Analysis on elemental volatilization behavior of titanium alloys during electron beam smelting

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ABSTRACT

Electron beam smelting is an effective technology for removal of inclusions from titanium alloys and improvement of metallurgical quality. However, since different element has different volatilization capacity, resulting in a large deviation in alloy composition, which affects the performance of titanium alloys. In this paper, the volatility trend of the components in a Ti-Al-Cr-Nb quaternary model alloy was evaluated and a calculation model for alloy composition change was established based on Langmuir's volatilization rate theory. The results show that, for the other three elements in the alloy, the order of relative volatility coefficient is Al > Cr > Nb. The mass fraction of Al in the alloy will be significantly reduced after smelting, which plays an important role in control of alloy composition. The effect of temperature on the change of alloy composition is greater than that of smelting time. When the temperature is over 2100 K, the composition changes too much in a very short time. The experimental results are consistent with the theoretical results, indicating the applicability of the model.

1. Introduction

Titanium alloys are widely used in aerospace, military and other fields, due to its low density, high specific strength and excellent performance at high temperature [1–4]. Especially, aviation industry has an extremely high demand for materials performance, which depends on the metallurgical quality of titanium alloys. The previous researches show that the purity of alloys has a great impact on their final performance [5,6]. However, the current preparation technology for titanium alloys can't meet the requirements for purity. In order to further improve the performance of titanium alloys, expand the service temperature and application area, it is necessary to develop an effective smelting technology for purification. The traditional vacuum arc remelting technology can't guarantee the complete elimination of metallurgical defects such as inclusions and segregation to obtain high-quality and clean titanium alloys ingot [7]. Electron beam smelting technology has the advantages of high energy density, high vacuum and good controllability, which can greatly improve the purity of titanium alloys [8]. Therefore, it is often used to prepare titanium alloys and improve its metallurgical quality.

The key of titanium alloys refining by electron beam smelting is to remove low-density and high-density inclusions, control volatile elements and ingot microstructure [9–13]. A lot of work has been done in these areas. Han et al. [14] studied the removal mechanism of low-density and high-density inclusions by adding specific inclusion particles to clean titanium alloys, and observed the microstructures of ingots with different melting time. Akhoninz et al. [15] studied the volatilization rate of Al in titanium alloys so that Al content can be controlled accurately. However, titanium alloys are complex systems composed of various elements, and different components in the system have different vapor pressure, as well as the volatilization capacity under high vacuum. Such behavior results in a large deviation in alloy composition, which affects the performance of titanium alloys. Therefore, it is a common problem to investigate and control the volatilization behavior of elements in titanium alloys during electron beam smelting.

In this study, from the perspective of element volatilization thermodynamics, the volatile coefficient of each element is obtained based on thermodynamics parameters, such as saturated vapor pressure and activity coefficient, in order to analyze their volatility. On this basis, Langmuir theory is used to calculate the volatilization rate of each element to investigate the influence of smelting parameters such as temperature and time on composition change. The volatilization rate of each element was obtained through the electron beam smelting experiments under different temperatures. The experiment values are compared with the theoretical values to obtain element volatilization regularity, which will provide a theoretical basis for precise control of

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Table 1
Parameters for Ti, Al, Cr and Nb used in Clausius-Clapeyron equation.

Element	A	B	C × 10^3	D	T/K
Ti	− 23200	− 0.66	–	13.865	1943–3562
Al	− 16380	− 1	–	14.445	933–2793
Cr	− 20680	− 1.31	–	16.685	2163–2945
Nb	− 37650	0.715	− 0.166	11.065	298–2741

the composition in multi-element alloy.

2. Elemental volatilization thermodynamics in multi-element alloy

Electron beam smelting is carried out in a high vacuum environment, and in such conditions volatile impurity can be removed effectively by evaporation. However, different elements show different degrees of volatilization. Firstly, from the view of thermodynamic, the elemental volatility was analyzed.

Under high temperature and high vacuum conditions, the volatilization of the element with high saturated vapor pressure is greater than that with low saturated vapor pressure, which is the theoretical basis for purification by vacuum evaporation [16,17]. The saturated vapor pressure of pure element p_i^0 (Pa) is only a function of temperature, which can be described by Clausius - Clapeyron equation:

$$\log p_i^0 = \frac{A}{T} + B\log T + CT + D \tag{1}$$

where T (K) is the absolute temperature; A, B, C and D are constants associated with the evaporation species which can be found in the thermodynamics handbook [18]. Table 1 shows the parameter values corresponding to the saturated vapor pressures of Ti, Al, Cr and Nb in pure matter. According to Eq. (1), the saturated vapor pressure can be calculated as a function of temperature, as shown in Fig. 1. The saturated vapor pressure of the four elements increases with the increase of temperature in the range of 1700–2500 K. The value of Al is the largest, which illustrates Al has the strongest volatility.

Under high temperature and high vacuum conditions, alloying elements can evaporate from the melt surface. Due to the different evaporation capacities, the composition of the elements entering the gas phase is different from that of the original liquid phase, resulting in the change of the liquid composition. Therefore, it is impossible to evaluate the volatility trend of the components independently from
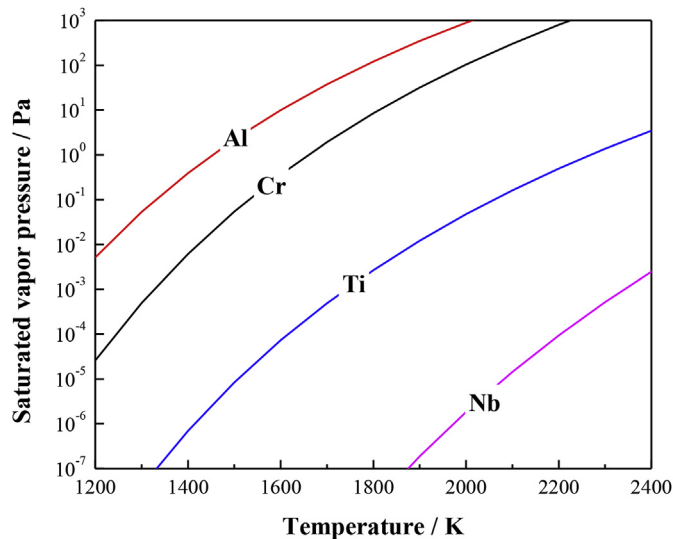

Fig. 1. Saturated vapor pressure of pure Ti, Al, Cr and Nb as a function of temperature.

their saturated vapor pressure. Then the relative volatility coefficient β is used to evaluate the volatile trend of alloying elements, which is expressed by the following equation [19]:

$$\beta = \frac{\gamma_i p_i^0}{\gamma_j p_j^0} \tag{2}$$

where γ_i and γ_j are activity coefficient of component i and j, respectively; p_i^0 (Pa) and p_j^0 (Pa) are saturated vapor pressure of component i and j in pure state.

There are three cases when β is used as a criterion to evaluate the volatile trend: (1) if $\beta = 1$, two components in the melt volatilize simultaneously, and the composition doesn't change after smelting; (2) if $\beta > 1$, the mass fraction of the component i in the melt is less than that in the vapor, which means the total volatilization of the component i is greater than that of the component j, resulting in the change of alloy composition; (3) if $\beta < 1$, the component j in the melt volatilizes more than component i, also resulting in the change of alloy composition.

For the above equation, the value of saturated vapor pressure can be obtained according to Eq. (1) using the parameters given in Table 1. There are two methods to obtain the activity coefficient of components in the melt: experimental measurement and thermodynamics calculation. For high active melt such as titanium alloys, it is very difficult to measure the activity coefficient experimentally. Generally, it can be obtained by theoretically predictions, using some empirical or semi-empirical models.

In this paper, we got the aid of a semi-empirical model which is called Miedema binary solution model to obtain the heat generation of binary alloy systems [20]. The binary calculation results were used to obtain the activity coefficient of the ternary alloy systems. Finally, two ternary alloy systems are combined to get the activity coefficient of the quaternary alloy.

In i-j binary alloy system, the relationship among the excess free energy G_{ij}^E (J/mol), the excess entropy S_{ij}^E (J/mol (J/mol·K)K) and the enthalpy change ΔH_{ij} (J/mol) is:

$$G_{ij}^E = \Delta H_{ij} - TS_{ij}^E \tag{3}$$

A high satisfactory equation relating S_{ij}^E and ΔH_{ij} in liquid binary system has been obtained by Gokcen [21], based on the free volume theory considering excess volumes of the alloys, as follows:

$$S_{ij}^E = 0.1 \times \Delta H_{ij} \left[\frac{T_{m_i} + T_{m_j}}{T_{m_i} \cdot T_{m_j}} \right] \tag{4}$$

where T_{mi} (K) and T_{mj} (K) are the melting point for the pure elements i and j. Therefore, if:

$$\alpha_{ij} = 1 - 0.1T \left(\frac{T_{m_i} + T_{m_j}}{T_{m_i} \cdot T_{m_j}} \right) \tag{5}$$

Then:

$$G_{ij}^E = \alpha_{ij}\Delta H_{ij} \tag{6}$$

As for a ternary system, the excess Gibbs energy can be expressed for the general case as:

$$G^E = G_{ij}^E + G_{jk}^E + G_{ik}^E + x_i x_j x_k (\alpha_1 x_i + \alpha_2 x_j + \alpha_3 x_k) \tag{7}$$

where x_i, x_j, and x_k denote the mole fractions of components in the melt, α_1, α_2, and α_3 are interaction parameters for the ternary solution. In view of the typical absence of experimental information on the thermodynamic properties of ternary solutions, the corresponding interaction parameters are usually put to zero, and the extra terms are omitted in Eq. (7)

In turn, the partial excess Gibbs energy $\overline{G_i^E}$, $\overline{G_j^E}$ and $\overline{G_k^E}$ are related to the integral thermodynamic functions, which are as follows: