Synthesis of a NbTi alloy by aluminothermic-reduction (ATR) in a water-cooled copper vessel

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Abstract

When hydrometallurgical processes are used to recirculate waste, they generate multiple material streams, most of them with a high content of potentially useful products. This applies especially for the ScaVanger project (Sustainable Supply of Scandium for the EU Industries from Liquid Residues from Chloride-Based TiO_2 Plants) where large quantities of TiO_2 and Nb_2O_5 are generated in a mixed hydroxide product (MHP). The challenge is to produce a sustainable metallic product from these materials. A possible usage of this metal alloy is the Nb-47Ti alloy, which is a common master alloy for superconductors, being used for example in medical magnetic resonance imaging.

In this work, the feasibility of producing a NbTi alloy with a 50:50 wt.-% composition ratio out from a synthetic precursor mixture of TiO_2 and Nb_2O_5 via ATR is investigated. The experiments were carried out in an innovative water-cooled copper vessel in order to avoid contaminations when using ceramic linings. Thermochemical modelling of generated input heat due to the reduction of the less noble metal oxides of niobium and titanium with aluminium showed, that large amounts of additional heat through booster addition are required for an autothermic process. The results in 10 kg-scale show how variable input heats in form of different amounts of booster additions influence the process flow, the separation of metal and slag and the reduction efficiencies of TiO_2 and Nb_2O_5. The targeted metal phase could be successfully formed via ATR with a direct dependency of the generated process heat and reduction efficiency of the metal oxides. As the heat input increases, the reduction efficiency decreases, whereas the metal-slag separation improves as the heat input increases. The results of the trials will also show the safety and usability of a water-cooled copper vessel as an innovative reactor for ATR in tested scale.

2 Introduction and motivation

NbTi alloys have become increasingly important in the field of superconductivity, particularly for their use in superconducting magnets. [1] The production of these alloys has traditionally been a complex and costly process, involving multiple steps and expensive powdering techniques. [2] The state-of-the-art process, which is shown in Figure 1, involves the production of titanium-sponge and pure niobium metal rods, which then will be alloyed in the electron beam melter (EBM). [3] However, recent advancements in ATR methods have opened new possibilities for more efficient and cost-effective production of niobium-titanium alloys. With the ATR, the possibility of directly reducing both metal oxides with aluminium is possible. The produced metal alloy consisting of niobium, titanium and aluminium must be refined afterwards in an EBM to evaporate the aluminium dissolved in the alloy. [4], [5]

Aluminothermic reduction is a well-established process in the metallurgical industry, known for its ability to produce high-purity metals and alloys through exothermic reactions. This method utilizes the high affinity of aluminium for oxygen, resulting in a rapid and strongly exothermic reaction that requires no external heat source. [6], [7] While aluminothermic processes have been extensively used in the production of various metals and ferroalloys, their application to niobium-titanium alloy production could represent a significant advancement in the field.

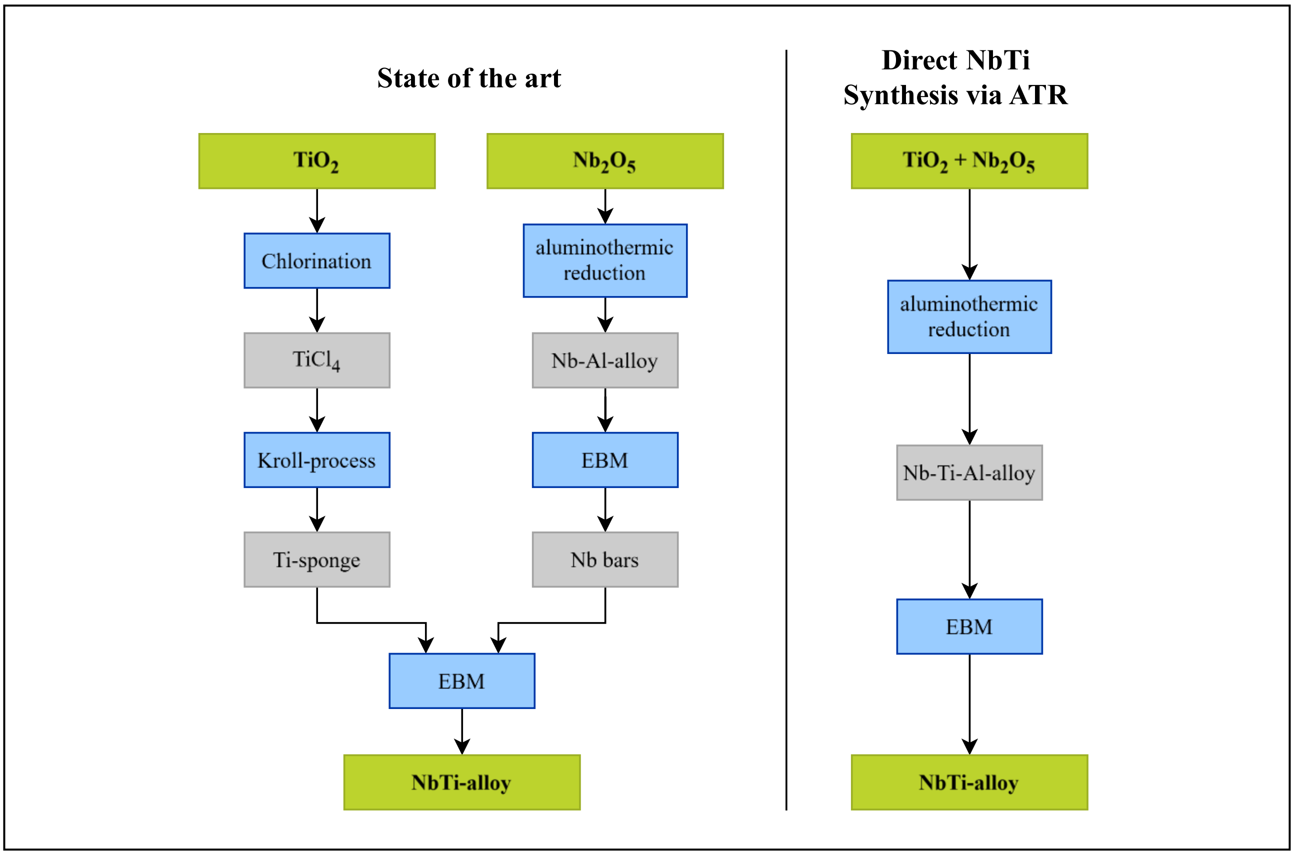

Figure 1: Process flow chart: State of the art (left) and new developed (right) NbTi-alloy production

Fundamentals of aluminothermic reduction

Metallothermic reduction refers to the pyrometallurgical extraction of metals or alloys by means of a generally highly exothermic reaction between the metal compound of the target metal and a less noble reducing metal, which is available at low cost. The metal compounds used in technical processes are almost exclusively oxides, chlorides and fluorides. Depending on the thermodynamic and technical conditions, the metals sodium, potassium, magnesium, calcium and aluminium as well as the semi-metal silicon are used as reducing metals. [8], [9] Metallothermic processes are also characterized by carbon-free metal extraction, which is why they are particularly suitable to produce refractory metals with high melting points, such as niobium and titanium, as these tend to form carbides. [10]

In the aluminothermic reduction, the reducing metal is aluminium. The metal phase consists of the reduced metal oxides and the slag consists of Al_2O_3 and unreacted metal oxides. Due to the high reaction enthalpies of the materials used, the ATR can be self-propagating. If the heat of formation of the reaction is not sufficient to create an autothermic process, there are various ways to generate the remaining heat for melting. [11]

Table 1 shows the reaction enthalpies of various metal oxides with aluminium.

Table 1: Heat generation of selected aluminothermic reactions calculated with FactSage 8.3 [12]

	ΔH_R [kJ/mol$_{Al}$]	**SH factor [Jg^{-1}]**
$TiO_2 + 4/3\ Al \rightarrow Ti + 2/3\ Al_2O_3$	- 129.3	- 1488.1
$4/10\ Nb_2O_5 + 4/3\ Al \rightarrow 8/10\ Nb + 2/3\ Al_2O_3$	- 268.0	- 2511.0
$1/2\ KClO_4 + 4/3\ Al \rightarrow 1/2\ KCl + 2/3\ Al_2O_3$	- 840.2	- 13535.3

The reaction enthalpies from literature data and empirical values from known systems can therefore be used to predict fairly accurately whether a metallothermic reaction will be self-propagating with the formation of a molten slag and metal phase. Besides the autothermic reaction, it is important to have a clear separation between the slag and metal layer. [10]

Since the heat content of the metal and slag obtained and the heat losses accompanying the process are approximately the same for the different metals, Shemtchushny has established the following rule to simplify the calculation:

$$SH = \frac{\sum H_R}{\sum m_{\text{input material}}} \tag{1}$$

SH: Shemtchushny factor [Jg^{-1}], H_R: Standard reaction enthalpy [J]

A metallothermic process is autothermal after initial ignition if the amount of heat released per gram of charge is at least 2300 J, recording to Shemtshushny. Considering more recent findings, however, the value of 2300 J/g is somewhat too low. In contrast to Shemtchushny, Dautzenberg formulates a specific heat effect of at least 2700 J/g. [13]

Figure 2 shows the comparison of the production of niobium and titanium oxide with carbon and aluminium in a Richardson-Ellingham diagram. The free enthalpy lines of niobium and titanium carbide formation are also shown. It can be seen from the Ellingham diagram that the reduction of titanium oxide to titanium with carbon to form CO is only possible from a temperature of around 1700 °C. However, the formation of titanium carbide is also preferred, as this has a more negative free reaction enthalpy at any temperature. The same applies to the conversion of niobium oxide to niobium with carbon. Here, the straight line of niobium carbide formation is also below the straight line of pure niobium metal formation for the entire temperature range. For the process, this would mean that titanium and niobium carbide formation would be preferred, and no pure titanium or niobium metal would form.

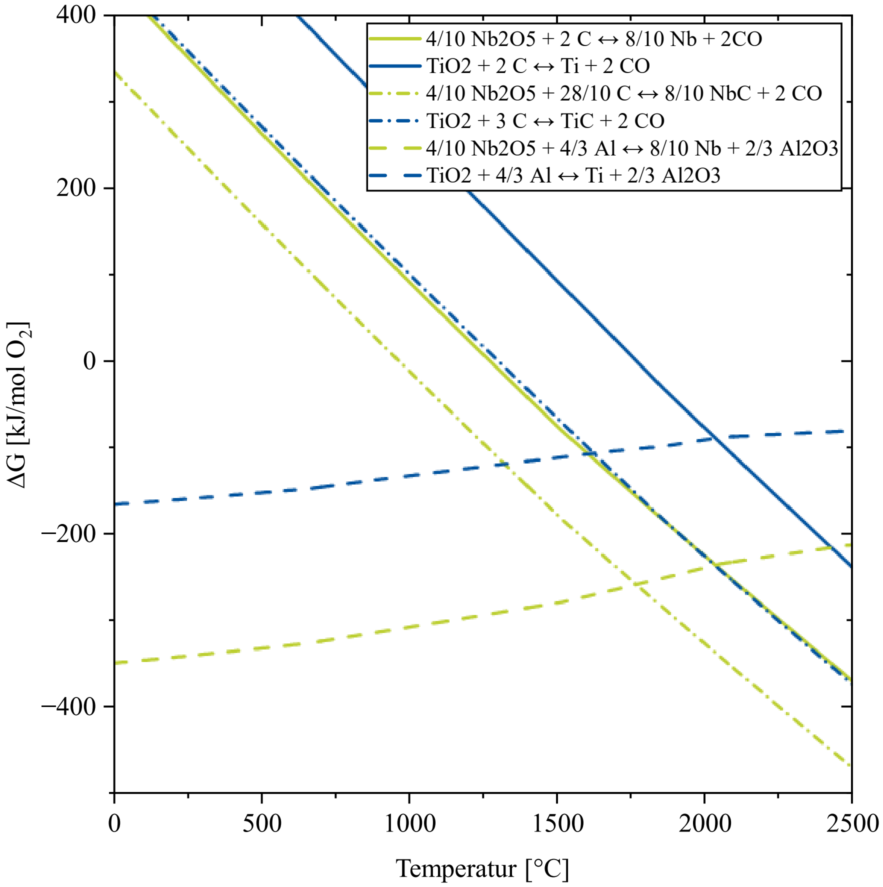

Figure 2: Gibbs free energy for different reduction reactions for Ti and Nb, calculated with FactSage^{TM} 8.3 [12]

Comparison of refractory reactor and water cooled copper vessel

Due to the high oxygen-affinity and -solubility of titanium, the interaction between the molten metal and the refractory in form of the dissolution equilibrium of the respective oxide is of central importance. [14] Metallothermic reactions are usually carried out in reactors lined with oxidic refractory material. These consist of a steel jacket, refractory bricks and a possible sacrificial oxide refractory layer as a contact surface to the molten phase. [10] Pure oxides, such as Al_2O_3, CaO, MgO and ZrO_2, or mixed oxides, such as CaO-MgO (dolomite), $MgAl_2O_4$ (MA spinel), $CaTiO_3$ (calcium titanate) and $CaZrO_3$ (calcium zirconate) are possible examples for refractory materials. [15] In previous studies by Maier et. Al [16], a corundum mass of Al_2O_3 is used as refractory material. The lining of these reactors is cost-effective and has good process engineering properties, such as high temperature resistance. However, refractory reactors have two significant disadvantages. On the one hand, these are the long cooling times of the molten material of 24 to 72 hours, depending on the size of the reactor, which limit the production capabilities. On the other hand, the corundum refractory material itself poses a problem regarding the process. The aluminium can dissolve from the refractory lining into the metal due to the high solubility of aluminium in titanium. Also, the oxygen bounded in the oxidic refractory material is in direct contact to the metal phase, which can result in the dissolution of oxygen into the metal melt. [15] The evaluation of the discussed aspects of both of the reactor types is shown in Table 2. For these reasons, the approach taken in this work is to use a water-cooled copper vessel as a reaction vessel. On the one hand, this offers fast cooling rates, and, on the other hand, the undesirable properties of the refractory material can be circumvented through the usage of a frozen slag layer between the copper and the melt (freeze lining). The challenge with the copper vessel lies in its design and manufacture, which is complex and expensive. In addition, critical attention must be paid during the process ensuring that sufficient cooling water is available, so the copper always remains well below its melting temperature of 1085 °C.

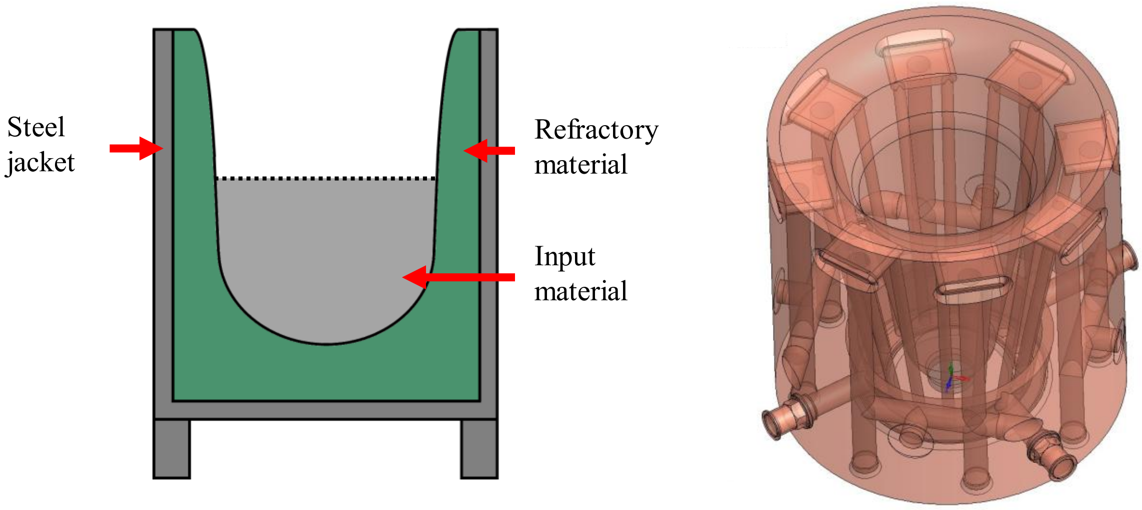

Figure 3: Refractory lined reactor (left) and water cooled copper vessel by Saar Metallwerke (right)

Table 2: Comparison of the two types of reactors

Category	**Refractory reactor**	**Water cooled copper vessel**
Production cost	++	--
Operation cost	-	+
Heat isolation	+	-
Interaction with melt	--	++
Cooling time	--	++

Materials and methods

This chapter focuses on the characteristics of the input materials followed by the description of the experimental setup and work. The experimental work was carried out in the IME of RWTH Aachen University.

Characterisation of input materials

Titanium oxide (TiO_2), niobium oxide (Nb_2O_5), potassium perchlorate ($KClO_4$), aluminum granules (Al) and quicklime (CaO) are used in the tests. Table 3 shows the materials used for the tests, assigned to the categories, such as reducing metal, the oxides which will be reduced to the metal and additives.

Table 3: Classification of the materials used

Category	**Input material**
Reducing metal	Aluminium granules
Oxides of alloying metals	TiO_2, Nb_2O_5
Additives	$KClO_4$

As the residual moisture in the material significantly influences the reaction due to the potential explosive vaporization of the water, it must be ensured that the materials used have the lowest possible residual moisture. The metal oxides TiO_2 and Nb_2O_5 have a residual moisture content of < 0.5 wt.% and are therefore not dried before the experiments. The CaO is pre-dried in a drying oven at approx. 650 °C for at least 12 hours before each test day to ensure that there is no residual moisture in the material due to the high hygroscopicity of CaO. The various input materials are shown in Figure 4.

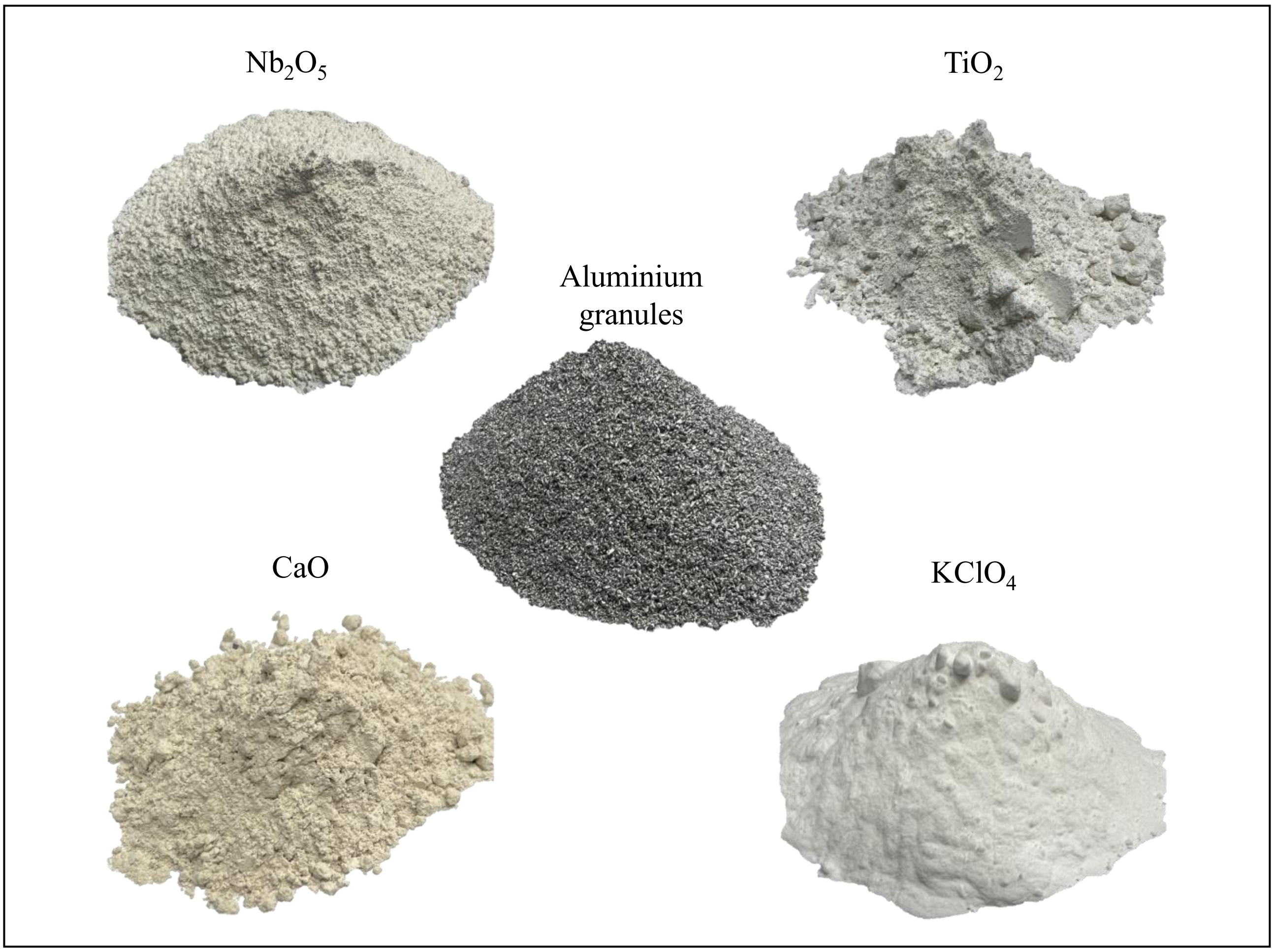

Figure 4: Input materials used for experimental work

Experimental setup

The experimental setup is consisting of the water cooled copper vessel, which is engineered and manufactured by Saar Metallwerke GmbH, the cooling water supply and a strong off gas system. The copper vessel has four cooling channels in the outer wall. These ensure sufficient cooling. A water meter is mounted at the outlet of each tube to monitor the cooling capacity. In addition, thermocouples are mounted in the wall of the vessel at various points, which can be used to monitor the vessel temperature. The vessel is conical in shape and has an outlet on the underside. This is used to discharge the material if it is directly cast in another vessel. In the case of these experiments, the outlet is closed with a plug made of Al_2O_3 refractory material.

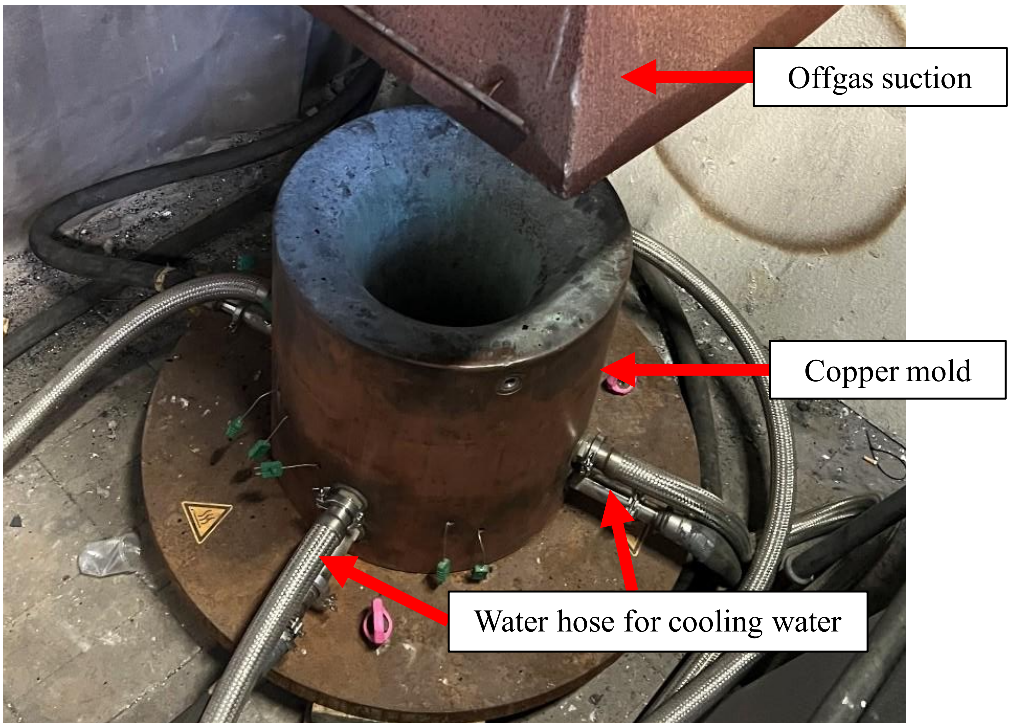

Figure 5: Experimental setup at IME with water cooled copper vessel by Saar Metallwerke

The experiments are initiated by igniting a mixture of mixed aluminum granules and $KClO_4$. This mixture is placed in a small sample bag, which is connected to a voltage source via a niobium metal coil wire with conducting cables. The initiation mixture is placed at the top of a small indentation in the combustion mixture. It is important to ensure that the ignition package is not too high on the surface of the combustion mixture so that the energy can be transferred effectively, and the activation energy of the combustion mixture is reached to ignite it. On the other hand, the ignition package must not be placed too deep in the combustion mixture, otherwise too much unburned combustion mixture will be ejected by the ignition. Figure 6 shows the combustion mixture in the copper vessel without the ignition package on the left and with the ignition package on the right. The conductor cables protruding from the combustion mixture are connected to a voltage source.

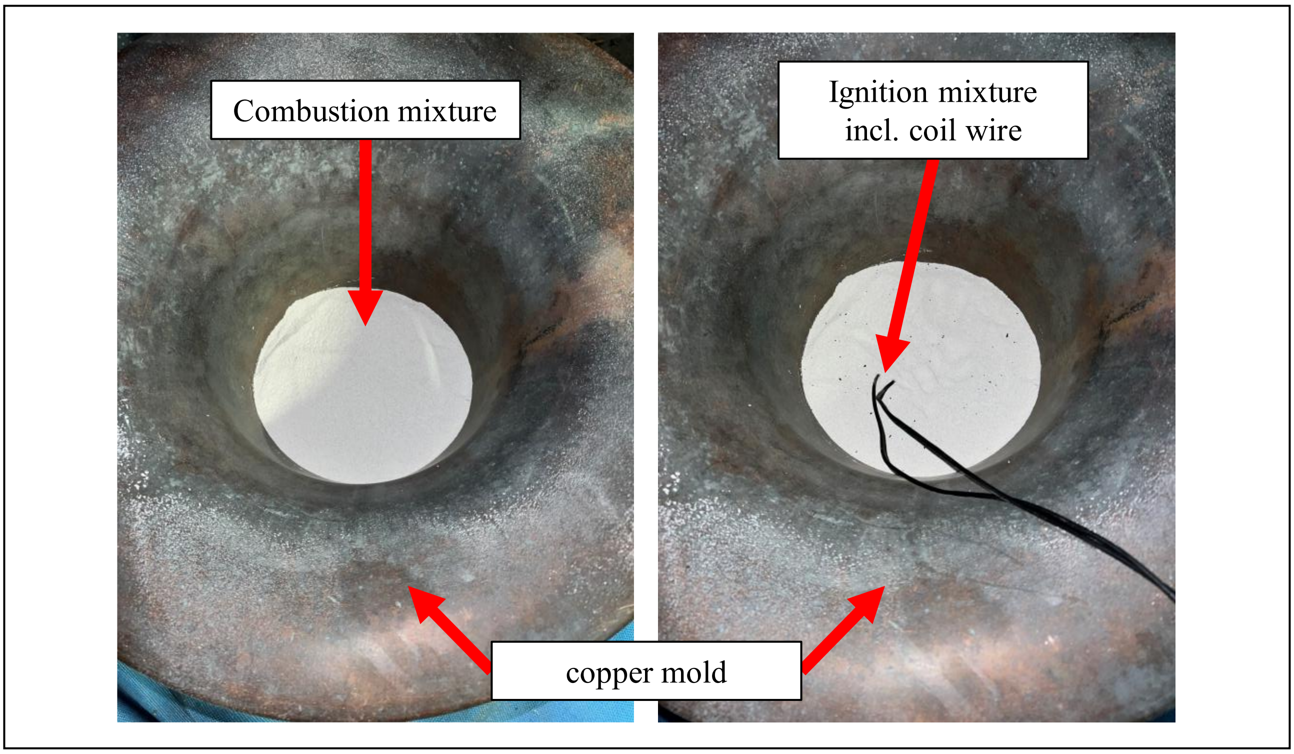

Figure 6: Combustion mixture (left) and combustion mixture with ignition mixture (right)

As soon as the ignition of the ignition package takes place, the wires are pulled out of the mixture as quickly as possible to avoid possible contamination of the target metal by the copper wire. After the reaction has ended and the metal and slag have solidified completely, the block is removed from the vessel by hand and the Al_2O_3 plug is separated from the metal.

Experimental work

In this work, the influence of the energy input based on the SH factor and the influence of the TiO_2 excess-input on the NbTi-alloy with a target composition of 50 wt.% Ti and 50 wt.% Nb is investigated. For the calculation of the charge masses, a complete reaction of the aluminium with the metal oxides is assumed. To lower the melting point of the slag and the activity of Al_2O_3 in the slag, enough CaO is added so that a theoretical slag composition of 81.15 wt.% Al_2O_3 and 18.85 wt.% CaO with a theoretical melting point of 1754 °C is produced. Since the reactions of the TiO_2-Nb_2O_5-Al system are not sufficient in heat generation for an autothermal process, $KClO_4$ is added to the mixture to balance the SH factor with its very high heat generation in the reaction with aluminium, as described before.

The parameters are carried out with 5 kg and 2.5 kg of target metal respectively. This serves to compare different total energy inputs and ratios of heat losses through the copper vessel. In experiments V1 and V2, a basic line system with a high SH factor of 3300 Jg^{-1} and without excess TiO_2 is investigated. Trials V3 and V4 are to investigate the influence of the TiO_2 excess addition on titanium and aluminium contents in the target metal in comparison to V1 and V2. For the TiO_2 excess, an excess of 50 wt.% is used in all experiments.

Table 4: Plan for carried out experimental trials with *) being TiO_2 excess addition of 50 %

Trial	SH [J/g]	Target metal [g]
V1	-3300	5000
V2	-3300	2500
V3*	-3300	5000
V4*	-3300	2500
V5*	-3100	2500
V6*	-3100	5000
V7*	-3200	2500
V8*	-3200	5000

For the excess titanium oxide, no reducing metal is added to the burn-off mixture, which increases the activity of TiO_2 in the slag, so that a higher conversion of the aluminum is achieved and thus the aluminum content in the target metal decreases and the titanium content increases. In experiments V7/V8 and V5/V6, the reduction in energy input measured by the SH factor is investigated in comparison to V3 and V4.

Results and Discussion

In this chapter the results of the experimental trials are being shown. An autothermal, sometimes explosive process sequence can usually be observed in the trials. The individual process steps can be recognized from Figure 7 (**A-D**). After ignition of the ignition mixture, a small volume of molten material burns into the combustion mixture (**A**). As soon as sufficient liquid melt has been produced, it burns downwards into the reaction mixture (**B**). In the trials with a quantity of 2.5 kg of target metal, a significantly slower burn-off is observed here. In addition, after the melt burns down, the collapse of the remaining ignition mixture from the edge area is not as explosive compared to the tests with 5 kg of target metal. As soon as the ignition mixture has collapsed, the melt continues to burn downwards (**C**). A critical point can be recognized when the ignition mixture collapses. The tests with SH factors of 3300 J/g show explosive behavior here. In this phase, a bubble rise can be seen throughout. As soon as the bubble rise largely stops, the end of the reaction has occurred, and the slag surface begins to solidify (**D**). For the infrared camera images, the emission value must be adjusted depending on the phase state.

As soon as the end of the reaction is reached, the slag solidifies first. It can be seen in some tests that liquid slag breaks through a frozen slag layer on the surface from below (see red dot in the middle in Figure 7: **D**). Compared to other reactors lined with refractories, complete solidification in the copper vessel is considerably faster with this alloy system, taking around 30 minutes.

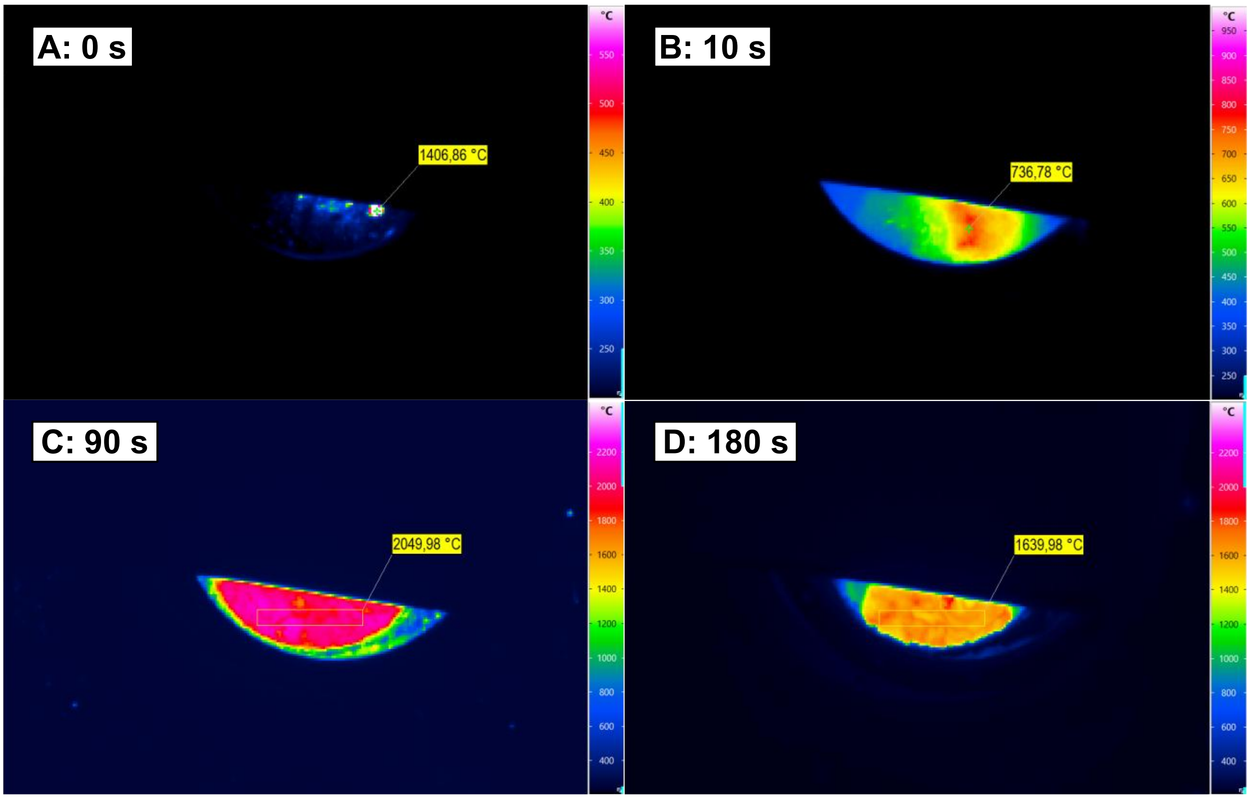

Figure 7: Reaction sequence V6, **A**: ignition, **B**: start phase, **C**: complete reaction, **D**: solidification

The metal-slag separation is good to very good in the tests with high energy input (see Figure 8). Only in the tests with a low target metal quantity of 2.5 kg and a lower SH factor (V5 and V7) it is not possible to achieve sufficiently good metal-slag separation. In experiment V8, the Al_2O_3 plug detached from the bottom of the copper vessel and floated to the top due to its low density. As a result, the molten liquid ran out of the vessel in an uncontrolled manner and the results of this experiment cannot be evaluated.

Figure 8: Metal from trial V6

Due to the partially insufficient metal-slag separation, no meaningful mass balance can be drawn up for the tests except for V1 and V6. This insufficient metal slag separation wasn't observed by Maier et al. [16], who also used titanium, but in lower concentrations, as part of a high entropy alloy (HEA). This HEA has a significant difference to the NbTi system used in this work. The rest of the metal oxides (Cr, Mo and V) produce more heat in the reaction with aluminium, so less $KClO_4$ addition is needed to reach high enough SH factors for a good metal slag separation. The known problem with high amounts of $KClO_4$ in the burn-off mixture is that the formed KCl gas has to escape the reaction and therefore creates more turbulence inside the reactor. Due to the created turbulence, the metal has not enough time to separate itself from the slag. The mass balance for tests V1 and V6 are shown in the table below.

Table 5: Mass balances and metal yields of carried out trials

Trial	$m_{metal, theoretically}$ **[g]**	$m_{metal, achieved}$ **[g]**	**Metal yield [%]**
V1	5000	4266.9	85.34
V6	5000	5732.3	114.65

The total metal yields of these trials are 85.34 % and 114.65 % respectively. When taking the metal composition into account, the NbTi yield is 65.71 % and 91.26 % respectively, which also represents their aluminium yields. The low titanium to niobium ratio in trials V1 to V4 is caused by too high SH factors resulting in too high reaction temperatures and therefore insufficient TiO2 reduction. Additionally, high SH factors are resulting in partial ejection of the burn-off mixture because of their rapid reaction and gas generation. This ejection of burn-off mixture is then causing low mass balance yields and therefore low metal yields.

Influence of TiO_2 excess

Trials V1/V2 and V3/V4 are considered for the influence of the excess titanium oxide, whereby V3 and V4 are each carried out with a 50 wt.-% excess addition of titanium oxide. Figure 9 shows the metal concentrations in the target metal of the tests investigated. The niobium content in the target metal increases from an average of 47.70 wt.% without excess to an average of 48.65 wt.% with excess. In addition, the titanium content in the metal increases from 29.50 wt.% to 31.65 wt.% with a sharp drop in aluminum concentrations. The concentration of aluminum in the target metal represents the greatest change here with a reduction of just under 30 %. The assumption that a higher activity of TiO_2 in the system leads to a higher concentration of titanium in the target metal and a better aluminum yield can thus be confirmed.

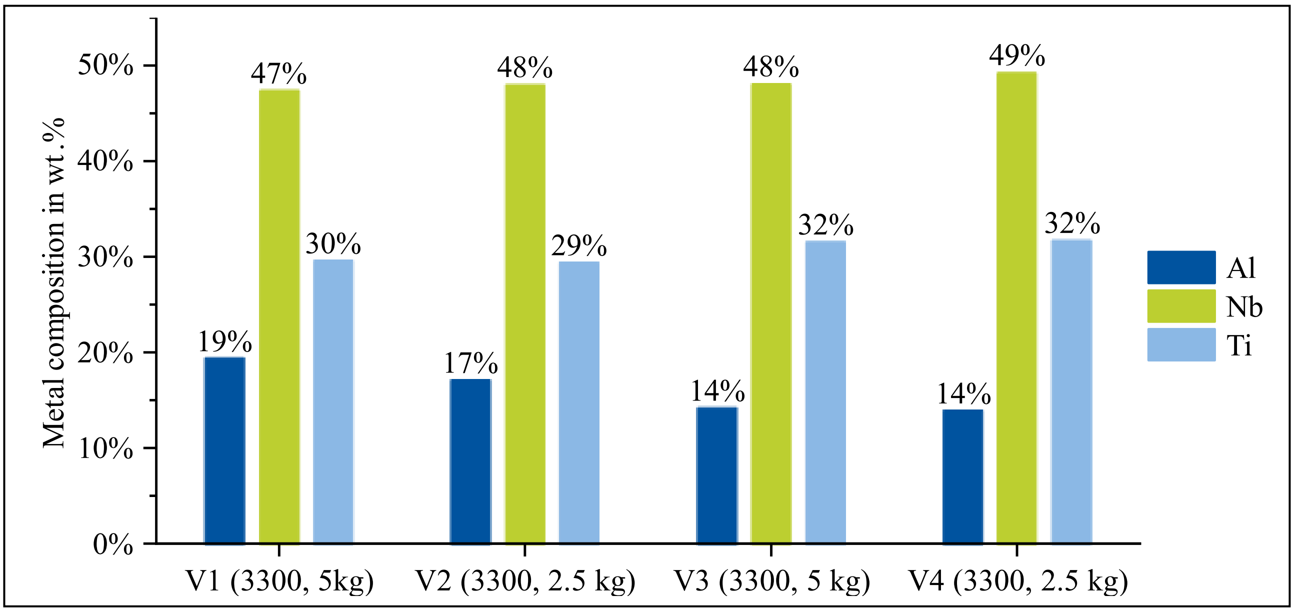

Figure 9: Metal composition for comparison of TiO_2 excess addition influence

Influence of energy density

To investigate the energy density, tests V3 to V8 are carried out with different SH factors from 3300 over 3200 to 3100 Jg^{-1}. The results of the tests are shown in Figure 10 with decreasing SH factor from left to right. It can be confirmed that the titanium yield, or the ratio of titanium to niobium, increases when the SH factor and thus the energy input into the system decreases. In addition, the total metal yield can be described based on the aluminum in the target metal, since an aluminum yield of 100 % would mean that either all the metal oxides have reacted with the aluminum to form aluminum oxide,

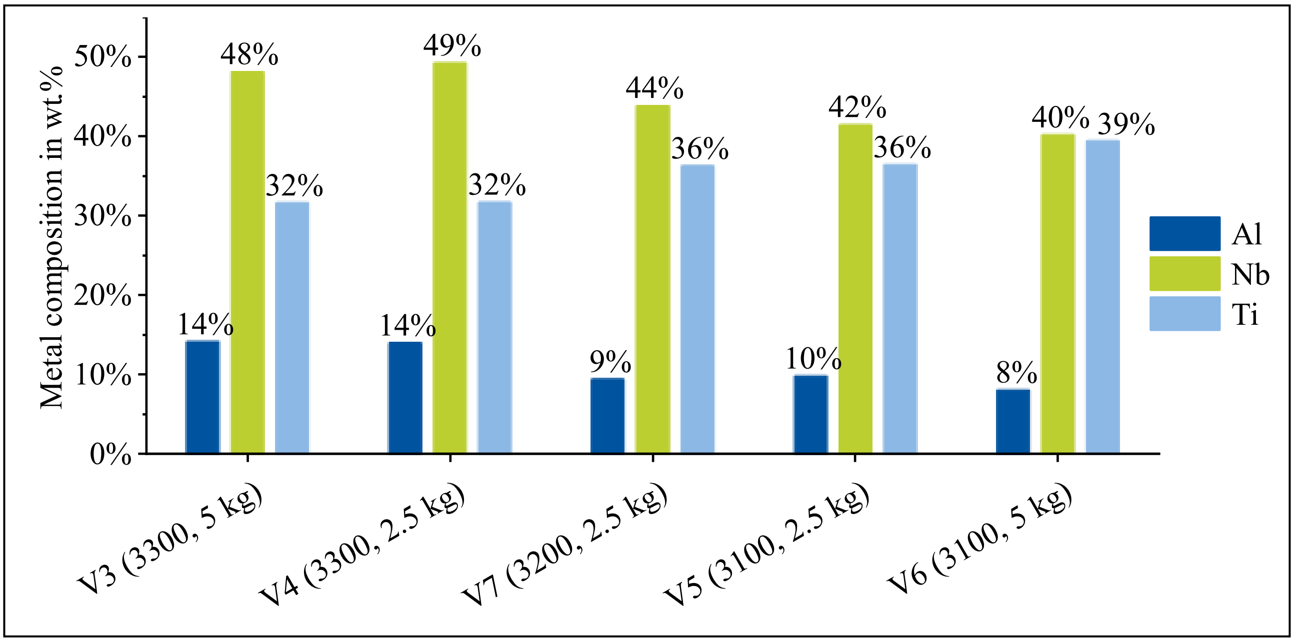

Figure 10: Metal composition for comparison of energy density influence

or the aluminum evaporates at the high prevailing temperatures. Since increasing evaporation with decreasing energy density is not thermodynamically possible, as a lower temperature is more likely to be reached in the system and the aluminum evaporation would have to decrease, it can be assumed that the aluminum is better converted with metal oxides. Figure 10 shows that the aluminum content also decreases as the SH factor decreases.

Conclusion and Outlook

Using the aluminothermic reduction, a metal alloy of NbTi was obtained from the respective oxides TiO_2 and Nb_2O_5. The water-cooled copper vessel enabled rapid cooling times compared to conventional refractory lined reactors. To achieve a good metal-slag separation, a slightly higher heat input is necessary to counter the heat losses through the rapid outside cooling. The influences of the excess addition of TiO_2 and the energy density on the composition of the target metal alloy and aluminum yield were investigated in a total of eight experiments. It was found that the excess titanium oxide leads to a higher aluminum yield and the titanium to niobium ratio is slightly improved. Due to the higher aluminum yield, the contamination by aluminum in the target metal is correspondingly lower. Energy density has a direct influence on the composition of the target metal. With decreasing energy density, the titanium to niobium ratio could be improved from around 0.40/0.60 (V3) to 0.49/0.51 (V6). In addition, the aluminum content was reduced from 14.10 wt% (V3/V4) to 8.97 wt% (V5/V6). For the trials V1 and V6, a mass balance could be drawn up and the NbTi yields are 65.71 % and 91.26 % respectively.

Although the experiments carried out in the course of this work established a fundamental dependence of the TiO_2 conversion on the energy density, no final energy density could be determined. It is therefore necessary to investigate even lower energy densities regarding an autothermal process and good metal-slag separation. In addition, it makes sense to measure the temperature of the process with a thermocouple in a protective tube and to adjust the energy density more precisely on this basis.

In view of the sometimes rapid a slightly explosive reaction of the burn-off mixture, as observed in this work, it is necessary to investigate the reduction of the booster quantity so that there is still good metal-slag separation. In addition, the experiments carried out as part of this study need to be scaled up to larger scales. The next step should be to use a target metal quantity of 20 kg to simulate the heat losses caused by conduction as realistically as possible. It is important to note that scaling up increases the total energy in the system considerably and therefore the heat losses due to conduction become relatively less. It is therefore necessary to investigate lower energy densities when scaling up the experiments. Furthermore, it is advisable to analyze the ATR regarding the oxygen and nitrogen content in the metal, as this has a considerable influence on the material properties and will be very high due to the open-atmosphere process. A possible way to decrease the oxygen and nitrogen content in the produced metal, the ATR could be done under inter gas atmosphere.

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