

Study on Thermodynamics and Kinetics for the Reaction of Magnesium Diboride and Water by Microcalorimetry

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Abstract

An exothermic reaction between MgB_2 and water was observed in our laboratory at high temperature, although no obvious reaction occurred at room temperature. The reaction process of MgB_2 and water was therefore studied by using microcalorimetry. The results showed that the reaction enthalpies of MgB_2 with water and the formation enthalpies of MgB_2 at $T = (323.15, 328.15, 333.15 \text{ and } 338.15) \text{ K}$ are $(-313.15, -317.85, -322.09, -329.27) \text{ kJ}\cdot\text{mol}^{-1}$, and $(-238.96, -237.73, -236.50, -234.30) \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The standard enthalpy of formation and standard molar heat capacity of MgB_2 obtained by extrapolation method are $-245.11 \text{ kJ}\cdot\text{mol}^{-1}$ and $246 \text{ J mol}^{-1}\cdot\text{K}^{-1}$, respectively. The values of activation energy E , pre-exponential factor A and the reaction order for the reaction of MgB_2 and water over the temperature range from 323.15 K to 338.15 K are $50.80 \text{ kJ}\cdot\text{mol}^{-1}$, $10^{4.78} \text{ s}^{-1}$ and about 1.346, respectively. The positive values of ΔG^\ddagger and ΔH^\ddagger and negative value of ΔS^\ddagger indicate that the reaction can take place easily above 314.45 K.

Keywords: Magnesium Diboride, Water, Microcalorimetry, Thermodynamics, Kinetics

1. Introduction

Since the discovery of the superconductive property of magnesium diboride (MgB_2) in 2001, its synthetic methods [1-4], single crystals growth [5], spectral properties [6], superconductive characteristics [7], applications [8] and synthesis reaction mechanism under vacuum [9] are widely researched lately. Up to now, the interactional properties between MgB_2 and solvents have never been investigated, however.

Boride is an important component of fuel-rich propellant, but it has difficulties in the ignition and combustion. One of the most effective methods to improve the performance of boron is to add combustible metals by chemical combination. In solid fuel ramjet's development, the propulsion application obtained by the reaction of Mg and water is the most popular topic of the water ramjet. For a deeper investigation of the potential applications of MgB_2 in special solid propellants, the reaction of MgB_2 and water was carried out by our laboratory to understand the physicochemical properties of MgB_2 in solid propellants. We found for the first time that the MgB_2 and water do not react visibly under room temperature, but

when the temperature rises, an exothermic reaction happens obviously. The aim of this work is to describe the thermodynamic and kinetic properties of the reaction, and the investigation will offer valuable suggestions for the application of MgB_2 on chemical propulsion aspect.

2. Experimental

2.1. Sample and Equipment

The sample (MgB_2) used in the experiment was prepared by Northwest Institute for Non-ferrous Metal Research. Its purity was improved from 95% up to 99.4% after recrystallized by our laboratory. The water was twice-distilled before use with its electrical conductivity being $(0.8 - 1.2) \times 10^4 \text{ S}\cdot\text{m}^{-1}$.

All measurements were made using a RD496-2000 Calvet microcalorimeter. Two replicates of each sample were tested. The enthalpy of dissolution of KCl (spectrum purity) in distilled water measured at 298.15 K was $17.234 \text{ kJ}\cdot\text{mol}^{-1}$, which was an excellent accord with the literature value $17.241 \text{ kJ}\cdot\text{mol}^{-1}$ [10], showing that the device for measuring enthalpy used in this work was reliable.

2.2. Experiments

2.2.1. The Reaction of MgB_2 and Distilled Water at a Heating Rate of $0.2 \text{ K}\cdot\text{min}^{-1}$

Certain amount of MgB_2 and distilled water were mixed in standard vessel at 298.15 K. The whole device was put into the furnace. A heating rate of $0.2 \text{ K}\cdot\text{min}^{-1}$ was employed from 298.15 K to 348.15 K. The product was dried under 313.15 K and the element analysis was then carried out.

2.2.2. Element Analysis

VarioE III element analysis equipment from German was employed to detect the content of H after the reaction. S4 Pioneer X-ray fluorescence spectrometer was used to determine the contents of both Mg and B, and the field emission scanning electron microscopy from FEI Company in Holand was also used to determine the contents of Mg, B and O.

2.2.3. The Reaction of MgB_2 and Distilled Water at Different Temperatures

The reaction of MgB_2 and distilled water was carried out at 323.15, 328.15, 333.15 and 338.15 K, respectively.

3. Results and Discussion

3.1. The Result of the Reaction of MgB_2 and Distilled Water at a Heating Rate of $0.2 \text{ K}\cdot\text{min}^{-1}$

The dependence of the heat flow of the reaction on reaction temperature (reaction time) was shown in **Figure 1**. From **Figure 1**, one can see that the reaction do not proceed at 298.15 K. When the temperature rises up to 312.15 K, the reaction of MgB_2 and water begins and the reaction rate reaches a maximal point when the temperature rises to 314.45 K.

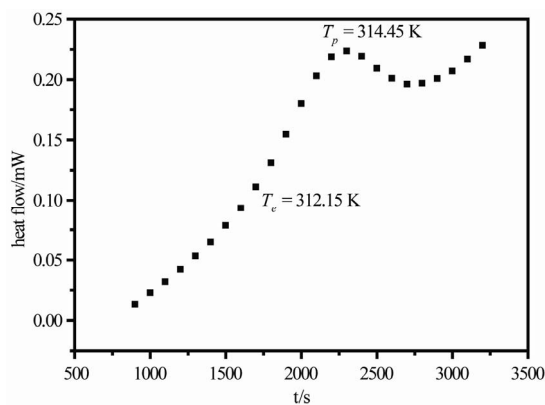
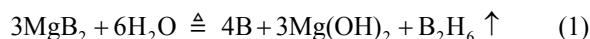


Figure 1. The heat flow curve of the reaction of MgB_2 and water at a heating rate of $0.2 \text{ K}\cdot\text{min}^{-1}$.

3.2. Element Analysis

The element H was determined by VarioELIII element analysis equipment for three times, and the results were 3.00%, 3.02% and 3.00%, respectively. The content of Mg was 36.63% by using the X-ray fluorescence spectrometer. The element analysis results obtained by the field emission scanning electron microscopy were shown in both **Figure 2** and **Table 1**.

From the results of the element analyses, the reaction can be deduced as



The results of the element analyses are close to the theoretical calculation: B 19.81%, Mg 33.43%, O 44.01%, H 2.75%.

3.3. The Standard Enthalpy of Formation of MgB_2

According to the Equation (2), we get the enthalpy of formation of MgB_2 as in Equation (3).

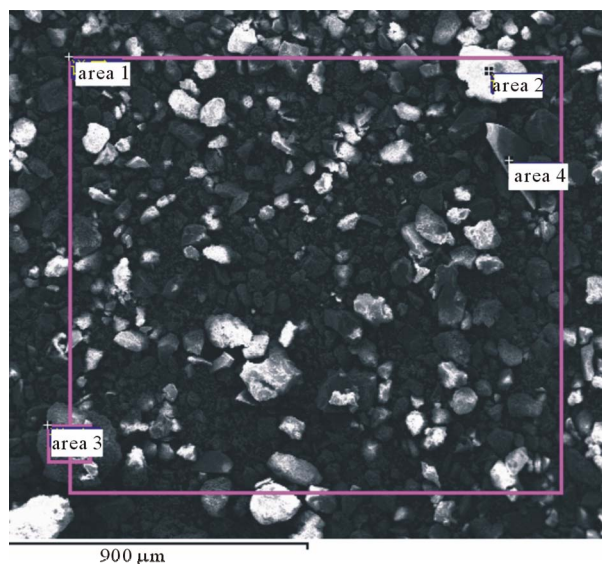


Figure 2. The electronic picture of the sample after the reaction.

Table 1. The content of each element.

No.	B	O	Mg	total
1	20.03	45.95	34.02	100.00
2	19.96	46.18	33.86	100.00
3	19.89	46.49	33.62	100.00
4	20.06	46.41	33.53	100.00

$$\Delta_r H_m = \Sigma \Delta_f H_p - \Sigma \Delta_f H_r \quad (2)$$

$$3\Delta_f H_m(\text{MgB}_2) = 4\Delta_f H_m(\text{B}) + 3\Delta_f H_m(\text{Mg}(\text{OH})_2) + \Delta_f H_m(\text{B}_2\text{H}_6) - \Delta_r H_m - 6\Delta_f H_m(\text{H}_2\text{O}) \quad (3)$$

where $\Delta_f H_m$ is the enthalpy of formation of each compound; $\Delta_r H_m$ is the enthalpy of reaction.

The enthalpy of formation of MgB_2 could be obtained by Equation(4) [11].

$$3\Delta_f H_m(\text{MgB}_2) = 4 \left[\Delta_f H_m^0(\text{B}) + \int_{298.15}^T c_B dT \right] + 3 \left[\Delta_f H_m^0(\text{Mg}(\text{OH})_2) + \int_{298.15}^T c_{\text{Mg}(\text{OH})_2} dT \right] + \left[\Delta_f H_m^0(\text{B}_2\text{H}_6) + \int_{298.15}^T c_{\text{B}_2\text{H}_6} dT \right] - \Delta_r H_m - 6 \left[\Delta_f H_m^0(\text{H}_2\text{O}) + \int_{298.15}^T c_{\text{H}_2\text{O}} dT \right] \quad (4)$$

Where c is the molar heat capacity and $\Delta_f H_m^0$ is the standard enthalpy of formation of each compound.

The determined reaction enthalpy of MgB_2 and water at different temperatures were listed in **Table 2**. Other necessary data for calculation were listed in **Table 3**.

By substituting the data taken from **Tables 2** and **3** to Equation (4), the formation enthalpies of MgB_2 at 323.15, 328.15, 333.15 and 338.15 K are -238.96 , -237.73 , -236.50 and -234.30 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Additionally, the standard enthalpy of formation, molar heat capacity and specific heat capacity of MgB_2 is -245.11 $\text{kJ}\cdot\text{mol}^{-1}$, 246 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and 5.36 $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, respectively, which indicates that MgB_2 has high thermal capacity compared to other compounds.

Table 2. The enthalpies of reaction of MgB_2 and water at different temperatures.

T (K)	$-\Delta_r H_m$ ($\text{kJ}\cdot\text{mol}^{-1}$)
323.15	313.55
328.15	317.85
333.15	322.09
338.15	329.27

Table 3. The parameters for calculation of the formation enthalpy of MgB_2 .

	c_p ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	$\Delta_f H^0$ ($\text{kJ}\cdot\text{mol}^{-1}$)
$\text{H}_2\text{O} (l)$	75.30	-285.84
$\text{B}(s)$	11.97	0
$\text{B}_2\text{H}_6(g)$	56.4	31.4
$\text{Mg}(\text{OH})_2(s)$	77.03	-924.66

3.4. The Kinetic Parameters of the Reaction of MgB_2 and Water

By putting the original data in **Table 4**, $-(dH/dt)_i$, $(H/H_\infty)_i$, H_∞ , $i=1,2,\dots,L$, into the kinetic equation (5) [12], the values of n and $\ln k$ listed in **Table 5** are obtained, where n is the reaction order and k the reaction rate constant.

$$\ln \left[\frac{1}{H_0} \left(\frac{dH}{dt} \right)_i \right] = \ln k + n \ln \left[1 - \left(\frac{H}{H_0} \right)_i \right] \quad i=1,2,\dots,L \quad (5)$$

From **Table 5**, one can see that the values of n are close at different temperatures, and $\ln k$ increase slightly with temperature rising.

The Equation (6) was applied to calculate the values of activation energy E and pre-exponential factor A by the slope and the intercept of the linear.

$$\ln k = \ln A - \frac{E}{RT} \quad (6)$$

The value of E is 50.80 $\text{kJ}\cdot\text{mol}^{-1}$ and A is $10^{4.78}$ s^{-1} .

With the data of E and A , the entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and Gibbs free energy of activation (ΔG^\ddagger) of the reaction processes of MgB_2 and water under different temperatures were obtained by Equations (7) and (8) and shown in **Table 6**.

$$\Delta G^\ddagger = RT \ln \frac{RT}{Nhk} \quad (7)$$

$$\ln \frac{k}{T} = \frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} + \ln \frac{k_B}{h} \quad (8)$$

where k_B is the Boltzmann constant (1.3807×10^{-23} $\text{J}\cdot\text{K}^{-1}$), and h is the Plank constant (6.626×10^{-34} $\text{J}\cdot\text{s}^{-1}$).

Table 6 The values of ΔG^\ddagger , ΔS^\ddagger and ΔH^\ddagger of the reaction process

The positive values of ΔG^\ddagger and ΔH^\ddagger , and the negative value of ΔS^\ddagger show that the reaction can easily take place when the temperature is high enough.

4. Conclusions

1) The reaction of MgB_2 and water will not happen until the environment temperature reaches 312.15 K.

2) The enthalpies of formation of MgB_2 at the temperatures of (323.15, 328.15, 333.15 and 338.15) K are (-238.96 , -237.73 , -236.50 and -234.30) $\text{kJ}\cdot\text{mol}^{-1}$, respectively. The standard enthalpy of formation of MgB_2 obtained is -245.11 $\text{kJ}\cdot\text{mol}^{-1}$.

3) The activation energy E and pre-exponential factor A of the reaction were obtained as 50.80 $\text{kJ}\cdot\text{mol}^{-1}$ and $10^{4.78}$ s^{-1} respectively. The values of n are close under different temperatures, and $\ln k$ increases slightly with temperature rising. The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and Gibbs free energy of

Table 4. The original data of the reaction process of MgB₂ and water at different temperatures.

T (K)	M (g)	m_{water} (g)	t (s)	$-(dH/dt)_r$ (mJ·s ⁻¹)	$(H/H_0)_i$	ΔH_r (kJ·mol ⁻¹)
323.15	0.0237	2.0010	300	2.5979	0.0349	-313.5
			600	2.6089	0.1117	
			900	2.5500	0.1837	
			1200	2.8444	0.261	
			1500	2.8764	0.3428	
			1800	2.6442	0.4219	
			2100	2.2974	0.4921	
			2400	1.9486	0.5524	
			2700	1.6397	0.6035	
			3000	1.3934	0.6465	
			3300	1.1892	0.6833	
			3600	1.0295	0.7148	
			3900	0.8948	0.7421	
			4200	0.7824	0.7659	
			4500	0.6912	0.7868	
328.15	0.0248	2.0008	300	1.3733	0.7485	-317.8
			600	1.1056	0.7834	
			900	0.9304	0.8121	
			1200	0.7702	0.8360	
			1500	0.6424	0.8559	
			1800	0.5498	0.8727	
			2100	0.472	0.8872	
			2400	0.4106	0.8996	
			2700	0.3597	0.910	
			3000	0.3181	0.9201	
			3300	0.2815	0.9285	
			3600	0.2528	0.9360	
			3900	0.2275	0.942	
			4200	0.2050	0.9489	
			4500	0.1869	0.9544	
333.15	0.0348	2.0011	300	5.8786	0.0333	-322.1
			600	8.2060	0.1682	
			900	9.0554	0.3347	
			1200	7.3002	0.4903	
			1500	5.2226	0.6072	
			1800	3.6957	0.6901	
			2100	2.6709	0.7492	

			2400	1.9952	0.7925	
			2700	1.5389	0.8253	
			3000	1.2169	0.8510	
			3300	0.9788	0.8715	
			3600	0.8043	0.8881	
			3900	0.6734	0.9019	
			4200	0.5703	0.9136	
			4500	0.4889	0.9235	
			4800	0.4260	0.9320	
338.15	0.0219	2.0006	300	9.0078	0.3364	-329.27
			600	6.7631	0.5705	
			900	4.2677	0.7286	
			1200	2.6545	0.8267	
			1500	1.7327	0.8893	
			1800	1.1941	0.9312	
			2100	0.8504	0.9604	

Table 5. The values of n , $\ln k$ and the correlation coefficient r for the reaction of MgB_2 and H_2O .

T/K	n	$\ln k$	r
323.15	1.390	-10.212	0.9999
328.15	1.317	-9.892	0.9988
333.15	1.389	-9.556	0.9987
338.15	1.289	-9.394	0.9891
mean	1.346		

Table 6. The values of ΔG^* , ΔS^* and ΔH^* of the reaction process.

T (K)	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* ($\text{J mol}^{-1} \text{K}^{-1}$)
323.15	391.37	142.29	-770.79
328.15	396.59	144.50	-768.23
333.15	401.74	146.69	-765.56
338.15	407.36	148.88	-764.38

activation (ΔG^\ddagger) of the reaction processes of MgB_2 and water under different temperatures show that the reaction can easily take place when the temperature is high enough.

5. Acknowledgements

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