

Calculating models on surface tension of RE₂O₃–MgO–SiO₂ (RE=La, Nd, Sm, Gd and Y) melts

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Abstract: A thermodynamic model was developed for determining the surface tension of RE₂O₃–MgO–SiO₂ (RE=La, Nd, Sm, Gd and Y) melts considering the ionic radii of the components and Butler's equation. The temperature and composition dependence of the surface tensions in molten RE₂O₃–MgO–SiO₂ slag systems was reproduced by the present model using surface tensions and molar volumes of pure oxides, as well as the anionic and cationic radii of the melt components. The iso-surface tension lines of La₂O₃–MgO–SiO₂ slag melt at 1873 K were calculated and the effects of slag composition on the surface tension were also investigated. The surface tensions of La₂O₃, Gd₂O₃, Nd₂O₃ and Y₂O₃ at 1873 K were evaluated as 686, 677, 664 and 541 mN/m, respectively. The surface tension of pure rare earth oxide melts linearly decreases with increasing cationic field strength, except for Y₂O₃ oxide, while Y₂O₃ has a much weaker surface tension. The evaluated results of the surface tension show good agreements with literature data, and the mean deviation of the present model is found to be 1.05% at 1873 K.

Key words: rare-earth oxide; surface tension; ionic radius; Butler's equation; calculating model

1 Introduction

Physical properties of elevated temperature melts are important parameters for high temperature related industries, such as iron and steel making, glass melting, ceramics sintering, controlling the rate of various reactions and the fluid flows [1]. Moreover, over the last few decades, since rare-earth elements including Sc, Y and lanthanides (Ln) have a common ionic valence (Z) of +3, and are known to be the most electropositive elements, it has been suggested that they are suitable sintering additives for Si₃N₄ [2]. Because the ionic radii (r) of the lanthanide elements decrease continuously with their increasing atomic number, which is known as lanthanide contraction, their cationic field strength ($\sigma_{\text{CFS}}=Z/r^2$, Z is the valence of the corresponding element, r is its ionic radius based on $r^{(\text{VI O}^{2-})}=0.14$ nm) also continuously changes with their atomic number. This causes consequent variations in various properties of rare-earth containing oxide and oxynitride glasses [3–9].

SHIMIZU et al [3] reported that the surface tension of rare earth (Y, Gd, Nd and La) containing 45.2%MgO–54.8%SiO₂ (mole fraction) melts linearly

decreases with the cationic field strength of RE³⁺. Conversely, the viscosity of rare earth (Y, Gd, Nd and La) containing 45.2%MgO–54.8%SiO₂ (mole fraction) melts linearly increases with the cationic field strength of RE³⁺. The similarly linear relationship between rheological and elastic properties and cationic field strength of corresponding rare earth elements was also observed in RE–Si–Mg–O–N glasses (RE=Sc, Y, La, Nd, Sm, Gd, Yb and Lu) [4,5] and the effect of rare earth on the thermal expansion and viscosity properties of soda–lime–silica was investigated [7–9]. However, it is difficult to find the appropriate surface tension data of elevated temperature melts due to the high temperature measurement and the complicated effect of components on surface tension.

Various models have been developed to predict the surface tension of molten slag melts. For slag with complicated interactions, TANAKA et al [10–12] applied a model considering the anionic and cationic radii of the component oxides as the model parameters to describe the surface tension, CHOI and LEE [13] calculated the surface tension using critically evaluated ionic surface distances of pure oxides. In addition, these two models were based on Butler's equation and

achieved consistent results compared to the data reported in the literature. However, to our best knowledge, there are no available reports on the surface tension evaluation model of rare-earth containing high temperature silicate melts.

Therefore, in order to systematically reveal the influence of rare earth on the surface tension of silicate melts, a thermodynamic model for determining the surface tension of RE₂O₃–MgO–SiO₂ (RE=La, Nd, Sm, Gd and Y) melts considering the ionic radii of the components and Butler's equation was developed. The temperature and composition dependence of the surface tensions in molten RE₂O₃–MgO–SiO₂ melts was reproduced by the present model using surface tensions and molar volumes of pure oxides, as well as the anionic and cationic radii of the melt components. The calculated surface tensions were compared with the experimentally obtained data for RE₂O₃–MgO–SiO₂ melts. In addition, the surface tensions of pure oxides of RE₂O₃ at 1873 K were evaluated and the iso-surface tension lines of La₂O₃–MgO–SiO₂ melts at 1873 K were also calculated.

2 Thermodynamic model for estimation of surface tension of molten slag

2.1 Butler's equation

Among various models suggested by previous researchers for the prediction of surface tension of liquid solutions, the present model is also based on the Butler's equation [14]. The surface tension (σ) of the molten slag system is calculated from

$$\sigma = \sigma_i^{\text{Pure}} + \frac{RT}{A_i} \ln \frac{a_i^{\text{Surf}}}{a_i^{\text{Bulk}}} \quad (1)$$

where subscript “*i*” refers to RE₂O₃, MgO or SiO₂; superscripts “Surf” and “Bulk” indicate the surface and bulk phases, respectively; *R* is the gas constant and *T* is the temperature, a_i^{Surf} and a_i^{Bulk} are the activities of the component *i* at the surface phase and the bulk phase, respectively; σ_i^{Pure} is the surface tension of the pure molten component *i*; and *A_i* is the molar surface area in a monolayer of pure molten component *i*, which can be figured out by

$$A_i = LN_0^{1/3} V_i^{2/3} \quad (2)$$

where *N₀* is Avogadro's number, *V_i* is molar volume of the pure molten component *i*, *L* is correction factor resulted from the surface structure and is usually set to be 1 for the molten salts and ionic oxide mixtures by TANAKA et al [1].

2.2 Hypotheses

Equations (3)–(7) for evaluating the surface tension of the AX–BY–CZ melts have been derived from

Butler's equation by considering the following assumptions [10–12]:

1) It has been known that molten ionic mixtures readily undergo surface relaxation due to spontaneous changes in the ionic distance at the surface, which causes the energetic state of the surface to approach that of the bulk state. Thus, the contribution from excess Gibbs energy terms is neglected in the Butler's equation.

2) In ionic substances, it is well known that their ionic structures depend upon the radii ratio of the cation to anion. In order to evaluate the ionic structures and physico-chemical properties of ionic materials, radii ratio of the cation to anion should be considered.

The relation between surface tension of slag melts and the *M_i* (substitute for the activities *a_i*) of components at the surface phase and the bulk phase conforms to Butler's equation:

$$\sigma = \sigma_i^{\text{Pure}} + \frac{RT}{A_i} \ln \frac{M_i^{\text{Surf}}}{M_i^{\text{Bulk}}} \quad (3)$$

where M_i^{Surf} and M_i^{Bulk} are the substitutes for the activities of the component *i* at the surface phase and the bulk phase, respectively. Taking CaO–Al₂O₃–CaF₂ slag melt as an example, Eq. (3) can be expressed as Eqs. (4)–(6):

$$\sigma_{\text{RE}_2\text{O}_3\text{-MgO-SiO}_2} = \sigma_{\text{RE}_2\text{O}_3}^{\text{Pure}} + \frac{RT}{A_{\text{RE}_2\text{O}_3}} \ln \frac{M_{\text{RE}_2\text{O}_3}^{\text{Surf}}}{M_{\text{RE}_2\text{O}_3}^{\text{Bulk}}} \quad (4)$$

$$\sigma_{\text{RE}_2\text{O}_3\text{-MgO-SiO}_2} = \sigma_{\text{MgO}}^{\text{Pure}} + \frac{RT}{A_{\text{MgO}}} \ln \frac{M_{\text{MgO}}^{\text{Surf}}}{M_{\text{MgO}}^{\text{Bulk}}} \quad (5)$$

$$\sigma_{\text{RE}_2\text{O}_3\text{-MgO-SiO}_2} = \sigma_{\text{SiO}_2}^{\text{Pure}} + \frac{RT}{A_{\text{SiO}_2}} \ln \frac{M_{\text{SiO}_2}^{\text{Surf}}}{M_{\text{SiO}_2}^{\text{Bulk}}} \quad (6)$$

where

$$M_i^p = \left(\frac{r_A}{r_X} \cdot n_i^p \right) / \left(\frac{r_{\text{RE}^{3+}}}{r_{\text{O}^{2-}}} \cdot n_{\text{RE}_2\text{O}_3}^p + \frac{r_{\text{Mg}^{2+}}}{r_{\text{O}^{2-}}} \cdot n_{\text{MgO}}^p + \frac{r_{\text{Si}^{4+}}}{r_{\text{SiO}_4^{4-}}} \cdot n_{\text{SiO}_2}^p \right) \quad (7)$$

Subscript *i* refers to RE₂O₃, MgO or SiO₂, subscripts “A” and “X” refer to the cations and anions of component *i*, respectively, n_i^p is the mole fraction of the component *i* in phase *p* (*p*=Surf or Bulk), *r_A* is the radius of the cation, and *r_X* is the radius of the anion. For example:

$$r_A = r_{\text{Si}^{4+}}, r_{\text{Mg}^{2+}}, r_{\text{RE}^{3+}} \quad (8)$$

$$r_X = r_{\text{SiO}_4^{4-}}, r_{\text{O}^{2-}} \quad (9)$$

where $r_{\text{SiO}_4^-}$ is considered to be the minimum anionic unit in SiO_2 , and the value of $r_{\text{Si}^{4+}}/r_{\text{SiO}_4^-}$ was experimentally determined to be 0.5 [1].

Data on the ionic radii were obtained from SHANNON et al [15,16], and the molar volumes of the pure oxides recommended by MILLS and KEENE [17] were used in the present model. These values are listed in Tables 1 and 2, respectively. The temperature dependences of the surface tension for pure RE_2O_3 , MgO and SiO_2 were collected from Refs. [10,18,19], as listed in Table 3.

Table 1 Radii of cationic and anionic ions

Ion	Radius/nm	$\sigma_{\text{CFS}}/(10^{-2} \text{ nm}^{-2})$
La^{3+}	0.114	2.31
Nd^{3+}	0.104	2.77
Sm^{3+}	0.100	3
Gd^{3+}	0.097	3.19
Y^{3+}	0.092	3.54
Mg^{2+}	0.066	
Si^{4+}	0.042	
O^{2-}	0.144	

Table 2 Temperature dependence of molar volume of pure components

Component	Temperature dependence of molar volume/($\text{m}^3 \cdot \text{mol}^{-1}$)
La_2O_3	$50.1[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
Nd_2O_3	$46.62[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
Sm_2O_3	$47.93[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
Gd_2O_3	$49.09[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
Y_2O_3	$45.22[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
MgO	$16.1[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$
SiO_2	$27.516[1+1 \times 10^{-4} \cdot (T-1773)] \times 10^{-6}$

Table 3 Temperature dependence of surface tension of pure components

Component	Temperature dependence of surface tension/($\text{mN} \cdot \text{m}^{-1}$)	
	Literature	Present work
La_2O_3	560 (2573 K) [18]	686 (1873 K)
Nd_2O_3	–	677 (1873 K)
Sm_2O_3	815 (2593 K) [19]	–
Gd_2O_3	–	664 (1873 K)
Y_2O_3	–	541 (1873 K)
MgO	$1770-0.636 T$ (1573–1873 K) [10]	–
SiO_2	$243.2+0.031 T$ (1773–2073 K) [10]	–

2.3 Model establishing

Based on the above study, the sequence of the established thermodynamic model for predicting the surface tension is shown in Fig. 1. As shown in Fig. 1, the parameter T is the absolute temperature, and n_i are the mole fractions of three components as RE_2O_3 , MgO and SiO_2 of RE_2O_3 – MgO – SiO_2 melts to represent chemical composition of the slags. In addition, M_i^p represents the relation of mole fraction of components, that is Eq. (7). Parameters A_i and σ_i^{Pure} used in the calculation are listed in Tables 2 and 3.

Figure 1 shows the sequences that M_i^{Bulk} can be calculated by mole fractions (or mass fraction) of components and Eq. (7). Further, σ and M_i^{Surf} can be calculated by M_i^{Bulk} , σ_i^{Pure} and A_i based on Eq. (7) and the Butler's equation.

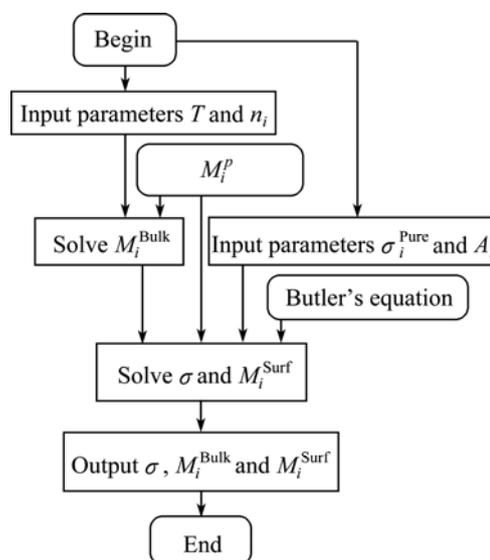


Fig. 1 Sequence of model for estimation of surface tension

The model stated above can be extended to multi-component slag systems, so long as the bulk phase and the surface phase both obey Eq. (7). Sample calculations have been made for ternary RE_2O_3 – MgO – SiO_2 slag melts.

3 Results and discussion

At a certain temperature, the calculation could be carried out with certain slag components. After linearization, Newton iterative method was used in Matlab software to gain all the surface tension of RE_2O_3 – MgO – SiO_2 slag melts.

3.1 Evaluating surface tension of RE_2O_3 at 1873 K

Since this calculating model has been verified in a lot of ternary molten slags, which includes not only such oxides as SiO_2 , Al_2O_3 , CaO , FeO , MgO and MnO , but

also surface-active components such as Na_2O , B_2O_3 and CaF_2 , the surface tensions of RE_2O_3 ($\text{RE}=\text{Y}$, Gd , Nd and La) at 1873 K are derived based on this calculating model and the surface tension of three different compositions of $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ slag melts [3] at 1873 K. The surface tensions of Y_2O_3 , Nd_2O_3 , Gd_2O_3 and La_2O_3 are 541, 664, 677 and 686 mN/m , respectively, as shown in Table 3 and Fig. 2. In Fig. 2, the surface tensions of pure RE_2O_3 melts at 1873 K are plotted as a function of the cationic field strength of RE^{3+} . Figure 2 obviously reveals that the surface tension of pure rare earth oxide melts linearly decreases with increasing cationic field strength, except Y_2O_3 oxides, while Y_2O_3 has a much weaker surface tension. The surface tensions obviously increase in the order of cationic radius of rare-earth (Table 3) from Y_2O_3 , Gd_2O_3 , and Nd_2O_3 to La_2O_3 . Figure 3 shows the temperature dependences of the surface tension of pure RE_2O_3 melts.

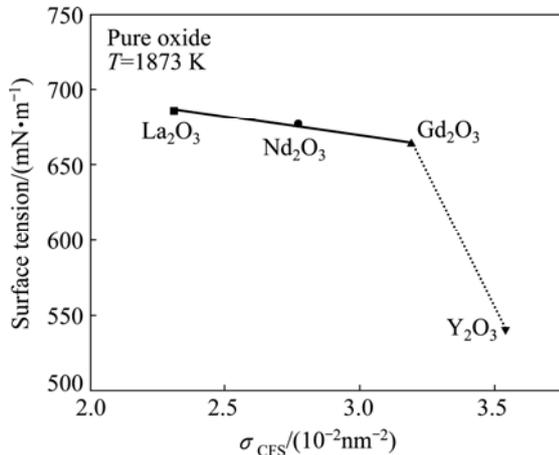


Fig. 2 Surface tension of pure RE_2O_3 melts at 1873 K

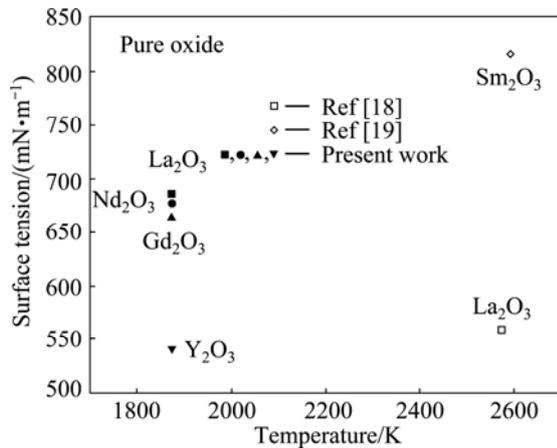


Fig. 3 Temperature dependences of surface tension of pure RE_2O_3 melts

LOFAJ et al [4,5] investigated the structure and physical properties (hardness, glass transition temperature and density) of Me-Mg-Si-O-N ($\text{Me}=\text{Sc}$, Lu , Yb , Y , Sm and La) oxynitride glasses and reported

that these properties varied linearly with radius of the Me^{3+} cation, moreover, depending on whether Me^{3+} belongs to the 3rd group (Sc and Y) of the periodic table of elements or the lanthanides, there were two distinct correlations. They have estimated that the deviations of physical properties from linearity were basically attributed to the considerable difference of atomic mass between lanthanide and non-lanthanide elements. However, in the present work, it is questionable whether the atomic mass will affect the surface tension of elevated temperature melts. This is experimentally evident that not only the cation size by itself but also the electronic structure of RE^{3+} cation has an influence on physical properties of high temperature melt. Furthermore, it is probable that the rare-earth oxide melts have a quite different microstructure in bulk and at surface.

3.2 Model evaluation

In order to evaluate the performance of the present model, the mean deviation is defined as

$$\bar{\sigma} = \frac{1}{N} \sum_{i=1}^N \left| \frac{\sigma_{\text{Calc}} - \sigma_{\text{Expe}}}{\sigma_{\text{Expe}}} \right| \times 100\% \quad (10)$$

where $\bar{\sigma}$ is the mean deviation, σ_{Calc} and σ_{Expe} [3] are the calculated and measured surface tensions, respectively, and N represents the number of the samples.

The surface tension data of melts of three different compositions in the system $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ ($\text{RE}=\text{La}$, Nd , Gd and Y) were measured in the early publication [3], which has been well represented by the present model. The comparison of the results between estimated surface tension data and the experimental surface tension data is shown in Fig. 4 and Table 4. The mean deviation computed by Eq. (10) is found to be

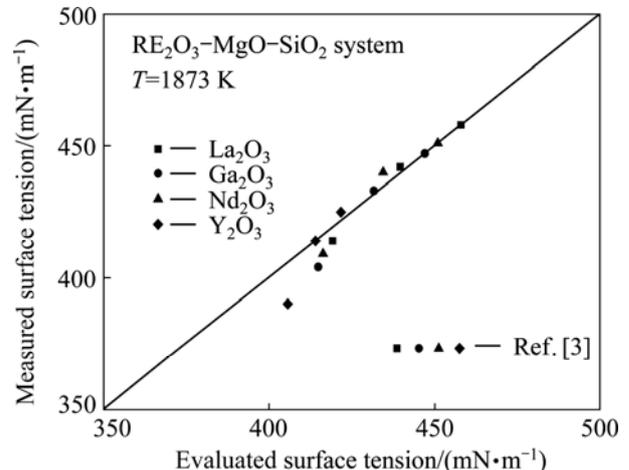


Fig. 4 Comparison of evaluated and measured surface tension for $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ system

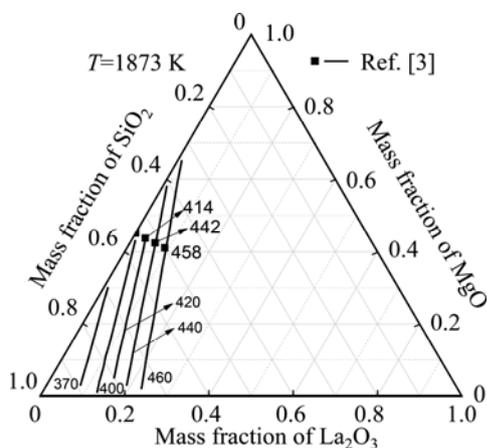
Table 4 Comparison of evaluated and measured surface tensions for RE₂O₃–MgO–SiO₂ system

Component	Surface tension of RE ₂ O ₃ –MgO–SiO ₂ system/(mN·m ⁻¹)	
	Measured [3]	Evaluated
La ₂ O ₃	414	419.2
	442	439.6
	458	458
Gd ₂ O ₃	404	414.8
	433	431.7
	447	447
Nd ₂ O ₃	409	416.3
	440	464.5
	451	451
Y ₂ O ₃	390	405.6
	414	414
	425	421.7

1.05% at 1873 K. Therefore, the present model provides a basal description of the surface tension variation of the RE₂O₃–MgO–SiO₂ system with regard to temperature and composition.

3.3 Model application

The calculated results for the iso-surface tension of the La₂O₃–MgO–SiO₂ system at 1873 K are shown in Fig. 5. These results are in good agreements with the literature values [3]. The iso-surface tension curves in Fig. 5, calculated using the current model, reproduce the composition dependence of surface tension for the La₂O₃–MgO–SiO₂ system, and show that its surface tension increases with the increase of La₂O₃ content and MgO content and decreases as SiO₂ content increases.

**Fig. 5** Calculated iso-surface tension lines of La₂O₃–MgO–SiO₂ system at 1873 K

4 Conclusions

1) Based on the ionic radii of the components and Butler's equation, a calculating model is developed for determining the surface tension of RE₂O₃–MgO–SiO₂ molten slags.

2) The surface tensions of La₂O₃, Gd₂O₃, Nd₂O₃ and Y₂O₃ at 1873 K are evaluated as 686, 677, 664 and 541 mN/m, respectively. The surface tension of pure rare earth oxide melts linearly decreases with increasing cationic field strength, except Y₂O₃ oxides, which has a much weaker surface tension.

3) The evaluated results for the surface tension from the present model show good agreements with literature values in RE₂O₃–MgO–SiO₂ ternary system. The mean deviation of the present model is found to be 1.05% at 1873 K.

4) The iso-surface tension lines of La₂O₃–MgO–SiO₂ slag melt are calculated. Surface tension of La₂O₃–MgO–SiO₂ slag decreases with increasing SiO₂ content and increases with increasing La₂O₃ content and MgO content.

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$\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ (RE=La, Nd, Sm, Gd 和 Y) 熔体表面张力的计算模型

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摘要: 基于熔体组元离子半径和 Butler 方程, 建立 $\text{RE}_2\text{O}_3\text{-MgO-SiO}_2$ (RE=La, Nd, Sm, Gd 和 Y) 熔体表面张力热力学计算模型。本模型利用纯组元的表面张力和摩尔体积以及熔体中各组元阳离子和阴离子半径可以获得 $\text{E}_2\text{O}_3\text{-MgO-SiO}_2$ 熔体表面张力随熔渣成分和温度的变化规律。计算 1873 K $\text{La}_2\text{O}_3\text{-MgO-SiO}_2$ 熔体等表面张力线并研究熔体成分对表面张力的影响。1873 K 的纯组元 La_2O_3 , Gd_2O_3 , Nd_2O_3 和 Y_2O_3 的表面张力通过本模型计算分别为 686、677、664 和 541 mN/m。除了 Y_2O_3 外, 纯稀土氧化物的表面张力随其阳离子磁场强度增加而呈线性减小, 而 Y_2O_3 的表面张力相对减小更多。表面张力的计算结果与文献数据一致, 1873 K 本模型平均偏差为 1.05%。

关键词: 稀土氧化物; 表面张力; 离子半径; Butler 方程; 计算模型

(Edited by Yun-bin HE)