Evaporation of multi-components in Ti-25Al-25Nb melt during induction skull melting process[①]

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[Abstract] Based on activity calculation model, the activity coefficients of Ti, Al and Nb components of Ti-25Al-25Nb (mole fraction, %) melt, the vapor pressures of corresponding components and the evaporation loss rates were calculated. Utilizing these activity coefficients and the vapor pressures, the relative evaporation coefficient is used to judge the evaporation tendency of these components. The evaporation tendency among the three components were compared and the result shows that the evaporation tendency is that: $Al \gg Ti > Nb$. Evaporation loss rate increases with the increase of melting temperature and decreases with the increase of chamber pressure. There exists an impeding pressure p_{impe} of Al element evaporation during induction skull melting process of Ti-25Al-25Nb alloy. The impeding pressure can be written as $p_{impe} = 8.1 p_e$, where p_e represents the equilibrium partial pressure. The calculation of evaporation loss of Al element also showed that when chamber pressure exceeds p_{impe}, the Al volatilization losses could be ignored. In order to prevent the evaporation loss of components, the pressure in the vacuum chamber should not below p_{impe}.

[Key words] Ti-25Al-25Nb alloy; ISM process; multi-components evaporation

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1　INTRODUCTION

Accurate composition is the precondition to achieve optimal properties of an alloy. During melting process, evaporation and oxidization are the main reasons for the change of the composition in a molten alloy. Titanium alloys have been applied widely in aerospace, chemical industry, metallurgy and sports apparatus due to the excellent corrosion resistance, high specific strength and fracture toughness[1]. For the high reactivity of elements in the molten status, titanium alloys are always melted under the vacuum condition so as to prevent the contamination. However, due to the high saturated vapor pressure of Al element that is an indispensable alloying element in almost all of the titanium alloys, there always exists its evaporation loss during the vacuum melting of aluminum-containing titanium alloys. Sometimes, the evaporation loss of Al arrives up to 8%(mass fraction) during the cold crucible induction skull melting (ISM) of gamma TiAl intermetallic compound. It could arrive up to 10% ~ 15% (mass fraction) by electron beam melting (EBM) process[2]. Undoubtedly, the over much evaporation loss can cause serious influence on gamma TiAl alloy's strength and ductility which are very sensitive to composition of the alloy. Unfortunately, up to now, the studies on evaporation behavior of alloy elements are very limited. These limited study are focused on the evaporation of single element of a molten alloy[3, 4]. In this study,

the authors investigate the evaporation behavior of Al, Nb and Ti elements during ISM process of Ti-25Al-25Nb(mole fraction, %) ternary alloy through theoretical calculation and analyze the effects of temperature in the molten alloy and pressure in the vacuum chamber aiming at providing a theoretical guidance to the melting practices of titanium alloys.

2　VAPOR PRESSURE AND EVAPORATION TENDENCY

At a certain melt temperature, the saturated vapor pressure of component i can be given as

$$p_i^e = x_i \cdot \gamma_i \cdot p_i^0 \qquad (1)$$

where p_i^e is the saturated pressure of component i, Pa; x_i is the molar fraction of component i; γ_i is the activity coefficient of i; p_i^0 is the saturated vapor pressure of pure element i, Pa. p_i^0 is dependent on the temperature and its value can be found out in thermodynamic handbooks.

Generally, activity coefficients of components in a molten alloy can be obtained by experimental measurement or theoretical calculation. However, for high activity of titanium alloy, it is difficult to experimentally measure the activity coefficient of the component. Up to now, many researchers have introduced their theoretical model to predict the component' activity coefficient of a molten alloy. Some of these models are prove to be reliable and accurate. In

this article, the model introduced in Ref. [3] was used to calculate the activity coefficients of Ti, Al, Nb components in molten Ti-25Al-25Nb alloy. The calculation results are listed in Table 1.

Table 1　Activity coefficients of Ti, Al, Nb elements of Ti-25Al-25Nb melt at different melting temperatures

Melting temperature/ K	γ_{Ti}	γ_{Al}	γ_{Nb}
2 100	0. 483	0. 075	0. 421
2 200	0. 504	0. 089	0. 456
2 300	0. 543	0. 105	0. 493

In order to calculate the saturated vapor pressures of Ti, Al, Nb elements in the Ti-25Al-25Nb melt, the following equations[5] can be used.

$$p_{Ti}^0 = 10^3 \exp(- 23\,200/ T - 0.66 \lg T + 10.86) \times \ln 10 \qquad (2)$$

$$p_{Al}^0 = 10^3 \exp(- 16\,380/ T - 1.0 \lg T + 11.44) \times \ln 10 \qquad (3)$$

$$p_{Nb}^0 = 10^3 \exp(- 26\,900/ T + 0.33 \lg T - 0.265 \times 10^{-3} T + 9.24) \times \ln 10 \qquad (4)$$

Table 2 shows these p_{Ti}^0, p_{Al}^0, p_{Nb}^0 at different melting temperatures. It can be seen that p_{Ti}^0, p_{Al}^0 and p_{Nb}^0 increase with increasing melt temperature. However, p_{Al}^0 is overwhelming bigger than p_{Ti}^0 and p_{Nb}^0 at the same temperature.

Table 2　Saturated vapor pressure of pure Ti, Al, Nb elements in Ti-25Al-25Nb melt at different melting temperatures

Melting temperature/ K	p_{Ti}^0/ Pa	p_{Al}^0/ Pa	p_{Nb}^0/ Pa
2 100	4. 16	1 219. 98	0. 83
2 200	12. 84	2 615. 83	3. 28
2 300	35. 83	5 237. 71	11. 48

Langmuir once pointed out that if the components in a melt evaporate in molecular status, the effect of their molecular masses on the evaporation cannot be ignored[6]. In Ref. [7], the authors defined a parameter, β, called relative evaporation coefficient to represent the evaporation tendency among components. As to components of a melt:

$$\beta = \frac{\gamma_i p_i^0}{\gamma_j p_j^0} \qquad (5)$$

where γ_i, γ_j are the activity coefficients of components i and j, respectively; p_i^0, p_j^0 are the saturated vapor pressures of components i, j of the melt.

When $\beta = 1$, the mass ratio of i to j in the vacuum chamber is equal to that of i to j in the melt. This means that the composition of the melt will not deviate from its original composition after the melting process. When $\beta > 1$, mass fraction of component i in the gas is bigger than its mass fraction in the melt, i. e. the evaporation loss of component i is larger than that of component j. This means the composition of the melt will deviate from its original composition after the melting process. If $\beta \gg 1$, comparing to the evaporation loss of component i, the evaporation of the component j can be ignored. When $\beta < 1$, it is obvious that the composition deviation of the melt is attributed to the evaporation of component j. Similarly, when $\beta \ll 1$, the evaporation of component i can be ignored comparing to the evaporation loss of component j. All of these were detailed in Ref. [7].

Using the data in Table 1 and Table 2, the relative evaporation coefficients between components of Ti-25Al-25Nb melt can be calculated with Eqn. (5). The calculation results are listed in Table 3. From Table 3, it can be seen that the evaporation loss tendency of Al element is overwhelmingly larger than that of Ti and Nb elements. For instance, when the melting temperature is 2 100 K, the evaporation tendency of Al is 45 and 262 times as magnitude as that of Ti and Nb elements respectively. While comparing Ti element with Nb element, the difference of their evaporation tendency is inconspicuous.

Table 3　Relative evaporation coefficients between components of molten Ti-25Al-25Nb alloy at different melting temperatures

Melting temperature/ K	Relative evaporation coefficient, β		
	β_1(Al: Ti)	β_2(Al: Nb)	β_3(Ti: Nb)
2 100	45	262	5. 8
2 200	36	152	4. 2
2 300	28	97	3. 5

3　EVAPORATION LOSS RATE OF COMPONENTS OF Ti-25Al-25Nb MELT

Under vacuum induction melting condition, the evaporating process of alloy elements, as shown in Fig. 1, includes the following steps: 1) the diffusion of evaporating elements in the liquid boundary layer. Due to the electromagnetic stirring action, the evaporating element in the melt transports to the very thin liquid boundary on the surface of the melt. The mass transport coefficient of this step is named as β_m(cm/ s); 2) the evaporation reaction ([M_i] = M_i(g)) in the liquid/ gas interface. K_m(cm/ s) represents the evaporation mass transfer coefficient of this step; 3) the migration of gaseous atoms in gas phase. The mass transfer coefficient of this step is named as β_g (cm/ s); 4) the condensation of the gaseous atoms in
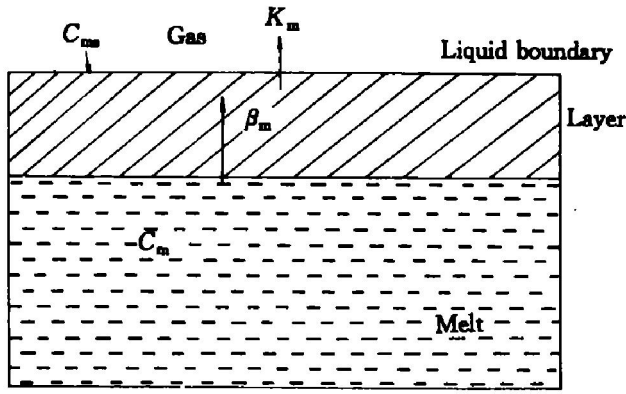
Fig. 1 Schematic of transfer process
during vacuum induction melting

(C_{ms} —Content of component in melt surface, $g \cdot cm^{-3}$;

C_m —Content of component in melt, $g \cdot cm^{-3}$)

the vacuum chamber surface. The mass condensing coefficient of this step is defined as K_c(cm/s).

All of the mass transfer coefficients β_m, K_m, β_g, K_c were detailed in Ref. [4]. The evaporation loss rate N_m of a component was also discussed in the Ref. [4]. The evaporation loss rate is given as follows[4].

$$N_m = C_m \frac{\beta_m \cdot K_m}{\beta_m + K_m} \qquad (6)$$

3.1 Mass transport coefficient (β_m) in liquid boundary layer

During the induction melting process, supposing the mass transfer of elements in the liquid boundary layer follows Machlin model[8], the transfer coefficient (β_m) of this step can be depicted as:

$$\beta_m = 2(2Dv/\pi r)^{1/2} \qquad (7)$$

where D is the diffusion coefficient of evaporating element, cm^2/s; v is the melt flowing speed in the liquid boundary layer, cm/s; r is the radius of the crucible, cm.

In ISM process, with increasing inputting power, the stirring effect becomes stronger, which increases D and v. At the same time, the melt temperature also increases. When other experimental conditions keep unchanged, we can hypothesize that D and v linearly depend on melt temperature T. Within a temperature scope (saying $T_1 \rightarrow T_2$):

$$D = D_1 + (D_2 - D_1) \frac{T - T_1}{T_2 - T_1} \qquad (8)$$

$$v = v_1 + (v_2 - v_1) \frac{T - T_1}{T_2 - T_1} \qquad (9)$$

where D_1 and D_2 correspond to the diffusion coefficient of the evaporation element in the melt when the melt temperature is T_1 and T_2 respectively. v_1 and v_2 correspond to the surface velocity of the melt when the melt temperature is T_1 and T_2. In our calculation, T_1 is the melting point temperature of the alloy and $T_2 = T_1 + 300$ K. D ranges from 10^{-5} cm^2/s to

10^{-4} cm^2/s[9], so $D_1 = 10^{-5}$ cm^2/s and $D_2 = 10^{-4}$ cm^2/s. Japanese researchers once pointed that v ranges from 6 cm/s to 21 cm/s[10]. Then $v_1 = 6$ cm/s and $v_2 = 21$ cm/s. Utilizing these data, β_m can be calculated.

3.2 Mass transportation coefficient, K_m

As far as the effect of chamber pressure on the evaporation reaction is concerned, the mass evaporation rate can be written as[11]:

$$N_m = K_L \varepsilon (p_i^e - p_{g(i)}) \sqrt{M_i/T_{ms}} \qquad (10)$$

Accordingly, K_m will be expressed as:

$$K_m = K_L \varepsilon (p_i^e - p_{g(i)}) \sqrt{M_i/T_{ms}} / C_{ms(i)} \qquad (11)$$

where T_{ms} is the temperature in the evaporating interface, K; p_i^e is given out by Eqn. (1); $p_{g(i)}$ is the partial pressure of component i in the gas space and it is discussed in detail in Ref. [4]; K_L is called as Langmuir constant ($K_L = 4.37 \times 10^{-4}$); ε is called condensation coefficient, for metals $\varepsilon = 1$. M_i is the atomic mass of component i.

During the calculation process, the content (C_{ms} and C_m) of the evaporating component will change with the calculation time. The evaporation loss rate (N_m) will also change with the time. According to our experiment condition, the charge melted is 5 kg, melting time is 6 min, and the evaporation surface area is the cross-section of the crucible that is 113 cm^2.

3.3 Calculation results and discussion

Fig. 2 shows the evaporation loss rate at different melting temperatures. It can be seen that the evaporation loss rate increases with the increase of the melting temperature.
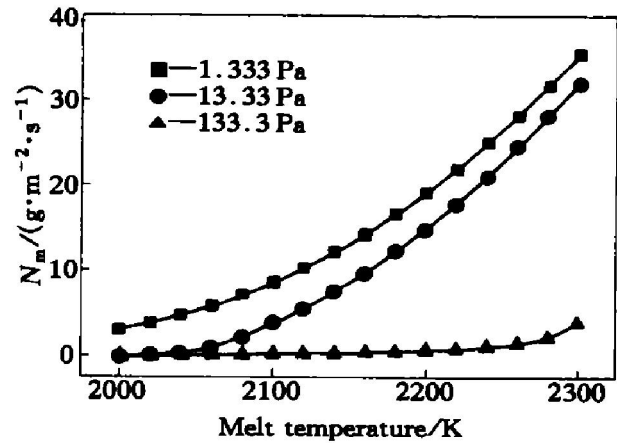

Fig. 2 Relationship between evaporation loss
rate (N_m) and melt temperature

Fig. 3 shows the relationship between the evaporation loss rate and the chamber pressure. At a certain melting temperature, the shape of the curve which shows the relationship between the evaporation
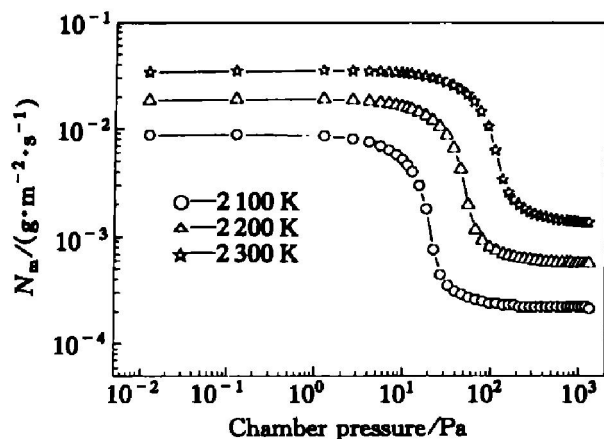
Fig. 3　Relationship between evaporation loss
rate (N_m) and chamber pressure

loss rate (N_m) and the chamber pressure is similar
with the experimental results that were gained from
the experiment carried out by other researchers[9, 12].

　　In Fig. 3, each curve of N_m —p can be obviously
divided into three parts. When the chamber pressure
p is less than a certain value, the evaporation rate
N_m reaches the maximum value and almost keeps un-
changed with declining the chamber pressure. This
value of chamber pressure can be defined as critical
pressure p_{crit} of the element evaporation. At the same
time, when the chamber pressure p is bigger than a
certain value, the evaporation rate N_m approaches a
minimum value and also nearly keeps unchanged with
the increase of the chamber pressure. In the same
way, this value of chamber pressure is defined as im-
peding pressure. When the chamber pressure increas-
es from p_{crit} to p_{impe}, the evaporation rate N_m sharply
decreases.

　　The critical pressure p_{crit} is very important in the
vacuum distillation process. Many metallurgists have
given lots of energy in it because when the chamber
pressure is less than p_{crit}, they obtained the maxi-
mum distillation rate which almost kept unchanged
with decreasing the chamber pressure. However, up
to now, we don't see any predecessor has given a
clear definition about the impeding pressure and its
calculation method. In this article, we give a defini-
tion about the impeding pressure and provide a simple
way to calculate its value based on its dependence on
the chamber pressure.

　　From Fig. 3, it can be seen that when the cham-
ber pressure is bigger than a certain value, the N_m
will tend to a minimum value and keep as a constant.
This minimum evaporation rate is defined as N_{min}.
Using a predefined error (saying 5% or less assigned
by the requested accuracy) and Fig. 3, we can define
an evaporation rate N_{impe} as the following:

$$N_{impe} = N_{min} + 5\% \cdot N_{min} \qquad (12)$$

Then the chamber pressure corresponding to N_{impe} is
defined as the impeding pressure p_{impe}. In our calcu-

lation, N_{min} corresponds to the evaporation loss rate
when the chamber pressure is the biggest value in our
calculation, saying 1 333 Pa. Table 4 shows the im-
peding pressure of Al element evaporation in Ti-25Al-
25Nb melt.

Table 4　Impeding pressure p_{impe} of Al element
and corresponding equilibrium partial pressure
p_e in melt of Ti-25Al-25Nb alloy

T / K	p_{impe}/ Pa	p_e/ Pa	p_{impe}/ p_e
2 100	188. 8	22. 9	8. 4
2 200	465. 0	58. 2	8. 0
2 300	763. 2	97. 5	7. 8

　　It is known that the vapor pressure of an element
in a solution is always used to depict the evaporation
characteristic of the solution. The equilibrium partial
pressure is a kind of this vapor pressure. Based on
this fact, the concerned equilibrium partial pressures
(p_e) are listed in Table 4. The values of p_{impe}/ p_e are
also listed in Table 4.

　　Table 4 shows that p_{impe}/ p_e tends to a constant.
Then we define a coefficient K_{impe} as follows:

$$K_{impe} = \frac{p_{impe}}{p_e}$$

　　As to molten Ti-25Al-25Nb alloy, K_{impe} is repre-
sented as the average value of p_{impe}/ p_e in different
temperatures, that is

$$K_{impe} = \frac{8.4 + 8.0 + 7.8}{3} = 8.1$$

So, the impeding pressure of Al element evaporation
in molten Ti-25Al-25Nb can be calculated by

$$p_{impe} = 8.1 p_e \qquad (13)$$

　　According to the definition of p_{impe}, it is reason-
able to increase the chamber pressure to detain the e-
vaporation of the element by refilling the vacuum
chamber with argon gas.

4 EVAPORATION LOSSES OF Al ELEMENT

　　Fig. 4 shows the relationship between the evapo-
ration loss of Al element and melt temperature at dif-
ferent chamber pressures. The evaporation loss of Al
element increases with the increase of the melt tem-
perature. But the effect of the melt temperature on
the evaporation loss of Al is different with different
chamber pressures. For example, when the melt
temperature is 2 100 K and chamber pressure is 1. 333
Pa, the evaporation loss of Al of the alloy melt is
29. 5 g and the simulation calculation also gives the
mole fraction of Al element decrease from to 0. 25 to
0. 241. However, with the same melt temperature
and different chamber pressure, saying 133. 3 Pa, the
evaporation loss of Al and the changing of chemical
composition can be ignored (evaporation loss of Al is

0. 76 g).

The effect of chamber pressure on Al volatilization losses at different melt temperatures is presented in Fig. 5. The relationship between the chamber pressure and the Al volatilization losses is similar to the relationship between the chamber pressure and the evaporation loss rate of Al. From Fig. 5, we can see that when chamber pressure is bigger than the impeding pressure, the evaporation losses of Al element could be ignored and the chemical composition of the alloy will meet the specification after being melted. In melting practice, we can refill the vacuum chamber with argon to meet this requirement.
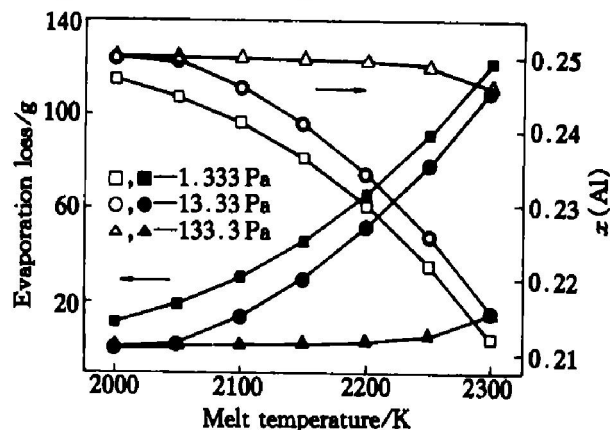

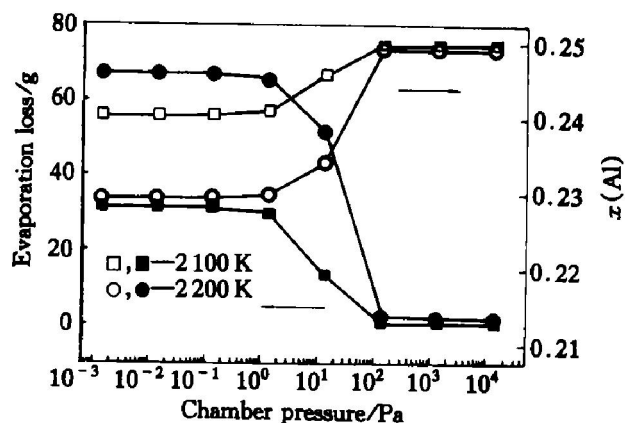**Fig. 4**   Effect of melt temperature on Al evaporation loss and its content at different chamber pressures

Fig. 5   Effect of chamber pressure on Al evaporation loss and its content at different melt temperatures

5   CONCLUSIONS

1) As to Ti-25Al-25Nb (mole fraction, %) alloy melting process, the evaporation tendency of Al element is at least as 28 and 97 times as those of Ti and Nb element respectively.

2) Evaporation loss rate and evaporation loss mass of Al element increase with the increase of the melt temperature.

3) When the chamber pressure is below the criti-

cal pressure, evaporation loss rate approaches the maximum value and keep almost unchanged. When the chamber pressure exceeds the impeding pressure, the evaporation loss rate will decline to a minimum value and almost keeps as a constant. When the chamber pressure increases from critical pressure to impeding pressure, the evaporation loss rate sharply decreases.

4) As to molten Ti-25Al-25Nb alloy, the impeding pressure of Al element evaporation can be written as $p_{impe}= 8. 1p_e$. In order to meet the specification of the alloy composition, the chamber pressure should be above p_{impe}.

[REFERENCES]

[1]   Eylon D, Newman J R. Titanium and Titanium Alloy Casting ASM Handbook (Formerly Tenth Edition) [M]. ASM International, 1992. 634– 639.

[2]   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– 624.

[3]   LIU Yuan. Study on the structure of Ti-15-3 alloy and its basic ISM process [D]. Harbin: Harbin Institute of Technology, (in Chinese), 1998. 23– 30.

[4]   GUO Jing-jie, LIU Gui-zhong, SU Yan-qing, et al. Control of Al content during ISM process of Nb3Al [J]. Transaction of Nonferrous Metals Society of China, 2000, 10(5): 571– 574.

[5]   LIANG Ying-jiao, CHE Yin-chang. Handbook of Thermodynamic Data of Inorganic Compounds [M], (in Chinese). Shenyang: North-east University Press, 1993. 324– 325.

[6]   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– 102.

[7]   LIU Gui-zhong, SU Yan-qing, GUO Jing-jie, et al. E-vaporation tendency of components in Ti-6Al-4V alloy melt [J]. Materials Science and Technology, (in Chinese), 2001, 9(2): 175– 177.

[8]   Machlin E S. Kinetics of vacuum induction refining-theory [J]. Transactions of the Metallurgical Society of AIME, 1960, 218(4): 314– 326.

[9]   YU Jing-lu, WEI Ji-he. Phenomenon of Heat and Mass Transportation during Metallurgical Process [M], (in Chinese). Beijing: Metallurgical Industry Press, 1981. 321– 322.

[10]   Tanaka T, Kurita K, Kuroda A. Mathematical modelling on liquid metal flow in a cold crucible coupled with heat transfer [J]. ISIJ International, 1992, 32(4): 572– 579.

[11]   KANG Xian-deng. Vacuum Metallurgy [M]. Shanghai: Shanghai Science and Technology Press, 1980. 44 – 46.

[12]   DAI Yong-nian. Vacuum Metallurgy of Nonferrous Metals [M], (in Chinese). Beijing: Metallurgical Industry Press, 1998. 55– 56.

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