Niobium As Mint Metal: Production – Properties - Processing

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Summary

For application as coin metal the used materials must be able to meet the demands in a wide range. This paper describes the selection criteria's for coin metals and gives an overview about the quality and production requirements needed for special collector coins. Niobium was selected as core metal for a special 25 Euro bi-metallic coin collectors series issued by the Austrian Mint. As counterpart Silver is used as surrounding metal.

A special feature of this bi-metallic coin is the use of coloured Niobium inserts. The combination of these materials with distinct different material properties, especially the deformation behaviour, and the use of the coloured Niobium insert makes an adaptation of production parameters and manufacturing philosophy necessary. Beside a general overview about the properties and applications of Niobium the paper describes the experience made during production of the bi-metallic coins.

Keywords

Niobium, properties, surface treatment, bi-metallic coin

1. Introduction

In the mid-term idea store of the Austrian Mint the issue of a collector's coin on the occasion of the 700 years anniversary of the city Hall / Tyrol was foreseen. The special commemorative coin should be a continuation of the so called "25 Euro Millennium Coin" series, which was started with the material combination Ag/Ti, focusing on telecommunication and mobility published in 2000 and 2001 respectively. For the third of this series a new material combination should be found. The number of coins of this collector's series is limited with 50.000 pieces per edition.

Between Austrian Mint and Plansee Aktiengesellschaft a project was started for identification of a metal, out of the production range of the Plansee group, which should allow a bridging between the history (700 years celebration of foundation of city Hall / Tyrol), Tyrol as production site for Niobium (manufacturing of the mint metal) and the high technology application of the mint metal (aerospace motive).

The Ag/Nb bi-metallic coin "700 Jahre Stadt Hall", published in 2003, combines the past and the future in an impressive way. The obverse side shows an earth observation satellite which is scanning symbolic the city map of Hall / Tyrol. The obverse side shows the motive of the "Guldiner", a historical coin which founds the tradition of Hall / Tyrol as historical mint place. The motive of the "Guldiner" is reflected and should give the impression of a coining die. As special feature and for intensification of the visual impression a unique material property of Niobium, the possibility to colour the surface by anodic oxidation, was used for the first time for coin manufacturing. For the 25 Euro bi-metallic coin "700 Jahre Stadt Hall" the Niobium surface was coloured blue (Figure 1).

Based on the big success of the first 25 Euro Ag/Nb bi-metallic coin the collectors series was continued with the 25 Euro Ag/Nb bi-metallic coin in 2004 on occasion of "150 Jahre Semmerringbahn" using a green coloured Niobium insert (Figure 2), and in 2005 on occasion of "50 Jahre Fernsehen" using a purple coloured Niobium insert (Figure 3). [1,2,3]

With this project, a new application for Niobium could be realized. Special challenge for the material producer is the high request to the optical appearance, which makes the development of special surface treatment techniques necessary. Furthermore, the colouring of the Niobium insert is an important feature which makes the development and establishment of advanced quality assurance tools necessary, to keep the quality level over the whole production amount of 50.000 pieces per edition.

Figure 1: Obverse and reverse side of 25 Euro bi-metallic coin “700 Jahre Stadt Hall” (edition 2003, 50.000 pieces)

Figure 2: Obverse and reverse side of 25 Euro bi-metallic coin “150 Jahre Semmeringbahn” (edition 2004, 50.000 pieces)

Figure 3: Obverse and reverse side of 25 Euro bi-metallic coin “50 Jahre Fernsehen” (edition 2005, 65.000 pieces)

2. From The Idea To The Coin

After definition of the project task by the Austrian Mint beginning of 2000, together with Plansee Aktiengesellschaft an assessment of candidate materials was made. In spite of intensive cooperation it lasts nearly two years until Niobium could be selected as that material, which fulfils the selection criteria's in the best way, that are: processibility, marketing strategy and quality criteria's. Also after start of production in October 2002 a continuation of the teamwork between the Austrian Mint and Plansee Aktiengesellschaft was necessary to fulfil the extreme quality request given by the colouring of the Niobium insert.

Two important features, the cooperation with an external partner in the design phase and the outsourcing of quality relevant production steps, required an implementation of new project management structures for the Austrian Mint. For the material producer the definition, development and establishment of advanced quality assurance methods was necessary. Furthermore, the establishment of a logistic network between three production sites was a common challenge for the project team. Important point for the successful project transfer and set up of a network between Austrian Mint and Plansee Aktiengesellschaft was the definition of a common target focusing on one specific product.

2.1 Requirements Profile For Coin Metals

Beside the before mentioned selection criteria's for the bi-metallic coins – correlation between material, production site and the design – also general criteria's must be fulfilled by a mint metal:

- workability at room temperature (for forming and striking)
- homogeneous surface structure (for optical appearance)
- colour (possibly contrast to the Ag ring)
- corrosion resistance (against contact corrosion to the Ag ring)
- availability of semi finished products (no special production)
- low tendency for cold welding (low tool wear during striking)
- material image (in combination with the design)
- material price

Based on the defined requirements profile the material program of Plansee Aktiengesellschaft, which is focused on the production of refractory materials and alloys based on powder metallurgical production techniques, was assessed. After pre-selection and stamping tests with candidate alloys, a market assessment was made under consideration of following criteria's:

- image
- possible future editions
- additional features like colouring of the metal by special surface treatments (decorative colouring like e.g. painting, printing or enamelling is not desired)
- price

On the basis of these assessment criteria's Niobium was selected as material of choice for the 25 Euro bi-metallic collector's coin series.

2.2 Quality Criteria's For Coin Production

In Figure 4 the production steps for the manufacturing of bi-metallic coins are given. Starting material for production of the Ag ring and the Niobium insert are melted ingots, which are cold rolled to sheet thickness of 2 mm. Intermediate heat treatment steps are applied if necessary. From the conditioned strips the Ag rings and Niobium inserts where punched with the necessary dimensions.

For the Ag rings no further special surface treatment is necessary before striking. For the Niobium insert before striking a special surface treatment is applied to optimize the surface structure and to realize the colouring of the blanks. The colouring is made by a so called anodic oxidation of the material. With this treatment, by electrochemical processing a very thin Niobium oxide layer is formed under controlled conditions.

By refraction of light in the oxide layer so called interference colours are created which gives the colouring of the Niobium. Depending on the processing parameters, the thickness of the oxide layer can be very well controlled, and gives the Niobium its noble appearance. Depending on the thickness of the layer different colours are producible. A special feature of this process is the fact, that the colouring layer is not deposited on the surface, but it is formed by commutation of Niobium in the surface area of the material. After colouring, the Niobium insert is assembled together with the Ag ring and stroked.

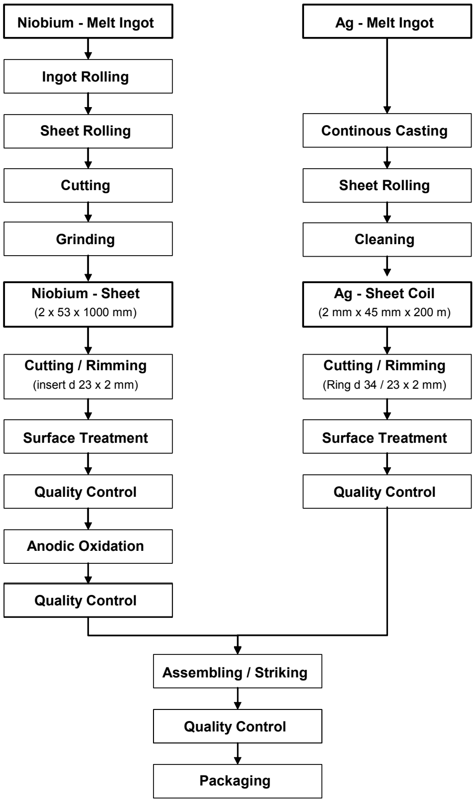

Figure 4: Production steps for manufacturing of bi-metallic Ag/Nb coins from the melt ingot to the coin.

Beside the purity of the metal and the homogeneity of microstructure, which influences the workability of the material, the so called “strike quality” of the coin is mainly influenced by the surface structure of the blank. One possibility for characterization of this property is the specification of the surface roughness. With this value, the surface condition as criteria for processing properties (e.g. deep drawing ability, formability) can be well specified. A definition of “optical quality” of the blank and the appearance of the coin after striking is not possible with this value.

The constant quality of the coins over the whole production campaign can be only guaranteed by repeated visual inspection and comparison with reference samples. The standardization of this “soft quality deciding facts” during production is only possible by intensive cooperation and information exchange of the different production departments. Beside the development and definition of the technical points the establishment of this interactive network between different production locations and a interdisciplinary project team between Austrian Mint and Plansee Aktiengesellschaft was one of the biggest challenge for project management. Retrospective it was the most important success factor for the realization of the 25 Euro bi-metallic Ag/Nb coin.

3. Niobium – Properties, Production And Application

With a melting point of 2468 °C belongs Niobium to the high melting metals and stands in the periodic system of elements, beside Vanadium and Tantalum, in group VA. Because of the unique material properties and the limited application fields these materials are also called as special metals or refractory metals. Particularly these specific material properties, which makes also special processes during mining, refining and production necessary, are the reason why these metals needs a very long time from its discovery to today’s technical application.

3.1 Refractory Metals Overview (ALLGEMEIN)

Metals are termed as “high melting” if the melting point lies above the melting point of Platinum (2054 K = 1772 °C). To this group of metals belong the elements of the groups IVA to VIIA of the periodic system of elements.

The high melting metals are divided in:

- the group of noble metals (Ruthenium, Rhodium, Osmium, Iridium and Platinum)
- the group of refractory metals (Zirconium, Hafnium, Niobium, Tantalum, Chromium, Molybdenum, Tungsten, Technetium and Rhenium)

Beside the high melting point also other special material properties and the unique combination of it are of importance for technical applications:

- low vapour pressure (important for high temperature / high vacuum application)
- high temperature strength (high temperature furnace components)
- creep resistance at high temperature (stiff high temperature furnace components)

- high Young's modulus (for elastic and stiff components, e.g. made of Tungsten)
- low thermal expansion coefficient (important for the electronic industry, e.g. for metal / ceramic material composites)
- high electrical and thermal conductivity (important for active and passive cooling elements for electronic industry)
- high corrosion resistance (for chemical engineering)

The specific properties and their unique combination of properties make the refractory metals suitable for many high performance applications in high technology, sometimes essential. [4] The production and processing is mainly made by use of powder metallurgical techniques, one of the core competences of the Plansee Aktiengesellschaft. From a technical point of view the most important refractory metals are Niobium, Tantalum, Molybdenum and Tungsten. Table 1 gives an overview about the physical and mechanical properties of this group of metals which are well established in the high technology application field as "standard materials".

3.2 Presence And Refining Of Niobium

With a content of 65 g/t is the amount of Niobium in the earth's crust comparable with that of Lead. The annual amount of mined Niobium ore is 40.000 tons, but only 5 % of the production is further refined for Niobium metal or alloy production. The bigger part (95 %) is used as FeNb as alloying element in the steel industry and as Niobium oxide in the catalytic converter and special glass production.

The main deposits which are industrial mined are located in Brasilia, Canada and Africa. In general, Niobium is found always together with Tantalum, Manganese and Iron. The ores were broken, grinded and refined by gravity separation or flotation. The Niobium ore is further purified by subsequent chemical treatment, depending on the used technique the Niobium concentrate is available as oxide, salt or chloride.

Further processing is made by use of carbothermic or aluminothermic treatment or by electrolysis in the dry way. The extracted Niobium raw-metal, which still contains high amounts of Carbon, Aluminium and Oxygen is the starting material for production of semi finished Niobium products. [6,7]

	Niobium	Tantalum	Molybdenum	Tungsten
Melting Point [°C]	2470	2996	2610	3410
Boiling Point [°C]	3300	6100	4800	6700
Crystal Structure	cubic body centred	cubic body centred	cubic body centred	cubic body centred
Density [g/cm³]	8,57	16,6	10,2	19,3
Young's Modulus [GPa]	110	186	290	358
Thermal Expansion Coefficient [10-6/°C]	7,1	5,9	5,4	4,5
Thermal Conductivity [W / m*K]	52	54	142	166
Electrical Resistance [Ohm * m]	14,8 * 10-8	13,5 * 10-8	5,2 * 10-8	5,5 * 10-8
Workability at Room Temperature	good	good	middle *)	bad *)
Ductile/Brittle Transition Temperature [°C]	- 150	- 260	- 20	300
Softening Temperature [°C]	ca. 1000	ca. 1400	ca. 1300	ca. 1600
Corrosion Resistance	high	Very high	low	low

*) depending on deformation degree and dimension

Table 1: Physical and mechanical properties of the refractory metals Niobium, Tantalum, Molybdenum and Tungsten [5]

3.2 Processing Of Niobium

Based on the special processing techniques, needed for refining and processing of Niobium, it lasts nearly 60 years from the discovery of the element in 1801 until the disengagement of the pure metal. Production of semi finished products in purities which allow a technical application is only possible since the middle of the 20th century.

After refining of the ores the Niobium raw material is available in the shape of metal sponge or metal powder. The processing to fully density and reduction of impurities (esp. the interstitial elements) is possible by powder metallurgical or melt metallurgical techniques.

By powder metallurgical processing the powder is shaped by die compaction and subsequent sintered in a temperature range of app. 2000 °C under high vacuum (10^{-6} mbar). During sintering a purification of Niobium is made by dissociation and evaporation of the interstitial compounds and the low melting metallic impurities. Also during sintering a further compaction of the shaped parts by diffusion happens and a sintering density of app. 95 % of theoretical density can be obtained. For melt metallurgical processing, due to the high melting point of Niobium, only crucible free melting is possible. Exclusive electron beam or electro arc melting furnaces with water cooled crucibles are used. The melting electrode is a consumable electrode which consists of the Niobium raw-material. During melting, the electrode is locally melted under high vacuum and allows the impurities to evaporate. After consolidation of the melt bath the ingots have 100 % of theoretical density. The obtained sintered or melted blocks are further processed by forging, rolling or drawing. Deformation is made at room temperature, necessary heat treatment operations must be performed under high vacuum. [7,8]

Niobium is room temperature ductile and a high deformation degree without intermediate heat treatment can be applied. The workability is comparable with stainless steel or copper. Typical wall thickness for tube manufacturing lies between 0,4 to 1 mm; for sheet manufacturing a thickness of 25 µm can be realized under mass production conditions. The quality of Niobium products is defined by the purity of the ingot material (esp. the elements Oxygen, Nitrogen, Hydrogen and Carbon), the microstructure of the semi finished product (grain size) and the surface roughness of the final product.

3.2 Physical And Mechanical Properties Of Niobium

The physical and mechanical properties of Niobium are mainly influenced by the purity of the metal, particularly already small amounts of interstitial impurities influences the properties in a negative direction, and the processing history (e.g. deformation degree). Typical physical and mechanical properties for technical grade Niobium (99,9 % purity) are summarized in Table 2. [9] Table 3 shows typical contents of impurities for technical grade Niobium semi finished products according ASTM specification. [10]

		Niobium (technical grade)
Lattice Constant at 20 °C [m]		$3{,}3004 \times 10^{-10}$
Atomic Radius [Angstrom]		$1{,}47 \times 10^{-10}$
Density [g/cm³]		8,56
Melting Point [°C]		2470
Boiling Point [°C]		4927
Specific Heat 20°C [J/kg*K]		270
Heat Capacity [J/mol*K]		25,2
Melting Heat [J/kg]		$298{,}5 \times 10^{3}$
Linear Coefficient Of Expansion [1/K]		$7{,}2 \times 10^{-6}$
Thermal Conductivity [W/m*K]		52,25
Electrical Conductivity [%-IACS]		13,3
Hardness HV10	annealed / as worked	60 – 110 / 110 - 180
Tensile Strength [Mpa]	annealed / as worked	250 – 350 / 350 – 500
Tensile Elongation [%]	annealed / as worked	25 – 40 / 5 – 25
Young's Modulus [Gpa]		104
Recrystallization Temperature [°C]		900 – 1527

Table 2: Physical and mechanical properties of Niobium [9]

		Niobium (technical grade)
Oxygen	[µg/g]	30
Nitrogen	[µg/g]	20
Hydrogen	[µg/g]	< 1
Carbon	[µg/g]	30
Iron	[µg/g]	< 50
Molybdenum	[µg/g]	< 100
Tungsten	[µg/g]	< 100

Table 3: Typical chemical analysis of technical grade Niobium semi finished products [10]

The influence of deformation degree on the mechanical properties is given in Figure 3. With increasing deformation degree tensile strength and hardness increases.

By application of high deformation degrees Niobium looses partly its ductility and tensile elongation is lowered to 10 %, but no embrittlement happens. The work hardening can be eliminated by stress relief annealing at 1100 – 1300 °C. Depending on the processing parameters grain coarsening happens by primary or secondary recrystallization.

The workability and mechanical properties of Niobium is very strong influenced by the content of interstitial elements, especially Oxygen, Hydrogen, Nitrogen and Carbon. For the mentioned elements Niobium has a high solubility at elevated temperatures and form stable compounds, which can't be decomposed also at very high temperatures and ultra high vacuum. Already Small amounts of interstitial elements give a strong increase on hardness and Niobium is loosing its room temperature ductility. The influence of the interstitial elements on the mechanical properties is given in Figure 4.

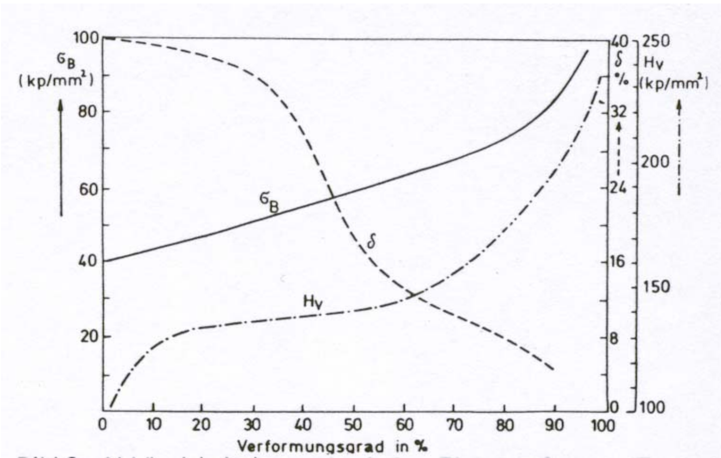

Figure 3: Mechanical properties of Niobium as function of deformation degree [8]

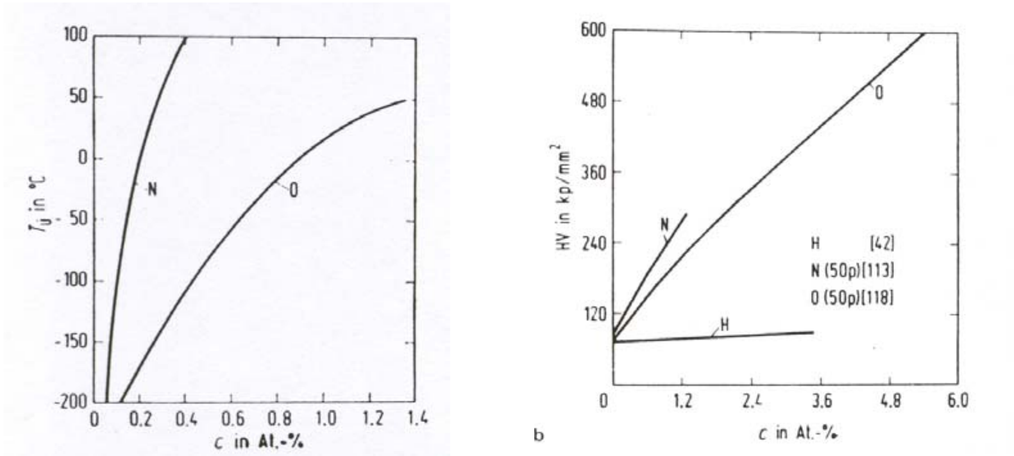

Figure 4: Influence of interstitial elements on the hardness (left) and the brittle/ductile transition temperature (right) of Niobium [11]

Beside the hardness also the other mechanical properties are strongly influenced by the interstitial impurities. A slightly increase in Oxygen content leads to a strong degradation of workability and weld ability. The brittle / ductile transition temperature, which lies for technical grade Niobium typically in the range of – 200 °C, is elevated by small amounts of Nitrogen or Oxygen to values above room temperature and as consequence, Niobium losses its good workability. Therefore to prevent embrittlement, for Niobium processing it is very important that all heat treatment operations are done under vacuum (10^{-6} mbar or better).

3.5 Chemical Properties Of Niobium

The corrosion resistance of Niobium is given by the formation of a very dense and adhesive oxide layer (not to mix up with the oxide layer which is responsible for the colouring of the Niobium). With exception of hydrofluoric acid, concentrated hot sulphuric acid and hot alkaline solutions Niobium shows good resistance against aqueous solutions (Table 4). In comparison to Tantalum the corrosion resistance of Niobium is not so excellent but far off better as that for stainless steel or Nickel based alloys used in chemical engineering. This is the reason, why Niobium plays not this important role in chemical engineering. Despite the lower price of Niobium (by a factor of 4 in comparison to Tantalum) the same expansive manufacturing techniques for construction of chemical apparatus must be used as for Tantalum. The good resistance against metalloid free liquid metals make Niobium applicable as construction material for cooler circuits. Niobium is strong attacked only from liquid Zinc and Aluminium by alloy formation.

	Vanadium	Niobium	Tantalum
Hydrochloric Acid (1:1)	less resistant	resistant	complete resistant
Hydrochloric Acid (concentrated)	not resistant	resistant	complete resistant
Nitric Acid (1:1)	not resistant	resistant	resistant
Sulphuric Acid (1:1)	less resistant	complete resistant	complete resistant
Sulphuric Acid (concentrated)	less resistant	resistant	resistant
Ammonia	less resistant	less resistant	resistant
Caustic Potash Solution (2n)	not resistant	less resistant	resistant
Caustic Potash Solution (50%)	not resistant	less resistant	not resistant
Nitrohydrchloric Acid	less resistant	resistant	resistant
Hydrofluoric Acid (10%)	less resistant	not resistant	less resistant
Hydrofluoric Acid (30%)	less resistant	less resistant	less resistant

Table 4: Corrosion resistance of Niobium in comparison to Vanadium and Tantalum at 100 °C [12]

3.6 Application Of Niobium

The biggest part of Niobium production is processed as FeNb in the steel industry. Niobium is used as alloying element for improvement of hot strength and non-scaling property of hot working steels.

The unique combination of material properties of Niobium and Niobium alloys is used in the aerospace industry, where extreme working conditions are demanded. After firing of satellite thrusters the combustion chamber is heated up within a few seconds from -100 °C up to operating temperatures of app. 1800 °C. These extreme heating conditions demands a high ductility over a wide temperature range (from -100 °C up to near below the melting point) and high elevated temperature strength of the material. Because of the excellent hot strength and the good ratio of tensile strength in comparison to density combustion chambers of research and telecommunication satellites are mainly made of the Niobium alloy C103 (Figure 5). To prevent corrosion caused by the propellant the combustion chamber is coated with an oxidation protection layer.

A special property of Niobium is the super conductivity which was discovered in 1911. Superconducting materials loose at temperatures near the absolute freezing point (-273 °C) its electrical resistance. In the superconducting condition electricity can be transported without losses. For use of this special property ultra-pure Niobium qualities must be used. So called Nb-RRR grades are characterized by very low content of interstitial elements (total amount of the elements Oxygen, Hydrogen and Nitrogen < 30 µg/g, see Table 3 for comparison) and can be reached only by repeated re-melting of the ingot. For Nb-RRR production under industrial scale the Niobium ingot is typically 8 times melted to reach a RRR value of > 300 or better (RRR = Residual Resistance Ratio, ratio between the electrical resistivity at room temperature and 4 Kelvin). By use of sheet rolling, deep drawing and welding so called resonant cavities are produced which are used as accelerator units in high energy physics research institutes (e.g. CERN, DESY). Over the whole production chain it must be guaranteed that no contamination with atmospheric oxygen or other gases take place to keep the RRR value high (Figure 6).

Furthermore Niobium is also used as component of the superconducting Nb_3Sn phase for production of superconducting cables and magnets for large test units in high-energy physics research institutes, for research on plasma fusion technology and in analytical devices for medicine technology. For this application Niobium rods are bundled, assembled in a copper container and subsequent processed by rolling and wire drawing to diameters below 3 mm and a length of over 500 m in one piece. At final diameter the Niobium filaments has a diameter of 10 µm or smaller. Superconducting wires contains typically 5000 Niobium filaments or more, separated from each other by a thin Copper layer. After drawing the wires are stranded to a cable and winded to magnets. In the final state the magnets are heat treated and the superconducting Nb_3Sn phase is formed.

Beside these “exotic” applications Niobium and Niobium alloys are also used in more common applications. For example in chemical engineering for heat exchangers, in high temperature furnace construction for heating and shielding elements, for process technology for getter materials and for lightning technology as components for sodium vapour lamps.

Figure 5: Combustion chamber for satellite thrusters made of hot strength Niobium alloy (thrust 200 N)

Figure 6: Superconducting resonant cavity made of ultra pure Niobium used as accelerator unit for high-energy physics [13]

4. Summary

Niobium belongs to the group of high melting metals and is a corrosion resistant, light-grey metal with good room temperature ductility. With edition of the 25 Euro bi-metallic coin on the occasion of the 700 years anniversary of the foundation of the historic city Hall / Tyrol in 2003, Niobium in combination with a blue coloured surface, was introduced for the first time as mint metal.

During production of the first 25 Euro bi-metallic Ag/Nb coin it was the first time for the Austrian Mint that, beginning with the idea collection, design and development phase and production an external partner was implemented and responsible for quality deciding production steps. A special challenge for the material producer was the adaptation of surface treatment techniques to the demands for mint production and the implementation of advanced quality assurance methods. Furthermore the striking conditions must be adapted to the special working behaviour of Niobium. Over two years an intensive cooperation between the Austrian Mint and Plansee Aktiengesellschaft was necessary for definition and implementation of criteria's which fulfil the processing-, marketing- and quality assurance demands.

From a material point of view, beside the development of a new application field for Niobium, the implementation of up to now not known quality criteria's for surface finishing for semi finished products and the development of a technique for colouring of Niobium with specified shade of colour was the challenge to overcome.

The big success of the first 25 Euro bi-metallic Ag/Nb coin supports the decision of the Austrian Mint to invest in this innovative product line in spite of the high realization risk. The series was continued in 2004 with the second edition "150 Jahre Semmeringbahn" with green coloured Niobium insert, and in 2005 with the third edition "50 Jahre Fernsehen" with a purple coloured Niobium insert. A continuation of the 25 Euro bi-metallic Ag/Nb collector's series is foreseen.

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