Denitrogenation and desulphurization during vacuum induction melting refining Ni-base superalloy①

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[Abstract] The denitrogenation and desulphurization behavior during vacuum induction melting (VIM) refining Ni-base superalloy using CaO crucible was studied. It has been found that the desulphurization process did not occur by only using CaO crucible. Combining with the results of XRD and composition analysis, the desulphurization mechanism of CaO crucible was proposed. Al addition limits effect on denitrogenation, but it is very important for desulphurization. Ti addition has adverse effect on denitrogenation. The increase of vacuum is a powerful measurement to accelerate the denitrogenation process.

[Key words] Ni-base superalloy; VIM (vacuum induction melting); CaO crucible; denitrogenation; desulphurization

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1 INTRODUCTION

Sulfur and nitrogen are both harmful trace elements in superalloys. Sulfur has intense harmful influence on the properties of Ni-base superalloys, even if there is a trace amount in them[1,2]. For example, when the sulfur content in M17 alloy is equal or above $2.0 \times 10^{-3}\%$, Ti_2SC (Y phase) appeared. Y phase became a crack initiation site and made creep rupture strength decrease evidently. Coarse primary TiN inclusion forms in liquid Ni-base superalloy when nitrogen content is above the saturation solubility. To many superalloys the nitride inclusion content is an order of magnitude higher than that of oxide inclusion[3]. The nitride inclusion remarkably affects the mechanical behavior of Ni-base superalloy. The result of previous investigation[4] showed that even if the nitrogen content in IN100 alloy is about $1.5 \times 10^{-3}\%$, the microporosity can be increased markedly, thus the nitrogen content of Ni-base superalloy must be controlled below $1.0 \times 10^{-3}\%$. Many researchers[5~7] have studied the desulphurization and denitrogenation in iron and steel during VIM (vacuum induction melting) using CaO crucible, but only a little in Ni-base superalloy[8~10]. Therefore it is of great significance to study desulphurization and denitrogenation of Ni-base superalloy using CaO crucible.

2 EXPERIMENTAL

The melting equipment was VIM-50/25F vacuum induction melting and casting furnace. The composition of the Ni-base superalloy was Ni-6Cr-5Co-

2Mo-6W (mass fraction, %). The CaO crucible was shaped by CIP (cold isostatic pressing) technology, its composition was CaO 98.6/ 99-SiO₂ 0.08/ 0.12-MgO 0.40/ 0.65-Al₂O₃ 0.08/ 0.15-S 0.005/ 0.008[11]. The nitrogen and sulfur contents in raw materials were Ni 2.6-Cr 36-Mo 15-W 10-Co 14 and Ni5-Cr 120-Mo 8-W 8-Co 39 (mass fraction, $10^{-4}\%$) respectively.

The samples were obtained by metal mold. During the melting process the liquid alloy was poured into the casting mold after a definite time. The samples were machined into d 4 mm × 40 mm bars and scraps respectively for chemical analyses. After washing ultrasonically in an acetone solution, they were analyzed by TC-436 ON and ICP-AES CS analyzers, whose precision was $\pm 10^{-4}\%$ when the nitrogen and sulfur contents were below $3.0 \times 10^{-3}\%$. The temperature was measured by W-Re thermocouple.

The air leak rate of the furnace was 1.4×10^{-2} Pa•m³/s. The vacuum was below 0.1 Pa during melting and refining process.

3 RESULTS AND DISCUSSION

3.1 Effect of CaO crucible on desulphurization

In the present study TiN and CrS were found in the master alloys which are shown in Fig.1. The sulfur content in the whole charge can be calculated to be about $1.4 \times 10^{-3}\%$. The sulfur content when the charge just melted is $3.5 \times 10^{-3}\%$ (Fig.2). Some sulfur in the crucible should go into the liquid metal. It is also shown in Fig.2 that after melting for 25 min at 1773 K, the sulfur content of the melting metal is

basically invariable. It shows that sulfur could not be taken off during melting and refining Ni-base superalloy by only using CaO crucible. When the sulfur content in CaO crucible was higher than that in the charge, it went into the liquid metal and made the sulfur content in the liquid metal increase.
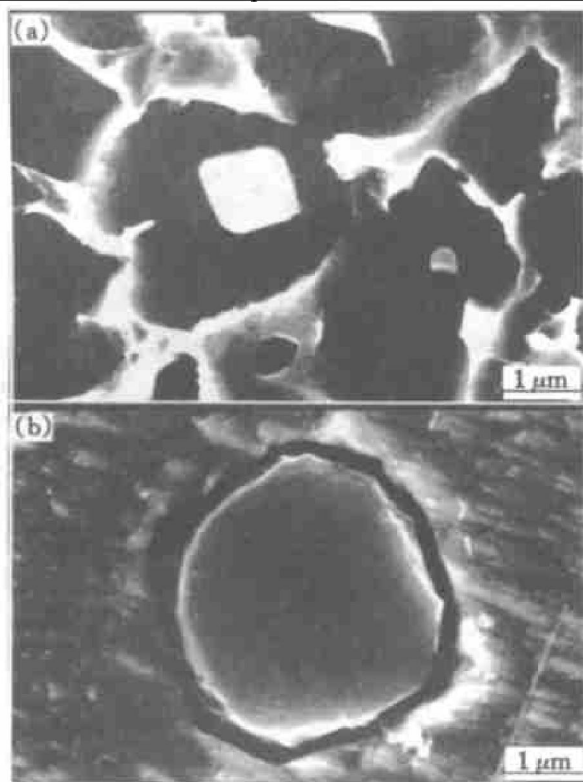

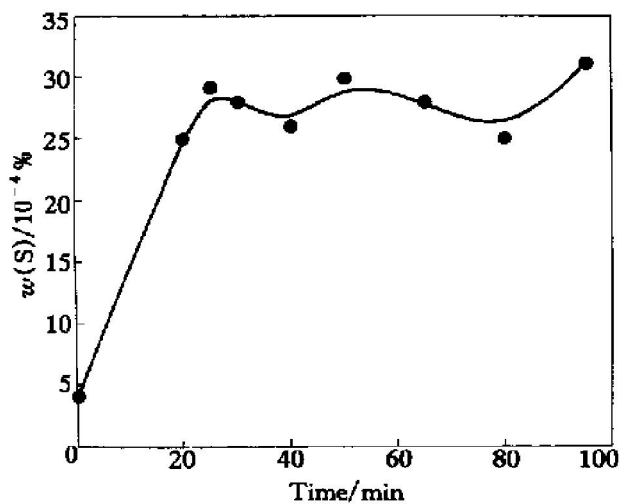**Fig. 1**　TiN and CrS inclusions in
Ni-base superalloy
(a) —TiN;　(b) —CrS

Fig. 2　Change of sulfur content during
refining at 1 773 K

3. 2　Effect of adding Al on desulphurization

Two modes of adding Al have been studied. One was adding 0. 5% Al once each test, the other was adding 0. 5% Al, twice each test, both the total

adding amount being 1% Al. Fig. 3 shows the change of sulfur content when adding Al once and twice. After 15 min of adding 0. 5% Al, the sulfur content decreased from $3. 0 \times 10^{-3}\%$ to $2. 0 \times 10^{-3}\%$. After 20 min it continued to decrease to less than $1. 0 \times 10^{-3}\%$. After 30 min, it dropped to less than $4 \times 10^{-4}\%$. The change of sulfur content when adding 1% Al (each time 0. 5% for two times) was similar to the change of adding 0. 5% Al once. After adding the second part of Al for 5 min, the sulfur content is about $(2 \sim 4) \times 10^{-4}\%$, and then it is kept at this level.
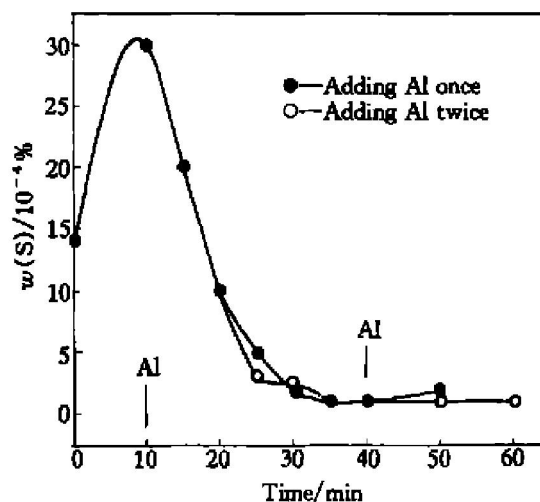

Fig. 3　Change of sulfur content
after adding Al at 1 773 K

3. 3　XRD and composition analysis of CaO crucible wall

In order to understand the reaction mechanism of desulphurization by CaO crucible, small pieces of CaO samples from the inner wall of the crucible before and after its use were separately taken, then ground into powder and analyzed by XRD obtaining results shown in Fig. 4. Fig. 4(a) proves that besides CaO there are some Ca(OH)$_2$, which is due to the absorption of water by CaO during the period of preparation of the
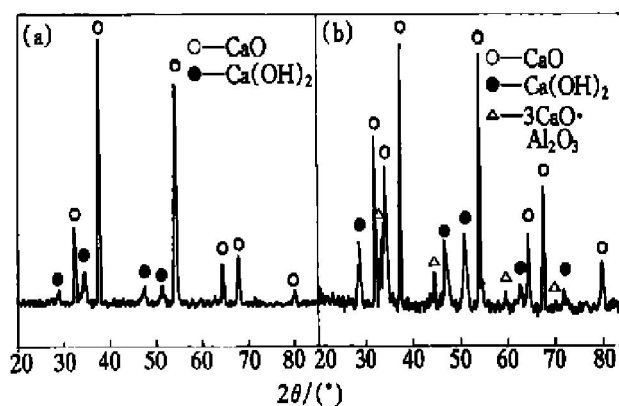

Fig. 4　XRD patterns of CaO powder
(a) —Before use;　(b) —After use

powder. Fig. 4(b) demonstrates that besides CaO and Ca(OH) $_2$, there exists $3CaO \cdot Al_2O_3$ which has lower melting point and strong desulphurization ability. CaO plays a major role to desulphurization, although it can not be confirmed that CaS exists in the experiment, this may be explained that the sulfur content in the powder is very low, so that the CaS formation is so little that it can not be examined clearly in the Fig. 4 of XRD diffraction.

Samples were taken from the inner wall of the CaO crucible after melting and then their sulfur contents were analyzed, which are shown in Table 1. It is known that the sulfur and aluminium contents of the inner wall surface of CaO crucible is 13~ 19 times and about 40 times higher than those of the initial CaO crucible respectively. The sulfur content of the alloy particles adhering on the inner wall of the CaO crucible is 100 times higher than that of the liquid alloy. These facts indicate again that the desulphurization reactions mostly happen between the interface of the liquid alloy and the inner wall of the CaO crucible.

Table 1 Sulfur and aluminium contents of CaO crucible wall

Samples No.	Sample place	S, Al content/ %	
		S	Al
1	To inner wall surface 0~ 1 mm (after smelting)	0. 067~ 0. 076	3. 99
2	To inner wall surface 3~ 6 mm (after smelting)	0. 078~ 0. 095	3. 95
3	Small alloy particles on inner wall (after smelting)	0. 033~ 0. 035	1. 33
4	CaO powder (before use)	0. 005	0. 11

3. 4   Results of denitrogenation

As there are some alloying elements in the Ni-base superalloy having strong affinity with nitrogen, which can intensely affect the denitrogenation process. Many investigations[10, 12, 13] have been studied about the influence of Cr on denitrogenation, and the results showed that Cr notably increases the nitrogen solubility in Ni-base superalloy and the difficulty of denitrogenation. In this experiment, the Ni-base superalloy contained 6% Cr, the refining temperature was 1 773 K, the vacuum of the furnace usually was about 0. 1 Pa, the results of the experiment are shown in Fig. 5, Fig. 6 and Table 2. It was known from Fig. 5 that after smelting, the nitrogen content decreases gradually with the increase of refining time. After refining for 60 min at 1 773 K, the nitrogen content decreased from $4 \times 10^{-4}\%$ to $1 \times 10^{-4}\%$, and for 80 min at 1 873 K it decreased from $5 \times 10^{-4}\%$ to $2 \times 10^{-4}\%$. While the charge just smelting, the nitrogen content depended on the time of the
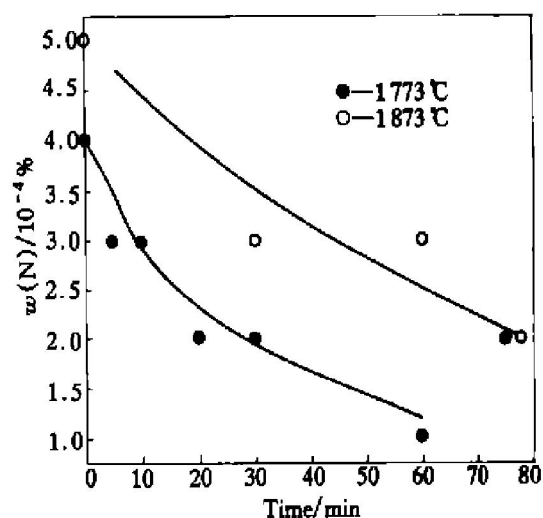

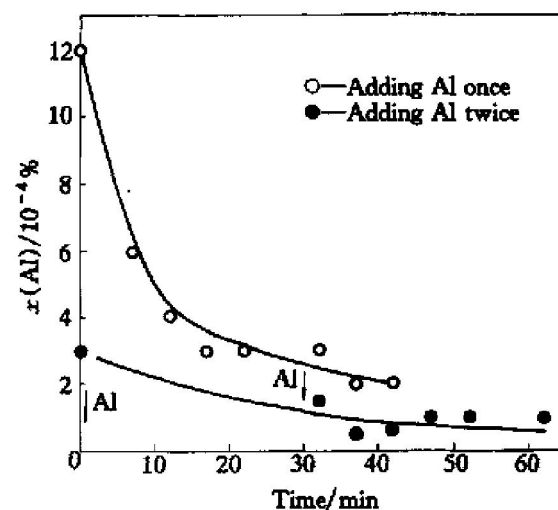**Fig. 5**   Change of nitrogen during refining at 1 773 K and 1 873 K

Fig. 6   Influence of adding Al on denitrogenation at 1 773 K

Table 2   Influence of adding 1% Ti on denitrogenation at 1 773 K

Heat	Pressure / Pa	$[N]_0$ $10^{-4}\%$	$[N]$ $10^{-4}\%$	$([N] - [N]_0)$ $10^{-4}\%$
1	0. 1	1	3	2
2	0. 1	10	7	− 3
3	0. 1	2	2*	0
4	0. 1	2	2	0
5	0. 1	2	2	0
6	6~ 19	2	3	1

Note: [1] ―[N] $_0$ is the nitrogen content before adding Ti;
[2] ―[N] is nitrogen content after adding Ti for 10 min;
[3] ―* is nitrogen content in liquid alloy after adding Ti for 6 min.

smelting period. It was known from Fig. 6 that adding Al promoted denitrogenation. After refining

for 42 min when adding 0. 5% Al once, the nitrogen content decreased from $12 \times 10^{-4}\%$ to $2 \times 10^{-4}\%$. Adding 0. 5% Al twice and refining for 62 min could make nitrogen content decrease from $3 \times 10^{-4}\%$ to $1 \times 10^{-4}\%$. The experiment results of adding 1% Ti to denitrogenation are shown in Table 2.

The denitrogenation effect was studied when totally adding 4% Al, each time 2% Al. The results were similar to that of adding 0. 5% Al. There was no evident difference.

3. 5　Calculation of nitrogen solubility in Ni-base superalloy

Many investigations showed that the relationship between nitrogen solubility in Ni-base superalloy and nitrogen partial pressure obeys to Sievert's law, by which the nitrogen solubility in Ni-base superalloy can be calculated. Because of lack of data of interaction coefficients between nitrogen and alloying elements, except Cr and Co, the other data were chosen from liquid Fe alloy and calculated approximately. The calculating results could be used to discuss qualitatively. The interaction coefficients of alloying elements to nitrogen used for calculation are listed in Table 3. Because [O], [N], [S] contents in the Ni-base superalloy were very low, the influences of e_N^N, e_N^O and e_N^S were neglected.

Table 3　Interaction coefficients of nitrogen with alloying elements at 1 873 K

j	$e_{N(Ni)}^{j}$	$e_{N(Fe)}^{j}$	e_N^{jj}
Cr	− 0. 101		0. 002 1
Co	− 0. 012*		
Al		− 0. 028	
Mo		− 0. 011	
W		− 0. 002	
Ti		− 0. 530	

Note: * calculated value.

For the dissolution of N_2 in liquid Ni-base alloy the equilibrium relation can be expressed as following

$$1/2N_2 = [N]_{Ni} \tag{1}$$

According to Sievert's law, the nitrogen solubil-

ity at different nitrogen partial pressures can be calculated by formula[2]

$$[N] = k \frac{\sqrt{p_{N_2}}}{f_N} \tag{2}$$

where p_{N_2} is the nitrogen partial pressure, Pa; f_N is the activity coefficient of nitrogen in Ni-base superalloy; k is the equilibrium constant of Eqn. (1).

According to Wada's data, $k = 0. 001 31\%$ at 1 773 K[13] was chosen and f_N could be calculated according to the data of Table 3. The result is $f_N = 0. 218$, and then the nitrogen solubility at different nitrogen partial pressures could be calculated. The influence of adding Al and Ti on nitrogen solubility could also be calculated in the same way. All the calculating results are listed in Table 4.

The data in Table 4 are the nitrogen solubility at 1 873 K, but the experiment results were got principally at 1 773 K. According to the experiment results of Wada[13] and Pehlke[9], the nitrogen solubility in Ni-base alloy at 1 773 K was a little higher than that at 1 873 K. The increment was about 7% ~ 15%, so that the experiment results could be discussed with the data in Table 4. The calculated results showed that the nitrogen content in Ni-6Cr-5Co-2Mo-6W alloy under 0. 13 ~ 1. 33 Pa at 1 773 ~ 1 873 K could be decreased from $5 \times 10^{-4}\%$ to $1 \times 10^{-4}\%$, which is shown in Fig. 5, as compared with the experimental results.

3. 6　Influence of vacuum on denitrogenation

It is known from Sievert's law that the increase of vacuum is an effective measurement to accelerate denitrogenation ratio, especially when the alloy contains strong nitride forming elements. For example to heat 6 in Table 2, the vacuum level was 6 ~ 19 Pa. After adding 1% Ti, the nitrogen content could be decreased from about $5 \times 10^{-4}\%$ to $4 \times 10^{-4}\%$. But at 0. 1 Pa. After adding 1% Ti, the nitrogen content could be decreased to below $2 \times 10^{-4}\%$. From the calculated results in Table 4, it can be concluded that the vacuum has evident effect on the decrease of nitrogen solubility in Ni-base alloy. The degree that nitrogen content approached to nitrogen solubility was decided by denitrogenation kinetics conditions.

Table 4　Influence of adding Al and Ti on nitrogen solubility at 1 873 K

p_{N_2}/Pa	[N]/$10^{-4}\%$				
	Master alloy	Master alloy+ 0. 5% Al	Master alloy+ 1% Al	Master alloy+ 4% Al	Master alloy+ 4% Al+ 1% Ti
$1. 01 \times 10^5$	60. 00	62. 00	64. 00	78. 00	264. 00
19	0. 82	0. 84	0. 87	1. 06	3. 58
6	0. 46	0. 48	0. 49	0. 60	2. 03
1. 33	0. 22	0. 23	0. 23	0. 28	0. 96
0. 13	0. 07	0. 07	0. 07	0. 08	0. 30

4 CONCLUSIONS

1) The desulphurization process does not occur only by using CaO crucible during the vacuum smelting process. Otherwise it is possible that the sulfur in the CaO crucible moves into the liquid Ni-base alloy and results in the increase of sulfur content in the liquid alloy.

2) Adding Al can make desulphurization process carry out obviously. $0.5\% \sim 1.0\%$ Al can desulphurize the liquid Ni-alloy from $3.0 \times 10^{-3}\%$ to $(2 \sim 4) \times 10^{-4}\%$.

3) Al reacts with CaO crucible and forms $3CaO \cdot Al_2O_3$ slag, which accelerate enormously the desulphurization process. The desulphurization process carries out between the interface of the $3CaO \cdot Al_2O_3$ slag on the inner wall of CaO crucible and the liquid alloy.

4) The nitrogen content can be reduced from $5 \times 10^{-4}\%$ to $2 \times 10^{-4}\%$ at $1873\,K$ and $0.1\,Pa$. Adding Al slightly accelerates the denitrogenation ratio when smelting in a CaO crucible. The nitrogen content could also be reduced from $4 \times 10^{-4}\%$ to $1 \times 10^{-4}\%$ at $1773\,K$.

5) Ti has adverse effect on denitrogenation process. Adding 1% Ti, the nitrogen content can be reduced from $5 \times 10^{-4}\%$ to $2 \times 10^{-4}\%$ at $1773\,K$ and $0.1\,Pa$. At $6 \sim 19\,Pa$ and $1773\,K$ the nitrogen content can be reduced from $5 \times 10^{-4}\%$ to $4 \times 10^{-4}\%$.

6) The nitrogen solubility of Ni-base superalloy is calculated at different pressure and amounts of Al and Ti addition. The increase of vacuum is a powerful measurement to denitrogenation.

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