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Control of Al content during ISM process of Nb₃Al^①

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[Abstract] The activity coefficients of components in Nb₃Al melt were calculated. On the basis of the activity coefficients, the evaporation behaviors, including the evaporation dynamic and the evaporation loss of Al in the Nb₃Al melt during the induction skull melting (ISM) process were studied systematically. The results show that the evaporation-controlling mode of Al in the alloy melt is a double controlling mode, i.e. the diffusion of evaporation element in melt boundary layer and the evaporation reaction, under the conditions that $p = 1.333$ Pa and the scope of melt temperature is 2235 ~ 2635 K. When the melt temperature is 2385 K (the superheat is 100 K), the evaporation-controlling mode varies from the double controlling mode to a single controlling mode (the evaporation reaction on the surface of melt) if the vacuum chamber pressure is above 133 Pa.

[Key words] Nb₃Al alloy; induction skull melting; Al evaporation

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1 INTRODUCTION

As a candidate for the next generation of high temperature structural materials, Nb₃Al-based alloys have been studied intensively. However, these studies focused only on the relationship between composition, microstructure, and heat treatment, hot work processing and various properties^[1~4]. Up to now, little attention has been put on the study of melting process. The melting process is an important factor restricting the application of these alloys because their properties are largely dependent on their components^[2~4]. Cold crucible induction skull melting (ISM) is regarded as an effective and practical method to melt reactive metals and alloys because the contamination of crucible materials and interstitial elements to the alloy melt is minimal. However, with the high level of the vacuum degree, the loss of the elements with high-saturated vapor pressure in the alloy melt will be very serious during the ISM process. As for the alloy of Nb₃Al with the high melt temperature, it is difficult to obtain the qualified nominal composition because the loss of Al element caused by its high vapor pressure can not be ignored. This paper is aimed at studying the Al content controlling during ISM process theoretically.

2 ACTIVITY OF Al IN Nb₃Al MELT

The evaporation loss of the element in the melt is strongly dependent on its equilibrium partial pressure. As for the equilibrium partial pressure, it can be defined as

$$p_{e(i)} = x_i \cdot \gamma_i \cdot p_i^0 \quad (1)$$

where p_i^0 is the equilibrium pressure of pure component i . For Al element, p_i^0 can be calculated by following formula^[5]:

$$\lg(p_{Al}^0/\text{Pa}) = -16236/T - \lg T + 14.14 \quad (2)$$

x_i is the mole fraction of element i in the alloy melt; γ_i is the activity coefficient of element i in the alloy melt.

2.1 Calculating formula for activity coefficient

In i - j binary system, component i is solute and component j is solvent. Based on Miedema model^[6] and Kohler Equation^[7], Ref.[8] has given the general formula to calculate the activity coefficient of component i as following:

$$\ln \gamma_i = \beta_j f_{ij} \left[\frac{A}{B} + x_j \left[\frac{ED + FC}{B} - GA \right] / B^2 \right] \quad (3)$$

where

$$\begin{aligned} \beta_j &= 1 - 0.1 T \left[\frac{T_{m(i)} + T_{m(j)}}{T_{m(i)} T_{m(j)}} \right] \\ f_{ij} &= 2 p V_i^{2/3} V_j^{2/3} \{ (q/p) [(n_{ws}^{1/3})_j - (n_{ws}^{1/3})_i]^2 - \\ &\quad (\phi_j - \phi_i)^2 - a(r/p) \} / \\ &\quad [(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_j^{-1}] \\ A &= x_i x_j [1 + \mu_4 x_j (\phi_i - \phi_j)] \cdot \\ &\quad [1 + \mu_5 x_i (\phi_j - \phi_i)] \\ B &= x_i V_i^{2/3} [1 + \mu_4 x_j (\phi_i - \phi_j)] + \\ &\quad x_j V_j^{2/3} [1 + \mu_5 x_i (\phi_j - \phi_i)] \\ C &= x_i [1 + \mu_4 x_j (\phi_i - \phi_j)] \\ D &= x_j [1 + \mu_5 x_i (\phi_j - \phi_i)] \\ E &= 1 + \mu_4 (\phi_i - \phi_j) (x_j - x_i) \\ F &= 1 + \mu_5 (\phi_i - \phi_j) (x_j - x_i) \end{aligned}$$

$$G = V_i^{2/3} [1 + \mu_i x_j (\phi_i - \phi_j)] + x_i V_i^{2/3} \mu_i (\phi_i - \phi_j) - V_j^{2/3} [1 + \mu_j x_i (\phi_j - \phi_i)] + x_j V_j^{2/3} \mu_j (\phi_j - \phi_i)$$

where $T_{m(i)}$, $T_{m(j)}$ are the melting point of component i and j , respectively; T is the melt temperature; V_i , V_j are the mole volume of i and j ; $(n_{ws})_i$, $(n_{ws})_j$ are the electron density of i and j ; ϕ_i , ϕ_j are the electron negativity of i , j , respectively; x_i and x_j are the mole fraction of component i and j ; p , r , q , a and μ are constant. The values of these parameters are supported by Ref. [6].

Based on the activity coefficient of component i , the activity coefficient of component j can be given by

$$\ln \gamma_j = \frac{1}{x_j} (\Delta H_{ij} \beta_j - x_i \ln \gamma_i) \quad (4)$$

where

$$\Delta H_{ij} = f_{ij} x_i [1 + \mu_i x_j (\phi_i - \phi_j)] x_j [1 + \mu_j x_i (\phi_j - \phi_i)] / \{ x_i V_i^{2/3} [1 + \mu_i x_j (\phi_i - \phi_j)] + x_j V_j^{2/3} [1 + \mu_j x_i (\phi_j - \phi_i)] \}$$

2.2 Calculated results and discussion

The calculated results of activity coefficients in Nb_3Al melt are shown in Fig. 1. From Fig. 1, it can be seen that the activity coefficients of Al and Nb (hereinafter referred to as $\gamma(Al)$ and $\gamma(Nb)$ respectively) increase with increasing the melt temperature. With increasing the temperature, the interaction forces between elements decline, which causes the increase of activity coefficients. For the attractive interaction force between element Nb and Al is strong, both $\gamma(Al)$ and $\gamma(Nb)$ are less than 1. At the same time, when the mole fraction of Al (hereinafter referred to as $x(Al)$) changes from 0.13 to 0.33, which may occur during the ISM process, $\gamma(Al)$ and $\gamma(Nb)$ are also shown in Fig. 1(b). It can be seen that, with the $x(Al)$ increase, the $\gamma(Al)$ increases, while the $\gamma(Nb)$ declines. The relationships between equilibrium partial pressure of Al (hereinafter re-

ferred to as $p_e(Al)$) and melt temperature and/or $x(Al)$ are also shown in Fig. 1(a) and (b).

3 CONTROLLING STEPS FOR EVAPORATION OF Al DURING ISM PROCESS OF Nb_3Al

Under the vacuum induction melting condition, the evaporation process of alloy elements, as shown in Fig. 2, includes three steps:

I. The diffusion of evaporating element in the liquid boundary layer. Due to the electromagnetic stirring action, the evaporating element in the melt is homogeneous. There only exists very thin diffusion boundary layer on the surface of the melt. The transferring rate coefficient of this step is named as β_m (cm/s).

II. The evaporation reaction ($[M_i] = M_{i(g)}$) in the liquid/gas interface. K_m (cm/s) represents the transferring rate coefficient of this step.

III. The migration of gaseous atoms in vacuum chamber. The transferring rate coefficient of this step is named as β_g (cm/s).

During the ISM process, in general, the step III has no effect on the evaporation process due to the high vacuum degree in the melting chamber and the big condensing surface. Thus only step I or/and II is likely to be the controlling step, which depends on the melt temperature, vacuum degree as well as the content of evaporating element.

3.1 Judging model for controlling step

In step I, the mass transferring rate N_m ($g \cdot cm^{-2} \cdot s^{-1}$) of evaporating element can be expressed as

$$N_m = \beta_m (\rho_m - \rho_{ms}) \quad (5)$$

where ρ_m ($g \cdot cm^{-3}$) and ρ_{ms} are the average content of the evaporating element in the inner and the evaporating surface of the melt, respectively.

In step II, the mass transferring rate N_m can be written as

$$N_m = K_m \rho_{ms} \quad (6)$$

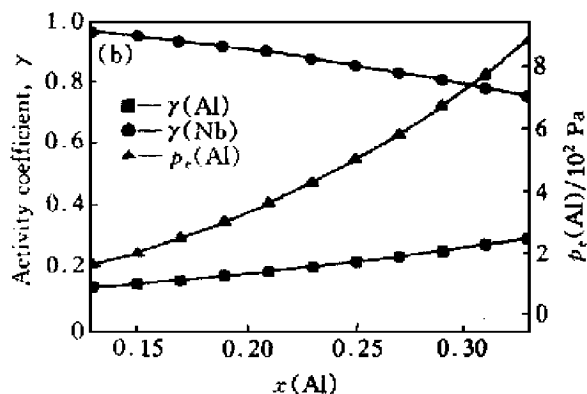
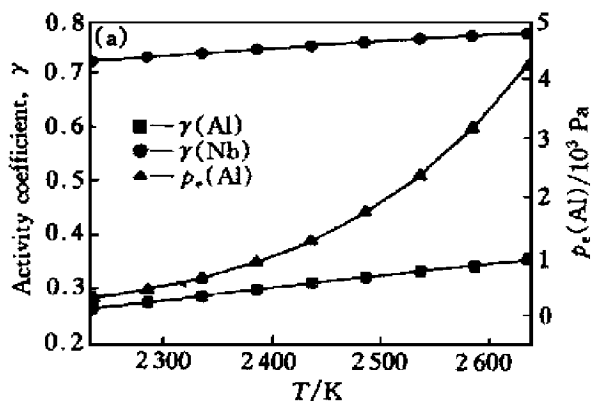


Fig. 1 Activity coefficients and equilibrium partial pressure of Al vs melt temperature (a) and mole fraction of Al (b) in Nb_3Al melt

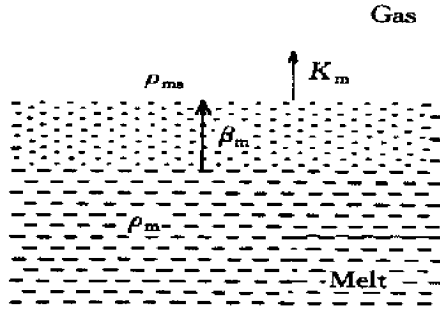


Fig.2 Schematic of evaporation process during vacuum induction melting process
(ρ_m and ρ_{ms} are the average content of the evaporating element in the inner melt and on the evaporating surface of the melt, respectively)

Since the evaporation of alloy element is a continuous process, Eqns.(5) and (6) should be equal. The rate of the whole evaporating process is

$$N_m = \frac{\beta_m K_m}{\beta_m + K_m} \rho_m = K \rho_m \quad (7)$$

where K is called the total mass transferring rate coefficient. It can be found from its formula that: if $K_m \ll \beta_m \Rightarrow K \rightarrow K_m$, in other words, the evaporation is controlled by the evaporating reaction in step II, this mode is called evaporating reaction controlling mode; If $K_m \gg \beta_m \Rightarrow K \rightarrow \beta_m$, that is, the evaporation is controlled by the diffusion in the liquid boundary layer in the step I and this controlling mode is called diffusion controlling mode. Contrarily, if the above-mentioned two instances do not exist, the evaporation will be controlled by both step I and step II, accordingly, this controlling mode is called double controlling mode.

3.1.1 Solution of β_m

Because during the induction melting process, the mass transfer of elements in the liquid boundary layer follows Machlin model^[9], the transferring coefficient of step I can be depicted as

$$\beta_m = 2(2 \frac{Dv}{\pi r})^{1/2} \quad (8)$$

where D is the diffusion coefficient of evaporating element; v is the melt's flowing velocity in the liquid boundary layer, according to our actual melting condition, v is about $15 \text{ cm} \cdot \text{s}^{-1}$, and in our calculation $v = 15 \text{ cm} \cdot \text{s}^{-1}$; r is the radius of the crucible, in this paper it is equal to 6 cm. In fact, D and v increase with the rise of melt temperature during ISM process, but the increasing trend is limited.

3.1.2 Solution of K_m

As far as the effect of chamber pressure on the evaporation reaction is concerned, the mass evaporation rate N_m can be written as^[10]

$$N_m = K_L \mathcal{E} (p_{e(i)} - p_{g(i)}) \sqrt{M_i / T_{ms}} \quad (9)$$

Accordingly, K_m will be expressed as

$$K_m = K_L \mathcal{E} (p_{e(i)} - p_{g(i)}) \sqrt{M_i / T_{ms}} / \rho_{ms(i)} \quad (10)$$

where T_{ms} is the temperature on the evaporating interface (K), $p_{e(i)}$ is the equilibrium partial pressure of component i at temperature T_{ms} , $p_{g(i)}$ is the partial pressure of component i in the chamber, K_L is called Langmuir constant ($K_L = 0.05833$ when the unit of $p_{e(i)}$ is Pa), \mathcal{E} is called condense constant, for metals $\mathcal{E} = 1$, M_i is the atomic mass of component i .

In the alloy system, the component's equilibrium partial pressure $p_{e(i)}$ is defined as Eqn.(1).

During the melting process, $p_{g(i)}$ varies with time. So the relationship between time and $p_{g(i)}$ must be found out. Fig.3 is a sketch map used to calculate $p_{g(i)}$. In Fig.3, Δn_i^t and Δn_i^{t+dt} represent the number of moles of component i volatilizing into the vacuum chamber within dt from time t to $t+dt$ and from time $t+dt$ to $t+2dt$ respectively. $\Delta n_{out(i)}^t$ and $\Delta n_{out(res)}^t$ represent the number of moles of volatile component i and the residual gases condensed or pumped out off the vacuum chamber within dt from time t to $t+dt$. n_{res}^t and n_{res}^{t+dt} are the mole number of the residual gases including inert gas and air in the vacuum chamber at t and $t+dt$ moment. n_i^t and n_i^{t+dt} represent the mole fraction of component i in the vacuum chamber at t and $t+dt$ moment, respectively. Before performing mathematical calculation, the following three hypotheses are necessary:

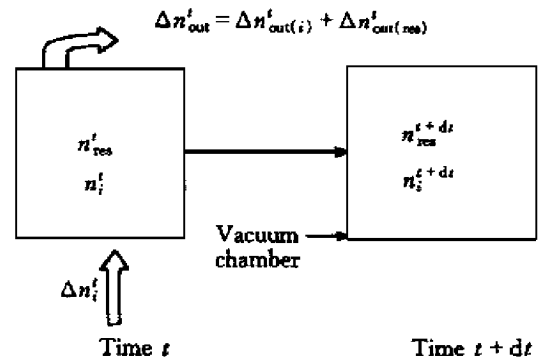


Fig.3 Sketch map for estimating partial pressure

1) Only one component such as Al in Nb₃Al melt volatilizes into the vacuum chamber.

2) The pressure (p) in the vacuum chamber always keeps a constant value, namely $\Delta n_i^t = \Delta n_{out}^t$.

3) Within a very short time-step ($t \rightarrow t+dt$), $\Delta n_{out(i)}^t \propto n_i^t$, $\Delta n_{out(res)}^t \propto n_{res}^t$.

Through a series of strict deduction, we can get the partial pressure ($p_{g(i)}^{t+dt}$) of component i in the vacuum chamber at the $t+dt$ moment as following:

$$p_{g(i)}^{t+dt} = \frac{RT'(n_i^t + N_{m(i)}^t S dt)}{V M_i} - \frac{R^2 T'^2 n_i^t N_{m(i)}^t S dt}{p V^2 M_i} \quad (11)$$

where S is the evaporating area (cm^2), T' is the temperature in the vacuum chamber and R is the gas

constant.

3.2 Judged results and discussion

It can be found from the above deducing process that K_m , N_m , ρ_m , ρ_{ms} , $p_{g(i)}$, $p_{e(i)}$, and so on all vary with time even if the melt temperature and vacuum degree are invariable. Thus an iterative computation must be operated to get their values at an arbitrary moment. The computing procedure is as follows:

$$\begin{array}{c}
 \left. \begin{array}{l} T_{ms} = T \\ p = p \\ x_i^0 = x_i \\ n_i^0 = 0 \\ n_{res}^0 = n_{res} \\ p_{g(i)}^0 = 0 \\ \rho_{ms}^0 = \rho_m^0 \end{array} \right\} \Rightarrow \left. \begin{array}{l} y_i^0 \\ N_{m(i)}^0 \\ K_{m(i)}^0 \\ \beta_{m(i)}^0 \end{array} \right\} \Rightarrow \left. \begin{array}{l} \rho_{ms}^{dt} \\ \rho_m^{dt} \\ y_i^{dt} \\ p_{g(i)}^{dt} \\ p_{e(i)}^{dt} \\ N_{m(i)}^{dt} \\ K_{m(i)}^{dt} \\ \beta_{m(i)}^{dt} \end{array} \right\} \Rightarrow \dots \Rightarrow \left. \begin{array}{l} \rho_{ms}^{\tau} \\ \rho_m^{\tau} \\ y_i^{\tau} \\ p_{g(i)}^{\tau} \\ p_{e(i)}^{\tau} \\ N_{m(i)}^{\tau} \\ K_{m(i)}^{\tau} \\ \beta_{m(i)}^{\tau} \end{array} \right\} \\
 \begin{array}{cccc} \text{Initial} & 0 & 0 + dt & \tau \\ \text{conditions} & \text{time} & \text{time} & \text{time} \end{array}
 \end{array}$$

Figs. 4(a) and (b) show the effect of melt temperature (T) and chamber pressure (p) on the transferring rate coefficients of element Al in the alloy melt. When p is 1.333 Pa and the temperature is in the scope of 2235 ~ 2635 K, the evaporation of Al is controlled by both its diffusion in the melt boundary layer and the evaporation reaction on melt and vacuum interface (double controlling mode). When the temperature is below 2550 K, it can be seen that $K_m < \beta_m$, which means the evaporation of Al is mainly controlled by the evaporation reaction on the interface. However, when the temperature is above 2550 K, it can be seen that $K_m > \beta_m$ and with the increase of the temperature, the β_m will become less than K_m . Under this condition, the evaporation of Al is mainly controlled by the diffusion of Al on the boundary layer. Fig. 4(b) shows that under certain temperature, increasing chamber pressure (p) means to impede the evaporation reaction, which causes the evaporation-

controlling mode to change from the double controlling mode to the single controlling mode of evaporation reaction. For example, it is obvious that the controlling mode changes from the double controlling mode to the single controlling mode under the conditions that the melt temperature is 2385 K and the chamber pressure (p) is above 133 Pa.

4 EVAPORATION LOSS OF Al

According to different controlling modes, the evaporation loss of Al can be given by relative equations. Under the condition of double controlling mode, the evaporation rate of Al can be given by Eqn.(7) and then the evaporation loss can be calculated.

Fig. 5 shows the evaporation loss of Al with different conditions of melt temperature, chamber pressure and original mass of alloy to be melted (hereinafter called charge of alloy). Some parameters, such as the evaporation area (S) and the holding time (τ) are given by the actual condition. In this article, S is 114.4 cm² and τ is 600 s. It can be found from Fig. 5 that with the increase of melt temperature (T) and/or decrease of chamber pressure (p), the evaporation loss of Al increases accordingly. The mole fraction of Al changed during ISM process is less than 3% with the condition of $p = 133.33$ Pa and $T < 2285$ K. If p is less than 1.333 Pa, to make the Al mole fraction changed be less than 3%, the melting temperature must be kept below 2285 K. However, in melting Nb₃Al process, generally, the heat degree is about 100 K. It means that the melt temperature should be around 2335 K. Under this condition, in order to make the Al mole fraction changed be less than 3%, the chamber pressure can not be below 133.33 Pa. In the other hand, with the same melting temperature and chamber pressure, the final percentage of Al in the alloy increases with increasing the original melting charge mass of alloy. So, in practical melting process, the charge of alloy to be melted should be as much as possible within the permission

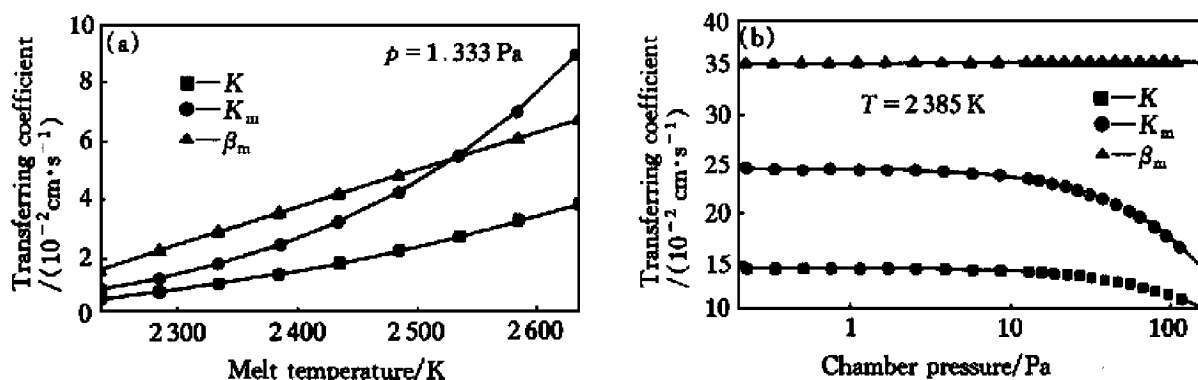


Fig. 4 Effect of melt temperature (a) and chamber pressure (b) on transferring coefficient of Al in Nb₃Al melt

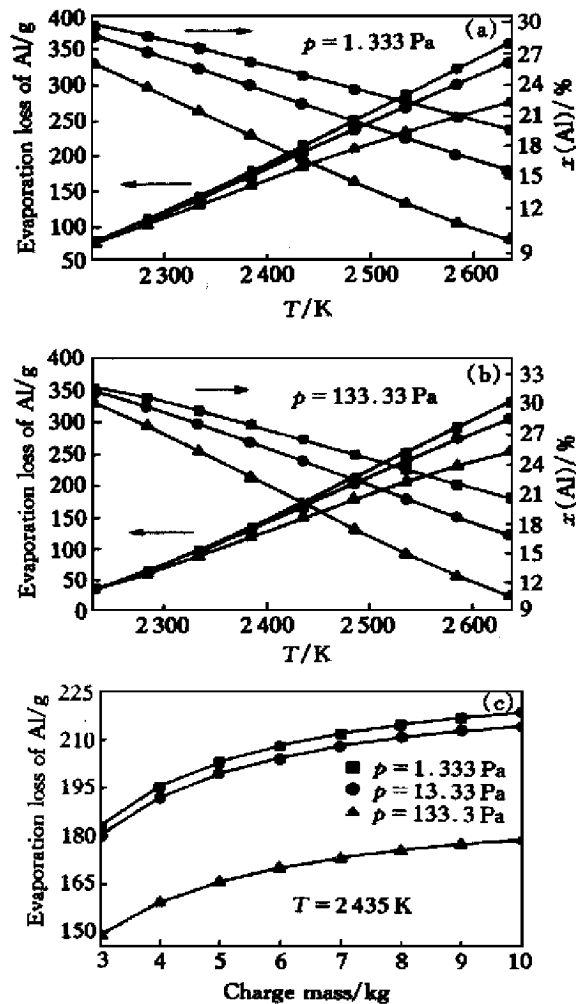


Fig.5 Evaporation loss of Al in Nb₃Al melt vs melt temperature and chamber pressure
For (a), (b): ■ — 7 kg charge;
● — 5 kg charge; ▲ — 3 kg charge;

content of the crucible.

5 CONCLUSIONS

1) When the temperature is 2335 K, $x(\text{Al})$ and $x(\text{Nb})$ in Nb₃Al melt are 0.21 and 0.75 respectively.

2) During ISM process, under the condition that $p = 1.333 \text{ Pa}$ and the melt temperature varies from 2235 K to 2635 K, the evaporation of Al is controlled by double controlling mode. The increase of chamber pressure means increasing the impeding force to evaporation reaction during the evaporation process. When the temperature is 2385 K, the evaporation-controlling mode of Al will change from double controlling mode to single controlling mode of the evaporation reaction under the condition of $p > 133.33 \text{ Pa}$.

3) With suitable superheat degree, to decrease the mole fraction change of Al, the p should be more than 133.33 Pa and the charge is as much as possible within permission content of the crucible.

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