

Thermodynamic analysis of Ti powder synthesized by SHS thermitreaction

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Abstract: According to the thermodynamics theories, the reactive Gibbs free energies, the reactive adiabatic temperature, the melting rate of Ti and the gasification mass of Mg in the Mg-TiO₂ and Al-TiO₂ systems were theoretically calculated and analyzed respectively. The results show that the reactions of Mg-TiO₂ and Al-TiO₂ are very easy to take place and the reaction of producing various suboxides of Ti may occur in Mg-TiO₂ and Al-TiO₂ reaction system; the adiabatic temperature of Mg-TiO₂ becomes lower with increasing mass fraction of Mg. The adiabatic temperature is below 1 800 K when the mass fraction of excessive Mg exceeds 25%; The adiabatic temperature of Al-TiO₂ also becomes lower with increasing mass fraction of Al, but it becomes higher with the preheat temperature increment. The adiabatic temperature plateau is the result of Ti melting endotherm; owing to the gasification of a great deal of Mg in Mg-TiO₂ reaction process, Mg should be properly excessive in order to get Ti.

Key words: self-propagating high-temperature synthesis(SHS); thermodynamic analysis; adiabatic temperature; Mg-TiO₂; Al-TiO₂

1 Introduction

Self-propagating high-temperature synthesis (SHS) provides an attractive promising alternative to the conventional methods of producing the advanced materials such as borides, carbides, silicides, aluminides, and other intermetallic compounds from powder mixture of metal and nonmetal elements, in respect that SHS superior in process economics and process simplicity[1-5]. The basis of studying the process of SHS lies in the thermodynamic analysis of combustion system, which can give us the information about reaction direction and extent as well as phase composition and stability at elevated temperature[6-7]. As for the formation of compounds, it has been demonstrated empirically that the reaction will not be self-sustaining unless the adiabatic temperature $T_{ad} \geq 1800$ K[8].

There are several varieties of thermitreactions and

the most commonly used involves reduction of the oxide with either Al or Mg[9]. The SHS of metallic titanium powders form Mg-TiO₂ initial mixtures was first carried out in ISMAN, Russia[10]. NERSISYAN et al[11] have synthesized nanocrystalline Ti Powder with Mg-TiO₂ system using NaCl as an inert diluent. LIANG et al[12-13] have synthesized Ti powder with Al-TiO₂ system and put forward the reaction mechanism.

In this study, reactive Gibbs free energies, reactive adiabatic temperature and the melting rate of Ti along with the gasification mass of Mg were calculated. the influence of the excessive Mg upon the adiabatic temperature, and the influence of the excessive Al and heating temperature in advance upon the adiabatic temperature in the Al-TiO₂ system were investigated.

2 Description of basis theory

2.1 Gibbs free energy

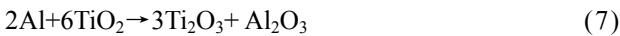
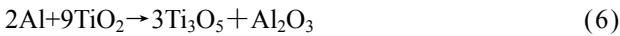
For any reaction system, the condition for the reaction

is[14]

$$\Delta G = \Delta H_{298}^{\Theta} - T \Delta \phi_T' < 0 \quad (1)$$

where $\Delta \phi_T'$ represents the Gibbs free energies function ($J/(K \cdot mol)$), and thus it can be viewed as the difference of Gibbs free energies of all the resultants and reactants. The more minus ΔG is, the easier the reaction will be.

All reactions that are probable to take place in the Mg-TiO₂ and Al-TiO₂ systems are shown as



2.2 Adiabatic temperature

For any binary reaction system:



When the thermodynamic effect is ΔH_{298}^{Θ} , the Kirchhoff formula can be adopted to calculate the $\Delta H_{T_0}^{\Theta}$ when the temperature is T_0 , that is

$$\Delta H_{T_0}^{\Theta} = \Delta H_{298}^{\Theta} - \int_{298}^{T_0} C_m^R dT \quad (11)$$

where ΔH_{298}^{Θ} means the difference between the summation of all the standard reaction enthalpy of the resultants and the summation of the standard reaction enthalpy of all reactants, T_0 is the initial reactive temperature, and C_m^R is the mole thermal capacity of the resultants.

Supposing that the reaction takes place under the adiabatic condition, and the exothermic heat is used to heat up the resultants, then the highest temperature that the resultants can reach is the adiabatic temperature. The adiabatic temperature can be calculated by

$$-\Delta H_{T_0}^{\Theta} = \int_{298}^{T_{ad}} C_m^R dT \quad (12)$$

where the minus denotes that the reaction is an exothermic one, T_{ad} is the adiabatic temperature.

In the most complicated cases, the reactive resultants experience a process of solid state phase change, melting and gasification. The formula for calculating the adiabatic temperature is

$$-\Delta H_{T_0}^{\Theta} = \int_{298}^{T_{tr}} C_m dT + \Delta H_{tr} + \int_{T_{tr}}^{T_m} C_m' +$$

$$\Delta H_m + \int_{T_m}^{T_B} C_m'' dT + \Delta H_B + \int_{T_B}^{T_{ad}} C_m''' dT \quad (13)$$

where C_m , C_m' , C_m'' and C_m''' represent the mole thermal capacities under the low temperature solid state, the high temperature solid state, liquid state and gaseity of the resultant, respectively, T_{tr} stands for the phase change temperature, and H_{tr} for the phase change heat, T_m for the melting point, and H_m for the melting heat, T_B for the boiling point, and H_B for the gasification heat. In Eqn.(13), the items on the right can be reduced according to the actual situation. The phase change rate under solid state, the melting rate and evaporation rate can be calculated by

$$P_k^A = \left(\sum n_i \Delta H_{T_0}^R - \sum n_j \Delta H_{T_c}^P \right) / (n_j \Delta H_k^A) \quad (14)$$

In this work, the calculation concerns about the phase change and melting of Ti, melting and gasification of Mg when it is excessive, and the melting when Al is excessive.

3 Design of experiment

Let the mass fractions of Mg, Al (x, y) be global variables, establish the correlation functions to calculate the melting rate of Ti, as well as the gasification rate of Mg and adiabatic temperatures for melting rates and gasification rates. Because most of the TiO₂ powder is the mixture of rutile and anatase, and anatase is in the major proportion of the mixture[15], the following calculations include rutile and anatase. The thermodynamic parameters used in the calculation can be found in Ref.[16].

4 Results and discussion

4.1 Change of free energy in synthesis reactions

Fig.1 shows the change of reaction free energy with

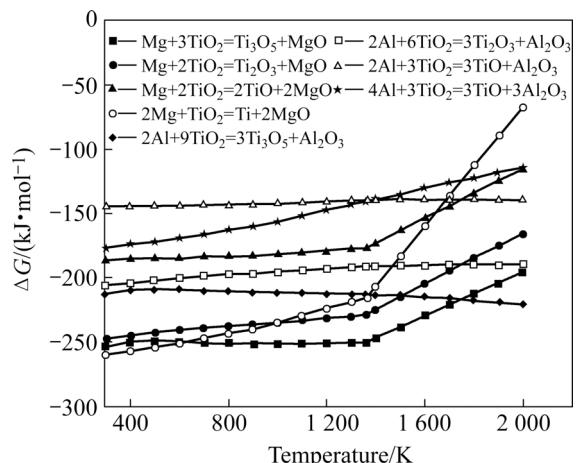


Fig.1 Relationship between reaction free energy and temperature for possible reaction systems of sorts

temperatures for reactions (2)–(9). It is obvious that all reactions can take place spontaneously and at the same time a great deal of heat is released during reaction, which makes SHS reaction easily occur and follow on.

For Mg-TiO₂ system, the reaction between Mg and TiO₂ occurs at 298–600 K, and the possibility of forming Ti is the highest. With rising of temperature and declining reduction of Ti, the main phase of the reactant is Ti₃O₅ between 600 and 1 000 K and the secondary reactant is Ti. When the temperature is above 1 000 K, the possibility of the appearance of Ti is lower than those for Ti₃O₅ and Ti₂O₃. When the temperature reaches 1 363 K, the $\Delta G-T$ curve of every possible reaction is changed, which results from the gasification of Mg at 1 363 K. When the temperature is above 1 600 K, the possibility of the appearance of Ti is lower than any other suboxide of TiO₂. Therefore, in order to obtain Ti, it is important to control the temperature in the reaction process.

For Al-TiO₂ system, ΔG of the reaction Al+TiO₂→Ti+Al₂O₃ rise perpendicularly with the increase of temperature and ΔG of the other suboxide shows a tendency of rising at the beginning and then declining. And this change is not obvious with the temperature variation. When the temperature is between 298 and 1 400 K, the main phase of the reactant is Ti₃O₅, and then Ti₂O₃, Ti and TiO. When the temperature is higher than 1 400 K, the possibility of the appearance of Ti is lower than that of TiO. So it is difficult for the reaction to take place. Like the Mg-TiO₂ system, in order to get Ti easily, the temperature in the reaction should be controlled properly.

Over all, the reducibility of Mg is stronger than that of Al, hence the reaction between Mg and TiO₂ takes place more easily than Al and TiO₂ at a low temperature. The change of ΔG between Mg and TiO₂ is obvious with the temperature variation. When the temperature reaches 1 363 K, ΔG changes greatly with the rising of temperature. When the temperature reaches 1 750 K, the possibility of reaction Mg+TiO₂→Ti+MgO is lower than that of the reaction Al+TiO₂→Ti+Al₂O₃ due to the gasification of Mg.

4.2 Adiabatic temperature of Mg-TiO₂ reaction

According to formula (5), supposing that the reaction takes place at 298 K ($T_0=298$ K) and neglecting the gasification of Mg, the adiabatic temperature curve can be figured out by the Matlab program, as shown in Fig.2.

Fig.2 shows that the adiabatic temperature falls with increasing mole number of Mg($n(\text{Mg})$). When Mg is excessive $w(\text{Mg})<20\%$, the adiabatic temperatures of the reaction of both rutile and anatase are higher than 1 800 K, which matches the empirical criterion put forward by MERZHANOV. Only when the adiabatic temperature meets the condition $T_{ad}\geqslant 1 800$ K, the SHS

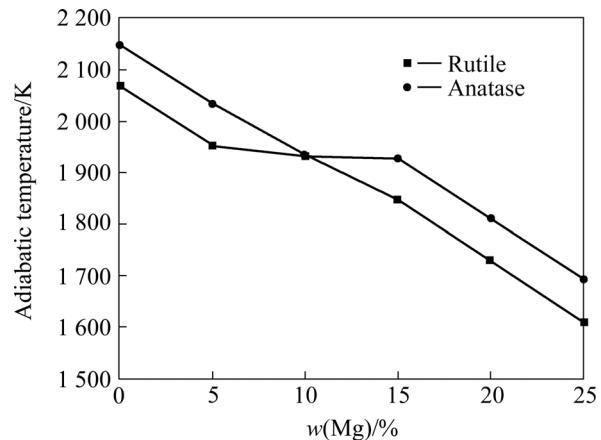


Fig.2 Effect of excessive mass fraction of Mg on adiabatic temperature

reaction can continue self-sustaining, otherwise, the outside energy is needed. When $w(\text{Mg})=25\%$, the adiabatic temperatures of the reaction between Mg and rutile or anatase are both lower than 1 800 K. Therefore, under the condition of no preheating, the mass fraction of excessive Mg may not be more than 25% in order to maintain the SHS reaction. Moreover, the synthetic temperature of Mg-TiO₂ reaction is much higher than that of the gasification of Mg, and in the process of the SHS reaction, the loss of Mg caused by gasification will lead to building up process and the structure of final resultants. As a result, in order to control the gasification of Mg, it is necessary to control the temperature in the building up process.

In Fig.2, it can also be found that when $5\% < w(\text{Mg}) < 10\%$ (rutile) or $10\% < w(\text{Mg}) < 15\%$ (anatase), a plateau appears in the curve of the adiabatic temperature, which is related with the melting of Ti. The melting rate of Ti can be calculated by formula (14). If $5.5\% \leq w(\text{Mg}) \leq 10.5\%$ (rutile) or $8.5\% \leq w(\text{Mg}) \leq 14\%$ (anatase), $0 \leq P_m^{\text{Ti}} \leq 1$. So when $5.5\% \leq w(\text{Mg}) \leq 10.5\%$ (rutile) or $8.5\% \leq w(\text{Mg}) \leq 14\%$ (anatase), the heat released during the reaction is just used for maintaining the melting of Ti and the temperature of reaction does not rise obviously.

4.3 Adiabatic temperature of Al-TiO₂ reaction and melting rate of Ti

Fig.3 shows the effect of excessive mass fraction of Al and preheating temperature on adiabatic temperature; Fig.4 shows the effect of excessive mass fraction of Al and preheat temperature on the melting rate of Ti.

It can be seen that for the same system, with the rising of preheating temperature, the adiabatic temperature and melting rate of Ti increase. The reason is that the initial temperature of the reaction rises when the total heat of the reaction increases, so the adiabatic temperature rises. For TiO₂ (rutile), when the preheating

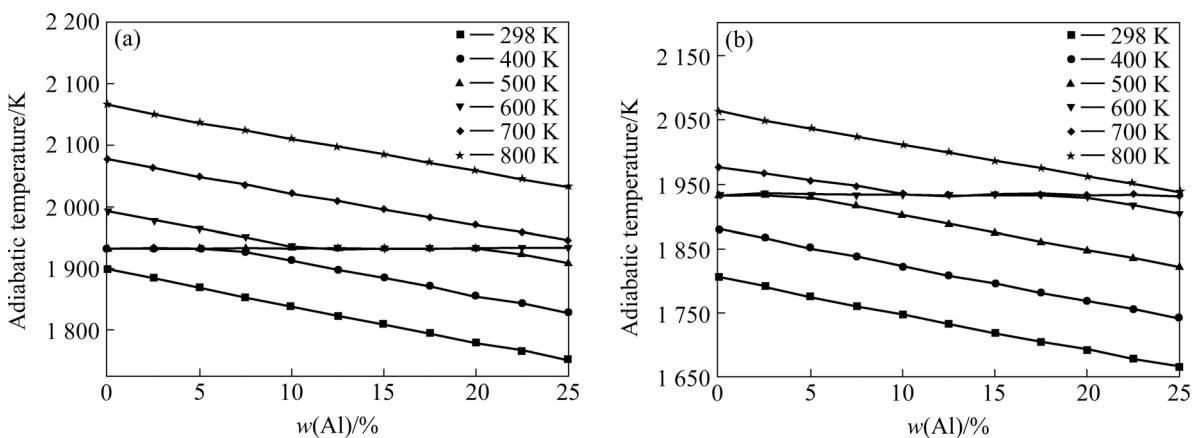


Fig.3 Effects of excessive mass fraction of Al and preheat temperature on adiabatic temperature of anatase (a) and rutile (b)

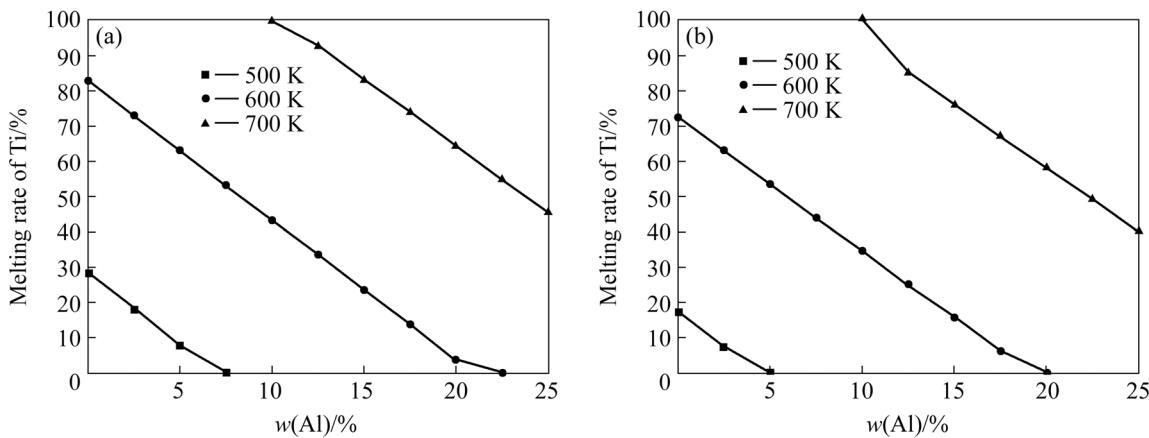


Fig.4 Effects of excessive mass fraction of Al and preheat temperature on melting rate of Ti of anatase (a) and rutile (b)

temperature reaches 500 K, the melting of Ti occurs. When the preheating temperature reaches 800 K, the melting of Ti occurs completely under the condition of $0 \leq n(\text{Al}) \leq 1$. When TiO_2 (anatase) is lower than 100 K, which is related to the standard reaction, heat of formation of TiO_2 (rutile) is higher than that of TiO_2 (anatase). No matter how changeable the temperature is, with the increase of Al content, both the adiabatic temperature and melting rate of Ti fall because excessive Al plays a role of dilution, making the raw material in unit volume reduced, the release of energy decreasing in unit time and unit volume, and causing the falling of the adiabatic temperature. Like the Mg-TiO₂ system, the plateau in the curve of the adiabatic temperature is resulted from the melting rate of Ti between 0 and 100%.

4.4 Gasification mass of Mg

Table 1 lists the gasification mass fraction of Mg at various excessive mass fractions of Mg.

It can be seen clearly from Table 1 that a great deal of Mg is gasified in the process of reaction. In order to make the reaction take place completely to get Ti, theoretically the mass fraction of Mg should reach 46.5%

or 51.0%. But, because of the suboxide produced in the reaction and the secondary reaction, the actual gasification mass of Mg may be smaller than that in Table 1. The data in Table 1 also show that with the increase of the mass fraction of Mg, the gasification mass of Mg correspondingly decreases. The reason is that excessive Mg as dilution in the reaction decreases the reaction temperature, so the gasification mass of Mg also declines. Hence during the reaction process, the properly excessive Mg can not only make up for the loss caused by the gasification of Mg for the high adiabatic temperature, but also lower the adiabatic temperature of the reaction to reduce the gasification of Mg. In order to reduce the gasification of Mg, it is necessary to control the synthetic temperature in the reaction process.

Table 1 Gasification mass mole of Mg at various excessive molar fractions of Mg

Sample	x(Mg)/%					
	0	5	10	15	20	25
Rutile	46.5	45.0	43.0	41.5	40.0	38.5
Anatase	51.0	49.5	48.0	46.0	44.5	43.0

5 Conclusions

1) By calculating the reactive Gibbs free energies of systems Mg-TiO₂ and Al-TiO₂, it is found that the SHS reaction can take place easily in these two systems. And the reaction can produce various suboxides of Ti, such as Ti₃O₅, Ti₂O₃ and TiO. With the rising of temperature, the possibility of forming Ti decreases.

2) The adiabatic temperature and the melting rate of Ti of the reactions with various quantity of Mg (rutile or anatase) are calculated theoretically. The adiabatic temperature of the Mg-TiO₂ reaction falls with the increase of the mass fraction of Mg; when the mass fraction of excessive Mg arrives at 25%, the adiabatic temperature is below 1 800 K. The adiabatic temperature of the Al-TiO₂ reaction falls with the increase of the mass fraction of Al in the same way, but the adiabatic temperature rises with the increase of preheating temperature. For both Mg-TiO₂ and Al-TiO₂ reactions, the plateau in the curve of the adiabatic temperature is resulted from the melting of Ti.

3) The calculation of the gasification mass of Mg for various quantity shows that a great deal of Mg is gasified in the reaction process. In order to make the Mg-TiO₂ reaction take place completely to get Ti, Mg should be excessive properly.

References

- [1] MUNIR Z A, ANSELMI-TAMNURINI U. Self-propagating exothermic reactions: The synthesis of high-temperature materials by combustion[J]. Mater Sci Rep, 1989, 3: 277–365.
- [2] VARMA A, LEBRAT J P. Combustion synthesis of advanced materials[J]. Chem Eng Sci, 1992, 47: 2179–2194.
- [3] MERZHANOV A G. Solid flames: Discoveries, concepts and horizons of cognition[J]. Combust Sci Technol, 1994, 98: 307–336.
- [4] MOORE J J, FENG H J. Combustion synthesis of advanced materials: part I. Reaction parameters[J]. Prog Mater Sci, 1995, 39: 243–273.
- [5] MOSSINO P. Some aspects in self-propagating high-temperature synthesis[J]. Ceramics International, 2004, 30: 311–332.
- [6] YIN Sheng. Combustion synthesis[M]. Beijing: Metallurgical Industry Press, 2002: 50–57.(in Chinese)
- [7] WANG L L, MUNIR Z A, MAXIMOV Y M. Thermite reaction: Their utilization in the synthesis and processing of materials[J]. Journal of Materials Science, 1993 28: 3693–3708.
- [8] MUNIR Z A, HOLT J B. The combustion synthesis of refractory nitrides part I. Theoretical analysis[J]. Journal of Materials Science, 1987, 22: 710–714.
- [9] MOORE J J, FENG H J. Combustion synthesis of advanced materials: part II . Classification, applications and modelling[J]. Prog Mater Sci, 1995, 39: 275–316.
- [10] MERZHANOV A G. Self-propagating high temperature synthesis: Twenty years of search and finding[M]. New York: VCH Publishers, 1990: 1–53.
- [11] NERSISYAN H H, LEE J H, WON C W. Combustion of TiO₂-Mg and TiO₂-Mg-C systems in the presence of NaCl to synthesize nanocrystalline Ti and TiC powders[J]. Materials Research Bulletin, 2003, 38: 1135–1146.
- [12] LIANG Shu-quan, ZHENG Zi-qiao, TAN Cheng-yu, YIN Den-feng, HU Wen-bin. The microstructure analysis of the combustion wave in Al-TiO₂ system by self-propagating high-temperature synthesis (SHS)[J]. Rare Metal materials and Engineering, 1993, 22(4): 42–45. (in Chinese)
- [13] LIANG Shu-quan, ZHENG Zi-qiao, TAN Cheng-yu, YIN Den-feng, HU Wen-bin. The structural macrokinetics of the Al-TiO₂ self-propagating high-temperature syntheses[J]. Material Science and Technology, 1993, 1(1): 34–39. (in Chinese)
- [14] JIN Yun-xue, ZHANG Er-lin. Self-propagating high-temperature synthesis technology and in situ composite materials[M]. Harbin: Harbin Industry Press, 2002: 8–9. (in Chinese)
- [15] SATTERFIELD C N. Heterogeneous catalysis in industrial practice[M]. New York: McGraw-Hill, 1980: 87–97.
- [16] YE Da-lun, HU Jian-hua. Practical data handbook of inorganic thermodynamics[M]. Beijing: Metallurgical Industry Press, 2002. (in Chinese)

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