

Article

Behavior of Nitrogen in GH4169 Superalloy Melt during Vacuum Induction Melting Using Returned Materials

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Abstract: The nitrogen behavior of superalloy melt GH4169 during the vacuum induction melting (VIM) process was clarified by using different proportions of returned materials including block-shaped returned material, chip-shaped returned material, and pure materials to produce a high-purity superalloy melt and provide guidance for the purification of the superalloy melt. For the nitrogen removal during the VIM process, the denitrification rate in the refining period reached 10 ppm per hour on average, which is significantly higher than 1 ppm per hour on average in the melting period. The denitrification reaction of superalloy melt GH4169 under extremely low vacuum pressure is controlled by both the mass transfer of nitrogen in the melt and the chemical reaction of the liquid–gas interface. The nitrogen removal of superalloy melts during VIM occurs through the two methods of gasification denitrification and nitride floatation because the nitrides begin to precipitate in the liquid phase at 1550 °C. A higher nitrogen removal rate can be obtained by increasing the proportion of chip-shaped material or decreasing the proportion of block-shaped material.

Keywords: vacuum induction melting; superalloy; denitrification; returned materials; nitrides



Citation: Gao, S.; Wang, M.; Xie, X.; Liu, M.; Bao, Y. Behavior of Nitrogen in GH4169 Superalloy Melt during Vacuum Induction Melting Using Returned Materials. *Metals* **2021**, *11*, 1119. <https://doi.org/10.3390/met11071119>

Academic Editor: Evgeny A. Kolubaev

Received: 31 May 2021

Accepted: 6 July 2021

Published: 13 July 2021

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1. Introduction

The Ni-based superalloy has been widely applied in the hot parts of aerospace turbine engines and chemical equipment [1]. The trace elements in superalloys can be classified into beneficial elements (e.g., C, B, Zr, Mg, Re, etc.) and harmful elements (e.g., H, O, N, S, Se, Te, Sb, Bi, Pb, Cu, etc.) [2]. Most of the harmful elements such as H, Se, Te, Bi, Pb, and Cu can be easily removed in the form of gas during the vacuum induction melting (VIM) process because of their low solubility in the melt or high vapor pressure. However, the highly harmful oxygen and nitrogen are difficult to remove because these impurities can easily contaminate the melt via the charge, refractory materials, and environmental gases. The removal and purification of oxygen, nitrogen and sulfur in the superalloy, and the control of segregation and precipitate, are gradually becoming the hotspots of superalloys [3–7].

The mechanical properties of a superalloy are influenced by the characteristics, size and morphologies of inclusions and carbides. Inclusions degrade the mechanical properties (e.g., tensile strength and fracture, specifically fatigue properties) of superalloys [8–12]. It was reported in [13] that the single mixed inclusions (oxide as the core, nitride as the shell) in the slab were mainly transformed to clusters during levitation melting of an Ni-based super alloy. The turbulent collision dominates the aggregation of inclusions, while Stokes collision dominates the floatation of inclusions. The morphologies of carbonitrides in Inconel 718 superalloy were changed from cluster block or single octahedral in ingots to skeleton-like after calcium treatment in the electroslag remelting (ESR) process due to the modification of oxide inclusions by Ca-treatment resulting in a change in precipitation and growth conditions for carbonitrides [14]. Song et al. [15] found that La added in

a 22Cr-14W-2Mo superalloy increases the heterogeneous nucleus of M₆C carbides and refines the carbides in the superalloy. It was reported in [16,17] that rare-earth elements can promote the phase transformation, counteract deleterious elements such as N, O, S, P, etc., and refine the microstructure of the superalloy due to their special physical and chemical characteristics [18]. Nitrogen and sulfur present in superalloys are treated as impurities in the charge materials and in each step of the alloy processing because they have a deleterious effect on the adherence of the oxide layer, which is a critical feature for the life span of the superalloy [19]. Ta-addition to Ti-containing Ni-based alloys can promote external alumina formation by forming a mixed Ti/Ta oxide compound, hence preventing the enhancement of chromia growth by Ti incorporation, which makes a positive contribution on oxidation resistance in SO₂ containing, high pO₂ environments [20].

In the practical production of nickel-based superalloys, castings with serious defects, such as sprues, runners, risers, etc., will inevitably be produced. These castings cannot be directly employed for the use in parts manufacturing. In addition, waste materials such as chips, corners and scrap parts are also generated during the processing [21,22]. The final weight of finished parts often only accounts for 30% of the weight of the original smelted alloy and even only 10% for some parts with complex shapes. More than 70% of the production of superalloys is in the form of sprues, runner, risers, scrap parts and cutting pieces. These scraps are similar in composition to the final product of the superalloy and can be used as returned materials to produce superalloy on the premise that harmful elements included in the returned materials can be well controlled.

For superalloys, nitrogen exists in solution or as nitride or carbonitride. Coarse primary TiN inclusions occur when the nitrogen content is higher than the saturated solubility of TiN at solidus. The content of such inclusions in the alloy is more than one order of magnitude larger than that of oxide inclusions, which will seriously affect the mechanical behavior of nickel-based superalloys [23]. In addition, the presence of Ti, Nb, and other elements with high affinity to nitrogen further increases the difficulty of nitrogen removal. With the continuous development of material science, superalloys require a strict control range of nitrogen content, which must be further reduced [24]. Therefore, it is important to study the denitrification reaction mechanism and nitride formation rule of the superalloy during vacuum smelting for further realization of low nitrogen control. The present work aimed to clarify the nitrogen behavior in the superalloy melt when returned materials are used to produce superalloy melt, and to provide guidance for the purification of superalloy melt.

2. Experimental Process and Methods

2.1. Material Preparation

Considering the influence of impurities and harmful elements in the returned materials on the cleanness of the superalloy, the returned materials must be cleaned before charging into the furnace. For the block-shaped returned material, the oxide layer of the surface was peeled off by machining, while the chip-shaped returned material was chopped and cleaned with a special cleaning agent (the components of which are confidential) as shown in Figure 1.

Three cases, listed in Table 1, were designed to investigate the behavior of nitrogen in superalloy melt during vacuum induction melting using different ratios of block-shaped and chip-shaped returned materials and pure materials. Block-shaped returned material (BRM) is mainly from the recycling of sprues, runners, risers, and scrapped superalloy machine parts. Chip-shaped returned material (CRM) is mainly from chips in the cutting and machining of the forging. The composition and cleanness of CRM are close to the final product, but the fluid oil adhering on the surface of CRM will cause the pickup of harmful elements during the melting process. Pure materials (PM) are high-purity main element alloys with very low residual elements.

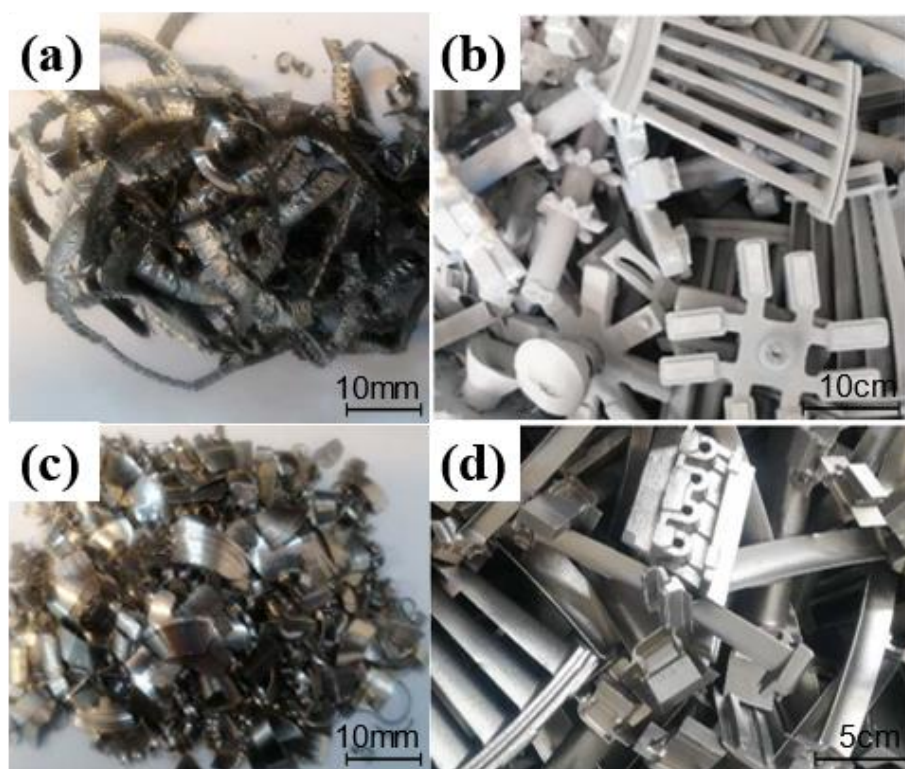


Figure 1. Returned materials before cleaning—(a) chip-shaped and (b) block-shaped—and after cleaning—(c) chip-shaped and (d) block-shaped.

Table 1. Experimental scheme with different mass ratio of return materials.

Scheme	Block-Shaped Returned Material	Chip-Shaped Returned Material	Pure Material
A	70%	/	30%
B	/	70%	30%
C	25%	45%	30%

A (70%BRM–0%CRM–30%PM); B (0%BRM–70%CRM–30%PM); C (25%BRM–45%CRM–30%PM).

In the three cases, the pure material was maintained at the same level of 30 wt%, and the returned materials in different cases were changed. Block-shaped and chip-shaped returned materials were used in the Case-A and Case-B, respectively. In Case-C, the mass ratio of block-shaped and chip-shaped returned material was 5:9.

2.2. Experimental Procedure

The industrial production route of GH4169 superalloy is “vacuum induction melting (VIM) → electroslag remelting (ESR) → vacuum arc remelting (VAR)”. Active metal elements (such as Ti) in GH4169 can easily be oxidized and nitrided when they are melted in the atmosphere, forming a large amount of inclusion. High quality products can only be obtained by vacuum smelting. VIM can greatly remove the harmful elements and gas in the melt through the excellent vacuum atmosphere, guaranteeing the precise chemical composition in the ingot, but it is difficult to eliminate the metallurgical defects (e.g., loose, shrinkage cavity, segregation) in the ingot. ESR is very efficient for deep desulfurization and inclusion removal, but macro-segregation is easily formed in the center of the ingot of ESR. VAR possesses the merit of refining the grain and improving the segregation, which guarantees the hot-machining performance of the superalloy. The process combination of VIM, ESR, and VAR provides the conditions for smelting a high-performance superalloy with returned materials.

The present study focused on the degassing and purification of melt during the VIM process. The superalloy was smelted in a 3-ton vacuum induction melting furnace (VIM-VIDP1000 manufactured by ALD in Hanau, Germany) with a certain ratio of returned materials (70%) and pure material (30%), and the total charging capacity of the alloy was about 2.3 ton per furnace. The air leak rate of the furnace was $32 \text{ Pa} \cdot \text{L} \cdot \text{s}^{-1}$. The ultimate vacuum degree of the VIM can reach 0.07 Pa, which is very beneficial for degassing and removing inclusions. The target chemical composition of superalloy GH4169 is listed in Table 2 (T.O and T.N represent the sum of free nitrogen and oxygen in metals and combined nitrogen and oxygen). In the smelting process, the target composition was based on the median value of the standard chemical composition with the consideration of effectively reducing the contents of harmful elements of oxygen and nitrogen in the melt to below 10 ppm and 55 ppm, respectively.

Table 2. Chemical composition of superalloy GH4169, wt%.

Elements	C	Mn	Ni	Cr	Mo	Al	Ti	Nb	Fe	T.O	T.N
Standard range	0.015–0.036	≤0.35	52.0–55.0	17.00–19.00	2.80–3.15	0.30–0.65	0.75–1.15	5.20–5.55	16.0–19.0	≤0.0025	≤0.010
Target control	0.023	/	53.5	18.0	2.95	0.6	0.95	5.45	17.0	≤0.001	≤0.0055

During the VIM process, the operation timing of the charge materials addition directly affects the loss of elements and the purification effect of the melt. Therefore, elements that are not easily oxidized and volatilized were charged before the induction heating, while the oxidized and volatile elements were added successively after the raw material was melted. Figure 2 shows the detailed operations during the VIM process. In order to reduce the loss caused by oxidation during the heating process, the vacuum pressure in the smelting chamber must be decreased to below 30 Pa before the raw material was charged. Then, the charge materials including pure nickel-plate ($\text{Ni} > 99.987 \text{ wt\%}$), pure iron ($\text{Fe} > 99.98 \text{ wt\%}$), molybdenum bar ($\text{Mo} > 99.99 \text{ wt\%}$), and returned materials (e.g., block-shaped material and chip-shaped material) were gradually added into the crucible in batches according to the target composition. The induction furnace started the heating operation to melt the charged materials after the first batch of about 200 kg of charge materials were added. The total melting time was about 5 h because the charge material was added eight times at 15 Pa pressure. The melting period lasted for about 5 h under the pressure of 15 Pa. At the end of the melting period, the nickel–niobium alloy ($\text{Ni} + \text{Nb} > 99.3\%$) and pure chromium ($>99.4\%$) were added into the melt for alloying. When the charging material was fully melted, Sample-1 was taken after 5 min using a vacuum sampler.

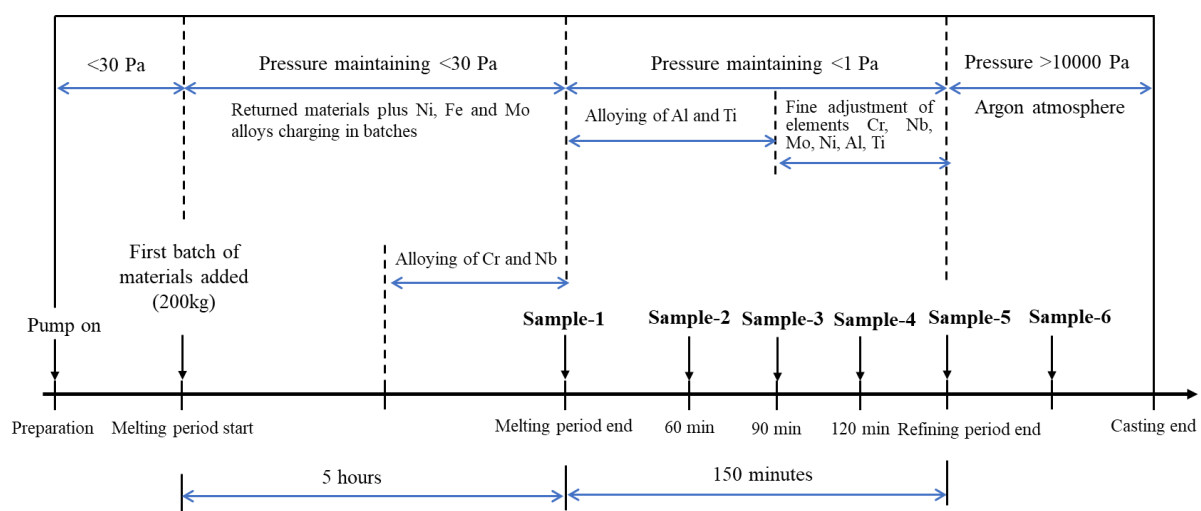


Figure 2. Detailed operations during the process of VIM.

After the vacuum pressure was decreased from 15 Pa to below 1 Pa, the process turned to the refining period. The alloying of aluminum and titanium and the fine adjustment of chemical composition were carried out based on the chemical composition of Sample-1, and the samples were taken at intervals of 30 min until the end of the refining period. When the target chemical composition of the superalloy melt was reached, the sample-5 was taken before the casting. Subsequently, the superalloy melt was poured into an ingot mould with Pa of protective argon atmosphere; meanwhile filling argon into the smelting chamber was applied to decrease the reoxidation of the casting process. The process of argon flushing and charging lasted about 30 min in the pouring period, and the actual pure pouring time was about 20–30 min.

All the samples were taken through the automatic sampling device fixed on the top of the smelting chamber. Specimens, including two rod-shaped specimens with ϕ 5 mm $\times$ 15 mm, one cubic-shaped specimen with 10 mm $\times$ 10 mm $\times$ 10 mm, and one cylinder-shaped specimen with size of ϕ 30 mm $\times$ 30 mm (height), were machined from the middle part of the samples for the analysis of nitrogen, inclusions, and chemical compositions after a standard metallographic process.

The nitrogen of the samples was analyzed using an automatic analyzer of oxygen and nitrogen (TCH 600, LECO, St. Joseph, MI, USA). The chemical compositions of the samples were analyzed via a Direct Reading Spectrometer (ARL iSpark 8860, Thermo Fisher, Waltham, MA, USA). The sizes, shapes, and chemical composition of the inclusions were characterized by an automatic inclusions analysis system (Evo18, Zeiss, Oberkochen, Germany), with a scanning area of 25 mm². The formation of inclusions and degassing of the superalloy melt under vacuum atmosphere were analyzed by using thermodynamic software and relevant databases (FactSage 7.2, codeveloped by Thermfact/CRCT, Montreal, QC, Canada, and GTT-Technologies, Herzogenrath, Germany).

3. Results and Discussion

3.1. Operation Curves and Chemical Composition of Superalloy Melt during Smelting Process

The smelting process of the superalloy includes three stages: melting period (300 min), refining period (150 min), and casting period (60 min). Figure 3 shows the operation curves of temperature and pressure at different stages. During the melting period, the materials were charged into the furnace in batches under a pressure of below 15 Pa until all the materials were fully melted, and the temperature changed between 1775 and 1800 K. When the pressure decreased from 12 Pa to below 1 Pa, the refining period started. The temperatures in the refining period were maintained between 1775 and 1800 K. After 150 min refinement, the high-purity superalloy melt was poured into an ingot mold with Pa of protective argon atmosphere, and the temperature of the casting process was controlled between 1755 and 1745 K. Table 3 shows the chemical composition of different cases during the smelting process.

3.2. Change of Nitrogen in the Superalloy Melt during Smelting Process

As shown in Figure 4, the square-, circle-, and triangle-marked curves represent Cases A, -B, and -C, respectively. It can be seen that in Case-C two data points are missing due to the sampling failure. The initial nitrogen of the charge materials changed between 70 and 80 ppm regarding different combinations of returned materials estimated by the calculation of materials charged and the initial chemical compositions in the raw materials. Then, it decreased to the range of 61 to 64 ppm after all the charge materials had been melted. The difference in nitrogen content for different returned materials narrowed at the melting endpoint. The denitrification rate of the melt maintained a very low level during the 5 h of the melting process, because the charge materials were added in batches to melt them gradually to avoid splashing. The denitrification rate in the refining period reached 10 ppm per hour on average, which is significantly higher than 1 ppm per hour on average in the melting period. Low vacuum pressure (<1 Pa) and good stirring conditions promote the removal of nitrogen in the melt. Despite the protection of argon atmosphere, the melt still

had a significant nitrogen pickup due to air leakage during the casting process. Case-B obtained the best denitrification effect and lowest nitrogen in the final product.

Figure 5 was obtained by the statistical treatment of the number density and average size of inclusions in the EVO results, and shows the change of quantity density and average size of nitride in the superalloy samples obtained during the refining process. In Figure 5, there is a difference in the number of nitrides in Case-A, -B, and -C. This difference may be caused by the difference in the number of oxides due to the bimodal effect of charging during the smelting period [25]. The surface area of different shapes of charge materials is different, which may lead to different oxide films brought in by them and may lead to different nitrogen compounds in the initial stage of refining [26].

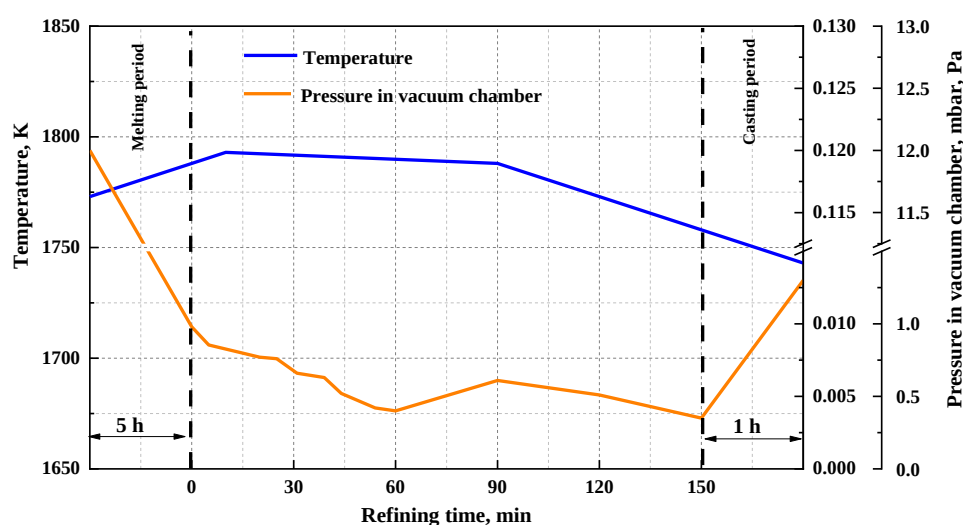


Figure 3. Operation curves of temperature and pressure at different stages.

Table 3. Chemical composition of different cases during the smelting process.

Case	Time/Min	C	Mn	Si	S	P	Ni	Cr	Mo	Al	Ti	Cu	B	Nb	Co	Fe
A (70%BRM-0%CRM-30%PM)	0	0.024	0.03	0.052	0.0008	0.01	54.69	19.01	2.80	0.32	0.68	0.018	0.003	5.14	0.14	16.16
	60	0.023	0.023	0.053	0.0008	0.009	53.75	18.38	2.95	0.56	0.92	0.018	0.003	5.38	0.29	16.74
	90	0.023	0.022	0.057	0.0008	0.013	53.89	18.36	2.97	0.56	0.93	0.017	0.003	5.43	0.29	16.66
	120	0.023	0.02	0.057	0.0008	0.011	53.79	18.36	2.96	0.56	0.92	0.017	0.003	5.4	0.29	16.72
	150	0.027	0.019	0.055	0.0007	0.009	54.23	18.34	2.99	0.61	0.99	0.016	0.003	5.43	0.3	16.71
	200	0.029	0.018	0.054	0.0007	0.011	53.97	18.24	2.97	0.6	0.98	0.015	0.005	5.39	0.3	16.75
B (0%BRM-70%CRM-30%PM)	0	0.021	0.032	0.052	0.0008	0.009	55.44	18.53	2.86	0.36	0.85	0.026	0.003	5.5	0.23	15.12
	60	0.024	0.019	0.053	0.0008	0.013	53.96	17.9	2.96	0.6	0.97	0.021	0.003	5.61	0.3	16.68
	90	0.023	0.019	0.055	0.0008	0.015	54.16	17.93	2.93	0.61	0.95	0.02	0.003	5.29	0.3	16.87
	120	0.023	0.017	0.053	0.0008	0.014	53.97	17.78	2.96	0.6	0.98	0.019	0.003	5.64	0.3	16.64
	150	0.023	0.016	0.053	0.0008	0.013	54	17.91	2.96	0.62	0.96	0.018	0.003	5.6	0.29	16.94
C (25%BRM-45%CRM-30%PM)	200	0.022	0.012	0.057	0.001	-	53.7	17.22	2.95	0.634	0.98	0.013	-	5.56	-	16.9
	0	0.03	0.032	0.064	0.001	0.01	54.83	18.47	2.88	0.36	0.64	0.02	0.003	5.34	0.17	16.7
	60	0.029	0.024	0.063	0.001	0.012	53.56	18.04	2.97	0.572	0.96	0.02	0.003	5.52	0.29	17.21
	90	0.028	0.018	0.069	0.002	0.013	53.73	17.9	2.99	0.57	0.96	0.02	0.003	5.554	0.29	17.17
	200	0.027	0.016	0.068	0.0015	0.012	53.4	17.89	2.97	0.58	0.96	0.014	0.0045	5.57	0.3	17.09

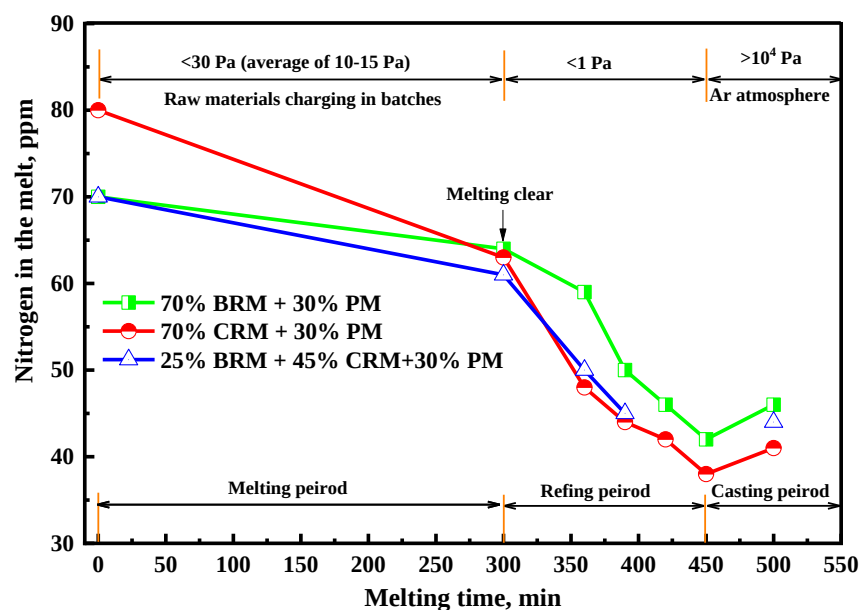


Figure 4. Change of nitrogen in the melt with smelting time.

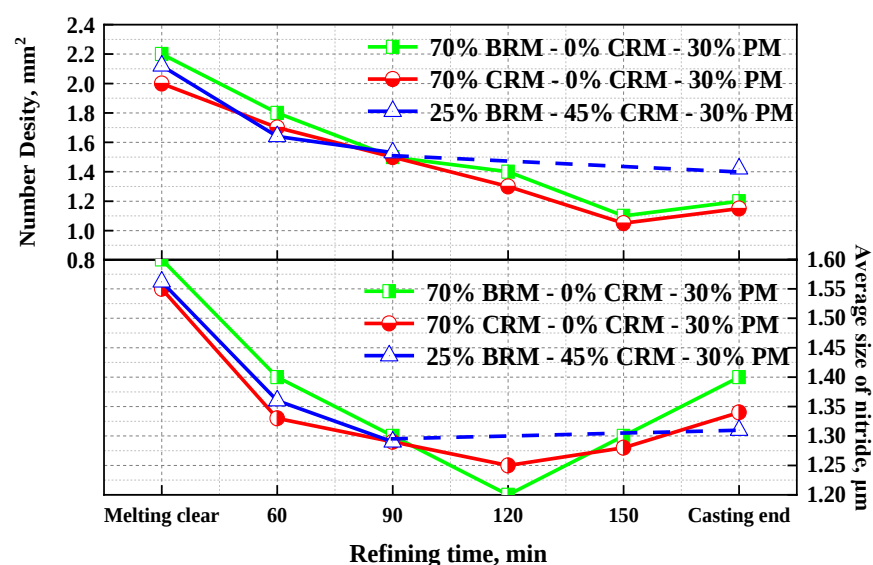


Figure 5. Change of quantity density and average size of nitride in the superalloy samples obtained.

With the refining time, the quantity density of nitrides in different cases shows a similar trend, changing from the average 2.1 per mm^2 at the melting endpoint to 1.1 per mm^2 at the refining end to 1.3 per mm^2 at the casting end. The trend of the variation in the quantity density of nitrides is consistent with that of the nitrogen content, i.e., as the nitrogen content continues to decrease, the quantity density of nitrides also decreases correspondingly. By comparison of the three cases, Case-C with 25% BRM plus 45% CRM plus 30%PM has the largest quantity density of nitride in the casting end, reaching 1.4 per mm^2 . The quantity density of nitrides decreases with the refining time, but the average size changes little, and remains in a range of 1 to 1.5 μm . The single returned material cases (Case-A and Case-B) can obtain lower total nitrogen than the mixed returned material case (Case-C).

3.3. Correlation of Denitrification and Nitrogen Solubility in the Superalloy Melt

Nitrogen in the superalloy exists in three forms: solid solution, compound, and gas, depending on the nitrogen content in the superalloy melt and its saturated solubility. The solubility of nitrogen in the melt and the partial pressure of nitrogen in the environment

obey Sievert's law [27,28]. The Gibbs free energy of reaction, as shown in Equation (1), can be calculated by Equation (2):

$$\frac{1}{2}\text{N}_2(\text{g}) = [\text{N}] \quad (1)$$

$$\lg K_N = -\frac{3630}{T} - 0.883 \quad (2)$$

where, K is the equilibrium constant expressed as $K_N = f_N[\%N](p_N/p^\theta)^{-0.5}$; $[\%N]$ is the dissolved nitrogen in the melt, wt%; p_N is the dimensionless nitrogen partial pressure of nitrogen; and f_N is the activity coefficient of nitrogen in the melt, which can be obtained by the Wagner model using the interaction coefficient of elements in Table 4.

Table 4. Interaction coefficient of the typical elements in the superalloy at 1873 K. Adapted from ref. [29–32].

Element	C	Cr	Ti	Nb	Mo	Fe
e_N^i	0.09	−0.1	−0.21	−0.072	−0.043	−0.021

The interaction coefficient of elements under an arbitrary temperature ($f_{N,T}$) can be calculated through the correlation of $\frac{\lg f_T}{\lg f_{1873}} = \frac{1873}{T}$ [33]. Based on the aforementioned equations, the change of nitrogen in the melt with respect to the partial pressure of nitrogen at different temperatures can be obtained, as shown in Figure 6.

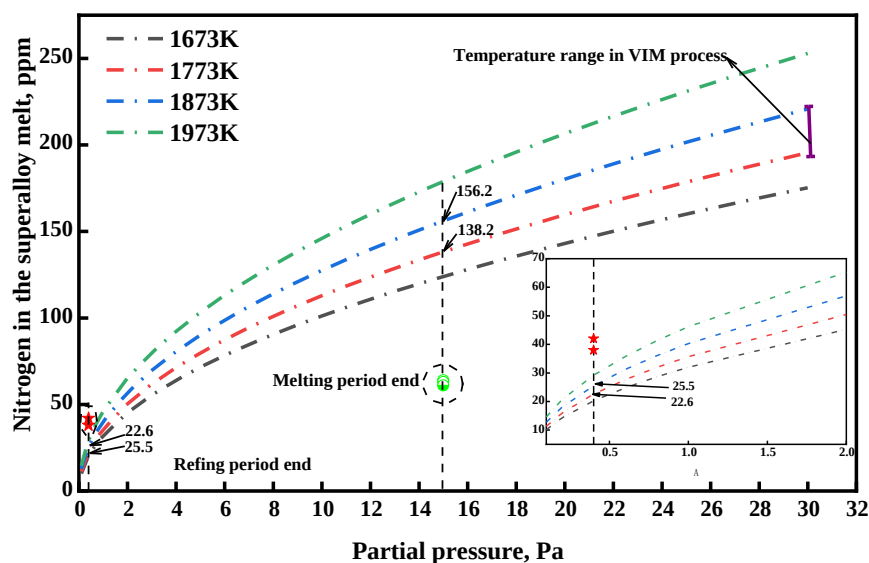


Figure 6. Nitrogen solubility at different partial pressures and temperatures.

It is shown in Figure 6 that, at the end of the melting period, the nitrogen content of 63 ppm on average in the melt is much lower than the theoretical solubility of nitrogen in the melt under the working pressure of 15 Pa. It indicates that the denitrification is difficult to take place under a pressure of 15 Pa after the superalloy is melted. As the pressure decreases to 0.5 Pa on average during the refining period, both nitrogen solubility and nitrogen content in the melt significantly decrease, although there is still a gap between the measured nitrogen in the melt and the theoretical solubility. The phenomenon mentioned above can be attributed to two aspects: (1) the precipitation of nitrogen has not yet reached equilibrium; (2) the nitrogen in the melt is not only in the form of solution. That is, the removal of nitrogen during the smelting process is greatly affected by the kinetic conditions and the chemical composition especially the nitrogen-affinity elements such as Ti, Nb, Al etc., which could form the nitrogen-based compounds.

It was reported in [34–36] that denitrification is a first-order reaction when the limiting step is the mass transfer of nitrogen from the interior of the liquid steel to the gas–liquid interface, while it is a second-order reaction when the denitrification rate is dominated by the chemical reaction of nitrogen atoms forming nitrogen molecules at the gas–liquid interface. Thus, the denitrification rate can be described via the first-order reaction model in Equation (3) or via the second-order reaction model in Equation (4). During the smelting process, the gas in the smelting chamber was continuously pumped out and the pressure in the chamber was maintained at a very low level which caused the N_2 partial pressure in the gas phase to be extremely low. Here, it is considered that the nitrogen content at the gas–liquid interface is in equilibrium with N_2 partial pressure approaching 0.5 Pa. Equations (3) and (4) are integrated, respectively, to obtain Equations (5) and (6). (Y_1 and Y_2 represent the first-order reaction and second-order reaction equations, respectively.)

$$\frac{dC_N}{dt} = -\frac{A}{V}k_1(C_N - C_{Ne}) \quad (3)$$

$$\frac{dC_N}{dt} = \frac{A}{V}k_2(C_{Ne}^2 - C_N^2) \quad (4)$$

$$Y_1 = -\ln \frac{C_{Ne} - C_N}{C_{Ne} - C_{N0}} = \frac{A}{V}k_1t \quad (5)$$

$$Y_2 = -\frac{1}{2C_{Ne}} \left[\ln \left(\frac{C_N - C_{Ne}}{C_N + C_{Ne}} \right) - \ln \left(\frac{C_{N0} - C_{Ne}}{C_{N0} + C_{Ne}} \right) \right] = k_2 \frac{A}{V}t \quad (6)$$

where, k_1 and k_2 are denitrification ratio constants of the first-order reaction and second-order reaction, $m \cdot s^{-1}$, $m \cdot s^{-1} \cdot \%^{-1}$; C_{N0} is the initial nitrogen content in the melt, wt%; t is the smelting time, s; A is the surface area of the superalloy melt, m^2 . V is the volume of the superalloy melt, m^3 . C_N is the nitrogen content in the melt at the time of t , wt%; and C_{Ne} is the nitrogen content at the gas/liquid interface in equilibrium with N_2 partial pressure, wt%.

The relevant data are derived according to Equations (5) and (6), the fitting result of the reaction order is shown in Figure 7, and the fitting parameters are shown in Table 5. According to the first-order reaction model, the mass transfer coefficient k_l is between 7.754×10^{-5} and 9.568×10^{-5} m/s. For the second reaction model, the rate coefficient k_c of the interface chemical reaction is between 0.0098 and $0.0127 m \cdot s^{-1} \cdot \%^{-1}$. The slope of the curve increases with the chip-shaped returned material, which indicates high CRM is beneficial for nitrogen removal under extremely low vacuum pressure. The average coefficients of determination, Y_1 and Y_2 , are both above 0.96. It can be deduced that the denitrification reaction of the superalloy melt under extremely low vacuum pressure is controlled by both the mass transfer of nitrogen in the melt and the chemical reaction of the liquid-gas interface.

3.4. Thermodynamic Consideration of Nitride Formation in the Superalloy Melt

During the smelting process of VIM, there are two main sources of nitrogen, i.e., the introduction of nitrogen from the charge materials and the absorption of nitrogen from air caused by the large leakage rate of the smelting chamber. The nitrogen can exist in three forms: solid solution, compound, and gas—depending on the nitrogen content in the superalloy melt and its saturated solubility. When the nitrogen content is lower than the saturation solubility, it presents mainly in the form of solid solution while the nitrogen may combine with the nitrogen-affinity elements such as Nb, Ti, Al etc., to form the compound or escape as a gas due to the effect of the vacuum atmosphere.

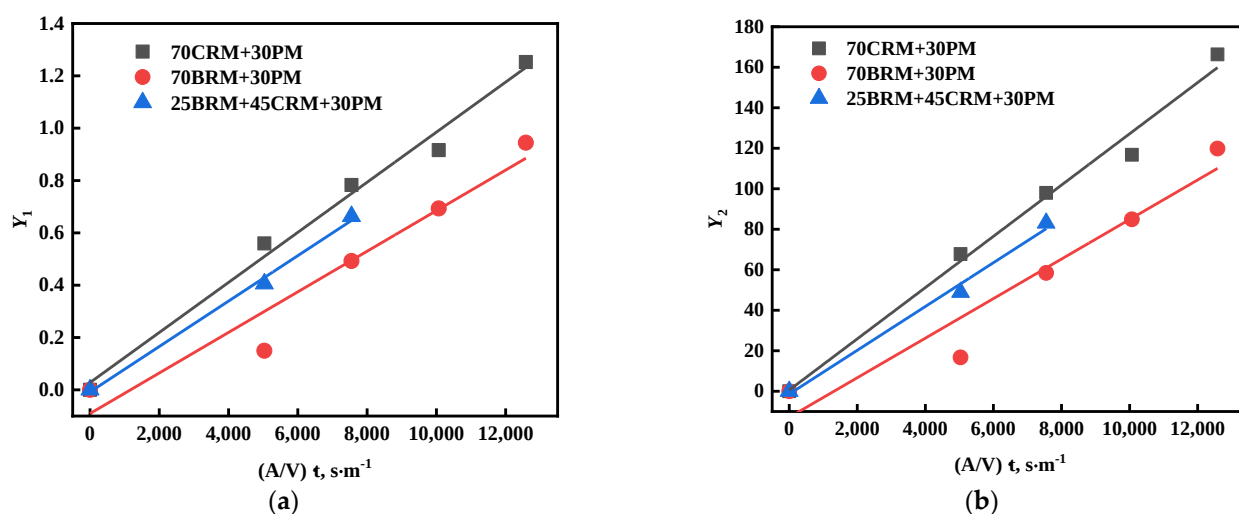


Figure 7. Data fitting of denitrification ratio: (a) the first order reaction model and (b) the second-order reaction model.

Table 5. R2 and Reaction rate k

Reaction Order	Raw Material	R ²
First-order reaction model	70 CRM + 30 PM	0.984
	70 BRM + 30 PM	0.923
	25 BRM + 45 CRM + 30 PM	0.992
Second-order reaction model	70 CRM + 30 PM	0.983
	70 BRM + 30 PM	0.909
	25 BRM + 45 CRM + 30 PM	0.984

It can be seen from Figure 8, that the liquidus and solidus temperature are 1355 °C and 1214 °C, respectively. A small amount of the oxides (M_2O_3 : mainly Al_2O_3 , Ti_2O_3 , and other oxides) co-exist with the liquid phase, while the nitride (MN: mainly TiN and (Nb, Mo)N) begins to precipitate in the liquid phase at 1550 °C, reaching the maximum at 1250 °C. The thermodynamic reactions are shown in Equations (7)–(11). It is indicated that many nitrides could already be present in the melt during the degassing process because the high content of nitride-forming elements such as Ti, Nb, Al existed in the returned materials. The precipitation of nitrides in the liquid-phase promotes the dissolved nitrogen in the melt transforming to nitrogen compounds and hinders the nitrogen desorption during the vacuum process. As shown in Figure 9, three typical inclusions, namely single-phase oxide inclusion, two-phase inclusion of titanium nitride wrapping oxide, and multiphase inclusion with three-layer structure, are found in the melt during the refining period. The fine oxide core provides favorable conditions for the precipitation of titanium nitride, which serves as the nucleation core of niobium and molybdenum nitride. The tendency of multiphase nucleation is related to the low degree of mismatch between particles.



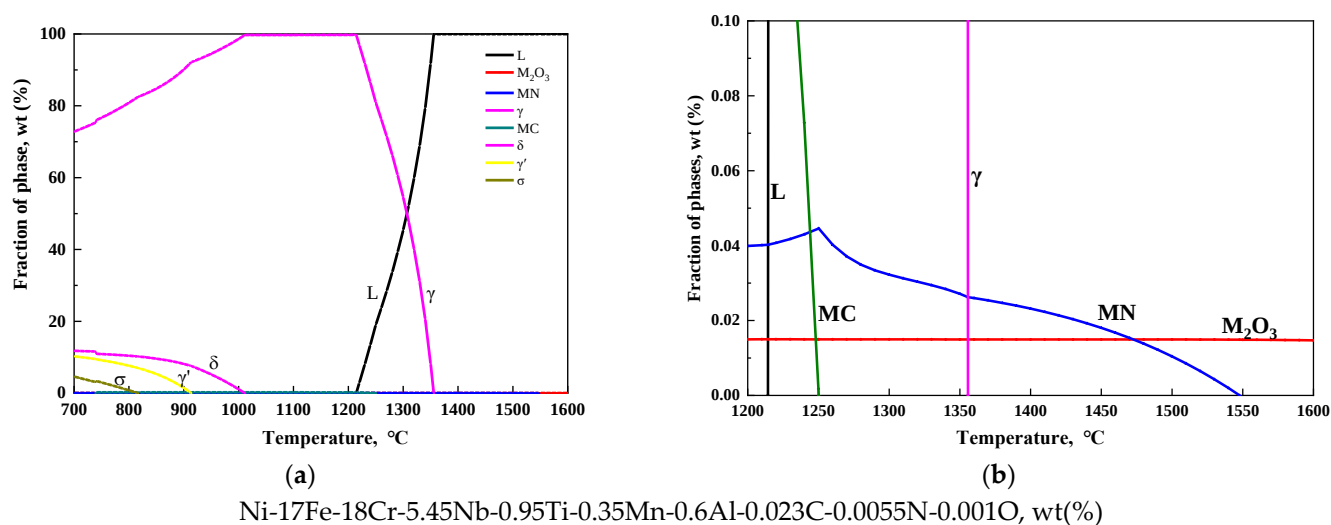


Figure 8. (a) Change of phases fraction in GH 4169 superalloy with temperature, and (b) local enlargement of precipitation phase.

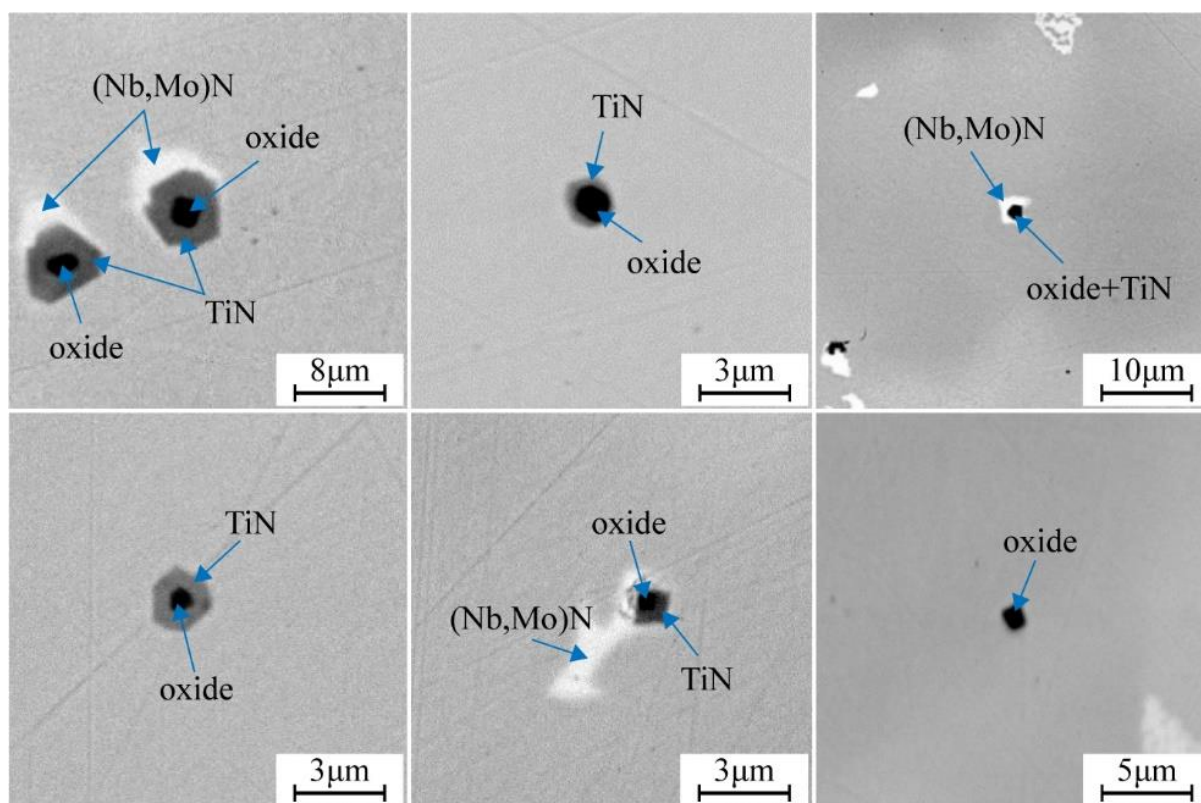


Figure 9. Typical inclusions in the melt during the refining period.

Figure 10 shows a typical multiphase inclusion with a three-layer structure, i.e., TiN grows on 1 μm of $MgO-Al_2O_3$ spinel core, and then (Nb, Mo)N grows on the TiN. This reveals that the formation of precipitates follows the sequence: $MgO-Al_2O_3$ spinel, TiN, and (Nb, Mo)N, which can be verified by the phase precipitation sequence in Figure 8.

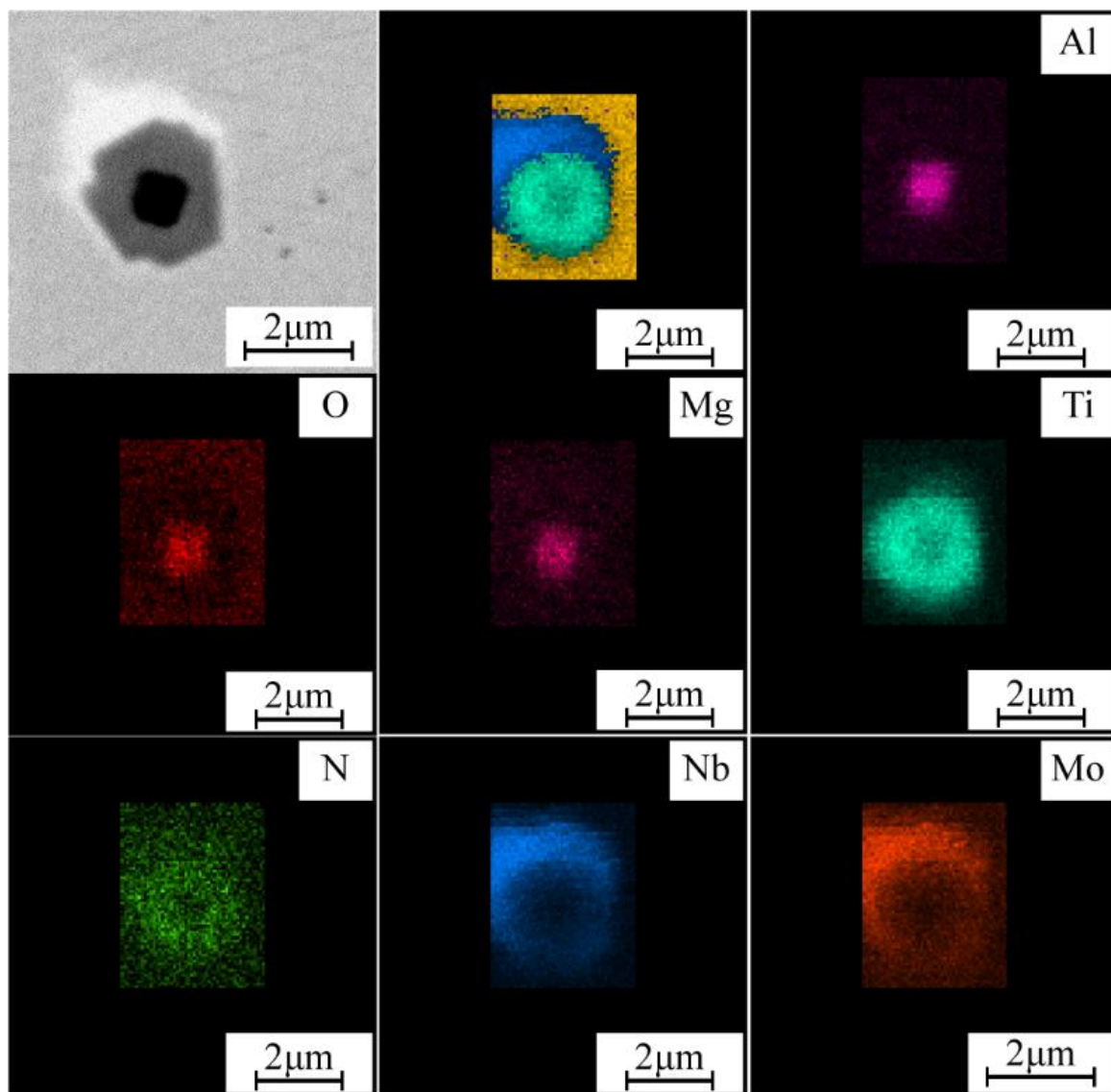


Figure 10. Mapping of a typical multiphase inclusion with a three-layer structure.

As shown in Figure 11, the denitrification rate coefficient increases with the amount of Nb and Ti content in the melt. Titanium and niobium are the formation elements of nitrides in the melt which can promote the formation of nitrides. It was concluded in Figure 8 that the nitride (MN) begins to precipitate in the liquid phase at 1550 °C, and many nitrides such as TiN and (Nb, Mo)N were formed on the oxides core, as can be seen in Figure 10. The denitrification of the superalloy melt in vacuum process is mainly composed of two parts, one is gasification denitrification depending on the pressure of the vacuum chamber, the other is nitride removal depending on the contents of the formation elements of nitrides in the melt. High initial titanium and niobium contents in the superalloy melt means more nitrides are formed during the smelting process, and a part of these nitrides will be removed by floatation. It is concluded in Table 1 that, during the melting process of returned materials, the initial content of Nb and Ti in different cases present a descending order as follows: Case-B, Case-C, Case-A. It can be seen in Figure 12 that the ratio of titanium and nitrogen in the melt increase with refining time and descends in order of Case-B, Case-C, Case-A. That means that the denitrification rate of the superalloy melt decreased with the proportion increase of the block-shaped returned material during the smelting

process. Thus, the block-shaped returned material is not conducive to the denitrification of the superalloy melt.

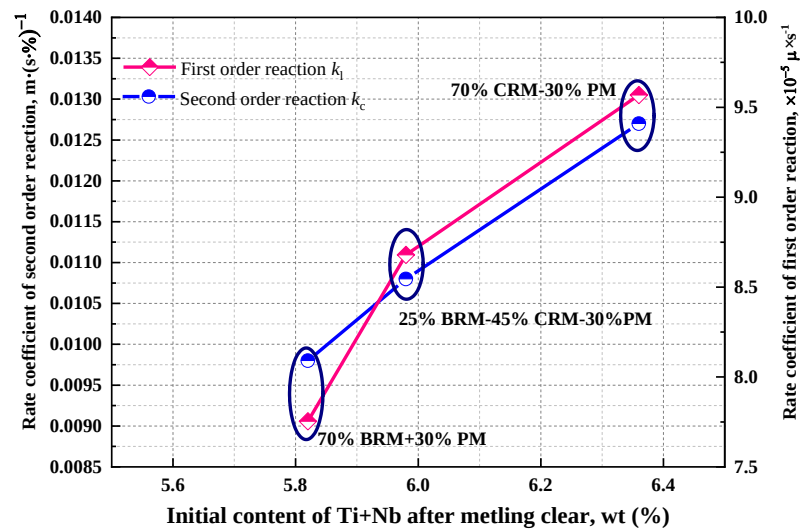


Figure 11. Mapping of a typical multiphase inclusion with a three-layer structure.

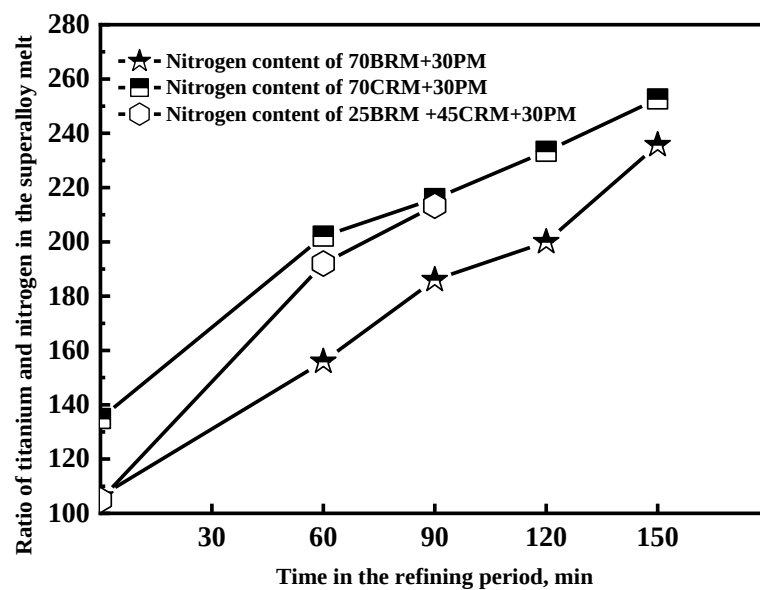


Figure 12. Ratio of titanium and nitrogen in the superalloy melt in the refining period.

4. Conclusions

- (1) The denitrification rates of superalloy melt GH4169 during the VIM process were 1 ppm per hour at the melting period and 10 ppm per hour in the refining period. Low vacuum pressure (<1 Pa) and good stirring conditions promote the removal of nitrogen in the melt.
- (2) The denitrification reaction of superalloy melt GH4169 under extremely low vacuum pressure is controlled by both the mass transfer of nitrogen in the melt and the chemical reaction of the liquid–gas interface. The average coefficients of determination for the first-order and second-order reaction are both above 0.96.
- (3) The liquidus and solidus temperature of GH4169 are 1355 °C and 1214 °C, respectively. A small amount of the oxide (M_2O_3) co-exist with the liquid phase, while the nitride (MN) begins to precipitate in the liquid phase at 1550 °C reaching the maximum at 1250 °C.

- (4) Three typical inclusions, namely single-phase oxide inclusion, two-phase inclusion of titanium nitride wrapping oxide, and multiphase inclusion with three-layer structure, are found in the melt during the refining period.
- (5) The denitrification of the superalloy melt during the vacuum process is due to the gasification denitrification and nitrides floatation, and the denitrification rate decreased with the proportion increase of the block-shaped returned material during the smelting process.

Author Contributions: Conceptualization, M.W. and Y.B.; methodology, S.G. and M.W.; software, X.X. and M.L.; validation, S.G., M.W. and M.L.; formal analysis, M.W. and S.G.; investigation, S.G. and X.X.; resources, M.W.; data curation, S.G., M.L. and M.W.; writing—original draft preparation, M.W. and X.X.; writing—review and editing, M.W. and S.G.; visualization, X.X.; supervision, M.W. and Y.B.; project administration, M.W.; funding acquisition, M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fundamental Research Funds for the Central Universities, grant number FRF-BD-19-022A. The authors wish to express gratitude for the financial support for their research.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The experimental materials were provided by the AVIC Shangda, and the experimental data were completed by engineers from the AVIC Shangda. The authors wish to express their gratitude for this necessary help.

Conflicts of Interest: The authors declare no conflict of interest.

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