PRODUCTION OF HIGH PURITY NIOBIUM MASTER ALLOYS

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Abstract

The metallothermic reduction of niobium oxide with aluminum is the most common production method for the production of high purity niobium containing masteralloys for the production of high grade nickel base superalloys. Usually ferro niobium (FeNb) and nickel niobium (NiNb) are used as masteralloy for this purpose. The aluminothermic production process and the two general plant designs, the reduction in ceramic vessels as well as in permanent copper moulds are described, taking into consideration theoretical aspects. Both production methods are suitable for masteralloy production and fulfill the requirements of the superalloy producers.

Introduction

Nickel base superalloys compete with steel products and even with titanium alloys. They provide the combined benefits of extreme corrosion resistance, heat resistance and very high strength at elevated temperatures. These properties are required for applications such as in land based turbines and aircraft turbine engines, petrochemical industry, on and off shore oil and gas production, power generation, thermal processing, automotive, paper industry and food processing.

Niobium has an important impact as an alloying element in nickel base superalloys. Niobium alloys have become increasingly important in industrial and aircraft applications, where superior heat and corrosion resistance are required. These types of superalloys contain up to 5 wt-% Niobium.

Nickel base superalloys are produced mainly by arc or induction melting (open as well as vacuum) and by mechanical alloying for very high specialized applications.

The alloying with niobium is carried out with the help of master alloys, e.g. nickel niobium and ferro niobium. The use of master alloys for alloying is advantageous. Due to their comparable low melting points the master alloys dissolve very quickly in the molten alloy. Combined with the high purity they enable the production of very homogeneous, high grade superalloys.

Requirements on High Purity Niobium Master Alloys

The purity and quality of high grade superalloys are influenced by the quality of raw materials, melting technology and of course by the quality of the master alloys. The requirements on high purity niobium master alloys therefore are more or less the same as the requirements on the final superalloys regarding the composition and the impurity content.

The impact of impurities on the properties of superalloys can be harmful as well as advantageous. In any case the impurities have to be kept within very tight tolerances in order to control the properties of the superalloys.

The development of suitable master alloys and the development of improved melting technologies, e.g. vacuum melting in the past 30 years, had a major impact on the improvement of the properties of superalloys. In particular, the electrochemical properties are dependent on the level of impurities in the alloy. Elements like sulfur, lead, selenium, tellurium, phosphorous, carbon and silicon are of major importance. The impact of these elements on the corrosion resistance is much higher than any difference in microstructure. The effect on the passivity is in accordance to the following order [1]:

$$S > Se > Te > P > C > Si$$

Other properties of superalloys are also impacted by impurities. The different types of superalloys require different grades of master alloys. Table I shows two typical specifications of FeNb and NiNb high purity master alloys respectively.

Table I Typical specification of high purity (hp) niobium master alloys

Alloy		FeNb 40:60 hp	NiNb 40:60 hp
Production method		metallothermic reduction	metallothermic reduction
Composition (wt.%)			
	Nb	min. 60 balance Fe	min. 58 balance Ni
	Al	max. 1.5	max. 1.0
	C	max. 0.1	max. 0.05
	Cr	max. 0.1	-
	Fe	-	max. 1.0
	P	max. 0.03	max. 0.03
	Pb	max. 0.005	max. 0.002
	S	max. 0.02	max. 0.01
	Si	max. 0.25	max. 0.25
	Ta	max. 0.25	max. 0.25
	Ti	max. 0.1	max. 0.1
	B	-	max. 0.005
	Se	-	max. 0.0002
	Sn	-	max. 0.001
	Ga	-	max. 0.006
	Sb	-	max. 0.001
	Ag	-	max. 0.0005
	Zn	-	max. 0.003
	As	-	max. 0.003
	Te	-	max. 0.001
	N	max. 0.05	max. 0.05
	O	max. 0.10	max. 0.10
Melting temperature		1630 °C	1280 °C
Specific weight		8.2 g/cm^3	8.8 g/cm^3

Method of Production

The most important method for producing niobium containing master alloys for superalloys is the metallothermic reduction by aluminum in one production step. In addition - but only for very special applications - metallothermic reduced master alloys are refined in vacuum induction furnaces (GfE – „Two Step Process“).

The raw material for the production of niobium master alloys is niobium oxide Nb_2O_5. The very tight specifications regarding impurities requires a pure niobium oxide. Table II showes a typical specification for niobium oxide suitable for master alloy production.

Table II Typical specification of niobium oxide for master alloy production

Nb_2O_5	min. 99.0 (wt.-%)
Ta	max. 0.25
Fe	max. 0.15
Si	max. 0.10
Ti	max. 0.10
C	max. 0.05
P	max. 0.01
S	max. 0.01

Material must be free of carbides and nitrides

Metallothermic reductions are carried out at a temperature where both the metal and slag are molten, to achieve a proper separation of the metal and slag phase, although the exothermic reduction at higher temperatures is less complete than at lower temperatures.

Theoretical Considerations [2]

The reduction of Nb_2O_5 by aluminum follows the formula:

$$3\,Nb_2O_5 + 10\,Al = 6\,Nb + 5\,Al_2O_3 \qquad -\Delta G°_T \tag{1}$$

The reaction is exothermic and the free energy $\Delta G°_T$ can be calculated in the temperature range between 298 and 2700 K with the formula:

$$\Delta G°_T = -925{,}3 + 0{,}1362 * T \text{ (kJ/mol}_{Nb2O5}) \tag{2}$$

The reduction of niobium oxide by aluminum does not take place in one step but in several steps via niobium suboxides. Reaction (1) therefore has to be divided into 3 subformulas:

$$3\,Nb_2O_5 + 2\,Al = 6\,NbO_2 + Al_2O_3 \qquad -\Delta G°_T \tag{3}$$

$$3\,NbO_2 + 2\,Al = 3\,NbO + Al_2O_3 \qquad -\Delta G°_T \tag{4}$$

$$3\,NbO + 2\,Al = 3\,Nb + Al_2O_3 \qquad -\Delta G°_T \tag{5}$$

The free energy, $\Delta G°_T$, can be calculated* as follows:

Table III Free Energy of the reaction of the metallothermic reduction of Nb2O5

Reaction	$-\Delta G°_T$ (kJ)			
	2000K	2100K	2200K	2300K
1	1,961	1,899	1,836	1,773
3	524	496	474	470
4	417	407	395	383
5	302	294	287	267

(*) calculated with GTT-Chemsage 4.0 program.

The magnitude of the free energy is an indication of the stability of a chemical compound. Table III shows, that the compound NbO (equation 5) is the most unstable compound in this system. The losses of niobium in the slag therefore has to be as NbO.

The equilibrium of the metallothermic reduction of niobium oxide by aluminum therefore will be controlled by equation (5). The equilibrium can be described as follows:

$$Kp = \frac{N^3_{Nb} * N_{Al2O3}}{N^3_{NbO} * N^2_{Al}} \tag{6}$$

From this equilibrium equation the NbO-content in the slag is dependent on the temperature and on the Al-content in the master alloy and can be derived as:

$$\ln NbO = \frac{\Delta G^o{}_T}{3*RT} - 2/3 \ln Al \tag{7}$$

$\Delta G°_T$	=	free energy	[kJ/mol]
N	=	moles	[-]
K_p	=	equilibrium constant	[-]
R	=	ideal gas law constant	[kJ/mol*°K]
T	=	temperature	[°K]

Figure 1 shows the dependency of NbO-content in the slag as a function of the Al-content in the master alloy at different temperatures.

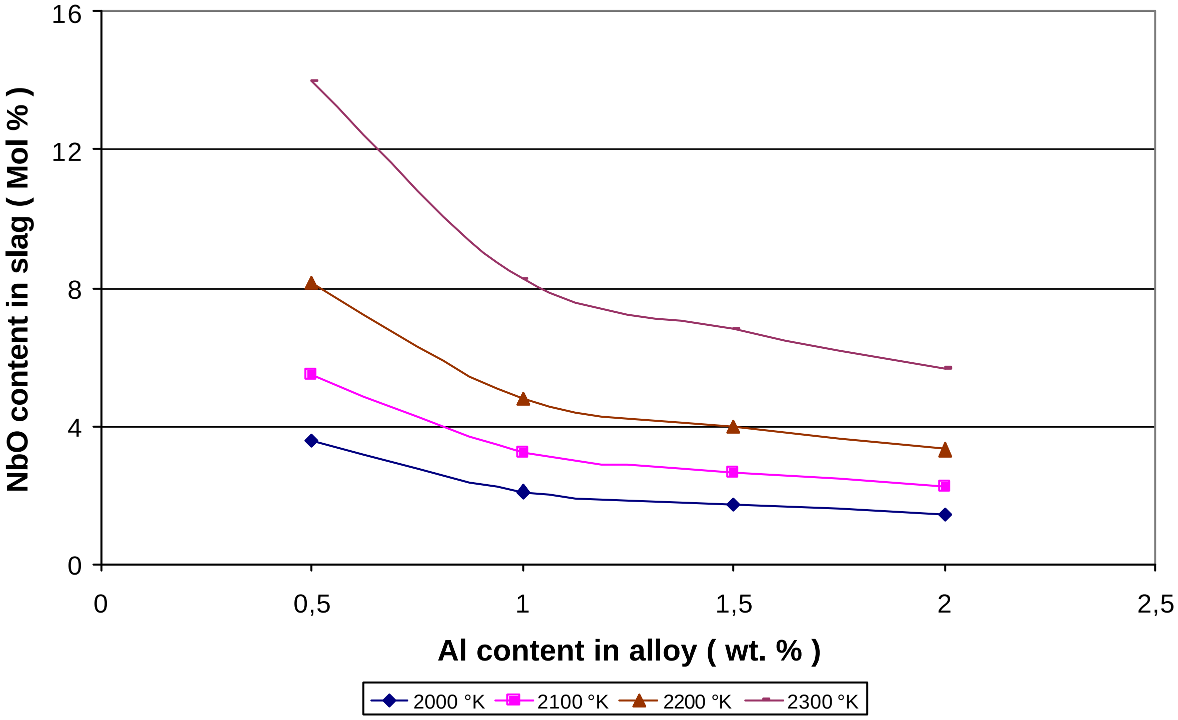

Figure 1: NbO-content in the slag for different temperatures and Al-content in the alloy.

It follows that the losses of NbO will be increased by increasing temperature of the melt and by decreasing the Al-content in the master alloy.

Production of Master Alloys

The theoretical consideration of the aluminothermic reduction of Nb_2O_5 shows, that the reduction should be done at temperatures as low as possible to achieve a high yield. Also the remaining Al content in the master alloy should be as high as possible for the same reason. But there are some discrepancies: due to the melting point of the master alloy of 1630°C (FeNb hp) and 1280°C (NiNb hp) respectively and the melting point of the Al_2O_3 slag of approximately. 2050°C, a working temperature of at least 2050°C in the system is needed to keep the slag and the metal molten to achieve a good separation of slag and metal. For economical reasons the remaining Al content in the master alloy should be as high as possible to get a high yield of Nb, but the requirements of the customer limit the Al content to max. 1%. A compromise between the requirements of the users and the thermodynamical behavior is therefore necessary.

For the formation of FeNb hp and NiNb hp, in addition to Nb_2O_5, Fe- and Ni bearing compounds or metals are necessary in the reaction. In the case of FeNb production iron oxide Fe_2O_3 is used, in the case of NiNb production nickel oxide NiO is used. The formation of the metals is in accordance with the equations (8) – (9):

$$Fe_2O_3 + 2\,Al = 2\,Fe + Al_2O_3 \qquad -\Delta G^\circ_T \tag{8}$$

$$3\,NiO + 2\,Al = 3\,Ni + Al_2O_3 \qquad -\Delta G^\circ_T \tag{9}$$

To keep all the components of the reaction system liquid, it is necessary to reach a certain reaction temperature. The energy to reach this temperature in general will be generated by the exothermic reaction between niobium oxide and aluminum. The formation of the metals according equations (8) and (9) also contributes energy to the reaction.

In practice the reaction system will lose energy during the reduction by radiation and convection. Depending on the size of the reaction vessel the heat loss could be too high. The heat generated by the chemical reactions in the system then is not enough to reach a temperature sufficient to melt all the components of the reaction system and to keep them molten for a timelong enough to enable a proper slag - metal separation. In this case boosters e.g. potassium perchlorate ($KClO_4$) have to be added to the reaction mixture to generate the required heat. The flow diagram (figure 2) explains the production process of FeNb hp and NiNb hp.

Plant Design

The aluminothermic reduction of niobium oxide is carried out on a production scale mainly in two basic plant designs:

I. Reduction in ceramic vessels

II. Reduction in permanent moulds

In plant design I, a vessel made of ceramic, mainly pure alumina is used for the topfiring of the reaction mixture. Usually, the vessel can be used only once and will be destroyed after the reaction and subsequent slag - metal separation. For every heat a new vessel is needed.

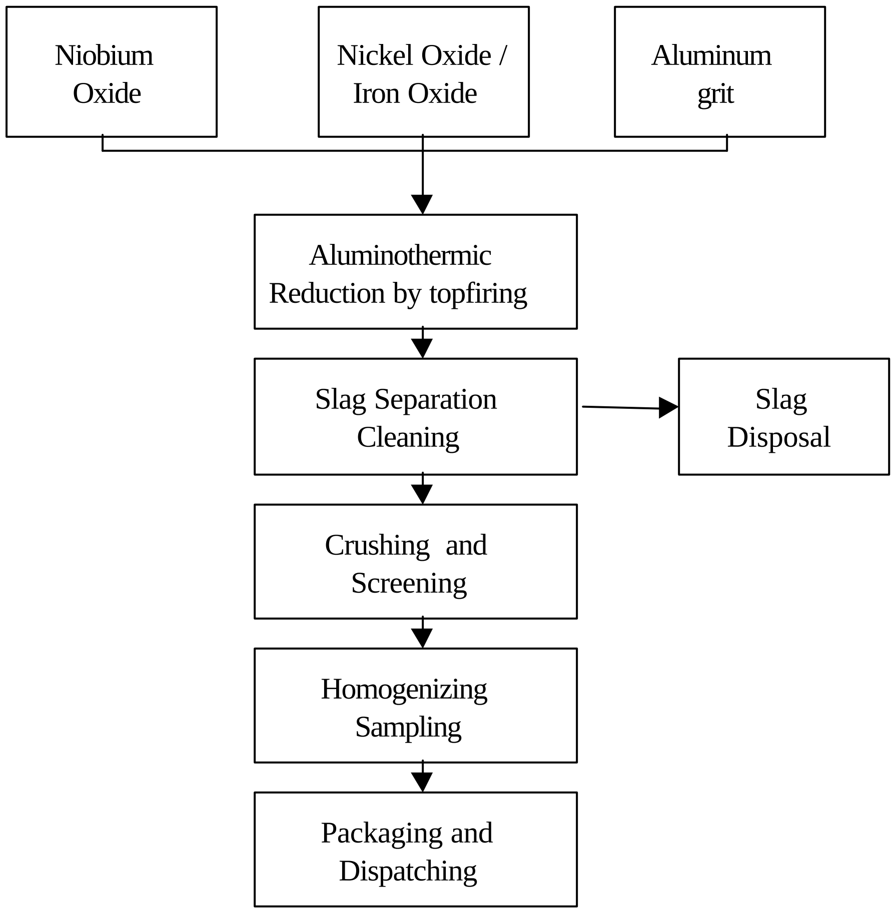

Figure 2: Aluminothermic production of FeNb hp and NiNb hp.

The main advantage of plant design I is the large size of the metal ingots. The mass of an ingot is usually on the order of 2,000 - 3,000 kg. The advantage of the big size is, that the metal ingot (and the slag) cool down very slowly over many hours, whereby a very good metal - slag separation can occur. This reduces the risk of slag inclusions in the master alloy. Developments in the past regarding the preparation of the ceramic vessel, especially the preparation of the ceramic surface of the vessel leads nowadays to very smooth metal surfaces with very low risk of slag inclusions. The manufacturing of the ceramic vessels is predominantly automated and can be done very cost effectively.

In plant design II a permanent mould, mainly consisting of copper is used for the reaction. Due to the high temperatures of the melt (>> 2000°C) the copper mould has to be water cooled by to avoid melting of the mould.

The main advantage of the copper moulds is, that the metal ingots have a very smooth and tight surface. The mould can be used several times.

A disadvantage is that ingot mass per heat is very small compared with plant design I and is about 50 - 100 kg. Due to the small ingot size and the necessary cooling of the mould, the melt freezes relatively quickly after the reaction. This can lead to lower yields and a poor slag - metal separation with the risk of slag inclusions in the master alloy.

Conclusion

The production of master alloys of NiNb and FeNb by aluminothermic reduction of niobium oxide and the corresponding oxides of the alloying partners leads to products with a very high purity and homogenity. All the requirements of the superalloy producers can be met. The processes described are very flexible regarding the composition of the masteralloy. Historically the processes are well established and are standard processes for master alloy production used for refractory metals. The processes are stable and cost effective.

References

(1) K. E. Volk, Nickel und Nickellegierungen (Berlin, Germany: Springer-Verlag, 1970).

(2) Alexander Arnold, private communication with author, RWTH Aachen, IME Metallurgische Prozeßtechnik und Recycling, Juni 2001.