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Thermodynamic Analysis of Intergranular Additives in Sintered Nd-Fe-B Magnet

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To get deeper insight into the effect of intergranular additives in sintered Nd-Fe-B magnet and consequently improve the properties better, the interaction between additives (oxide, nitride, and carbide) and Nd-rich phase in the temperature range of 298.15-1400 K was analyzed thermodynamically. It can be found that the oxide additives became less stable than nitrides and carbides. Except for calcium oxide, almost all oxides could react with Nd from Nd-rich phase. To be different from oxide additives, the mechanism of nitrides and carbides was defined with various elements, either reaction with Nd from Nd-rich phase or not. The two different mechanisms would show different effects on the microstructure and hence properties of magnet. The thermodynamic analysis had a better agreement with the experimental information.

Keywords : sintered Nd-Fe-B magnet, intergranular additives, thermodynamic analysis, experimental verification

1. Introduction

Due to the outstanding magnetic properties, the production of sintered Nd-Fe-B magnets has grown rapidly and its application has been expanded extensively. However, poor thermal stability, limited corrosion resistance, and coercivity much less than the theoretical maximum have seriously restricted its further application. In order to overcome these weaknesses, many investigations have been made previously. It has been reported that the coercivity and corrosion resistance can be improved by alloying additions, such as the first type dopant element (Cu, Al, Ga, and Mg, etc.) and the second type dopant element (Nb, Zr, Ti, and Mo, etc.) [1-3]. But this also accompanies with the reduction of other properties, such as remanence and Curie temperature, due to the dilution effect of the magnetization. Recently, more and more workers focus mainly attention on the intergranular additions for avoiding that. The adopted method is mainly powder blending [4, 5]. Previous studies have shown that the additions of the metal powders (such as Cu, Al, Ga, and Nb) are effective in avoiding or inhibiting the reduction of other properties on the basis of improved coercivity and corrosion resistance [6-9]. Besides that, the compound additives are proved to be effective as well. Heh *et al*. have reported that the additions of fine nitride powders can homogenously improve the coercivity and remanence. Among them, BN, AlN, Si_3N_4, and TiN are the most effective. This is attributed mainly to the modification of intergranular phase probably resulting from the reaction between nitrides and the Nd-rich phase [10, 11]. Moreover, oxide additions have been also investigated widely. Previous results show that the additions of fine oxides powders (such as MgO, ZnO, and CaO) can enhance the coercivity considerably, which arises from the new intergranular Nd-O-Fe-M phase [12, 13]. Unfortunately, this is together with the reduction of remanence, whereas the problem of which can be solved through minor additions of their nanopowders [14, 15]. Although many studies have been made into the effect of compound additions on final magnetic properties, few have sought to first identify the mechanism between compounds and Nd-rich phase. In the present work, this is analyzed thermodynamically in detail, with the aim of using the resulting information to improve the properties better.

2. Thermodynamic Analysis

2.1. Oxide additives

As well known, oxygen plays a very important role in the magnetic properties of Nd-Fe-B magnet [16]. Therefore, the mechanism of oxide additives is analyzed first.

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Here we choose four representative oxides, which are the oxides with high and low melting point of the first type dopant element (Al_2O_3 and Bi_2O_3), the oxide with high melting point of the second type dopant element (TiO_2), and very stable calcium oxide (CaO), respectively. First of all, a chemical thermodynamic analysis is made on the reaction between Al_2O_3 and Nd from Nd-rich phase. The reaction between them may be as follows:

$$2Nd + Al_2O_3 \rightarrow Nd_2O_3 + 2Al \quad (1)$$

Based on the thermodynamic data [17], the standard molar Gibbs energy of formation ($\Delta_f G_m^\ominus$) for Al_2O_3 and Nd_2O_3 in the temperature range of 298.15-1400 K is depicted in Fig. 1. It can be seen that, $\Delta_f G_m^\ominus$ values for Nd_2O_3 are more negative than those for Al_2O_3, indicating that Nd_2O_3 is more stable than Al_2O_3. Therefore, the reaction (1) may carry out spontaneously. To further verify this, the standard molar Gibbs energy of reaction ($\Delta_r G_m^\ominus$) is calculated, as shown in Fig. 2. It is clearly shown that $\Delta_r G_m^\ominus$ values are all negative in the temperature range of 298.15-1400 K, and become more negative with increasing temperature. This implies that the reaction (1) can assuredly carry out spontaneously and is easier at higher temperature. The resultant Al can modify the grain boundary phase, thereby improving the coercivity and corrosion resistance. Small amounts of Nd_2O_3 can play a role on the refinement of $Nd_2Fe_{14}B$ grains, which is also beneficial to the improvement of coercivity and corrosion resistance.

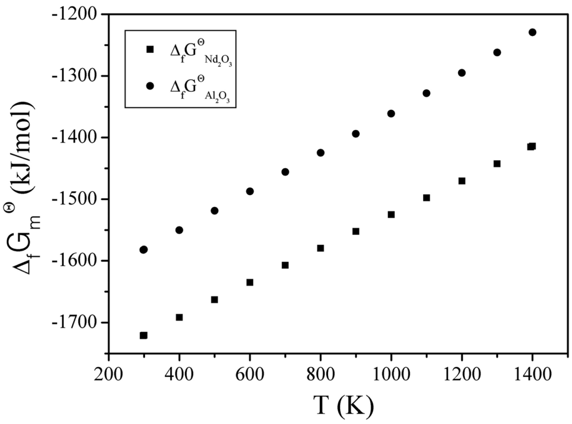

Fig. 1. $\Delta_f G_m^\ominus$ for Al_2O_3 and Nd_2O_3 at 298.15-1400 K.

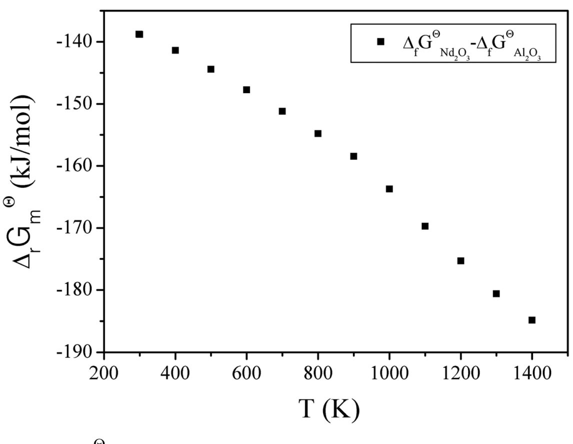

Fig. 2. $\Delta_r G_m^\ominus$ for reaction (1) at 298.15-1400 K.

Secondly, we investigate the probability of reaction between TiO_2 and Nd from Nd-rich phase. The reaction equation can be given by:

$$4Nd + 3TiO_2 \rightarrow 2Nd_2O_3 + 3Ti \quad (2)$$

According to the thermodynamic data [17], $\Delta_r G_m^\ominus$ values for reaction (2) are calculated and shown in Fig. 3. As can be seen, $\Delta_r G_m^\ominus$ values are all negative in the temperature range of 298.15-1400 K, indicating that the reaction (2) can carry out spontaneously during sintering. $\Delta_r G_m^\ominus$ values become less negative with increasing temperature, which is different from that for Al_2O_3, but $\Delta_r G_m^\ominus$ values are much smaller than those for Al_2O_3. This implies that TiO_2 is more prone to react with Nd from Nd-rich phase compared to Al_2O_3. Moreover, the resultant Ti belongs to the second type dopant element with high melting point. So it can form binary boride phase. The reaction can be written as:

$$Ti + 2B \rightarrow TiB_2 \quad (3)$$

Due to $\Delta_f G_m^\ominus = 0$ for simple substance Ti and B, $\Delta_f G_m^\ominus$ values for TiB_2 equal to $\Delta_r G_m^\ominus$ for reaction (3). Therefore, $\Delta_r G_m^\ominus$ for reaction (3) is negative according to reference [17], hinting that TiB_2 precipitates can be formed at the grain boundaries during sintering process. TiB_2 precipitates effectively inhibit the movement of grain boundaries, leading to the refinement of $Nd_2Fe_{14}B$ grains, thereby improving the coercivity and corrosion resistance. Thus, the addition of appropriate amounts of TiO_2 can improve

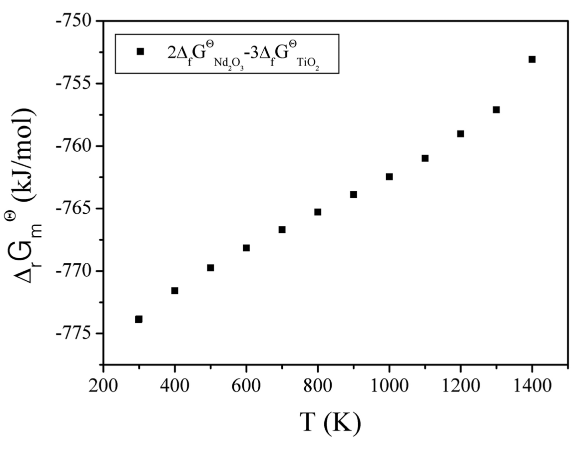

Fig. 3. $\Delta_r G_m^\ominus$ for reaction (2) at 298.15-1400 K.

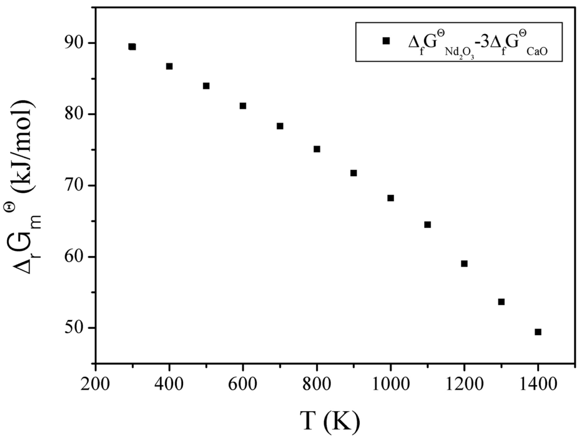

Fig. 4. $\Delta_r G_m^{\Theta}$ for reaction (5) at 298.15-1400 K.

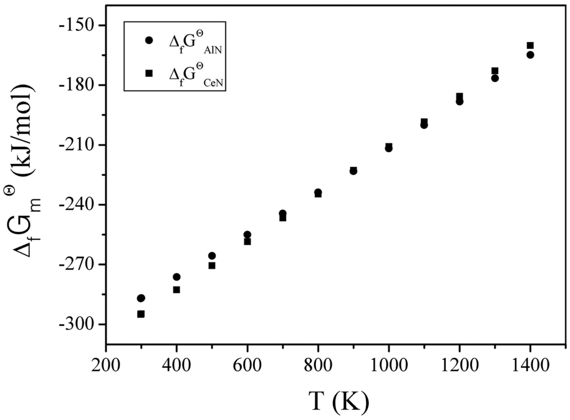

Fig. 5. $\Delta_f G_m^{\Theta}$ for AlN and CeN at 298.15-1400 K.

both the coercivity and the corrosion resistance.

Using the same method, we analyze the role of Bi_2O_3 and CaO. The reactions between Bi_2O_3 or CaO and Nd from Nd-rich phase may be as follows:

$$2Nd + Bi_2O_3 \rightarrow Nd_2O_3 + 2Bi \tag{4}$$

$$2Nd + 3CaO \rightarrow Nd_2O_3 + 3Ca \tag{5}$$

$\Delta_f G_m^{\Theta}$ values for Bi_2O_3 are negative and much more positive than those for Nd_2O_3 [17]. This indicates that Bi_2O_3 is much easier to react with Nd from Nd-rich phase, which is proved by the negative $\Delta_r G_m^{\Theta}$ for reaction (4), with the value of $-1229.3 \sim -1211.6$ kJ/mol in the range from 298.15 K to 1400 K. Compared with Al_2O_3 and TiO_2, the reactivity of Bi_2O_3 is higher, and its melting point is much lower. Therefore, it may induce better densification and modification of microstructure, thereby improving the magnetic properties and corrosion resistance. To be different from Al_2O_3, TiO_2 and Bi_2O_3, CaO is very stable and do not react with Nd from Nd-rich phase, resulting from the positive $\Delta_r G_m^{\Theta}$ for reaction (5) (as shown in Fig. 4). In other words, Ca can act as deoxidant to increase the effect of Nd content and hence improving the densification of sintering. In addition, the resultant stable CaO particles or the addition of its nano-scale powders can refine the grains by inhibiting the movement of grain boundaries, thus improving the magnetic properties and corrosion resistance.

2.2. Nitride additives

In order to investigate the effect of nitrides, AlN, Mg_3N_2, VN, and ZrN are chosen as examples in this paper. They are all with higher melting point. Firstly, we explore the mechanism of AlN as intergranular additive. The reaction between AlN and Nd from Nd-rich phase can be given by:

$$Nd + AlN \rightarrow NdN + Al \tag{6}$$

On the basis of the thermodynamic data [17], the standard molar Gibbs energy of formation ($\Delta_f G_m^{\Theta}$) for AlN and NdN in the temperature range of 298.15-1400 K is shown in Fig. 5. Here we use $\Delta_f G_m^{\Theta}$ for CeN instead of that for NdN, because $\Delta_f G_m^{\Theta}$ for NdN is not found in the reference and Ce and vicinal Nd both belong to the light rare earth element. It is clearly shown that $\Delta_f G_m^{\Theta}$ values for CeN and AlN are nearly same. It can be inferred that the reactivity of reaction (6) is lower, even if it can carry out. This is also proved by $\Delta_r G_m^{\Theta}$ values for reaction (6), as depicted in Fig. 6. As can be seen, whether AlN is reactive or not depends on the temperature, but the whole reactivity is lower. Therefore, the effect of AlN on the microstructure and properties of magnet is more complicated. On the contrary, Mg_3N_2 can react with Nd from Nd-rich phase as the following reaction (7) due to the negative $\Delta_r G_m^{\Theta}$ values (as shown in Fig. 7).

$$2Nd + Mg_3N_2 \rightarrow 2NdN + 3Mg \tag{7}$$

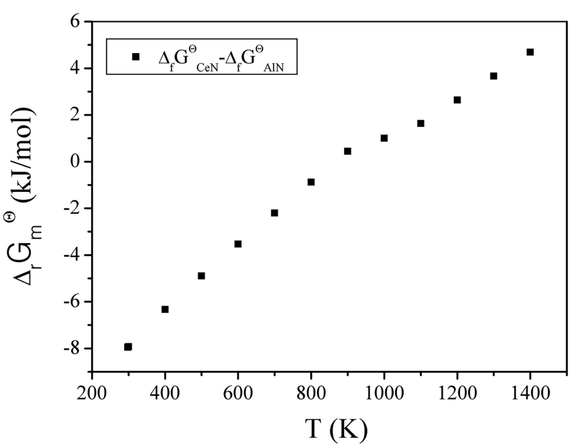

Fig. 6. $\Delta_r G_m^{\Theta}$ for reaction (6) at 298.15-1400 K.

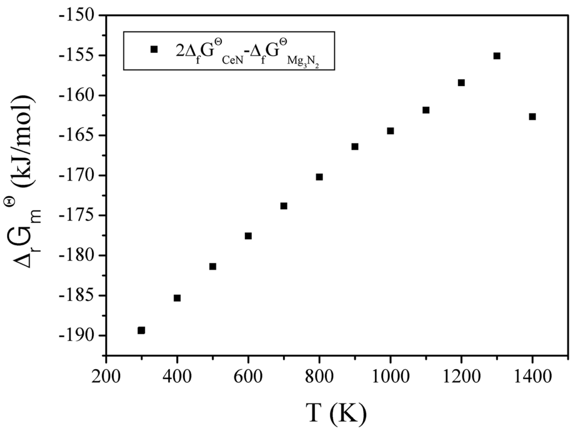

Fig. 7. $\Delta_r G_m^\Theta$ for reaction (7) at 298.15-1400 K.

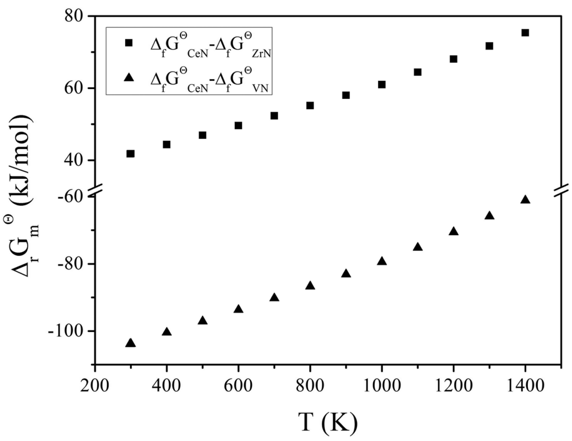

Fig. 8. $\Delta_r G_m^\Theta$ for reaction (8) and (9) at 298.15-1400 K.

The resultant Mg with low melting point can be beneficial to the liquid sintering and the formation of new intergranular phase, Thereby enhancing the magnetic properties and corrosion resistance.

Similarly, we investigate the mechanisms of nitrides of high-melting metals Zr and V. The results in Fig. 8, calculated from the data of reference [17], show that $\Delta_r G_m^\Theta$ for reaction (8) and (9) is greater and less than zero, respectively. It can be deduced that reaction (9) can carry out spontaneously, but reaction (8) can not. Therefore, the intergranular addition of nano-scale ZrN powders can inhibit the grain growth according to Zener model, consequently improving the coercivity of magnets. Moreover, the resultant V can form V-Fe-B phase at the grain boundaries, likewise, playing a role of grain refinement.

$$Nd + ZrN \rightarrow NdN + Zr \tag{8}$$

$$Nd + VN \rightarrow NdN + V \tag{9}$$

2.3. Carbide additives

Except for oxides and nitrides, carbides will be also important additives. However, in the sintered magnets, they do not get enough attention. In this section, we take SiC, TiC, and WC as examples to elucidate the mechanism of their intergranular addition in sintered Nd-Fe-B magnets. SiC may react with Nd from Nd-rich phase to form Si and Nd_2C_3, the equation can be expressed as:

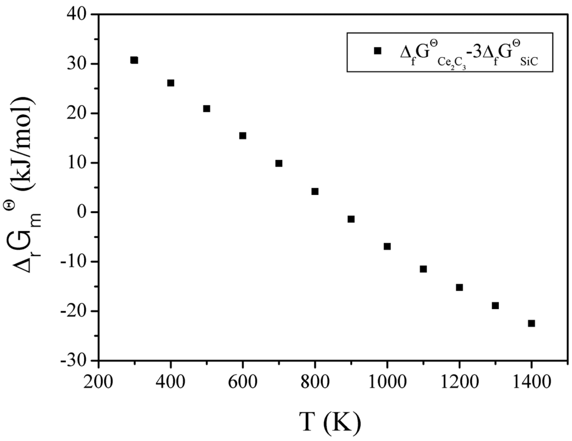

Fig. 9. $\Delta_r G_m^\Theta$ for reaction (10) at 298.15-1400 K.

$$2Nd + 3SiC \rightarrow Nd_2C_3 + 3Si \tag{10}$$

Similarly, $\Delta_f G_m^\Theta$ values for Nd_2C_3 are replaced by those for Ce_2C_3 [17]. It can be seen from the calculation that when temperature $T < 792$ K, $\Delta_r G_m^\Theta$ for reaction (10) is greater than zero, contrarily, $\Delta_r G_m^\Theta$ is less than zero, as shown in Fig. 9. Therefore, reaction (10) can carry out spontaneously during sintering process. The resultant Si can dissolve in Nd-rich phase, modifying the grain boundary phase, thereby improving the magnetic properties and corrosion resistance of magnets [18].

Additionally, the mechanism of TiC and WC are also investigated. The reaction between TiC or WC and Nd from Nd-rich phase may be as follows:

$$2Nd + 3TiC \rightarrow Nd_2C_3 + 3Ti \tag{11}$$

$$2Nd + 3WC \rightarrow Nd_2C_3 + 3W \tag{12}$$

$\Delta_r G_m^\Theta$ for reaction (11) was calculated through $\Delta_f G_m^\Theta$ values for TiC and Ce_2C_3, as presented in Fig. 10, suggesting that reaction (11) can not occur owing to $\Delta_r G_m^\Theta >$ 0. Therefore, TiC can exist stably at the grain boundaries in the temperature range from 298.15 K to 1400 K, which is similar with ZrN. According to the above discussion, the intergranular addition of appropriate amount of TiC nanopowders is also an effective way to improve the coercivity and corrosion resistance in sintered Nd-Fe-B magnets by grain refinement. Contrarily, $\Delta_r G_m^\Theta$ values for reaction (12) are all negative and decrease with increasing

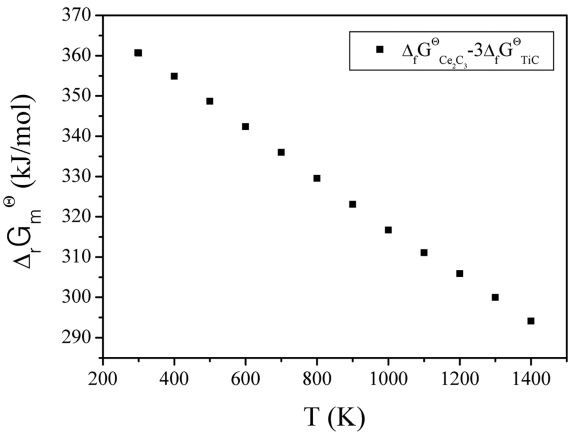

Fig. 10. $\Delta_r G_m^\Theta$ for reaction (11) at 298.15-1400 K.

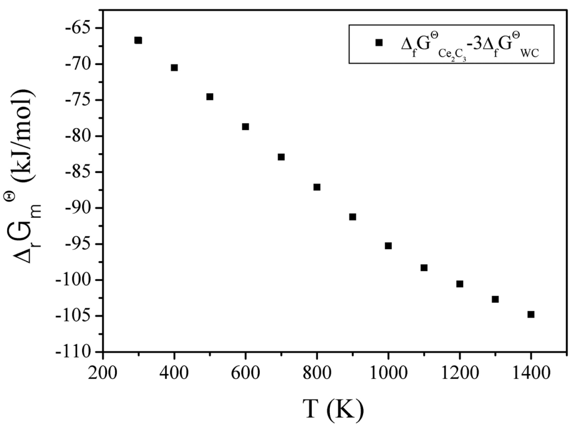

Fig. 11. $\Delta_r G_m^\Theta$ for reaction (12) at 298.15-1400 K.

temperature (as shown in Fig. 11). This indicates that WC can react with Nd from Nd-rich phase. The resultant W can form W-Fe-B intergranular phase, which improves the coercivity and corrosion resistance of magnets due to the refined grains and modified grain boundaries.

2.4. Summary on various additives

Based on the thermodynamic analysis, the mechanisms of various additives are investigated, as summarized in Table 1. The oxide additives are less stable than nitrides and carbides. Except for calcium oxide, almost all oxides can react with Nd from Nd-rich phase, thereby modifying the intergranular phase and then improving the properties of magnet probably. Moreover, calcium can be employed as deoxidizer, reducing the oxygen content in magnet. This is also beneficial to the improvement of the magnetic properties. On the other hand, the nitrides of low melting elements (such as Mg, Ga, Si, and Zn) and high melting elements (such as V, Nb, and Mo) are not stable, and they can react with Nd from Nd-rich phase, forming corresponding elements and neodymium nitrides. This is helpful to modify the grain boundary phases, thereby enhancing the magnetic properties and corrosion resistance. However, the nitrides of Zr and Ti are stable and can play a role of inhibition of grain growth. The carbides were similar with the nitrides. Among them, the carbides of the elements (such as Zn, Si, W, and Mo) can react with Nd from Nd-rich phase, whereas the carbides of the elements (such as Ti, Zr, Nb, and V) are stable.

3. Experimental Verification

The effects of intergranular additives on sintered Nd-Fe-B magnets have been also verified by our and other researchers' experimental results. Our results show that, SiO_2 added to intergranular region can react with Nd from Nd-rich phase, thereby modifying the intergranular phase and refining the matrix phase grains. The optimization of microstructure contributes to the improvement of intrinsic coercivity (H_{cj}), remanence (B_r) and corrosion resistance [19]. Likewise, Beseničar *et al.* have reported that the

Table 1. The standard molar Gibbs energy of reaction ($\Delta_r G_m^\Theta$) for variously possible reactions at 1340 K (in kJ/mol)

Additives	Reaction equation	$\Delta_r G_m^\Theta$	Remarks
SiO_2	$3SiO_2+4Nd \rightarrow 2Nd_2O_3+3Si$	−849.81	Reactive
Al_2O_3	$Al_2O_3+2Nd \rightarrow Nd_2O_3+2Al$	−179.98	Reactive, oxides of the first dopant elements Cu, Ga, Mg, Sn, and Zn are similar
TiO_2	$3TiO_2+4Nd \rightarrow 2Nd_2O_3+3Ti$ $Ti+2B \rightarrow TiB_2$	−755.97 −87.50	Reactive, oxides of the second dopant elements Mo, Nb, V, W, and Zr are similar
Bi_2O_3	$Bi_2O_3+2Nd \rightarrow Nd_2O_3+2Bi$	−1221.78	Low-melting oxide, very easy to be reactive
CaO	$3CaO+2Nd \rightarrow Nd_2O_3+3Ca$	54.32	Not reactive, Ca can be as deoxidizer
Mg_3N_2	$Mg_3N_2+2Nd \rightarrow 2NdN+3Mg$	−155.39	Reactive, nitrides of the first dopant elements Ga, Si, and Zn are similar
AlN	$AlN+Nd \rightarrow NdN+Al$	4.55	Reactive below 940 K
VN	$VN+Nd \rightarrow NdN+V$	−65.24	Reactive, nitrides of the second dopant elements Nb and Mo are similar
ZrN	$ZrN+Nd \rightarrow NdN+Zr$	72.13	Not reactive, nitride of the second dopant element Ti is similar
SiC	$3SiC+2Nd \rightarrow Nd_2C_3+3Si$	−20.47	Reactive above 792 K
WC	$3WC+2Nd \rightarrow Nd_2C_3+3W$	−103.55	Reactive, carbide of the second dopant elements Mo is similar
TiC	$3TiC+2Nd \rightarrow Nd_2C_3+3Ti$	298.56	Not reactive, carbides of the second dopant element Nb, Zr, and V are similar

intergranular addition of ZrO_2 has a positive influence on the magnetic properties, temperature coefficients and corrosion resistance of Nd-Fe-B magnets [20]. TEM examination reveals that the added ZrO_2 may be reduced by Nd from Nd-rich phase to form Nd_2O_3 and Zr, and the resultant Zr can also form ZrB_2 plate-like phase. The formed Nd oxides and ZrB_2 phase modify the microstructure of Nd-Fe-B magnet, thereby improving its properties. Besides, the intergranular additions of nitrides can also improve the magnetic properties and corrosion resistance of Nd-Fe-B magnets. As reported that, BN, AlN, Si_3N_4, and TiN are the most effective for enhancing the magnetic properties of magnet [10, 11]. Small addition of BN can result in a maximum 20% increase in H_{cj}. Chemical compositions analysis indicates that BN particles react with Nd and dissolve in the Nd-rich phase during sintering. As a result, the microstructure is modified and thus H_{cj} is increased. Moreover, the addition of Si_3N_4 can also improve the corrosion resistance of Nd-Fe-B magnet [21]. According to the EDX results, Si has been dissolved in Nd-rich phase, indicating that the added Si_3N_4 can react with Nd from Nd-rich phase to form Si and NdN. This leads to the modification of intergranular phase and optimization of microstructure, and thus improves the magnetic properties and corrosion resistance of Nd-Fe-B magnet. In addition, the intergranular addition of WC has been proved an effective method to increase coercivity [22]. The formation of W-Fe-B phase confirms the reaction of WC with Nd from Nd-rich phase. And the refined grains are the main reason for improving coercivity. Overall, the thermodynamic analysis can well explain the effect of intergranular additives on the microstructure and properties of Nd-Fe-B magnet, and can be used to improve properties better.

4. Conclusions

The effects of intergranular additives (oxide, nitride, and carbide) in sintered Nd-Fe-B magnets were analyzed thermodynamically. The standard molar Gibbs energy of reaction ($\Delta_r G_m^\ominus$) between the additives and Nd-rich phase in the temperature range of 298.15-1400 K was calculated. The thermodynamic calculations indicated that almost all oxides additives apart from calcium oxide were less stable than nitrides and carbides, and could react with Nd from Nd-rich phase. However, nitrides and carbides either reacted with Nd from Nd-rich phase or not. In both mechanisms, the effects of nitrides and carbides on the microstructure and properties of magnet were different. In addition, the thermodynamic analysis had been verified by the experimental results. This would be an important guide for better improving the properties of magnet.

Acknowledgments

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