of the boron powder turned liquid metal lithium from white bright to blue bright. By continuing stirring and raising the temperature, the liquid alloy became viscous. At last, the second exothermal reaction occurred below 530℃. In addition to the above experimental phenomena that have been mentioned in refs. [7,12], it was found that the second exothermal reaction will also take place if the temperature was kept at just above 450℃ for a sufficiently long time. In order to investigate the possibility of self-propagating high-temperature synthesis (SHS), a hot iron rod (about 700℃) was put into the melting at a temperature range of 400—490℃ without inducing the second explosion reaction.

2.2 Density

For the Li-33wt%B alloy, between the first and second reaction (450℃) the density was 0.71 g/cm^3, while after the second reaction and after being cold extruded, the density was 0.83 g/cm^3.

2.3 Influence of boron powder types

For the large batch reaction synthesis, each batch weighed 100 g, with the composition of Li-33.3wt%B. Three types of boron powder were used——crystalline boron powder (＜149 μm), amorphous boron powder (＜2 μm), and pretreated amorphous boron powder (＜149 μ m). With crystalline boron powder as raw material, both boron and lithium were put into the crucible at the same time. Slowly increasing the temperature and stirring properly around 330℃, we separated the two exothermal reactions perfectly. Taking amorphous boron powder as raw material, at first the boron powder floated on the surface of molten lithium. The first reaction did not take place around 330℃. At about 400℃, the temperature of the melting increased abruptly and the two reactions finished at the same time and could not be controlled. Taking pretreated amorphous boron powder as raw material, if all the powder was added in one batch, the two reactions were difficult to separate; if the power was added stepwise in many small batches, the two reactions was easy to separate.

2.4 Distribution of boron compound in the middle alloy

Taking coarse crystal boron particle (500—840 μm) as raw material, many crucibles of Li-33.3wt%B alloy were melted in small batches. From 340 to 500℃ , the heating rate was kept in 1℃/min. The crucibles were taken out of the furnace at 350, 370, 400, 425, 450, 475 and 500℃, respectively. It was found that all samples consisted of two parts——soft and hard part. Of course, the soft part was lithium-rich and the hard part boron-rich. Below 400℃ the hard part was evidently near to the pure boron particle. Above 425℃, with the increase in temperature, the boundaries between hard part and soft part became more and more obscure and the soft parts became harder gradually. Put-

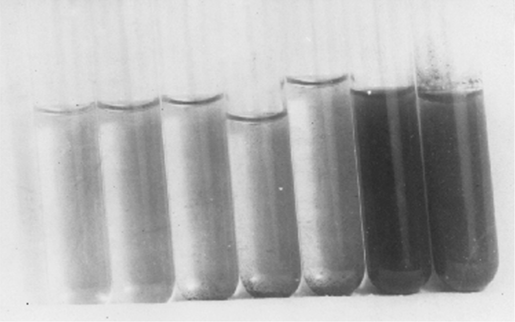

Fig. 2. Comparison of Li-B contents in soft parts at different temperatures. From left to right, the samples are taken out at 350, 370, 400, 425, 450, 475 and 500℃, respectively.

ting the same quantity of soft part into pure water, we found that below 425℃, the solution was light, and above 450℃, the solution was dark (fig. 2). The color of the water solution of the alloy of the alloy reflected the boron content in the solution. So the Li-B products that had undergone the first reaction did not diffuse into liquid lithium till 425℃.

3 Mechanism of reaction synthesis of Li-B alloy

3.1 First exothermal reaction

Refs. [7, 12, 13] showed that only the pure lithium diffraction pattern can be found in the XRD for the samples experiencing just the first reaction. Even in the *in-situ* XRD experiments by Wang[7], no other diffraction pattern was found. The present experiments show that before the second exothermal reaction, the boron had distributed over all part of the melting alloy (2.4). The density of middle alloy (Li-33.3wt%B) was 0.71 g/cm^3, very near to the value 0.72 g/cm^3 calculated according to the simple mixture of Li and B, showing that in the middle alloy boron distributed in the form of elemental boron, rather than in the form of compound with rigid chemical composition. This result offers a new support to Li-B solution model proposed by Wang[7].

Experimental phenomena in synthesis experiments show that there are three stages in the first exothermal reaction. When the temperature of the melting metal is up to 330℃, the first exothermal reaction between boron particle and liquid lithium begins. It first takes place at the surface of the boron particles instantaneously. This is the first stage of the reaction. As mentioned in chapter 2.4, below 400℃ the reacted Li-B product is still attached on the surface of boron particle. According to the differential scanning calorimetry (DSC) analysis[8], the composition ratio of the reacted products should be LiB_3. As no related diffraction pattern is detected by XDR, this product is not in stable crystalline state. In this case, only through diffusion of lithium in LiB_3 can the reaction continue. This process is the second stage of the first exothermal reaction. With an increase in temperature, the LiB_3 dissolves into liquid lithium (fig. 2). This is the third stage of the reaction.

In the first stage, assume that the boron particle is spherical with radius r_0, and initial reaction depth Δr_0. Then the reacted volume for a single particle is

$$\Delta V = \frac{4}{3}\pi r_0^3 - \frac{4}{3}\pi (r_0 - \Delta r_0)^3. \tag{1}$$

When Δr_0 is very small, $\Delta V = 4\pi r_0^2 \Delta r_0$.

Denote the weight percent of boron in raw mixture by W_B. Then the volume percent of boron in raw mixture is

$$V_B = \frac{W_B / d_B}{(W_B / d_B + (1 - W_B) / d_{Li})},$$

where d_B and d_{Li} are densities of elemental B and Li, respectively.

The number of boron particles in unit volume of raw mixture is

$$N_B = V_B/(\tfrac{4}{3}\pi r_0^3) = 3V_B/(4\pi r_0^3). \tag{2}$$

So the reacted total volume of boron is

$$V_B' = N_B \cdot \Delta V = V_B\left[1-\left(1-\frac{\Delta r_0}{r_0}\right)^3\right].$$

Accordingly, the reacted mole number of boron is

$$M_B' = V_B' \cdot d_B / M_B,$$

in which M_B is atomic weight of boron. So the heat released per unit volume in the first stage is

$$Q' = M_B' \cdot Q_B, \tag{3}$$

in which Q_B is the caloric in first reaction per mole of boron. According to experimental result of Dallek[8],

$$Q_B = 18 \pm 4 \text{ KJ/mol}.$$

Substitute the related formulae into formula (3). Then

$$Q' = \left[1-\left(1-\frac{\Delta r_0}{r_0}\right)^3\right]\cdot Q_B \cdot \frac{W_B}{M_B}\Bigg/\left(\frac{W_B}{d_B}+\frac{1-W_B}{d_{Li}}\right). \tag{4}$$

Substitute numerical values[14] into formula (4). Then

$d_B = 2.535(\text{g/cm}^3)$, $d_{Li} = 0.534(\text{g/cm}^3)$, $M_B = 10.81$, $Q_B = 18$ KJ/mol,

$$Q' = 1.665\left[1-\left(1-\frac{\Delta r_0}{r_0}\right)^3\right]\Bigg/\left(1.873\times\frac{1}{W_B}-1.478\right). \tag{5}$$

If Δr_0 is very small, then

$$Q' = 4.995\cdot\frac{\Delta r_0}{r_0}\Bigg/\left(1.873\times\frac{1}{W_B}-1.478\right). \tag{5$'$}$$

Formula (5′) shows that the caloric released instantaneously in the first stage will increase with a decrease in particle size of boron or with an increase in boron content. Especially, the caloric is in inverse proportion to particle radius, showing that the radius of boron particle is a key factor controlling instantaneous caloric released in the first stage. If the particle size is too small, the superfluous caloric released will ignite the second exothermal reaction. That is why for small boron particle (2 μm) the reaction synthesis of Li-B alloy is difficult to control, but for great boron particle (149 μm), the case is different.

In the second stage, in order to continue the reaction it is necessary to diffuse Li atoms through the Li-B shell on the surface of boron particle. Ernst[9] also indicated that at primary stage Li atoms wedge into the lattice of boron and make the particle of boron swell. With the increasing size of boron particle, much long time would be needed to complete the diffusion, making the first reaction insufficient even though the second reaction has already taken place.

Johnston model can be used to describe the dynamical procedure of the second stage [15]. In this model, the integrated formula of dynamical equation is expressed by traverse rate G

$$F_k(G)=1-\frac{2}{3}G-(1-G)^{2/3}=\frac{2DMC_0}{R_0^2\rho n}\cdot t=K_\mathrm{k}t\,, \tag{6}$$

where D is the diffusion parameter of Li in $\mathrm{LiB_3}$; M, the atomic weight of $\mathrm{LiB_3}$; C_0, the concentration of Li at lithium rich end; ρ, the density of $\mathrm{LiB_3}$; n, the atomic number of Li to form $\mathrm{LiB_3}$ for an atom B; K_k, the reaction rate constant of Johnston dynamical equation.

The dynamical equation shows that the reaction rate constant K_k strongly depends on particle radius of boron. Without the dissolution of $\mathrm{LiB_3}$ to liquid lithium, the first reaction is very difficult to complete fully for the big size particle of boron.

With the increase in temperature, $\mathrm{LiB_3}$ begins to dissolve into Li liquid and the diffusion speed of Li in $\mathrm{LiB_3}$ increases. The reaction begins to enter the third stage. The result in sec. 2.4 shows that the third stage starts at about 425℃. When the temperature is up to about 450℃, the middle alloy solution gradually turns into sticky state, which indicates that an LiB compound, the product of the second reaction, begins to nucleate and the second exothermal reaction begins.

3.2 Second exothermal reaction

Above 450℃, the molten alloy becomes more and more sticky, due to a small amount of LiB compound dispersed in the molten middle alloy[12,13]. But at this moment(450—490℃), self propagating high-temperature synthesis (SHS) cannot be triggered by plugging a 700℃ iron rod into the molten alloy (sec. 2.1), showing that the little amount of caloric released in the formation of LiB compound is not enough to evoke an exploding reaction. In this stage, the thermal activated reaction is very weak, and the exothermal rate of the system is lower than the sum of endothermic rate and cooling rate of system. The second exothermal reaction can be separated into two stages, that is, nucleation pregnancy and exploding reaction.

For the first stage, in order to produce stable LiB compound in the solution of Li-B, the energy barrier associated with the newly formed boundary between two phases must be overcome. It is a thermal activated procedure as follows:

$$N=N_0\mathrm{e}^{-\frac{E_1}{kT}}, \tag{7}$$

where E_1 is the energy barrier to be overcome in nucleation of Li-B compound; N the nucleated number in unit volume; N_0 the position number that can nucleate in unit volume, proportional to the atomic number of boron in unit volume A_B, $N_0=N_0'A_\mathrm{B}$; k the Bolzmann constant; T the experimental temperature. Above a critical temperature, as soon as a particle of LiB nucleates, it will grow up subsequently. So the total nucleated number in volume V_0 is the sum of the total nucleated number in time t.

$$N_1 = \int_0^t N \cdot V_0 dt \ .$$

The growth of a single LiB crystalline grain is also a thermal activation process, with the line growth rate

$$\upsilon = \upsilon_0 \mathrm{e}^{-\frac{E_2}{kT}}, \tag{8}$$

where E_2 is the activation energy related to boron in the Li-B solution.

Because the Li-B compound is fibrous[5,6], and grows along c axis[6], the volume growth speed of a single fiber is

$$V' = 2S_0\upsilon = 2S_0\upsilon_0 \mathrm{e}^{-\frac{E_2}{kT}},$$

where S_0 is the cross section of an LiB fiber.

The whole volume growth speed is

$$V'_{\text{total}} = N_1 \cdot V' = 2N_0V_0S_0\upsilon_0 \left(\int \mathrm{e}^{-\frac{E_1}{kT}} dt\right) \cdot \ \mathrm{e}^{-\frac{E_2}{kT}}.$$

Then the total exothermal rate in reaction is

$$Q' = V'_{\text{total}} \cdot \Delta Q = 2\Delta Q N_0V_0S_0\upsilon_0 \mathrm{e}^{-\frac{E_2}{kT}} \int \mathrm{e}^{-\frac{E_1}{kT}} dt, \tag{9}$$

where ΔQ is the caloric released in the formation of a unit volume of LiB compound.

At the same time, besides the caloric released in reaction, there are the absorption of the molten materials and cooling of the system in melting procedure. In the case of determinate experimental condition, both of them are stable. Then the total rate of thermal consumption is

$$Q'_2 \ = Q'_1 \ (\text{absorption}) + Q'_2 \ (\text{diffusion}).$$

Only when the total exothermal rate is greater than the total rate of thermal consumption, does the exploded reaction take place. That is,

$$Q' > Q'_2 \ .$$

In practice, the temperature of the melting alloy changes with time. In this case, it will be difficult to carry out the integration in eq. (9). If isothermal processes at different temperatures are assumed, the problems will be simplified. The relationships between parameters of several processes in the second reaction will be also revealed.

According to isotherm assumption, formula (9) becomes

$$Q' = 2\Delta Q N_0V_0S_0\upsilon_0 \mathrm{e}^{-\frac{E_2}{kT}} \mathrm{e}^{-\frac{E_1}{kT}} t. \tag{10}$$

Therefore, the total exothermal rate Q' is proportional to time t.

Simplifying formula (10), we have

$$Q' = P_1 \mathrm{e}^{-\frac{E}{kT}} t, \tag{11}$$

where $P_1 = 2\Delta Q N_0 V_0 S_0 \upsilon_0$, and $E = E_1 + E_2$.

The thermal activation energy of the growth of the lithium boron fiber, E_2, is only involved with the fluctuation movement of one atom, but the thermal activation energy of the nucleation of the lithium boron compound, E_1, is involved with the fluctuation movement of many atoms. Therefore, E_2 is much smaller than E_1, $E \approx E_1$. The dynamical procedure of the reaction synthesis of lithium boron alloy had been studied by Ernst[9] with differential scanning calorimetry (DSC). It can be known from experimental results in this paper[9] that the thermal activation energy controlling the second reaction is 6.21×10^{-19} J, which belongs to the nucleation activation energy of lithium boron compound, E_1, according to the viewpoint of this paper.

When the second reaction enters the critical state, without heating the furnace by electricity, the total rate of thermal release is equal to the total rate of thermal consumption

$$Q' = Q_2' = Q_1' \text{ (absorption)} + Q_2' \text{ (diffusion)}.$$

As the process has been assumed to be isothermal, $Q_1' \text{ (absorption)} = 0.$ So the critical exothermal rate equals the thermal diffusion rate of the furnace. Therefore whether the second exploding reaction will take place or not depends on the competition between the exothermal rate and the thermal diffusion rate of the melting system. The thermal diffusion rate of the furnace at different temperatures has been measured in this work, with the lithium boron raw materials substituted with the same volume of metal tin to model the isothermal condition in practical synthesis. Results show that in the temperature range from 250 to 550℃, a proportional relationship can be obtained.

$$Q_2' \text{ (diffusion)} = 0.4757T - 177.4, \tag{12}$$

where the unit of the $Q_2' \text{ (diffusion)}$ is W, and that of T is K.

Experiments show that the exploding reaction will take place 50-min stirring at 450℃, meaning that at this moment the exothermal rate of the melting has approached to the thermal diffusion rate of the furnace. So formula (11) will be equal to formula (12), and the value of the constant P_1 can be determined ($P_1 = 6.354\times10^{25}$ W). Drawing exothermal rate $Q' = P_1 e^{-\frac{E}{kT}} t$ and thermal diffused rate $Q_2' \text{ (diffusion)} = 0.4757T - 177.4$ in the same figure (fig. 3), we can clearly find that the pregnant time for the second exploding reaction is strongly dependent on the reaction temperature. The reason is as follows: that with increasing reaction temperature, the thermal diffusion rate increases in proportion, but the exothermal rate increases exponentially. Therefore the pregnant time required to initiate the second exploding reaction becomes shorter and shorter. Under the limited measuring precision, there is an upper limit temperature (around 530℃) for the second exploding reaction.

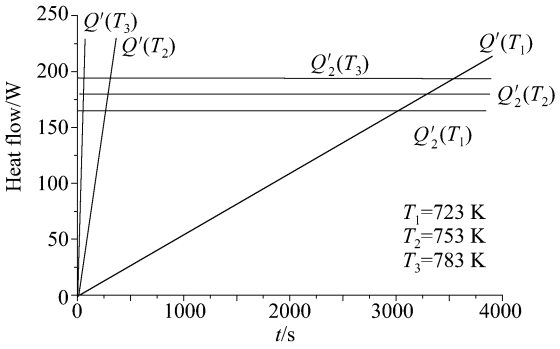

Fig. 3. Pregnant time for the second exploding reaction vs. temperature.

4 Conclusions

(1) In the course of preparing Li-B alloy, if taking amorphous boron as raw material, we found it difficult to control the first reaction; if taking crystalline boron (particle size$<$149 μm), it will be easy to control the reaction.

(2) The middle sample between the first and second exothermal reaction had a density of 0.71 g/cm^3, very near to the calculated value, 0.72 g/cm^3, according to the mixture of Li and B.

(3) The first exothermal reaction can be divided into three stages. The first stage is an instantaneous reaction on the boundary between boron particles and lithium melting, in which the caloric released is inversely proportional to particle size of boron powder. The second stage is a reaction between boron in the core of the particle and the lithium that has diffused through the product LiB_3 on the surface of the boron particle. This process can be described by Johnston model in solid reaction and is also strongly related to the particle size. When the temperature is up to 425℃, the product LiB_3 dissolves into the Li liquid. That is the third stage of the first exothermal reaction. At the same time, the second exothermal reaction begins. The second exothermal reaction is completed through nucleation and growth of the last Li-B compound. It can be further divided into two stages, i.e. the nucleation pregnant stage and the exploded reaction stage. When the concentration of the particle nucleated is high enough, the exploding reaction takes place. The lower the temperature, the longer the time needed to induce exploding reaction.

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