

Production of High Purity Niobium Masteralloys

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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) will be 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 fulfills 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 in land based turbines and aircraft turbine engines, chemical industry, on and off shore oil and gas production, power generation, thermal processing, petrol chemistry, automotive, paper industry and food processing.

Niobium has an important impact as an alloying element in nickel base superalloys. Niobium alloys have become increasingly importance in industrial and aircraft applications, where superior heat and corrosion resistance is required. This type of superalloys contains up to 5 wt-% Niobium.

Nickel base superalloys will be 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 will be done 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 dissolves very quick in the molten alloy. Combined with the high purity they enables the production of very homogeneous, high grade superalloys.

Requirements on High Purity Niobium Master Alloys

The purity and quality of high grade superalloys will be impacted by the quality of raw materials, melting technology and of course by the quality of the used master alloys. The requirements on high purity niobium master alloys therefore are more or less comparable to the requirements on the final superalloys regarding the composition and the content of impurities.

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

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



But also the other properties of superalloys are impacted by the impurities. The different types of superalloys requires different grades of master alloys. Table I shows two typical specifications of NiNb high purity respectively FeNb high purity master alloys.

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 of production for niobium containing masteralloys for the production of superalloys is the metallothermic reduction with aluminum in one production step. Besides this - but only for very special applications - metallothermic reduced masteralloys will be refined in vacuum induction furnaces (GfE - „Two Step Process“).

The raw material for the production of niobium master alloys is niobium oxide Nb₂O₅. The very tight specifications regarding impurities requires a pure niobium oxide. Table II shows a typical specification for niobium oxide suitable for master alloy production.

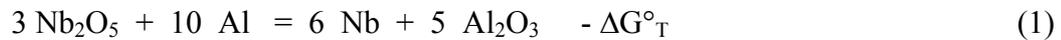
Table II Typical Specification of Niobium Oxide for Master Alloy Production

Nb ₂ O 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 will be carried out on a temperature level where the metal is molten as well the slag, to gain a proper separation of the metal and slag phase, although the exothermic reduction on higher temperatures is less complete than at lower temperatures.

Theoretical Considerations [2]

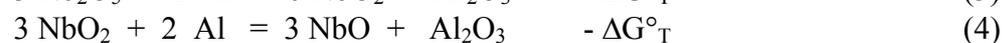
The reduction of Nb₂O₅ by aluminum follows the formula



The reaction is exothermic; the free energy ΔG°_T can be calculated in the temperature range between 298 and 2700 K with the formula

$$\Delta G^\circ_T = -925,3 + 0,1362 * T \quad (\text{kJ/mol}_{\text{Nb}_2\text{O}_5}) \quad (2)$$

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



The free energie - ΔG°_T was be calculated* as follows:

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

Reaction	- ΔG° _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 amount of the free energy is an indication for the stability of a chemical compound. Table III shows, that the compound NbO (equation 5) is the most stable 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 therefor will be controlled by equation (5). The equilibrium can be described as follows:

$$K_p = \frac{N_{Nb}^3 * N_{Al_2O_3}}{N_{NbO}^3 * N_{Al}^2} \quad (6)$$

From this equilibrium equation the calculation formula for the NbO-content in the slag dependent from the temperature and the Al-content in the master alloy can be derived as

$$\ln NbO = \frac{\Delta G_T}{3*RT} - 2/3 \ln Al \quad (7)$$

ΔG° _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 from temperature and Al-content in the master alloy.

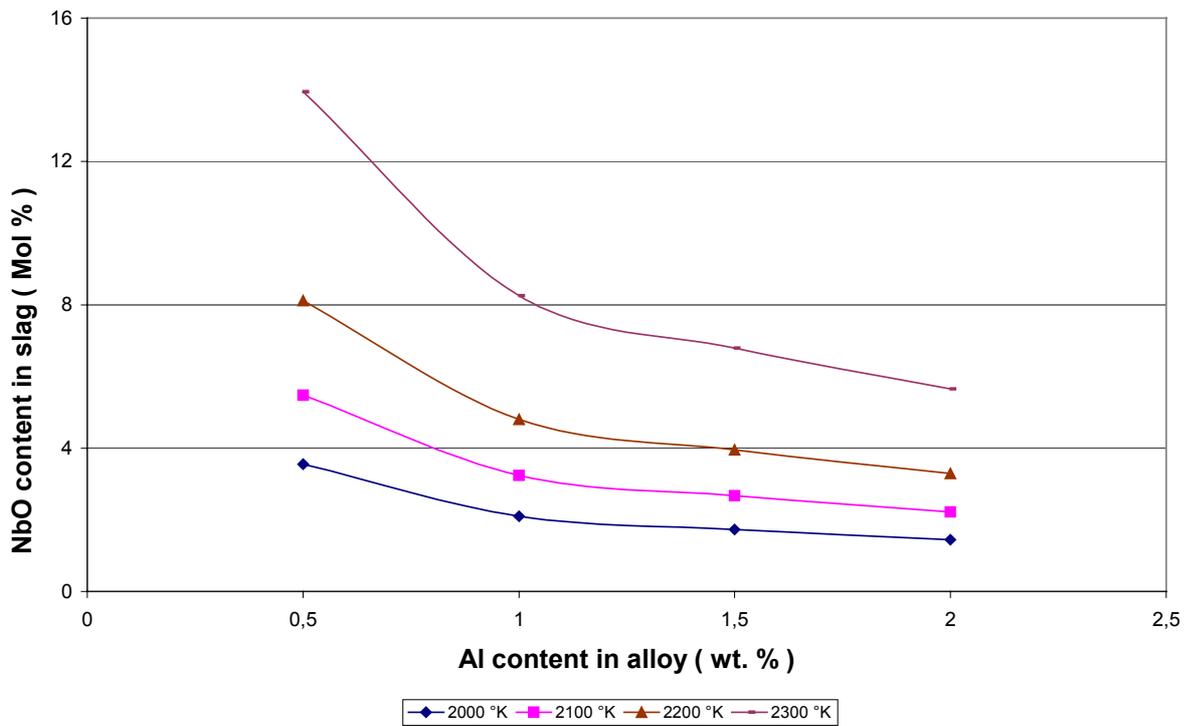


Figure 1: NbO-content in slag in dependency of temperatures and Al-content in the alloy

Figure 1 shows that the losses of NbO will be increase 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 reach 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 $1630^\circ C$ (FeNb hp) respectively $1280^\circ C$ (NiNb hp) and the melting point of the Al_2O_3 slag of appr. $2050^\circ C$ we need at least a working temperatures of more than $2050^\circ C$ in the system 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 regarding Nb, but the requirements of the customers limits the Al content to max. 1%. A compromise between the requirements of the users and the thermodynamical behaviour therefore is necessary.

For the formation of FeNb hp and NiNb hp beside Nb_2O_5 also Fe- and Ni bearing compounds or metals are necessary in the reaction system to form the alloys. In case of FeNb production iron oxide Fe_2O_3 , in case of NiNb production nickel oxid NiO will be used. The formation of the metals is in accordance with the formulas (8) – (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 to equations (8) and (9) also contributes energy to the reaction system and enables to gain the required temperature.

In practice the reaction system will lose energy during the reduction by radiation and convection. Depending on the size of the reaction vessel the lost heat could be too high. The generated heat by the chemical reactions in the system is not enough, to reach the sufficient temperature to melt all the components of the reaction system and to keep them molten for a certain time to enable a proper slag - metal separation. In this case boosters e.g. potassium perchlorate ($KClO_4$) has 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 :

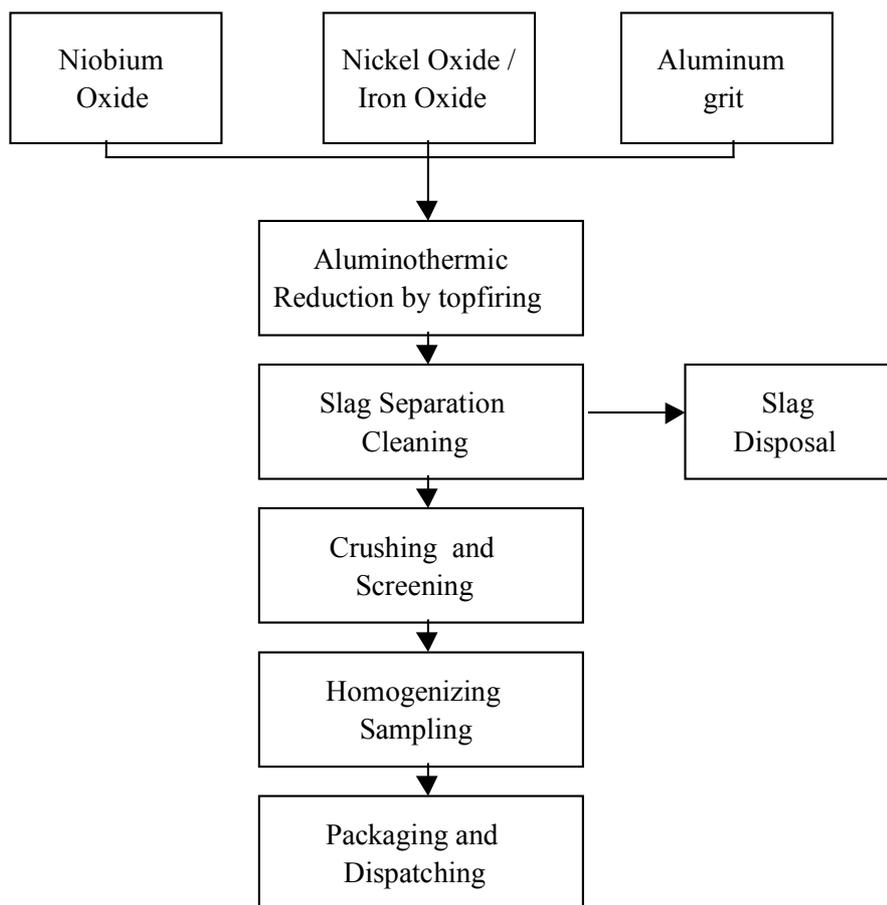


Figure 2: Aluminothermic Production of FeNb hp and NiNb hp

Plant Design

The aluminothermic reduction of niobium oxide will be carried out in technical 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 will be 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 has to be built.

The main advantage of plant design I is the big size of the metal blocks. The weight of a metal block is usually in the level of 2.000 - 3.000 kg / block. The advantage of the big block size is, that the metal block (and the slag) cool down very slow over many hours, whereas a very good metal - slag separation can occur. This reduces the risk of slag inclusions in the masteralloy. The 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 for slag inclusions. The manufacturing of the ceramic vessels is almost automated and can be done very cost effective.

In plant design II a permanent mould, mainly consisting of copper will be used for the reaction. Due to the high temperatures of the melt ($\gg 2000^\circ\text{C}$) the copper mould has to be cooled by water to avoid the melting of the mould.

The main advantage of this metal moulds is, that the metal block has a very smooth and tight surface due to the usage of a copper vessel. The mould can be used several times.

Disadvantageous is, that block weight per heat is very small compared with plant design I and is in the level of 50 - 100 kg / block. Due to the small block size and the necessary cooling of the mould, the melt will be frozen relatively fast after the reaction. This could lead to lower yields and a bad slag - metal separation with the risk of slag inclusions in the masteralloy.

Conclusion

The production of masteralloy consisting of NiNb and FeNb by aluminothermic reduction of niobium oxide and the correspondent oxides of the alloying partners lead to products with a very high purity and homogeneity. All the requirements of the superalloy producers will be fulfilled. The described processes are very flexible regarding the composition of the masteralloy. The processes itself are well established since decades and are the standard processes for masteralloy production based on 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