



**Recovery of Tungsten, Niobium and Tantalum occurring as by-products in
mining and processing waste streams**

(TARANTULA)

D7.8 Validation of the produced Nb in special steel manufacturing

SUMMARY FOR PUBLICATION

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Abbreviations and acronyms

Ar ₃	Temperature during cooling at which austenite begins to transform to ferrite.
AMT	Ammonium metatungstate
APT	Ammonium paratungstate
ATP	Average traded price
AOD	Argon oxygen decarburisation
BF	Blast furnace
BN	Boron nitride
CAGR	Compound annual growth rate
CBMM	Companhia Brasileira de Metalurgia e Mineração
CC	Continuous casting
CRM	Critical raw material
DES	Deep eutectic solvent
EAF	Electric arc furnace
ESR	Electroslag refining
FeNb	Ferroniobium
FeW	Ferrotungsten
GA	Grant Agreement
HSE	Health, Safety and Environment
HSLA	High strength low alloyed steel
HSS	High speed steels
ICP	Inductively coupled plasma
IL	Ionic liquid
LNG	Liquefied natural gas
MTU	Metric ton unit
NASX	Non-aqueous solvent extraction
PSD	Particle size distribution
PV	Photovoltaics
SBQ	Steel bar quality
T	Temperature
TGA	Thermal gravimetric analysis
T _{nr}	Temperature of non-recrystallization (It is the temperature below which recrystallization does not occur)
Q&T	Quenched and tempered
VAR	Vacuum arc remelting
WP	Work package
XRD	X-ray powder diffraction
YoY	Year over year
YS	Yield strength



Executive summary

When this deliverable was conceived during the TARANTULA proposal preparation it was described as the “validation of the produced Nb in special steel manufacturing (task 7.6)”. On the course of the project, the prototype validation of the most promising route was selected for W, as it has been already described and justified in previous deliverables. This fact was not an obstacle for the experimental validation on steel since the required Nb content in a -lab scale ingot steel (as described in the Grant Agreement of TARANTULA project) is really low and the necessary amount of material could be reached in lab conditions. Figure 1 presents the basic workflow defined among the consortium for the Nb validation: TEC and KUL produced the Nb₂O₅ at lab scale, and SINTEF was responsible to obtain the metallic Nb to produce ferroniobium for a suitable addition to molten steel.

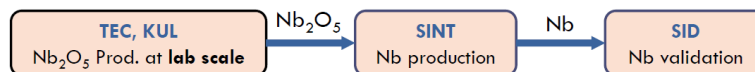


Figure 1. Basic flowsheet for Nb validation in steel manufacturing.

This deliverable summarises the main requirements that ferroniobium should accomplish for a go-to-market strategy. The study is focused on ferroniobium because this alloy is the primary Nb marketable product accounting for more than 90% of niobium market worldwide. As it was not possible to obtain the experimental ferroniobium raw material in TARANTULA (the main reasons are explained next), a desk work is described instead.

Additionally, and given that tungsten was selected in Task 7.1 as the most promising route for the prototype validation, a W desk work validation has been also included in this report. In this case, as W applications are much wider than steel manufacturing, different materials have been evaluated from the market strategy (tungsten trioxide, tungsten metal and ammonium paratungstate).

Although, for the moment, the evaluated TARANTULA tungsten-containing products do not present the purity requirements to be commercially exploited without any further research, the general approach for the recovery of niobium/tantalum and tungsten along the project has been proved to be highly valuable.



1. Introduction to niobium validation

Niobium can be found in several deposits around the world and there are more than 90 types of niobium-containing minerals. However, in terms of economic viability for extraction, only two minerals are profitably obtained: columbite (presenting 76% as a maximum level of Nb_2O_5 and pyrochlores) and tantalite. Brazil has the largest concentration of exploitable Nb deposits, at >97% by mass [1].

In 2022, the mine production of niobium was estimated to reach a total of 79,000 metric tons worldwide. Brazil was the largest producer of this transition metal, with an estimated production of 71,000 metric tons, around the 90% of the total world production (Figure 2 [1]). In fact, most of the production is concentrated in Companhia Brasileira de Metalurgia e Mineração (CBMM), the world's largest niobium producer. Considering the current world consumption, the mine in Brazil presents reserves to last for 500 years, however, this element was considered as a CRM by the European Commission on 2014, 2020 and 2023 due to scarce availability in Europe.

CBMM's niobium production in 2021 amounted to nearly 100 thousand metric tons (see Figure 3 [2]), from which ferroniobium productions amounted to nearly 92 thousand metric tons, the 92% of the company's niobium output. In other words, **the dominant niobium product all over the world is ferroniobium, and it is mainly dedicated to the steel production.**

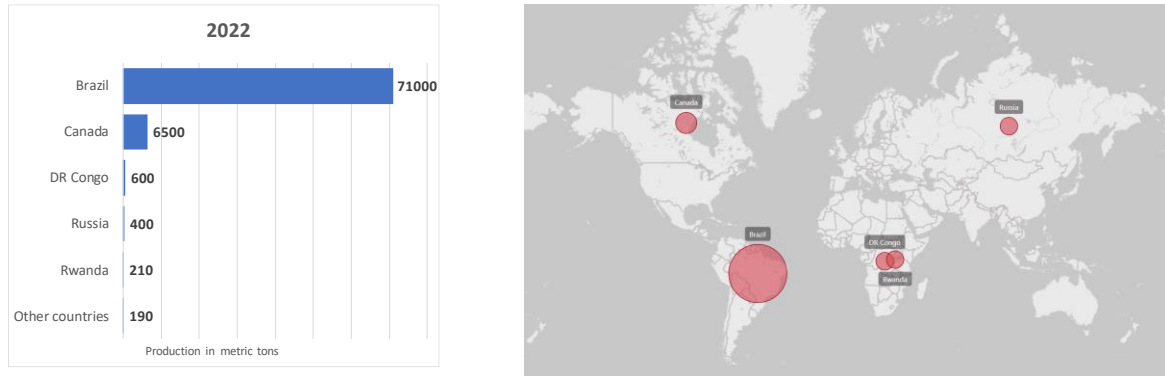


Figure 2. Niobium mine production worldwide in 2022, by country.

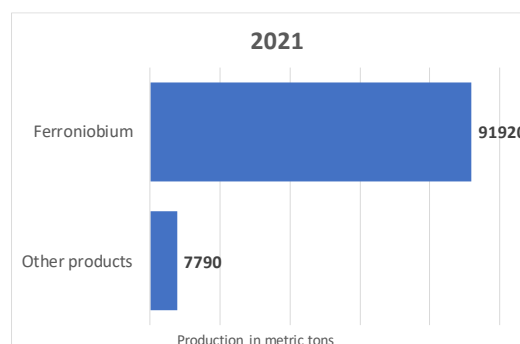


Figure 3. Niobium production of CBMM in 2021, by product.



1.1. Niobium in modern steels

It is well known that niobium is added to a wide range of steels for improving processing, microstructure, properties and performance [2]. Nb can act in a wide variety of steels and Fe-containing alloys, for ambient and high temperatures, in multiple ways such as solid solution, micro-carbide formation, and the formation of intermetallic phases.

Although niobium was discovered in 1801, it was in 1965 when it became a viable commercially produced ferroalloy suitable for addition to steel. From 1965 on, ferroniobium started to be used in the steel industry as a microalloying element, prior to this date only vanadium and titanium had been used for this purpose.

The main application field of Niobium are high-strength low-alloy steels (HSLA), where Niobium is added as Ferroniobium [3]. This market accounts for 90% of niobium usage (Structural, automotive, pipelines and others, see Figure 4) and is responsible for most of the increase in overall consumption of this element.

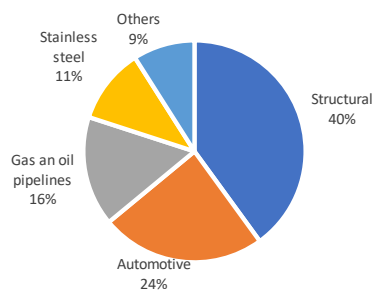


Figure 4. Distribution by sector application of ferroniobium – 2018 data.

The use of niobium as a microalloying element in steel for grain refinement is widespread [4]. Microalloyed steels were developed in the second half of the twentieth century, being one of the biggest breakthroughs in the development of new steels. In these materials, small amounts of niobium, vanadium or titanium are added and significant grain refinement is obtained due to the delay in the recrystallization caused by precipitates of carbon-nitrides of these microelements.

The precipitation process of carbon-nitride $Nb(C,N)$ strongly influences the final microstructure and properties of products. Precipitates inhibit the recrystallization of austenite, which leads to the reduction of the size of the ferrite grains after transformation of non-recrystallized austenite. A new generation of steels called high strength low alloyed (HSLA) steels was developed on this basis.

Since niobium can act as either a solute or precipitate in austenite, each role with different final effects, it is important to recognise where the niobium would be during rolling, and this



will vary with the rolling practice. During rolling different microstructural changes can be seen (recovery, recrystallization, grain size growth...) that can modify the final microstructure and properties of the as-rolled steel. In Figure 5a, it can be seen how for each subsequent rolling pass, the grains are initially deformed, the new grains start to nucleate and a recrystallization takes place. In each rolling pass the grain size is reduced, until the temperature of non-crystallization (T_{nr}) where the austenite grains are non-longer reduced in size and finally transform to ferrite when reaching A_{r3} temperature. However, the use of niobium increases the T_{nr} and reduces de A_{r3} at the same time, increasing the temperature range where the austenite can be deformed without suffering the recrystallization (Figure 5b). The deformation below T_{nr} produces pancaking and more nucleation points for the ferrite. The overall effect is the reduction of the ferrite-pearlite final grain size in microalloyed steels.

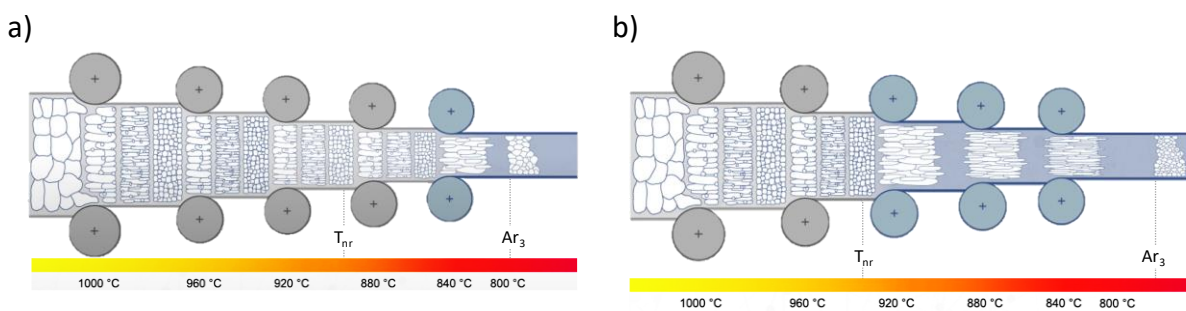


Figure 5. Recrystallization, nucleation and grain refinement during steel rolling: a) Plain C-Mn steel; b) C-Mn with niobium.

Nevertheless, the hardening effect induces by niobium in steel is a complex topic as it can be seen in Figure 6. Niobium has a three-fold influence on the mechanical properties of steel as: grain size refinement during thermomechanical hot forming, precipitation hardening and lowering the γ to α transition temperature.

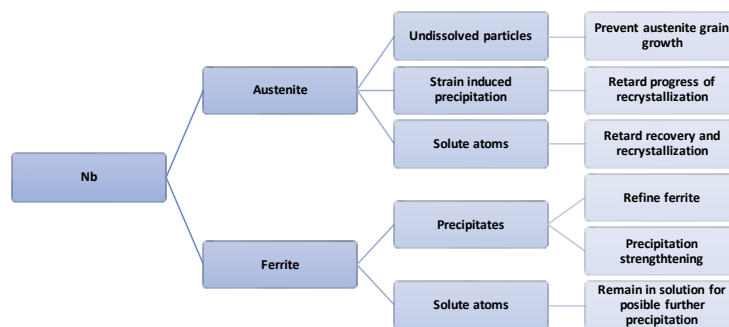


Figure 6. Different hardening effects of Nb in steel.

Figure 7 shows the contributions of five strengthening mechanisms on yield strength (YS) level of a 700 MPa strip, and the main elements contributing to each of them [4]. As it can be seen the effect of niobium is highly remarkable even if it is used in low concentrations.



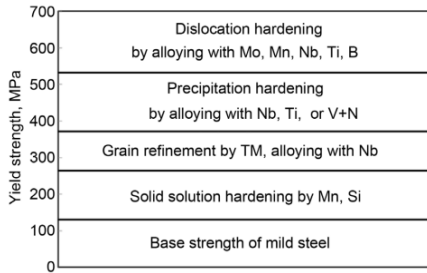


Figure 7. Strengthening mechanisms yielding to the yield strength level of 700 MPa.

Steel Category	Niobium Content Range (Wt %)
Medium Strength Structural Steel	0.015-0.06
Lower Strength Linepipe (X60)	0.02-0.06
Higher Strength Linepipe (X70/X80)	0.04-0.1
Automotive Steel (including trucks)	0.01-0.08
Stainless Steels	0.3-1.0

Figure 8. Typical Nb content in different steel grades.

1.2. Niobium steel grades at SIDENOR

SIDENOR is a steel company, leader in the European steel industry for the production of **special steel long products**. It is also an important supplier of cold finished products in the European market. The company has production centers in Basque Country, Cantabria and Catalonia as well as business delegations in Germany, France, Italy and the U.K.

The company is at the frontline of the sector thanks to their intense research commitment. Having one of the largest R&D centers in the European steel sector, SIDENOR’s technological developments offer optimization of products and processes. In fact, SIDENOR participates in TARANTULA project through its R&D unit: SIDENOR INVESTIGACIÓN Y DESARROLLO.

SIDENOR’s steel production capacity exceeds one million tons annually, primarily destined to the automobile, machinery, capital equipment, railway, energy, mining and petrochemical industries. A full range of rolled products (wire rods, bars, flats, billets), cold finished (cold-drawn, peeling/turning and straightening) and continuous casting semi-finished products (billets, blooms and rounds) are provided in different steel grades: carbon steels, free cutting steels, alloyed steels, spring steels, micro alloyed steels, cold forming steels, ...(Figure 9).

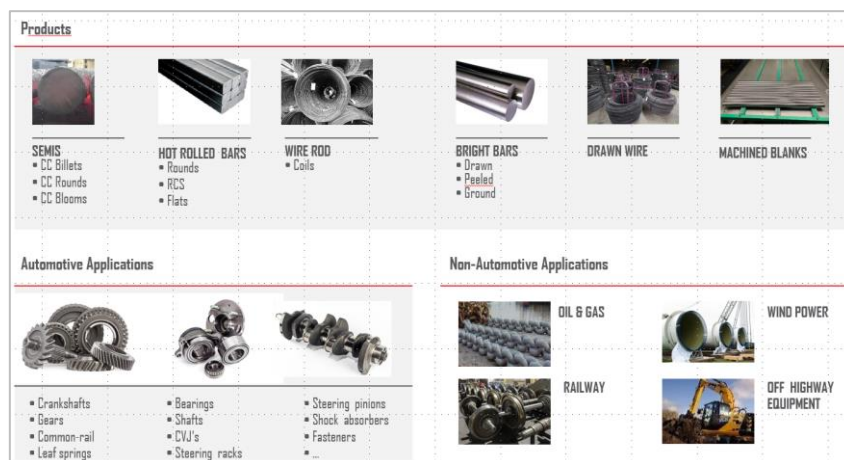


Figure 9. SIDENOR’s SBQ portfolio.



In 2022, the total annual sales reached 645,000 tons, from which around 2% comprised steel grades containing niobium. This amount seems to be small in comparison with HSLA micro alloyed strip producers where most of the steel grades consider niobium additions. Anyway, the final application of SIDENOR products is wide and only specific applications requires the addition of this element.

1.2.1. Innovative microalloying technology for case hardening steels

SIDENOR niobium containing grades are used in different final applications: micro alloyed steel for forged components, spring steels, steering racks, and gears. Of special interest is the NANOCEM PLUS technology developed by SIDENOR due to a market demand on case hardened pieces. Figure 10 presents the commercial brochure of this innovative technology [5].



Figure 10. Commercial brochure of NANOCEM PLUS by SIDENOR.

Case hardening, also called carburizing, is a heat treatment process that hardens the surface of a metal substrate while maintaining a softer core. For low carbon steel grades (with carbon contents between 0.1 and 0.3 wt% C), which have poor hardenability on its own, the case-hardening process involves infusing additional carbon into the surface layer. Carburizing is a diffusion-controlled process usually performed around 950 °C for up to 10 hours, so the longer the steel is held in the carbon-rich environment the greater the carbon penetration will be and the higher the carbon content.



NANOCEM PLUS is an innovative technology specially developed for the high temperature carburizing ($T > 1000$ °C) of gears, shafts, wheels, planetaries and any carburized components, particularly those subjected to fatigue loading. Increasing the carburizing temperature is it possible to reach the same case hardened depth in a much shorter time, usually around 2 hours time (see Figure 11). However, austenitic grain size is temperature-dependent and at higher temperatures, grains grow and coalesce. NANOCEM PLUS was developed to specifically prevent austenite coarsening due to the presence of micro precipitates at high temperatures. The overall effect on Ti and Nb microalloying technology is shown in Figure 12.

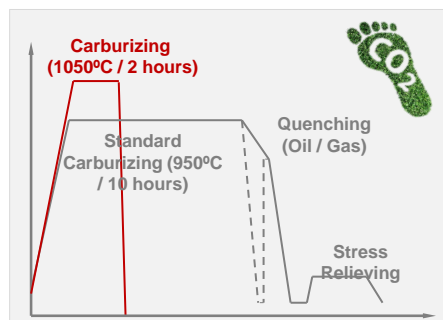


Figure 11. Comparison of thermal cycles: standard carburizing (950°C – 10h) vs high temperature carburizing (1050°C- 2h).

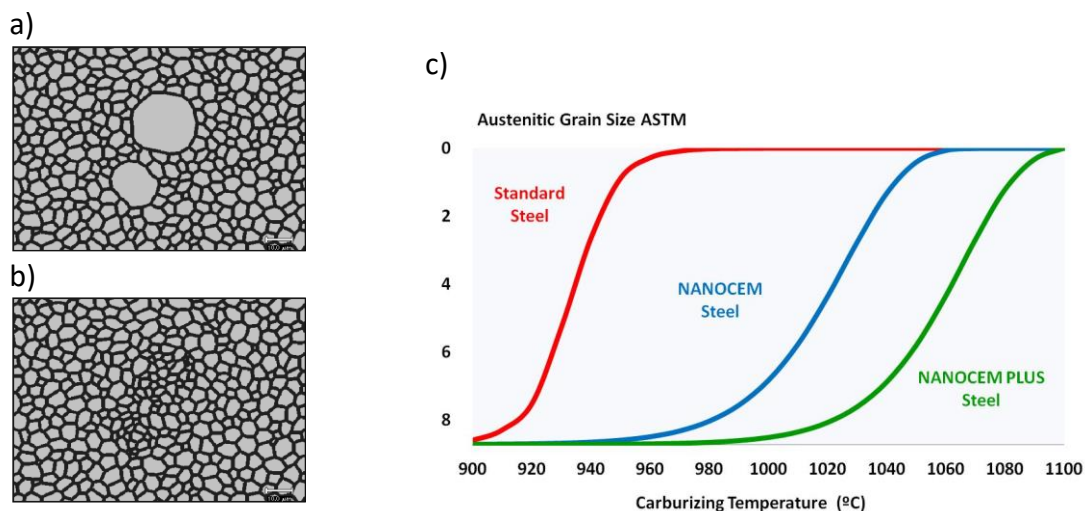


Figure 12. a) Austenitic grain size in standard grade; b) Austenitic grain size in NANOCEM PLUS; c) Austenitic grain size distribution: standard grades vs NANOCEM PLUS.



There are several advantages provided by NANOCEM PLUS technology over standard grades:

- NANOCEM technology can be applied to all usual case hardening steels.
- It allows carburizing process at temperatures up to 1050 °C, while maintaining a fine grained microstructure.
- Shorten the treatment time 3 times as the high temperature speeds up the carbon diffusion in the austenite.
- Increased case depth since the higher diffusion rate allows obtaining a deeper case, maintaining the component quality.
- Cost reduction ($\approx 5\%$ of the total component cost), increasing productivity and reducing quality problems.



2. Validation of the produced Nb in steel

The objective of the deliverable was the validation of the niobium, obtained by other partners' technologies on the frame of TARANTULA project, for the production of special steel for the automotive market.

For that purpose, an industrial heat was not considered since several tens of kilograms of FeNb would have been requested and TARANTULA could not handle so much material. Therefore, some experimental heats at laboratory scale would be initially produced by vacuum induction furnace (30-40 kg ingot). The validation stage would consist of the comparison of two experimental heats with the same target chemical composition manufactured at SIDENOR's research laboratory. One of the heats would be manufactured with commercial ferroniobium for reference comparison, while a second experimental ingot will be produced with Nb from TARANTULA project as a raw material (Figure 13).

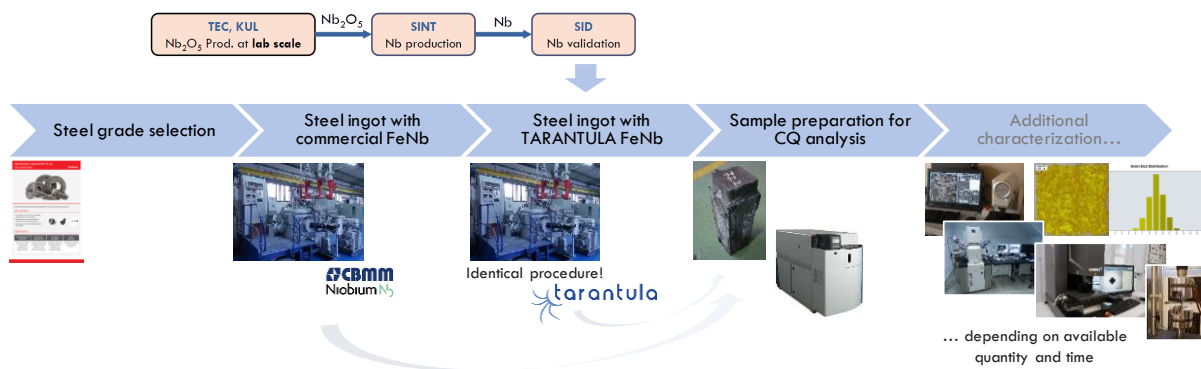


Figure 13. Flowsheet for the validation of the produced Nb at lab scale.

2.1. Ferroniobium addition to molten steel at industrial scale

Figure 14 summarises the main existing special steel manufacturing routes. Nowadays, most of the steel production considers continuous casting (in the centre of the figure), whereas only some specific products require ingot casting (not consider in Figure 14). SIDENOR manufacturing process is highlighted in red in Figure 14. It comprises 100% of scrap, EAF for the steelmaking, secondary metallurgy in the ladle, continuous casting, and rolling to bars and wires depending on the required diameters. Several requirements of the product and the process must be accomplished to assure a good yield of niobium contribution in steel.





Figure 14. Steelmaking routes based on CC and types of steel products.

2.1.1. Minimizing the loss of niobium due to oxide formation

Independently of the processing route, BF or EAF route, niobium must be added to the molten steel during secondary metallurgy or refining in the ladle. Ferroniobium should not be added during primary steelmaking when the oxygen is high in order to avoid the formation of oxides, so, it should be added in the ladle when the steel has been killed, that means when strong deoxidizers like Al and Si have already done their work. The Ellingham diagram in Figure 15 [6] establishes how niobium’s affinity for oxygen is also lower than that of other microalloying elements such as V and Ti. This diagram helps to define the addition sequence of elements in order to avoid the formation of non-desired inclusions in molten steel.



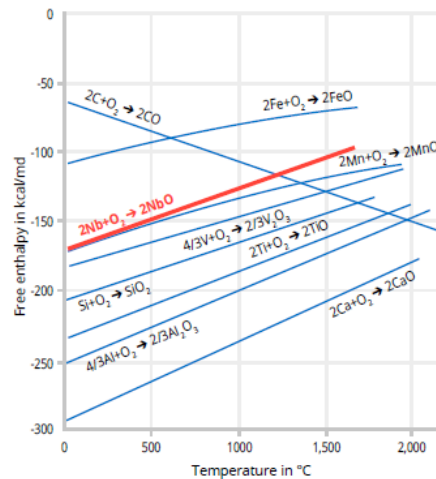


Figure 15. Ellingham diagram showing relative stabilities of different oxides.

2.1.2. Homogenization of niobium in molten steel

Another important factor during FeNb addition to molten steel is the stirring. The density of FeNb is about 8.1 g/cm^3 while 7.1 g/cm^3 of liquid steel. Therefore, without an adequate stirring, the FeNb particles will tend to sink in the melt [7]. Figure 19 shows a delivery system of FeNb particles to the ladle [8], in which argon gas of electromatic stirrers are used to promote mixing of the FeNb and liquid steel.

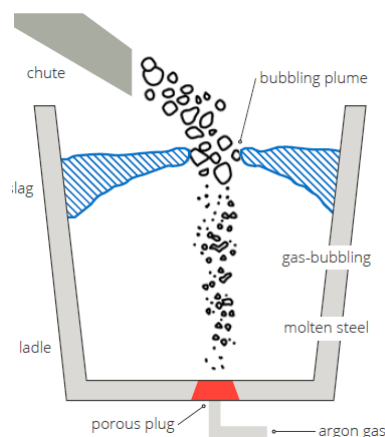


Figure 16. Scheme of the system for the addition of the FeNb particles to the ladle.

Nevertheless, dissolution time will be affected by factors such as particle size and temperature. Smaller particles may be carried away by the strong convection currents associated with the high temperatures of the materials in the ladle, or even they can be collected directly into the de-dusting system. Typically, a particle size distribution of 5-50 mm produces an optimum yield. A viable alternative for particles below 5 mm could be the



additions in cans or cored wire. Table 1 shows different FeNb commercial products by CBMM, such as lumps, fines and briquettes.

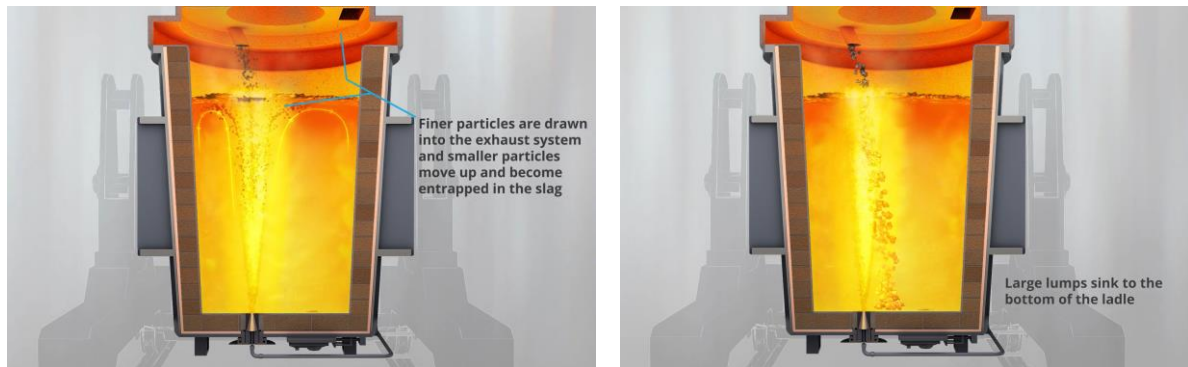


Figure 17. Considerations on FeNb particle size during steelmaking addition: a) Too fine particles; b) too large particles.

Table 1. Different ferroniobium products by CBMM.

Lump	Fines	Briquette
		
Sizing: 5-50 mm Packaging: <ul style="list-style-type: none"> ○ Drum: 250 kg ○ Big Bag: 1000 kg ○ Customized 	Sizing: < 5 mm Packaging: <ul style="list-style-type: none"> ○ Can: Up to 10 kg ○ Drum: 250 kg ○ Big Bag: 1000 kg ○ Customized 	Sizing: 25 mm x 45 mm x 60 mm Packaging: <ul style="list-style-type: none"> ○ Drum: 200 kg ○ Customized

2.1.3. Why ferroniobium is required for niobium addition to molten steel

The melting point of niobium 2477°C is much higher than that of iron 1538 °C. The addition of iron significantly reduces the melting point reaching a minimum of 1370 °C at about 15 %Nb. In the Fe-Nb system (Figure 18 [9]) there is an eutectic reaction around 1500 °C and 60% Nb.



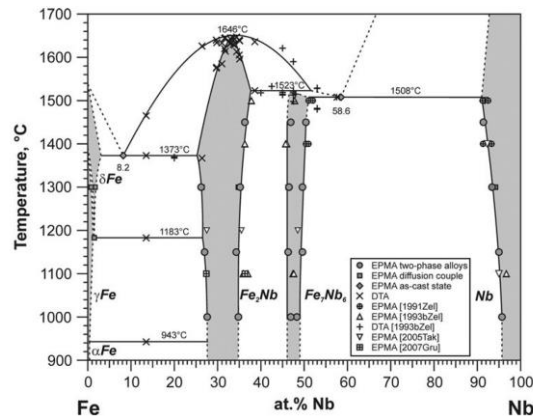


Figure 18. Phase diagram of the binary Fe-Nb system.

The higher the temperature the more rapid is the dissolution rate. During secondary metallurgy in the ladle, the temperature rounds 1600 °C, so the FeNb should be dissolved if enough time is provided. This same low melting point in the Fe-Nb system was used for the ferroniobium preparation at SINTEF.

2.1.4. Standard Specification for Ferroniobium

ASTM A550 specification [10] covers three different grades of ferroniobium, designated as low-alloy steel grade, alloy and stainless steel grade, and high-purity grade. Chemical requirements for each grade are specified in Table 2 and Table 3.

Table 2. Chemical Requirements for FeNb according to ASTM A 550.

Element	Composition, %		
	Low-Alloy Steel Grade	Alloy and Stainless Steel Grade	High-Purity Grade
Columbium ^B	60.0–70.0	60.0–70.0	60.0–70.0
Tantalum, max	5.0	2.0	0.50 ^C
Carbon, max	0.5	0.3	0.10
Manganese, max	3.0	2.0	0.50
Silicon, max	4.0	2.5	0.40
Aluminum, max	3.0 ^D	2.0 ^D	2.0 ^E
Tin, max	0.25	0.15	0.02
Phosphorus, max	0.10	0.05	0.02
Sulfur, max	0.10	0.05	0.02

Table 3. Supplementary Chemical Requirements for FeNb according to ASTM A 550.

Element	Composition, %		
	Low-Alloy Steel Grade	Alloy and Stainless Steel Grade	High-Purity Grade
Chromium	1.00	1.00	0.10
Tungsten	1.00	0.5	0.05
Titanium	1.00	1.0	0.10
Lead	0.25	0.01	0.01
Cobalt	0.25	0.05	0.05



However, chemical specification of standard FeNb by CBMM [11] is more restricted than the one for low-alloy steel grade in ASTM A550, and this should be considered as the minimum quality to be reached by TARANTULA Nb product for steelmaking, since this is the reference product for SIDENOR.


Table 4. Ferroniobium Standard Chemical Specification (wt%).

Nb	Si	Al	P	C	S	Ta	Fe
63.5 min.	3.0 max.	2.0 max.	0.22 max.	0.20 max.	0.04 max.	0.20 max.	balance


Figure 19 and Figure 20 present a ferroniobium certificate provided by CBMM to SIDENOR together in one product delivery. The possible negative effect of trace elements reported in Figure 20 is summarised next (it should be noted that some of the list of elements appearing next could be intentionally added in some other grades with the aim of modifying their final mechanical properties):

- Silicon: Si is the strongest solid solution hardener of ferrite after C, N and P, so it should be specially controlled for steel grades subjected to subsequent cold forging. It presents also a high affinity to oxygen, so it can promote decarburation at hot rolling and hot forging temperatures.
- Aluminium: It is a strong deoxidizer forming really strong alumina oxides, which are really harmful for machining operations. The sequence addition during secondary metallurgy allows controlling the formation of oxides and the decantation to the slag. If nitrogen is present in the melting bath it should also form Aluminium nitrides which are especially harmful in fatigue applications.
- Phosphorus: It is one of the elements that promotes fragilization to the most. It is responsible of the tempering fragilization in Q&T steels. Its content is reduced as much as possible in the last step of the EAF, so if it is added in the ladle it will remain in the last product.
- Lead: Its use in steel is almost prohibited apart from free cutting steels. In free cutting steel it is intentionally added to improve machinability as it is poorly soluble in steel and forms metallic inclusions of low melting point.





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CRL 0502

Analysis Report

Date: 23 Feb 2021
 Report Number: 33637
 Version: 1
 Product: FERRONIUBIUM
 Country of Origin: Brazil
 REF. #: 4500416005
 Packaging: Steel drums - 200 kg on pallets
 Lot: 01.051577
 Lot Quantity (Kg): 48,000.00
 Labware Number: 2860333
 Sampling Plan: 24496
 Customer: CBMM EUROPE B.V.
 Address: 96 WTC H-TOWER, LEVEL 11- ZUIDPLEIN
 City: AMSTERDAM-1077 XV
 Country: NETHERLANDS

Result:


Element	Result	Uncertainty	K	Analysis Date	QL	Method
Nb (%)	65.9	0.2	1.96	22 Feb 2021	NA	ABNT NBR 16420:2015

Notes:

- 1 - Analysis Methodology:
ABNT NBR 16420:2015 (Analysis by ICP-OES)
- 2 - Reported results refer to the entire lot.
- 3 - Sampling is performed according to the ISO 4552-2:1987, IT-DEBE-02 method .
- 4 - Uncertainty in the certified value is calculated as $U=k \cdot U_c$ where K is the coverage factor for a 95% coverage probability and U_c is obtained from the standard Uncertainty. U is the expanded uncertainty which includes the contribution of the volume, weight, calibration curve and other contributions of the measuring system.
- 5 - The recognition status and scope shall be checked at the address www.Inmetro.gov.br/credenciamento/laboratoriosAcreditados.asp
- 6 - % Nb testing refers to the Nb content in the FeNb product.
- 7 - This certificate may only be reproduced in its entirety.
- 8 - The unit "%" is used to represent "g/100g".

Report Number: 33637 V.1
 Lot: 01.051577
CBMM - Informação Restrita

Page: 1/1



Approved by: CLEBER REINALDO DA CUNHA
 Title: LAB LEADER II
 Professional Registration: CRQ 02411797 2nd Region

This product was manufactured in a plant whose management system is certified accordance with the requirements defined in ISO 9001, ISO 14001, ISO 45001 and ISO 27001

Figure 19. Commercial Ferroniobium: Certificate of analysis (part1).




Companhia Brasileira de Metalurgia e Mineração

Córrego da Mata S/N - Araxá - MG
38.183-970 - Brazil
Tel: +55 (34) 3669-3000- Fax: +55 (34) 3669-3300

Analysis Report

Date: 23 Feb 2021
Report Number: 33637 A
Version: 1
Lot: 01.051577

Element	Result	Analysis Date	QL	Method
Si (%)	2.1	22 Feb 2021	0.57	ABNT NBR 16419:2015
Al (%)	0.9	22 Feb 2021	0.26	ABNT NBR 16419:2015
P (%)	0.18	22 Feb 2021	0.028	ABNT NBR 16419:2015
Pb (%)	0.094	22 Feb 2021	0.0165	ABNT NBR 16419:2015
Fe (%)	29.2	22 Feb 2021	NA	ABNT NBR 16420:2015
C (%)	0.14	22 Feb 2021	0.0390	ABNT NBR 16417:2015
Ta (%)	0.13	22 Feb 2021	0.051	ABNT NBR 16419:2015
S (%)	0.01	22 Feb 2021	0.0032	ABNT NBR 16417:2015
N (%)	0.05	22 Feb 2021	0.0100	ABNT NBR 16418:2015

Size Distribution		
Screen (mm)	% Accumulated Retained	Method
50	0.00	ITL-PRAM-04
5	97.87	ITL-PRAM-04

Legend:

-- = Not Analyzed

NA = Not Applicable

QL = Quantification Limit

Notes:

1 - Analysis Methodology:

ABNT NBR 16420:2015 (Analysis by ICP-OES)

ITL-PRAM-04 (Sieving analysis)

ABNT NBR 16417:2015 (LECO CS Determinator)

ABNT NBR 16418:2015 (LECO ONH Determinator)

ABNT NBR 16419:2015 (Analysis by XRF)

2 - Reported results refer to the entire lot.

3 - Sampling is performed according to the ISO 4552-2:1987, IT-DEBE-02 method . Sample is prepared according to ITL-PRAM-02, ITL-PRAM-03 and ITL-PAIH-02.

4 - This certificate may only be reproduced in its entirety.



Report Number: 33637 A V.1

Page: 1/1

Approved by: CLEBER REINALDO DA CUNHA

Title: LAB LEADER II

Professional Registration: CRQ 02411797 2nd Region

Lot: 01.051577

CBMM - Informação Restrita

This product was manufactured in a plant whose management system is certified accordance with the requirements defined in ISO 9001, ISO 14001, ISO 45001 and ISO 27001

Figure 20. Commercial Ferroniobium: Certificate of analysis (part2).


- Carbon: It is a main component of steel together with Fe. It cannot be considered a trace element in low alloyed steel, however, in some stainless steel grades it should be limited to the minimum. The higher the carbon content in liquid steel the smaller the solubility of niobium.
- Tantalum: Tantalum increases ductility, strength and steel melting point.
- Sulphur: During solidification, the residual liquid is enriched in sulphur, so it is finally concentrated in segregated regions, which could lead to defects called “ghost lines”. Sulphur also deteriorates isotropy and mechanical properties of the steel.
- Nitrogen: If other nitride formers are present in the bath, nitrogen combines to form precipitates which are really strong and stable at high temperatures.

2.2. Production of FeNb on the frame of TARANTULA project

SINTEF has validated the Nb₂O₅ material produced at lab scale in WP4 by TEC and KUL, and produced Nb metal from it by using direct electrochemical de-oxidation method. The metal product obtained was analysed by SINTEF using XRD, and the different phases were quantified by Rietveld refinement method with TOPAS software (cf. Table 5). The results showed highly crystalline Nb metal powder being formed, along with some NbFe₂. Besides, metal carbides (NbC_{0.5}, Nb₂C and Nb₆C₅) and calcium carbonate are present as important impurities. Moreover, un-reduced FeO and SiO₂ is found, stemming from the impurities present in the input Nb₂O₅ material.

SIDENOR delivered 500 g electrolytic Fe to SINTEF to prepare the ferroniobium material required for niobium addition into steel. The plan was to melt the Nb metal produced with the provided Fe to reach ferroniobium material (Nb 65%) to partner SID,

However, the high impurity content (carbides, carbonates and oxides) in the metal produced, prevented the melting process.

2.3. Experimental validation of FeNb at lab scale

For the validation of the produced Nb in steel, the grade 17NiMoCrNb6 was selected. This is a NANOCEM PLUS variant specially designed for carburizing gears requiring a special austenitic grain size control.

Experimental casting at lab scale is a process that try to simulate the industrial process of steel manufacturing. Of course, the process is not exactly comparable, because all the industrial procedure carried out in three different installations (EAF, secondary metallurgy and



continuous casting) is resumed in only one piece of lab equipment, the vacuum induction furnace.

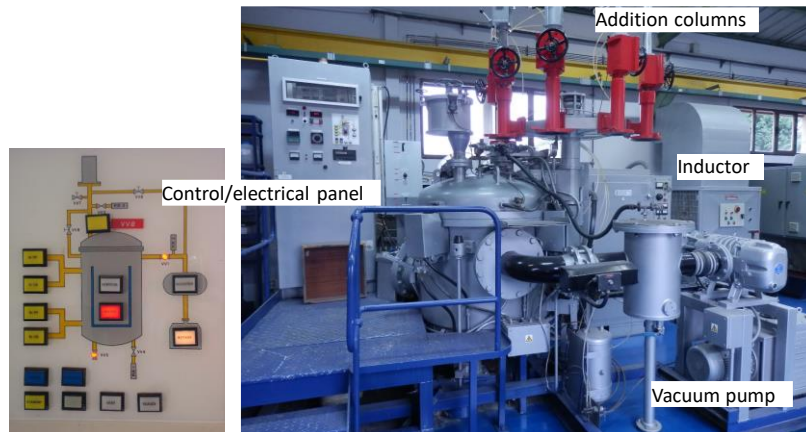


Figure 21. Vacuum induction furnace VMC 030.

SIDENOR INVESTIGACIÓN Y DESARROLLO owns a vacuum induction furnace VMC 030 with a maximum steel load of 45 kg (Figure 21). It can reach a maximum vacuum of 0.002 mbar, and it is supported by oxygen activity measurement and gas injection stirring. It allows the design of new steel grades and the evaluation of different parameters and additions during the elaboration process. Refining processes such as deoxidation and desulphuration can also be considered.

The procedure starts with the preparation of the elements to be added. For the iron matrix, electrolytic iron is employed. This high-quality iron reduces the addition of non-desired alloying elements. It is usually cut in slices that are deposited at the bottom of the crucible.

The ingot mould is prepared (Figure 22) with a layer of BN painting to prevent steel ingot from sticking to the walls. Then, a layer of glass fiber is added, and a top riser is mounted in the top. The main purpose of the top riser is to control the upper shrinkage of the ingot during cooling and to retire the slag that could be poured during tapping. Finally, a safety ring is added.



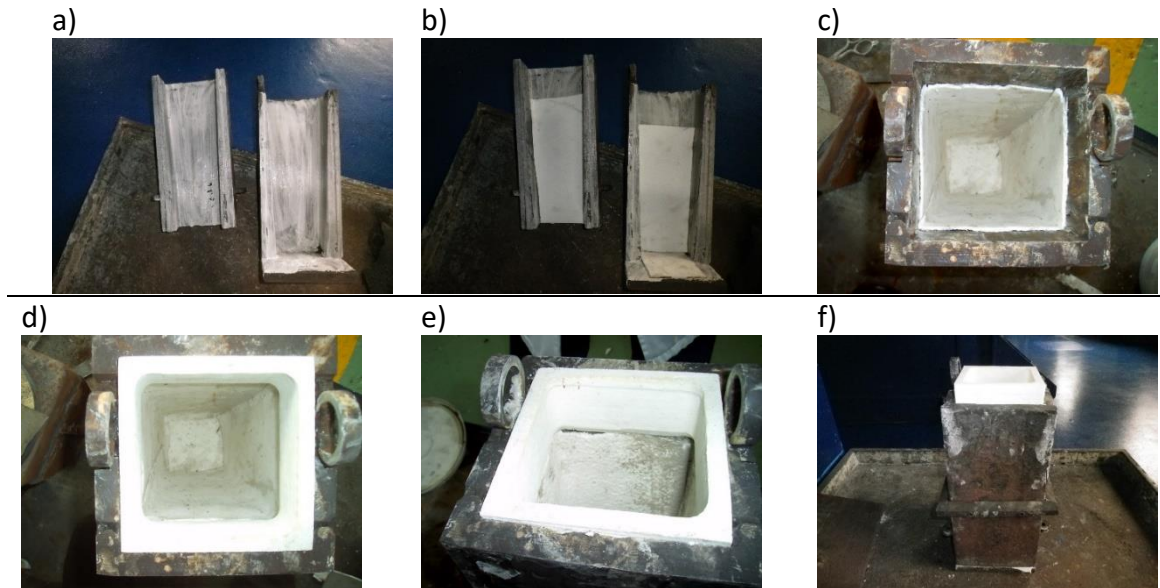


Figure 22. Preparation of the ingot mould: a) BN painting; b) glass fiber; c) assembled ingot mould; d & e) top riser, f) ingot mould assembling with safety ring.

The ingot and the melting crucible are placed inside the vacuum chamber (Figure 23).



Figure 23. Melting crucible: a) general view; b) crucible in dump position; c) crucible with electrolytic iron and ingot mould inside the vacuum chamber.

The melting procedure starts holding a vacuum inside the vacuum chamber. When the power is increased, the electrolytic iron begins to melt (Figure 24a). This first step lasts for 1h 20 min. Before finishing iron melting, Ar gas is inserted in the vacuum chamber render the inert atmosphere down to 200 mm Hg. Once the iron melting is completed (after 2h -2h 30 min), a new vacuum step and a new addition of Ar are done. In this moment the high C foundry is added, and then all the alloying elements following the proper sequence (alloying sequence can take between 30 min and 1h 30 min). Once again, vacuum is held, the temperature is controlled by Celox and finally the liquid steel is poured into the ingot mould. Temperature cannot go over 1600 °C, otherwise it could cause the perforation of the crucible endangering operators' safety.

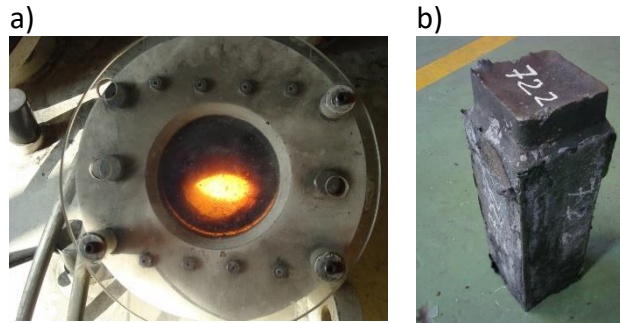


Figure 24. a) View of the liquid steel bath; b) as-cast ingot (the knock-off feeder with smaller dimensions can be seen in the upper part).

2.3.1. Inability to produce FeNb due to Nb₂O₅ precursor impurities

Unfortunately, it was not possible to get a FeNb raw material produced on the frame of the TARANTULA project. The experimental trials to get the ferroniobium only reached from the niobium oxide (produced at lab scale in WP4) to the metallic phase.

As it can be seen in Table 5, the metallic niobium presented considerably amounts of impurities, hindering the subsequent alloying step to reach the FeNb. For the industrial validation only the FeNb makes sense to be used. Under industrial conditions, Nb is always added to the molten steel as FeNb, so a hypothetical validation trial using the “metallic Nb” from TARANTULA would not resemble the future industrial implementation.

Table 5. Chemical composition (wt%) of the metallic niobium produced by SINTEF after reducing the niobium oxides from TEC and KUL. Results obtained by Rietveld refinement method of the XRD diffractograms using TOPAS software.

Sample	Nb	NbFe ₂	CaCO ₃	Nb carbides			SiO ₂	Graphite	FeO
				NbC _{0.5}	Nb ₂ C	Nb ₆ C ₅			
KUL #1	39.79	14.28	17.47	13.54			2.74	7.66	4.53
				1.99	6.75	4.8			
KUL #2	44.78	12.81	17.03	11.66			2.58	7.05	4.09
				1.29	5.91	4.46			
KUL #3	28.25	6.29	3.71	5.24			3.2	49.11	4.2
				0.62	2.47	2.15			
TEC #2	45.5	20.17	11.54	12.47			3.4	0	6.92
				1.91	7.61	2.95			
TEC #3	52.49	24.99	8.08	7.33			2.33	0	4.79
				1.47	4.4	1.46			

In case the material was obtained, the results of the chemical composition would have been added to the corresponding spreadsheet in order to evaluate into consideration the possible effect in the final ingot chemical composition. Although the impurities of the metallic product



are known, that does not provide enough information as to quantify the traces element in the hypothetical ferroniobium. Therefore, as no experimental material was achieved no comparison was made to the commercial FeNb.

The lack of experimental FeNb for the validation implies that it is not possible to apply TARANTULA solution in steelmaking nowadays. However, there is still one open door for the future development of FeNb alloy, not taking the metallic Nb as precursor, but the corresponding oxide. Current industrial exploitation of FeNb, using different oxides minerals as precursors, considers the aluminothermic reduction process for ferroniobium manufacturing. This process starts mixing Nb_2O_5 concentrate with Al or Fe-Al, hematite or iron scrap and fluxing agents in an EAF. After separation of the aluminium containing slag, a metallic phase as ferroniobium (64-69%) is obtained [additional info on this procedure can be found in annex, page 41]. This procedure was not considered in TARANTULA, and further research will be necessary in order to be adapted to the Nb_2O_5 obtained in WP4.



3. Introduction to tungsten validation

As Covid pandemic was hard on many industries all over the world and the start of Ukraine War had a significant influence on the military sector as one Tungsten End Use segment the current Tungsten market is still quiet dynamic and still trying to find its way back to a stable market. Consequently, current and reliable data is hard to evaluate. Thus, for the evaluation of the present case the data from the last 3 years are presented, including some potential forecasts.

In 2020 world tungsten refinery and production suffered from COVID-19 restrictions especially the “Zero COVID” strategy in China. However, since then the tungsten market is recovering and 2021 First and End Use volume increase:

First Use volume: 113 kt (+18 % YoY)

End Use volume: 102 kt (+10% YoY)

The main growth drivers were:

- Defense expenditure programs (provoked by war in Ukraine)
- Mining & construction (many new projects related but not limited to critical raw materials e.g., US IRA program)
- Oil & Gas but also increasing LNG investments (Ships, Terminals, Pipelines)
- Renewable Energy (Wind, Solar PV ...)
- Aviation (Superalloys)

Whereas still existing growth obstacles being:

- High energy prices (especially in Europe)
- Ukraine crisis
- Ongoing shortage of chips (semiconductors) and supply chain disruptions
- Lack of (skilled) workforce

Figure 25 left shows the first use segments for tungsten in 2016 [12, 13]. It is reasonable to assume that the distribution among these segments has not shifted significantly and tungsten carbide products are still by far the most important segment for tungsten. In 2021 this segment accounted for around 65 %. This is followed by the steels and superalloys, tungsten metal products and Chemicals and others. Chemicals being tungsten containing compounds are sodium tungstate (Na_2WO_4), tungstic acid (H_2WO_4) or ammonium meta tungstate (AMT; $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$). Also illustrated in Figure 25 is the structure of the End Use of tungsten products with mining and construction as well as transport being the largest consumers [14]. Both use mainly tungsten carbide-based products.



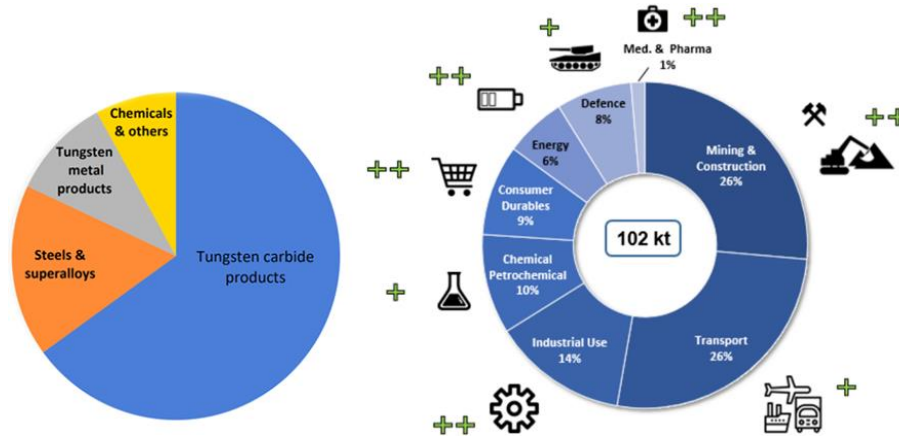


Figure 25. Tungsten First Use Segments 2016 (left) and Tungsten End Use Structure 2021 (right).

Depending on the first and end use a certain tungsten quality is prerequisite. This includes both chemical purity and physical properties like particle morphology or size distribution. Therefore, it is crucial to know both first use segments and end use market to evaluate a market for a potential product and to develop a go-to-market strategy.

Main producer of tungsten still is China which improved its position to around 36 % in 2021 whereas Europe still accounts for 20 % worldwide production. With a predicted annual growth of 2.8 % CAGR (mainly due to Mining and construction, energy, defense) the total tungsten End Use will increase from 102 kt in 2021 to 135 kt 2031.

- New/promising developments:

Start-ups like Nyobolt Limited and research institutes are investigating the use of tungsten-based products like APT, AMT or tungsten oxides as an anode material for batteries which could lead to batteries with higher electrochemical performance and faster charging. Also coating of the cathode active material is currently under investigation. Even with a low weight percentage in the overall battery the amount needed to satisfy the growing demand for battery material could represent an interesting future tungsten market.

The properties of tungsten also makes it a possible candidate as a neutron shield for potential fusion reactors. The best tungsten compound for this application will probably be in the form of tungsten boride. However, this potential market is certainly still far in the future.

- Tungsten price indication:

As ammonium paratungstate (APT) (in the form of the tetrahydrate) represents the most important intermediate from which almost all other tungsten products like oxides, tungstic acid, ammonium metatungstate, but also tungsten metal powder and tungsten carbide are produced. APT is the commonly traded tungsten product. Consequently, it functions as the



reference for pricing tungsten [15]. In Figure 26 the price development of APT is presented in \$ per mtu of WO₃ content in APT (metric tons unit, equivalent to 10 kg). Once for the last 5 years (Figure 26, left) and in more detail for the last 12 month (Figure 26, right).

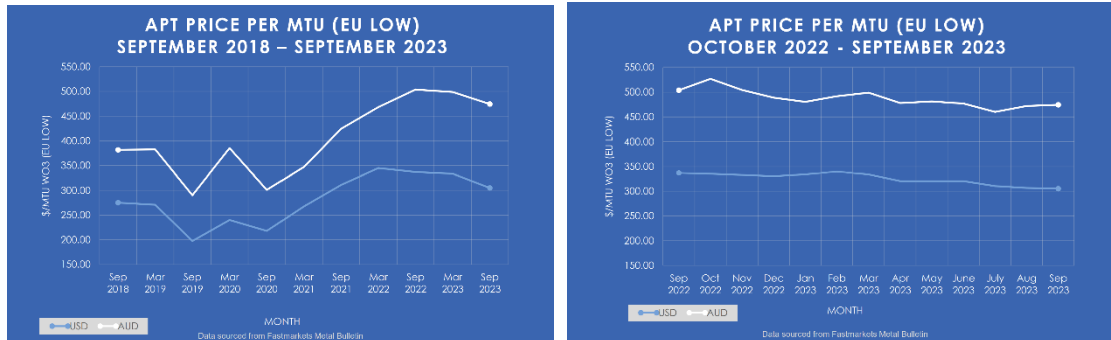


Figure 26. APT price in \$/MTU WO₃ over last 5 years on half-year basis (left) and 1 year on a monthly basis (right).

The tungsten content normally is expressed as WO₃. To clarify that and make potential additional calculations (or recalculations) easier to understand, Table 6 shows the W-content in mass percentage for both APT and tungsten oxide (top). Furthermore, Table 6 illustrates the W value in the ATP price as it is converted from \$/MTU WO₃ into \$/kg W in form of APT.

Table 6. W-content in APT and WO₃ (top) and ATP price converted from \$/mtu in \$/kg (bottom).

	Formula	W-content [m.-%]
Ammoniumparatungstate (APT)	(NH ₄) ₁₀ (H ₂ W ₁₂ O ₄₂)·4 H ₂ O	70.4
Tungsten trioxide	WO ₃	79.3
Tungsten metal	W	100

	\$/mtu	\$/kg
WO ₃ content in APT	320	32
W	254	25

As mentioned above, knowing the first and end use of the tungsten product gives one an idea about the product specifications. Both a deviation in chemical purity or physical properties can mean that the product is useless for that specific segment. However, since all tungsten products, due to high material costs almost without exception end up in high performance materials the product specifications are typically very high. Not having a high purity or specific physical properties would end up in an underperforming material which then could be better and more economically replaced by a lower priced material.



4. Desk work validation of tungsten

4.1. Production of W products on the frame of TARANTULA project

In the following paragraphs the W-based materials produced within the present project are presented and a rough estimate for a potential application is given. The products include tungsten oxide (WO_3), tungsten metal and ammonium paratungstate (APT).

4.1.1. Tungsten trioxide

Tungsten oxide might be one of the tungsten products with the broadest variation concerning its specifications. This is based on the fact that tungsten oxide powders are used a lot for tungsten coatings in the field of (petrochemical) catalysis. However, also high purity is normally required in this field. The manufacturing process is based on dissolving the tungsten precursors in e.g. ammonia containing aqueous solutions before getting coated onto the catalyst materials. This dissolving step allows the separation of certain impurities. Furthermore, a calcination step can occur which represents an additional purification step. Impurities like P or S can form volatile compounds during this heat treatment and be separated from the tungsten product.

As one can imagine, due to the dissolving step, also the requirements for the physical properties like particle size distribution or morphology is comparably low. However, as indicated already, “low” chemical purity still means WO_3 content of at least 99.5 %.

Following the calcination step the tungsten oxide is obtained as yellow powder indicating the successful calcination of the precursor. This is further confirmed by powder XRD characterization and comparison with existing patterns of WO_3 .

Potential discussions with certain downstream partner on their specific dissolving and potential calcination conditions might give a possibility of evaluating an economically application for the produced tungsten oxide quality. One potentially more expedient processing of the obtained tungsten quality could be the production of tungstic acid. State-of-the art production processes are based on the dissolving and acidic recrystallization of the tungsten units. By recrystallization one can take great influence in the separation of especially P (as phosphoric acid). By this value-adding process (tungstic acid is normally more expensive based on the W-content compared to WO_3) the specification of common tungstic acid might be reached and the value-add also justifying the additional process step including acid consumption.



Summarizing, the production of tungsten oxide out of pretreated tungsten tailings using DES leaching and IL extraction was successful. Although, current specifications are not fully met for all impurities the underlying process flowsheet was confirmed. Further investigations are needed for go-to-market strategy and economically estimations.

4.1.2. Tungsten metal

Tungsten metal is normally considered the tungsten product with the highest requirements. This accounts for both chemical and physical properties. This can be based on the fact, that a great part of the metallic tungsten goes into the military sector for shielding or ammunition having very high material requirements. Thus, tungsten contents of minimum 99.95 % are required for these applications. However, also comparable low-grade tungsten metal exists and can be used in the steel industry due to the potential of high dilution.

Within this project, tungsten metal was produced by SINTEF based on tungsten oxide powder obtained by KUL/TEC, using direct electrochemical de-oxidation process and graphite as anode material. Figure 27 shows the quality of the obtained tungsten metal. As indicated by the black colour, carburization of the tungsten occurred during the reduction process. This is further confirmed by XRD analysis which also shows the degree of carburization. Following the XRD patterns, the presence of tungsten carbide, i.e., WC and W_2C was confirmed. Beside tungsten and tungsten carbide also pure graphite and $CaWO_4$ are part of the obtained product. By detailed Rietveld analysis the metallic tungsten content is 13 wt% as shown in Table 7. Having more than 50 % carbide material in the final product indicates the intrinsic obstacle of using graphite as electrode material in the reduction process.

A particle size analysis in the Figure 28 shows a trimodal distribution indicating three different main (primary) particle sizes. Imagining each fraction represents a specific product compound, e.g. metal powder, carbide powder and/or scheelite and graphite further investigation of the different fractions could open a way to an effective and easy purification step by sieving, thus, enabling a higher product quality. Also, the size range of the final fraction somewhere between 1 and some hundreds of micrometres would be suitable for potential end use. Commercial products can vary between nano grade materials with some 100 nm in diameter up to several hundreds of μm provided the size distribution of the final product is comparably narrow.

In conclusion, a powder containing 13 wt% of the desired chemical compound cannot be used in the end use sector of course. Especially Ca and Carbon in the form of tungsten carbide are known to make the tungsten metal parts like shielding etc. brittle and fragile. Therefore, the specifications in commercial tungsten metal powder are varying between 5 and 50 ppm. So, the obtained tungsten metal powder produced within this project cannot be used in this field



without further purification steps. However, the general concept of reducing tungsten oxide to its metallic form with the proposed process was proven.

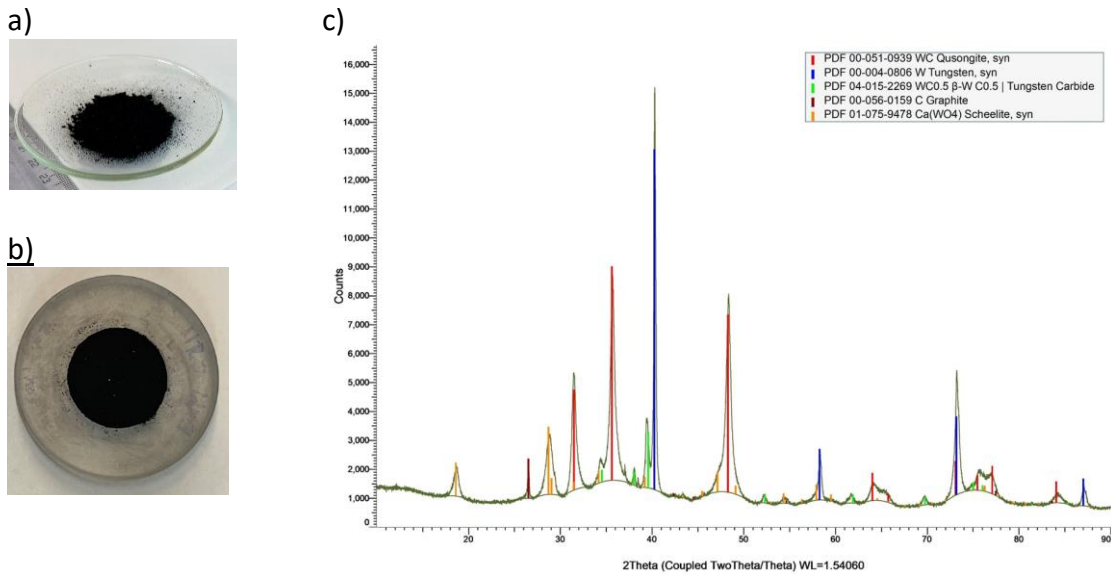
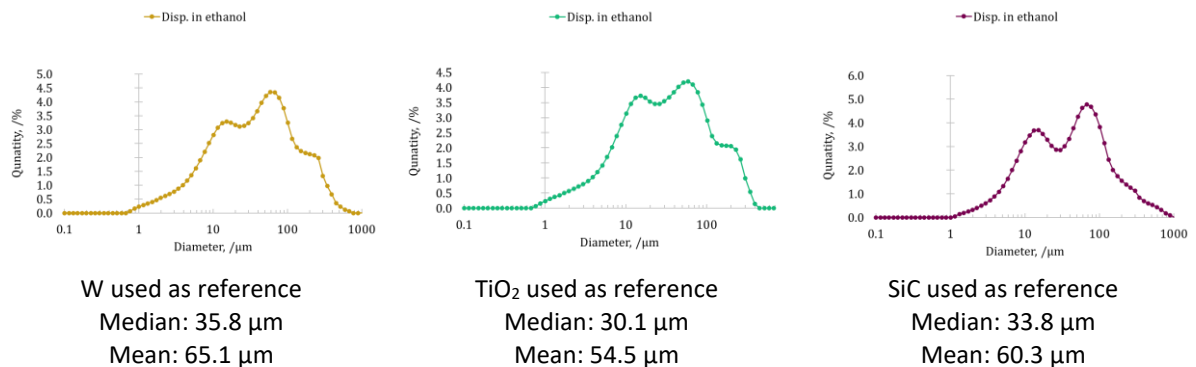


Figure 27. W metal product obtained by SINTEF with graphite anode from WO₃ obtained by KUL: a) powder, b) Sample in the XRD holder, c) XRD pattern.

Table 7. Chemical composition of the cathode product obtained by SINTEF after XRD and Rietveld analysis.

Chemical component	W	WC	W ₂ C	CaWO ₄	C (graphite)
wt%	13	47	8	18	14

Figure 28. Particle size distribution obtained by SINTEF with HORIBA Partica LA-960 Laser Scattering PSD Analyzer and using ethanol as the liquid metal.



4.1.3. Ammonium paratungstate

Tungsten concentrates are converted predominantly into APT. APT is then converted to various powders, which are used in downstream metals, alloys or tungsten-based chemicals. Thus, APT represents the main intermediate product for almost all tungsten product manufacturers. Therefore, the purity requirements for APT can differ a lot depending on the desired final product. Also, physical properties can be depending on the APT. It should be noted that the WO_3 crystals obtained by calcination of APT are known to be isomorph to the precursor APT crystals. In summary, APT is the most important tungsten intermediate and thus the tungsten compound traded on a commercial scale. A typically traded APT product is the “Tungsten APT Price CIF Rotterdam” with minimum 88.50 % WO_3 content. In theory the tungsten oxide content in APT is 88.77 %. So still the impurity level of commercially traded APT is quite high. However, considering the APT going into almost exclusively high-performance materials the high standard quality is comprehensible.

the APT produced within this project at the pilot by TEC, obtained as white powder, by crystallization after DES leaching and IL extraction/reextraction was further used to produce the above-described tungsten oxide. Initial analysis of the white powder indicated a tungsten content lower than the commercial one. Based on this finding (and further analysis) the obtained white powder must consist of some volatile (by-) products which evaporate or decompose during the subsequent calcination step.

There is an open way for increasing the quality of this APT powder obtained within this project significantly by low temperature thermal treatment.

In general, every calcination step can be considered as a potential purification. Especially the phosphorous content can significantly be decreased from APT to tungsten oxide by evaporation/sublimation of P_2O_5 . Sulphur can be effectively reduced by the high temperature treatment as well. On the other hand, impurities like Al, Si, Ca or Ti are not expected to undergo separation from tungsten by calcination as e.g. the oxides are not known to be volatile. So, the impurity level of these elements relative to the tungsten content should be more or less the same in the APT as in the tungsten oxide. Consequently, the expected impurity level, especially for P as well as Al, Si, Ca and Ti will still be notable compared to commercially available APT. So, a specific downstream product must be evaluated. As low impurity levels for these elements are crucial for hard metal or catalytical applications the processing to tungsten metal powder and use in the steel or superalloy industry must be considered. In this first use segment, the dilution of these impurities by blending with other materials is possible.

Summarizing, the general layout of producing APT from scheelite tailings can be confirmed. Further optimization for the solvent extraction and crystallization step will increase the product quality. As tungsten application and product portfolio is broad, further optimization



of the herein presented process should be forged ahead with focus on tailor made product qualities. By focusing on one specific downstream partner and product quality, also the economics will benefit from further optimizing this process for the recovery of this critical raw material.

4.1. Use of tungsten in steel

Tungsten is known for its tendency to form extremely hard and stable carbides, which is the reason for using tungsten in high-speed and tool steels, as well as many hard metal alloys. Today tungsten is used as an alloying element in different steel grades [16]:

- High Speed Steels (HSS): In general terminology they are often simply called tungsten steels. These grades consume most of the tungsten used in steelmaking.
- Hot work tool steels
- Cold work tool steels
- Plastic moulds tool steels
- Heat and creep resistant steels
- Corrosion resistant stainless and valve steels.

When added to steel, tungsten forms tungsten carbides or complex carbides with other carbide forming elements, such as chromium, molybdenum and vanadium. The addition of tungsten will produce a larger carbide volume than other alloying elements at the same carbon level.

The most important property of tool steel is good wear resistance and tungsten (next to vanadium), is the most effective carbide forming element for increasing wear resistance. However, to get this effect, a careful heat-treatment practice is required (see Figure 29 for the tempering temperature effect on hardness).

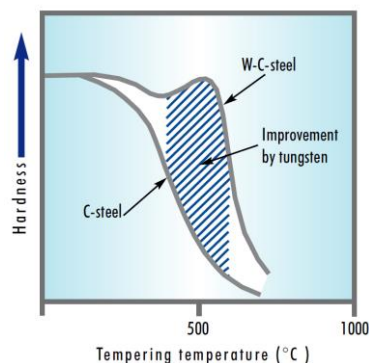


Figure 29. Effect of tungsten on hardness after tempering: W-C steel vs C-steel.



Most of the tungsten used in steelmaking today is used for tool steel, in particular high speed steels, where tungsten has remained the major alloying element in most grades. However, this segment of steel only refers to less than 0.03% of the global steel market, and thus tungsten containing steels constitute a very narrow niche [16].

Tool steels grades are specially well suited for hot and cold forming and for cutting tools applied on metals, wood and polymers. Their suitability comes from their distinctive hardness, resistance to abrasion and deformation, and their ability to hold a cutting edge at elevated temperatures.

According to their W content (in weight percentage), tool steels can be classified into four groups:

- High speed steels with W content of 1.5-20%
- Hot work steels with 1.5-18%
- Cold work steels with 0.5-3%
- Plastic mould steel with W content of ~ 1%.

4.2. Tungsten steel grades at SIDENOR

The experimental validation of TARANTULA outputs in task 7.6 “Validation of the produced Nb in steel” was focused -as per GA- on niobium, but not on tungsten. In the previous sections it has been highlighted the wide application of tungsten for (mainly tool) steel production. However, when TARANTULA was conceived, the tungsten experimental validation in steel was not considered, as SIDENOR practically does not manufacture tungsten steels. As it can be seen in SIDENOR portfolio on tool steels (Figure 30), only the steel grade MAGNO considers W as an alloying element. SIDENOR facilities are not optimised for tungsten, and only few steel grades with relative W content could be manufactured.



TOOL STEELS

Steels with resistance to wear, toughness and thermal shocks. We can highlight 3 steel families: steels for cold working, steels for hot working and steels for the production of plastic moulds.

Applications:

- Steels used in the production of gauges, dies, drills, moulds for thermoplastic materials.



Cold and hot working

Standard equivalents				Chemical composition (average values in %)									
SIDENOR	EUROPE EN	GERMANY DIN	Stand	FRANCE AFNOR	C	Mn	Si	Cr	V	W	Ni	Mo	V
MAGNO	95MnWCr5	95MnCrW8	1.2510	90MnWCrV5	0,95	1,10	0,25	0,50	0,10	0,50			
ATOR14	55NiCrMoV7	56NiCrMoV7	1.2714	55NiCrMoV7	0,55	0,70	0,25	1,00			1,70	0,50	0,10
FINORV	X40CrMoV5.1	X40CrMoV5.1	1.2344	X40CrMoV5	0,39	0,40	1,00	5,00				1,40	1,00

Steels for moulds of plastic materials

Standard equivalents				Chemical composition (average values in %)										
SIDENOR	EUROPE EN	GERMANY DIN	Stand	FRANCE AFNOR	C	Mn	Si	Cr	Ni	Mo	V	S	Cr+Ni+Mo	
EBRO-C45	C45W	C45W	1.1730		0,45	0,65	0,30						0,010 max	0,45 max
EBRO-2311	40CrMnMo7	40CrMnMo7	1.2311	40CMD8	0,38	1,10	0,30	1,70		0,20	0,10		0,010 max	
EBRO-P20	35CrMo8			35CrMo8	0,34	0,80	0,35	1,85		0,42	0,10		0,010 max	
EBRO-2312	40CrMnMoS8.6	40CrMnMoS8.6	1.2312		0,40	1,50	0,35	1,85		0,20	0,10		0,06	
EBRO-2738	40CrMnNiMo8.6.4	40CrMnNiMo8.6.4	1.2738	40CMND8	0,39	1,40	0,30	1,85	1,00	0,20	0,12		0,005 max	
PLASTINOX	XC40Cr14	X42Cr13	1.2083	X40Cr14	0,40	0,50	0,80	13,50			0,20		0,005 max	

Figure 30. SIDENOR portfolio on tool steels.

Anyway, when the tungsten worksheet was selected in WP6, the validation as desk study of tungsten in steel was considered as additional value for the project. Although SIDENOR does not produce these grades on a large scale, SIDENOR INVESTIGACIÓN Y DESARROLLO has experience in developing new steel grades containing tungsten as an alloying element on the frame of other European projects (e.g. RFCS-TOOLSTEEL¹⁷).

4.3. Ferrotungsten addition to molten steel at industrial scale

With a density of more than 19 g/cm³ and a melting point of 3410 °C; metallic tungsten cannot be directly used in standard steelmaking practices. The use of tungsten steel was limited until 1893 when the ferrotungsten was introduced in the market. The system W-Fe (Figure 31) forms the basis of the industrial ferrotungsten alloy [18]. Commercial ferrotungsten contains up to 80% tungsten, and it is obtained from tungsten ore concentrates in an electric furnace. Several advantages are associated with FeW: a lower melting point temperature, faster dissolution in the steel melt and a higher tungsten yield, all leading to a lower steel price. Even so, ferrotungsten has a very high melting temperature (2400 to 2800 °C), which makes the melting procedure very slow.



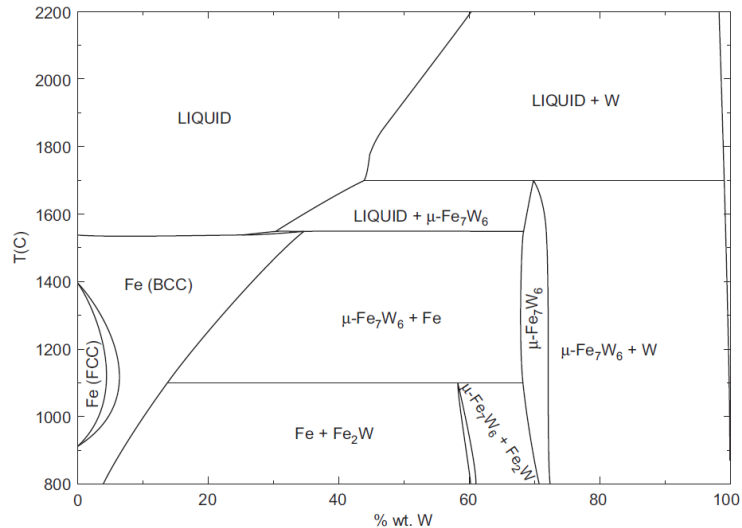


Figure 31. Phase diagram of the binary W-Fe system.

Today tungsten also can be added to the steel melt as scheelite ore concentrates. The different tungsten concentration are:

- Ferrotungsten: 75-80%
- Scheelite ore concentrates: 35-70%

Once again, the European Union needs to deal with the scarcity of supply of FeW. The worldwide production of ferrotungsten is located out of the European Union concentrated in three different countries: China, Russia and Vietnam.

Opposite to the previous manufacturing route described for Nb steels, tungsten steels are not mostly produced by continuous casting, as ingot casting is more suitable. Tungsten containing steels are commonly manufactured via: EAF, AOD, ladle furnace, ingot casting, refining, hot forming, heat treatment and machining route. Tungsten is added as scrap of ferrotungsten directly to the arc furnace to produce a base melt which is further refined in the secondary metallurgy. Additions of tungsten for final adjustment in this stage is made by ferrotungsten.



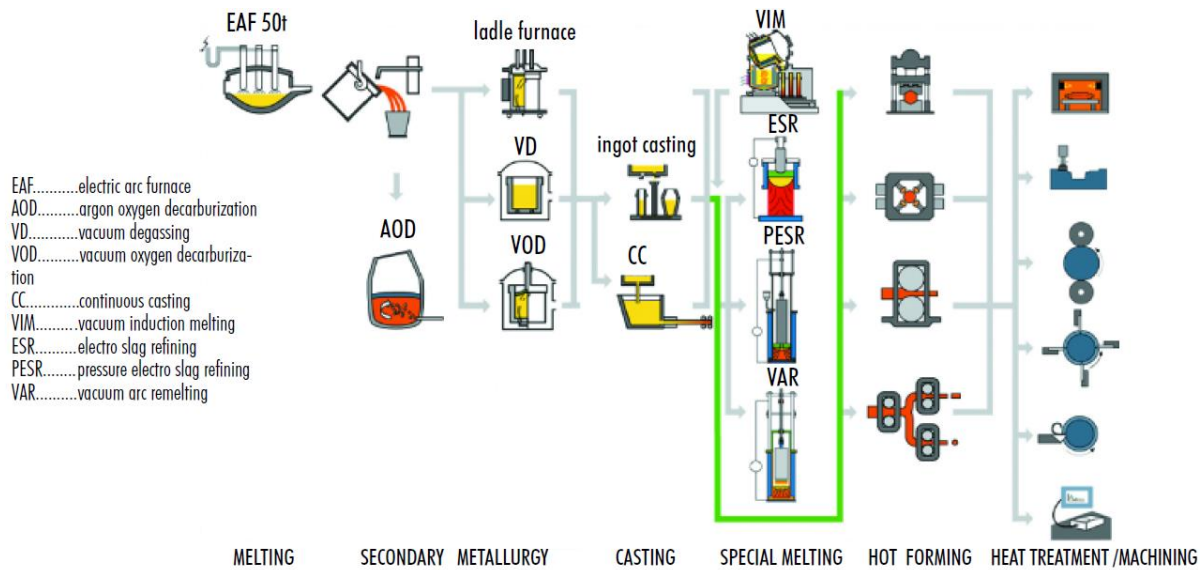


Figure 32. Steelmaking route of the tungsten alloyed steels (highlighted in green).

Additional stages of refining such as ESR or VAR (Figure 32) can be applied to improve cleanliness (in terms of oxide inclusions and reduction on sulphur content), to induce a uniform as-cast microstructure and to minimize carbide segregation.

4.3.1. Standard Specification for Ferrotungsten

Standard ferrotungsten is commercially available in several grades, as they are described in ASTM A 144 [19]. The major difference is defined by the alloy production method, which is reduction by either aluminium or carbon and silicon. This also determines the amount and distribution of impurities. The density of ferrotungsten is high (14 to 15.5 g/cm³), as is its melting temperature (~2700 °C), so it dissolves in the steelmaking furnace slowly and tends to sink at the bottom [36].

Table 8. Chemical Requirements for FeW according to ASTM A 144-02.

Grade	Primary Compositions, max, %, Unless Otherwise Shown						
	Tungsten	Carbon	Phosphorus	Sulfur	Silicon	Molybdenum	Aluminum
A	85.0–95.0	0.050	0.010	0.020	0.10	0.20	0.10
B	75.0–85.0	0.10	0.020	0.020	0.50	0.35	0.10
C	75.0–85.0	0.60	0.060	0.050	1.0	1.0	...
D	75.0–85.0	0.60	0.060	0.050	1.0	3.0	...



Table 9. Supplementary Chemical Requirements for FeW according to ASTM A 144-02.

	Manganese	Copper	Nickel	Arsenic	Antimony	Tin	Bismuth	Total: Arsenic, Antimony, Tin	Total: Arsenic Antimony, Tin, Bismuth
A	0.10	0.50	0.05	0.010	0.010	0.010	0.010	...	0.040
B	0.30	0.07	0.05	0.020	0.020	0.020	0.030	...	0.090
C	0.75	0.10	...	0.10	0.080	0.10	...	0.20	...
D	0.75	0.10	...	0.10	0.080	0.10	...	0.20	...

4.3.2. Inability to produce FeW due to WO₃ precursor impurities

Once tungsten flowsheet was selected for upscaling in the pilot plant, and considering the previous experience of SIDENOR INVESTIGACIÓN Y DESARROLLO in casting W-containing steels at the lab scale, a tentative experimental validation at lab scaled was considered.

In this case, the approach was comparable to Nb route.. For FeW the necessary amount of material was much higher (considering 1% of tungsten content in the final grade, a purity of 75% and a yield of 90%, at least 592 g of FeW would be requested for a 40Kg ingot).

Unfortunately, the boundary conditions for FeW production were far from the optimum ones. As reported in Table 7 (page32) the metal W presented large amounts of impurities (mainly as carbides, oxides and graphite, thus preventing the melting process.



5. Conclusions

Experimental validation of the produced Nb and W in special steel manufacturing requested both elements as the corresponding ferroalloys. However, nor ferroniobium or ferrotungsten has been obtained on the course of TARANTULA. Different difficulties were encountered to obtain both ferroalloys, since metallic phases were considered as the precursors. Neither metallic Nb or metallic W fulfilled the purity requirements to proceed towards the ferroalloying step. Metallic Nb presented high graphite, carbides and CaCO_3 content, while metallic W was mainly contaminated by carbides, CaWO_4 and graphite. As a consequence, a desk work validation was performed in both cases.

For the niobium application on steel manufacturing, the requirements of the ferroniobium have been described: purity degree, impact of impurities in final product, granulometry, etc. The experimental procedure has been described by the selection of the suitable NANOCEM PLUS grade, and the yield of the commercial FeNb has been proved in lab conditions. Further research on the FeNb production from TARANTULA Nb_2O_5 precursor mirroring the current industrial production from mine minerals has been also suggested.

A desk work validation of TARANTULA W output has been carried out. In this case, apart from the ferrotungsten use in steelmaking, different products have been evaluated:

- Tungsten trioxide was successfully produced out from tungsten tailings using DES leaching and IL extraction, although the specifications are not fully met for all the impurities. Further investigations will be needed for go-to-market strategy.
- Tungsten metal only represented a 13 wt% of the metallic phase, so it cannot be commercially exploited in the current situation without further purification steps.
- APT powder is obtained with contamination from the solvent extraction process. A thermal treatment method (at low temperature) was found to significantly increase APT content in the product to >99%. Focus on specific downstream product to optimize the process in order to diminish the impurity levels could open a way for industrial use.



6. Annexes

6.1. Aluminothermic reduction process for Ferroniobium manufacturing

The ferroniobium production process (Figure 33), the most widely used Nb product, starts with mixing the refined ore concentrate with Al or an Fe-Al alloy, a source of Fe such as hematite or iron scrap, and some fluxing agents like lime or fluorite [1, 20]. This mixture is transferred to an electric arc furnace and is heated until all the mass melts (Figure 34 shows some images of the EAF step).

The molten mixture separates in two phases: a slag phase that contains mainly Al_2O_3 and a metallic phase containing the melted ferroniobium. The slag phase is syphoned off, cooled and stored, and the metallic phase is directed to molds and after cooling, is unmolded and crushed to an adequate size.

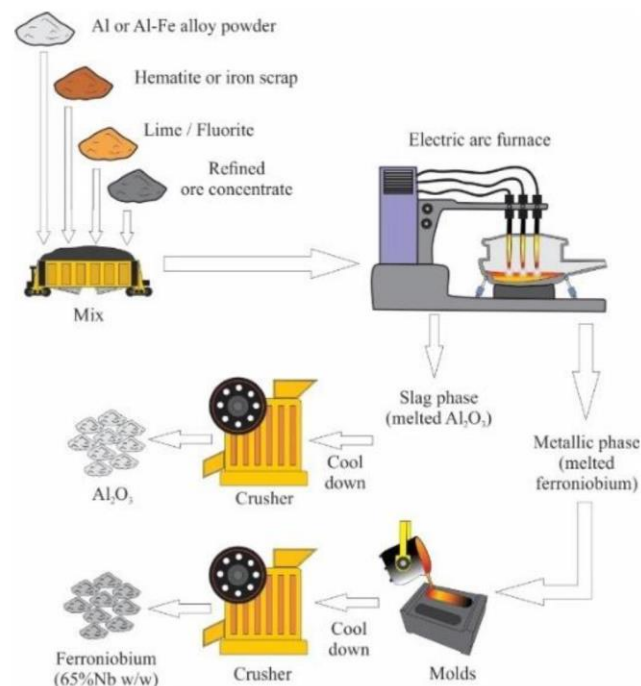


Figure 33. Ferroniobium production process by the aluminothermic reduction process.



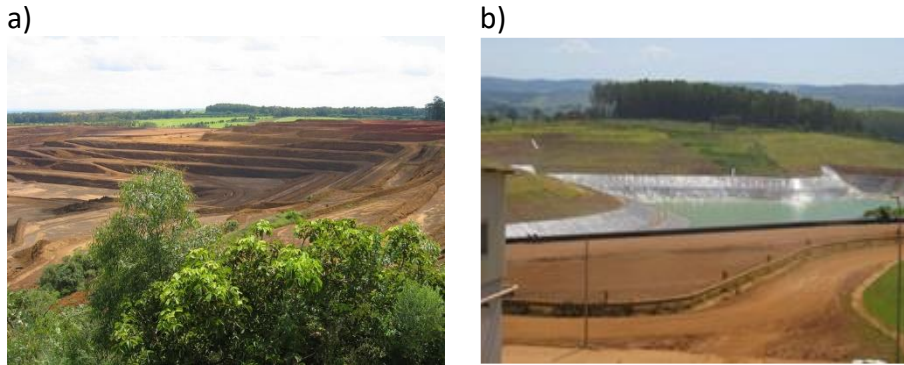



Figure 34. a) The open cast mine; b) Floatation process of enhance the niobium content of the ore.

Table 10. Production of FeNb by the aluminothermic reduction process

	<p>The ore contains about 2 wt% or niobium in the form of pyrochlore (containing Nb₂O₅ in the form (Ca,Na)₂(Nb,Ta,Ti)₂O₆(OH,F)) [21]. It is first enriched by floatation and then heated in an EAF with aluminium and iron.</p> <p>The aluminium reacts to liberate niobium which dissolves in the iron to produce ferroniobium.</p> <p>Here the slag (alumina rich) is being tapped.</p>
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The best extraction of niobium is achieved via the reduction by aluminium, which has favourable thermodynamics for the reaction between Nb₂O₅ and aluminium [22].

$3\text{Nb}_2\text{O}_5 + 10\text{Al} = 6\text{Nb} + 5\text{Al}_2\text{O}_3$ (~1000 kJ/mol oxide Nb₂O₅) but less favourable for the reaction $3\text{Nb} + 2\text{Al} = 3\text{Nb} + \text{Al}_2\text{O}_3$ (~165 kJ/mol oxide NbO). The temperatures of the aluminothermic process reach 1800 °C to 2000 °C and the extraction of niobium into the alloy approaches 99.8%.



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