[Article ID] 1003- 6326(2002)02- 0222- 05

Change law of real vapor pressure of Al element in Ti-xAl (x = 25~ 50) melt during ISM process①

LIU Gui-zhong(刘贵仲), SU Yan-qing(苏彦庆), GUO Jing-jie(郭景杰),
DING Hong-sheng(丁宏升), JIA Jun(贾 均), FU Heng-zhi(傅恒志)
(School of Materials Science and Engineering, Harbin Institute of Technology,
Harbin 150001, China)

[Abstract] A new model was established to calculate the real vapor pressure of the Al element in the molten Ti-xAl (x = 25~ 50, mole fraction, %) alloy. The effects of the holding time, chamber pressure, mole fraction of Al and melting temperature on the real vapor pressure of Al element in the vacuum chamber were analyzed. Because of the impeding effect of the real vapor pressure on the evaporation loss rate, within a short time (less than 10 s), the real vapor pressure tends to a constant value. When the chamber pressure is less than the saturated vapor pressure of the Al component, the real vapor pressure of Al is equal to the chamber pressure. While when the chamber pressure is larger than the saturated vapor pressure, the real vapor pressure is equal to the saturated vapor pressure of the Al element of the same condition.

[Key words] real vapor pressure; Al element; ISM process; Ti-xAl melt

[CLC number] TG 248 **[Document code]** A

1 INTRODUCTION

Titanium alloy have been widely studied in recent years for its high thermal stability and good creep-resistance[1~ 4]. In vacuum melting process of TiAl alloys, because of the high temperature of the melt and the high vacuum degree in the vacuum chamber, the evaporation loss of the volatile element is very serious. For instance, the evaporation loss of Al element in the TiAl melt can arrive up to 10% ~ 15% (mole fraction) by electron beam melting (EBM) process[5]. Undoubtedly, the large quantity of evaporation loss will cause serious influence on the strength and ductility of the gamma TiAl alloy that is very sensitive to its composition. The notable effect of the real vapor pressure of the volatile element in a molten alloy on its evaporation loss has been noticed by some metallurgists[6~ 8] as follows:

$$N = K_{\mathrm{L}}\varepsilon(p_i^e - p_{g(i)})\sqrt{M_i/T_{\mathrm{ms}}} \qquad (1)$$

where N is the evaporation rate, g•cm^{-2}•s^{-1}; K_{L} is the Langmiure constant and equal to 4.37×10^{-4}; ε is 1; p_i^e is the saturated vapor pressure of the component i in a melt, Pa; $p_{g(i)}$ is the real vapor pressure of the component i, Pa; M_i is the atomic weight of i; T_{ms} is the melt temperature on the melt surface. However, they did not give any way to calculate $p_{g(i)}$. In our practice of melting some reactive alloy via vacuum Induction Skull Melting (ISM)[9~ 12], we find that the effect of $p_{g(i)}$ on the evaporation loss rate is obvious. In this paper, a new model was established to theoretically calculate the real pressures of the volatile elements.

2 THEORY MODEL

The schematic diagram of ISM furnace is shown in Fig. 1.

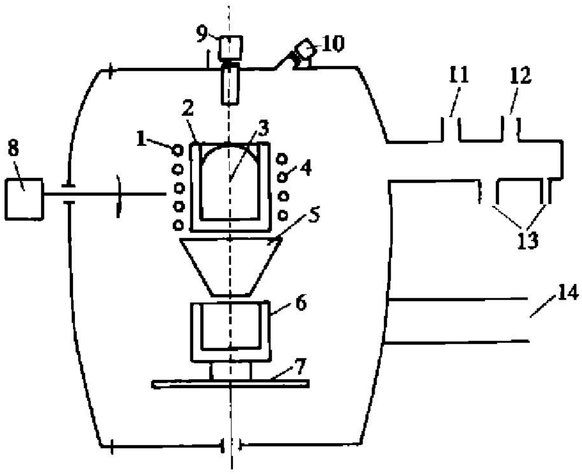

Fig. 1 Schematic diagram of ISM furnace
1 —Induction coil; 2 —Water-cooling copper crucible;
3 —Melt; 4 —Skull; 5 —Tundish; 6 —Permanent mold;
7 —Centrifugal pouring dish; 8 —Tilting facility;
9 —Optical pyrometer; 10 —Pick-up camera;
11 —Inlet of iner; 12 —Inlet of air; 13 —Vacuometer interface;
14 —Attach to vacuum pump system

Fig. 2 shows the schematic of this theoretic model based on the ISM melting process. In Fig. 1, Δn_i^t and $\Delta n_i^{t+\mathrm{d}t}$ are the mole numbers of the component i entering the vacuum chamber via evaporating within

---

① **[Foundation item]** Project (G2000067202- 2) supported by the National Key Fundamental Research and Development Program

[Received date] 2001- 06- 25; **[Accepted date]** 2001- 11- 19

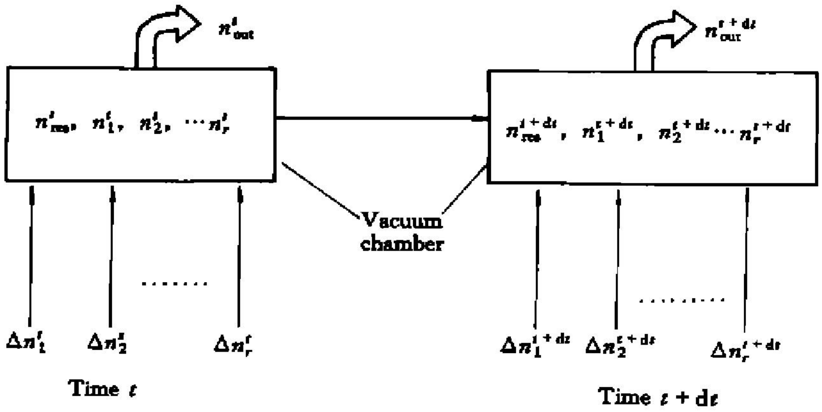

Fig. 2 Schematic diagram of mole number of gases in vacuum chamber

dt from time t to $t+$ dt and from time $t+$ dt to $t+$ 2dt respectively; n^t_i and $n^{t+\mathrm{d}t}_i$ are the mole numbers of the component i in the vacuum chamber at time t and time $t+$ dt. n^t_{res} and $n^{t+\mathrm{d}t}_{\mathrm{res}}$ represent the mole numbers of residual gas in the vacuum chamber at time t and time $t+$ dt. n^t_{out} and $n^{t+\mathrm{d}t}_{\mathrm{out}}$ are the mole numbers of gas pumped out off the vacuum chamber and condensed on the surface of the wall of the vacuum chamber within dt from time t to $t+$ dt and from time $t+$ dt to $t+$ 2dt respectively. r is the number of evaporation components in the molten alloy.

To the calculation model, there are three hypotheses:

1) The gas in the vacuum chamber follows the ideal gas law.

2) The whole pressure, p, in the vacuum chamber always keeps as a constant value, namely $\sum_{i=1}^{r}\Delta n^t_i = n^t_{\mathrm{out}}$ and $\sum_{i=1}^{r}\Delta n^{t+\mathrm{d}t}_i = n^{t+\mathrm{d}t}_{\mathrm{out}}$.

3) Within a very short time step $(t \to t+\mathrm{d}t)$, $\Delta n^t_{\mathrm{out}(i)} \propto n^t_i$, $\Delta n^t_{\mathrm{out(res)}} \propto n^t_{\mathrm{res}}$.

Just as mentioned in hypothesis 1) and 2), the whole pressure (p) in the vacuum chamber (hereinafter is called as chamber pressure) is always kept as a constant value, then

$$\sum_{i=1}^{r} n^t_i + n^t_{\mathrm{res}} = \sum_{i=1}^{r} n^{t+\mathrm{d}t}_i + n^{t+\mathrm{d}t}_{\mathrm{res}} = \frac{pV}{RT'} \tag{2}$$

where V is the effective volume of the vacuum chamber (occupied by gases), T' is the temperature of the gas in the vacuum chamber, generally 310 K, R is the gas constant. According to hypothesis 3), the mole number of the component i pumped out off the vacuum chamber within dt (from time t to $t+$ dt) can be given by

$$n^t_{\mathrm{out}(i)} = n^t_{\mathrm{out}} \frac{n^t_i}{\sum_{i=1}^{r} n^t_i + n^t_{\mathrm{res}}} \tag{3}$$

Then, the mole number of the component i in the vacuum chamber at time $t+$ dt is

$$n^{t+\mathrm{d}t}_i = (n^t_i + \Delta n^t_i) - n^t_{\mathrm{out}(i)} \tag{4}$$

Substitute Eqn. (3) into Eqn. (4), then

$$n^{t+\mathrm{d}t}_i = (n^t_i + \Delta n^t_i) - \left(\sum_{i=1}^{r}\Delta n^t_i\right)\frac{n^t_i}{\sum_{i=1}^{r} n^t_i + n^t_{\mathrm{res}}} \tag{5}$$

And the real pressure $(p^{t+\mathrm{d}t}_{\mathrm{g}(i)})$ of the component i in the vacuum chamber at time $t+$ dt is

$$p^{t+\mathrm{d}t}_{\mathrm{g}(i)} = \frac{n^{t+\mathrm{d}t}_i}{\sum_{i=1}^{r} n^{t+\mathrm{d}t}_i + n^{t+\mathrm{d}t}_{\mathrm{res}}} \cdot p \tag{6}$$

Substitute Eqn. (5) and Eqn. (2) into Eqn. (6), then

$$p^{t+\mathrm{d}t}_{\mathrm{g}(i)} = \frac{RT'(n^t_i + \Delta n^t_i)}{V} - \frac{R^2T'^2 n^t_i\left(\sum_{i=1}^{r}\Delta n^t_i\right)}{pV^2} \tag{7}$$

If the evaporation loss rate of the component i, that is N^t_i (g·cm^{-2}·s^{-1}), can be given out, then Δn^t_i can be given as the following:

$$\Delta n^t_i = \frac{N^t_i S \cdot \mathrm{d}t}{M_i} \tag{8}$$

where S is the area of the evaporation surface (cm^2). Substitute Eqn. (8) into Eqn. (7), we get

$$p^{t+\mathrm{d}t}_{\mathrm{g}(i)} = \frac{RT'(n^t_i M_i + N^t_i S \cdot \mathrm{d}t)}{VM_i} - \frac{R^2T'^2 n^t_i\left(\sum_{i=1}^{r}\frac{N^t_i S \cdot \mathrm{d}t}{Mi}\right)}{pV^2} \tag{9}$$

Ref. [12] gives the method to calculate the evaporation loss rate.

From Eqn. (9), it can be seen that $p^{t+\mathrm{d}t}_{\mathrm{g}(i)}$ depends on the chamber pressure p, evaporation loss rate N^t_i and holding time. The evaporation loss rate N^t_i is mainly controlled by the melting temperature T, chamber pressure and the mole fraction of the volatile component in the molten alloy[13]. The detailed discussion of the evaporation loss rate N_i^t has been carried out in Ref. [12].

In this paper, the calculating time is 300 s; evaporation surface is 113 cm^2; volume of vacuum chamber is 3 m^3; charge mass is 5 kg. All the calculation results are based on the hypothesis that the calculation begins when the solid alloy is completely melted, and during the holding time the composition of the melt is homogeneous.

3 RESULTS AND DISCUSSION

Fig. 3 shows the relationship between the real vapor pressure of Al in the Ti-50Al (mole fraction, %) melt (this pressure is hereinafter called $p_{g(Al)}$) and the holding time.

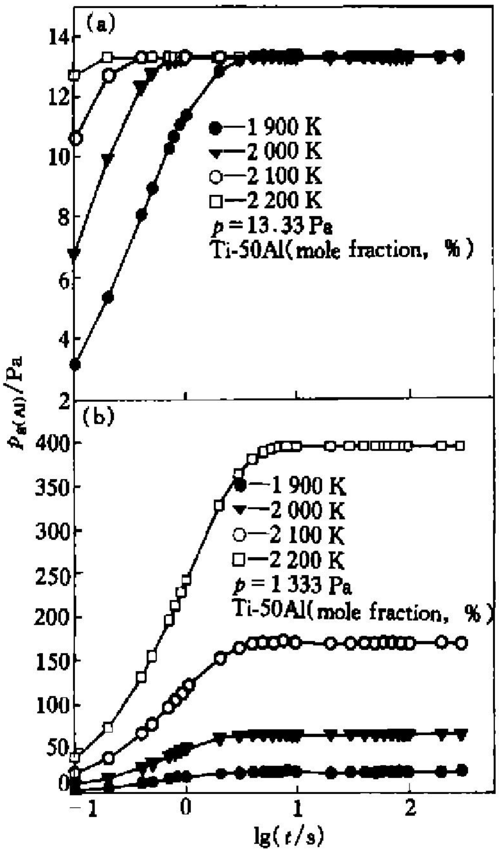

Fig. 3 Relationship between $p_{g(Al)}$ and holding time

From Fig. 3, it can be seen that within a short time (less than 10 s), $p_{g(Al)}$ tends to a constant value. In Fig. 3(a), when holding time is larger than 10 s, $p_{g(Al)}$ is equal to the chamber pressure. This is the reason that when the melt temperature is equal to or larger than 1 900 K, the saturated vapor pressure of the Al element (which will be called as p^e_{Al}) in the Ti-50Al (mole fraction, %) is larger than the chamber pressure (13.33 Pa). From Eqn. (1) and hypothesis 2 (chamber pressure is a constant), $p_{g(Al)}$ is equal to the chamber pressure and the evaporation of Al will continue with the increase of the holding time. However, in Fig. 3(b), p^e_{Al} is less than the chamber pressure (13.33 Pa). With increasing the holding time, $p_{g(Al)}$ increases until equal to p^e_{Al} of the same temperature. From Eqn. (1), the evaporation rate of Al element is zero and $p_{g(Al)}$ is equal to a constant.

Fig. 4 shows the relationship between $p_{g(Al)}$ and p at different melting temperatures and the mole fraction of Al element.

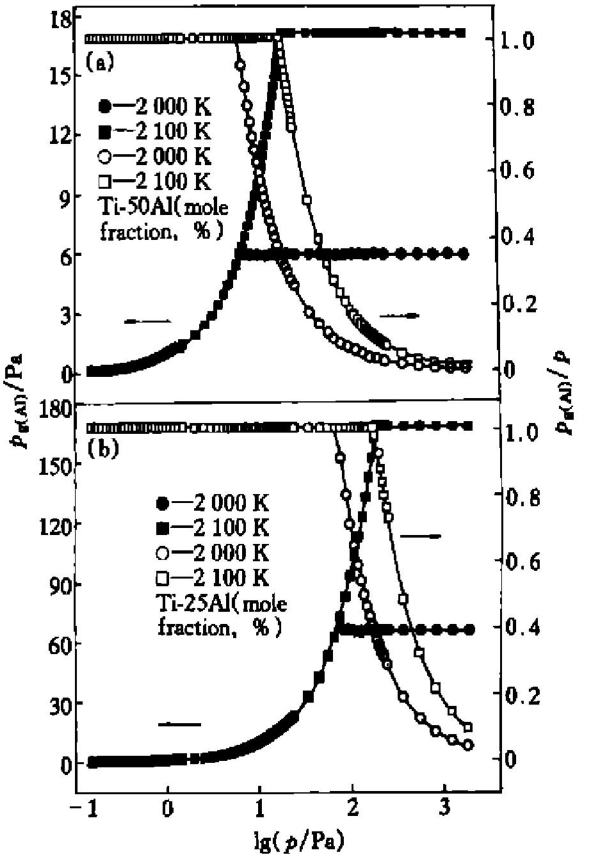

Fig. 4 Relationship between $p_{g(Al)}$ and p at different melting temperatures and mole fraction of Al

From Fig. 4, it can be seen that $p_{g(Al)}$ increases and tends to a constant with increasing p. In fact, it is obvious that this constant is p^e_{Al} of the same melt temperature. Before $p_{g(Al)}$ is equal to the constant, $p_{g(Al)}/p = 1$. Undoubtedly, after $p_{g(Al)}$ is equal to the constant, $p_{g(Al)}/p < 1$ and decreases with increasing p. In Fig. 4, if p is less than p^e_{Al}, $p_{g(Al)}$ is equal to p. Otherwise, if p is larger than p^e_{Al}, $p_{g(Al)}$ is equal to p^e_{Al}.

Fig. 5 gives the relationship between $p_{g(Al)}$ and the mole fraction of Al in the molten alloy. When p is larger (for example 1 333 Pa), $p_{g(Al)}$ increases with the increase of the mole fraction of Al, which is shown in Fig. 5(b). In Fig. 5(a), when the melt temperature is 2 100 K, p^e_{Al} of the Al element in molten Ti-xAl (x = 25% ~ 50%, mole fraction) is always beyond 13.33 Pa and p^e_{Al} is equal to p (13.33 Pa). However, if the melt temperature is

1900K, when mole fraction of Al element is less than 0.44, $p^e_{\mathrm{Al}} < p$ and $p_{\mathrm{g(Al)}}$ is equal to p^e_{Al}. If the mole fraction of Al element is bigger than 0.44, p^e_{Al} is larger than p and $p_{\mathrm{g(Al)}}$ is equal to the chamber pressure p. From Fig. 5, it can be seen that $p_{\mathrm{g(Al)}}$ is more liable to tending to its constant value at the high melting temperature and the bigger mole fraction of Al component.

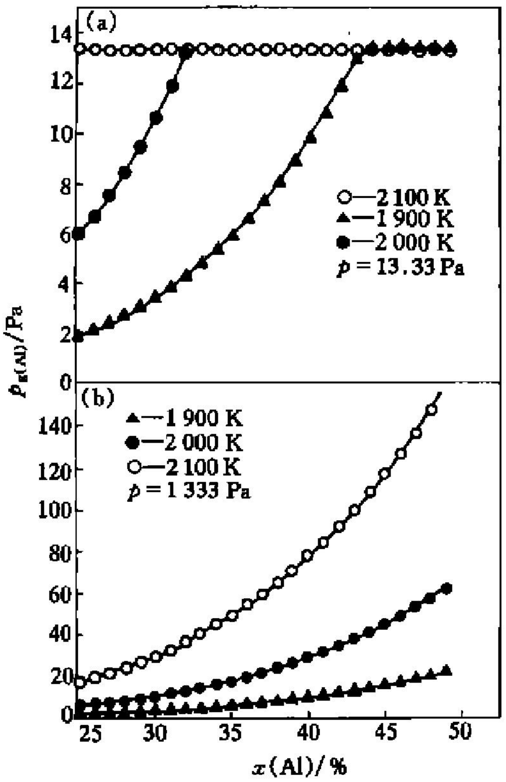

Fig. 5 Relationship between $p_{\mathrm{g(Al)}}$ and mole fraction of Al in melt

The relationship between $p_{\mathrm{g(Al)}}$ and the melting temperature is shown in Fig. 6. When p is larger, that is 1333Pa, $p_{\mathrm{g(Al)}}$ increases with increasing the melting temperature, which is shown in Fig. 6(b). However, when p is smaller, such as 13.33Pa, the effect of the melting temperature on $p_{\mathrm{g(Al)}}$ is complex with different contents of Al component in the melt, as shown in Fig. 6(a). In molten Ti-50Al (mole fraction, %), within the temperature range of 1900K to 2200K, p^e_{Al} is always larger than p, so that $p_{\mathrm{g(Al)}}$ is equal to p. In Ti-25Al (mole fraction, %) melt, $p_{\mathrm{g(Al)}}$ increases with increasing the melting temperature when the temperature is below 2075K. But when the melt temperature is larger than 2075K, $p_{\mathrm{g(Al)}}$ tends to 13.33Pa as that of the Ti-50Al (mole fraction, %) melt.

A melting practices for the Ti-34% Al (mass fraction) alloy has been developed with the process conditions: melting power of 300kW, charge mass of 3kg, vacuum pressure of p = 1.33Pa, the melt temperature is about 1950K. The initial Al content of 3kg charges is 1020g. After the melting process, the evaporation loss of Al is 39.61g as listed in Table 1. Utilizing Eqn. (1), the theoretical calculation values of Al evaporation at the condition of the real vapor pressure is equal to zero and not equal to zero are all listed in Table 1. From Table 1, it can be seen that the effect of $p_{\mathrm{g(Al)}}$ on the evaporation loss is obvious.

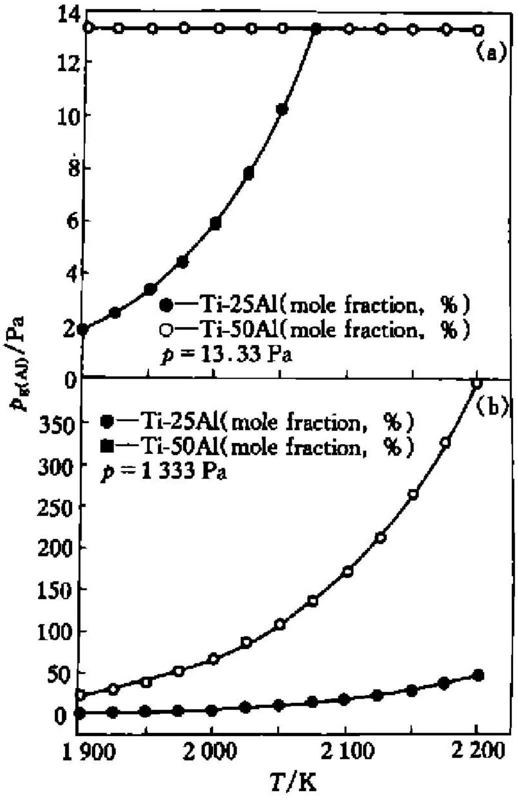

Fig. 6 Relationship between $p_{\mathrm{g(Al)}}$ and melting temperature at different p

Table 1 Theoretical and experimental evaporation loss of Al (g)

Experimental loss of Al	Theoretical evaporation loss of Al	
	$p_{\mathrm{g(Al)}} \neq 0$	$p_{\mathrm{g(Al)}} = 0$
39.61	43.03	55.13

4 CONCLUSIONS

1) Based on three hypotheses, a model to calculate the real vapor pressure of the volatile elements in a molten alloy is established and the equation represented the real vapor pressure is deduced.

2) Within a short time step (less than 10s), $p_{\mathrm{g(Al)}}$ of the Al element in the melt arrives at a constant. This constant is the chamber pressure when the chamber pressure is 13.33Pa. When the chamber pressure is 1333Pa, the constant is equal to p^e_{Al} of the same condition.

3) If p is larger than p^e_{Al}, with the increment of the mole fraction of the Al element or the melt temperature, $p_{\mathrm{g(Al)}}$ increases and is equal to p^e_{Al} of the

same condition. If p is less than p^{e}_{Al}, $p_{\mathrm{g(Al)}}$ is a constant and equal to p.

[REFERENCES]

[1] Anderson C D, Hofmeister W H, Bayuzick R J. Solidification kinetics and metastable phase formation in binary Ti-Al [J]. Metallurgical and Materials Transactions, 1992, 23A: 2699- 2709.

[2] Powell A, van Den Avyle J, Damkroger B, at el. Analysis of multicomponent evaporation in electron beam melting and refining of titanium alloys [J]. Metallurgical and Materials Transactions, 1997, 28B: 1227- 1240.

[3] HUANG Bai-yun, HE Yue-hui, WANG Jian-nong. Improvement in mechanical and oxidation properties of TiAl alloy with Sb addition [J]. Intermetallics, 1999, 7(8): 881- 887.

[4] HUANG Bai-yun, HE Yue-hui. Grain refined TiAl alloy by rapid deformation [J]. Materials Science& Engineering, 1997, 240A: 709- 717.

[5] Sakamoto K, Yoshikawa K, Kusamichi T, et al. Change in oxygen contents of titanium aluminides by vacuum induction cold crucible induction and electron beam melting [J]. ISIJ International, 1992, 32(4): 616- 629.

[6] DAI Yong-nian. Vacuum Metallurgy of Nonferrous Metals [M], (in Chinese). Beijing: Metallurgical Industry Press, 1998. 314- 316

[7] Ozberk E, Guthrie R I L. A kinetic model for the vacuum refining of inductively stirring copper melts [J]. Metall Trans, 1986, 17B(3): 87- 101.

[8] KANG Xian-deng. Vacuum Metallurgy [M], (in Chinese). Shanghai: Shanghai Science and Technology Press, 1980. 216- 219

[9] GUO Jing-jie, SHEN Wen-bin, SU Yan-qing, et al. Analysis of overflow critical value for TiAl based alloy during the process of centrifugal casting [J]. Trans Nonferrous Met Soc China, 1999, 9(2): 207- 212.

[10] GUO Jing-jie, LIU Yuan, SU Yan-qing. Evaporation behavior of components in Ti-15-3 melt during ISM process [J]. Trans Nonferrous Met Soc China, 1998, 8(4): 539- 543.

[11] GUO Jing-jie, SU Yan-qing, JIA Jun. A mould materials used for TiAl alloy calcai [J]. Trans Nonferrous Met Soc China, 1998, 8(2): 216- 220.

[12] GUO Jing-jie, LIU Yuan, SU Yan-qing, et al. Evaporation behavior of aluminium during the cold crucible induction skull melting of titanium alloys [J]. Metall Trans, 2000, 31B(4): 837- 846.

[13] GUO Jing-jie, LIU Gui-zhong, SU Yan-qing, et al. Control of Al content during ISM process of Nb_3Al [J]. Trans Nonferrous Met Soc China, 2000, 10(5): 571- 575.

(Edited by HUANG Jin-song)