COCIR
Brussels, Belgium

MRI superconductor recycling

Review of methods and their viability for recovery of niobium from MRI superconductor cables - DRAFT

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1 Introduction

MRI with high field strength electromagnets are manufactured with superconducting cables. These contain fine filaments of niobium/titanium alloy embedded in a copper matrix. When each MRI is manufactured about 17kg of scrap is generated per MRI and the rest becomes available for recycling when the MRI reaches end of life. Currently MRI superconductor scrap is usually not recycled and so COCIR has asked RINA to investigate potential recycling processes and their viability.

2 MRI SUPERCONDUCTING MAGNETS

MRI use large circular electromagnets that consist of a fine niobium/titanium (NbTi) wire embedded in a supporting copper matrix. The superconducting coil wound and then supported by filling gaps between wires with a resin. This combination of materials makes recycling difficult as the niobium and copper have a reasonable metal value, but first must be separated from the resin and then from each other.

3 MARKET AND MATERIAL QUANTITIES

COCIR has estimated the market for MRI in 2017, including the waste per magnet (typically, 17 kg per MRI are wasted in the production process) as follows:

EU MRI sold in 2017	912	MRI units
Cu:NbTi	4,575.2	Kg/unit
Cu	4,117.68	Kg/unit
NbTi	457.52	Kg/unit
Nb	212.75	Kg/unit

The above quantities are calculated using the following assumptions on the composition of the wire (NB wire composition varies considerably).

Cu:NbTi	10%	Can be from 7 to 11%
Nb	46.5%	
Ti	37%	

In addition, if a viable recycling process is available, superconductor scrap sourced globally can be recycled, which is estimated to be about three times the EU total.

4 PROPERTIES OF SUPERCONDUCTOR MATERIALS

Recycling of superconductor cables requires the separation of copper from niobium-titanium. The chemistry of copper, niobium and titanium are very different and this can be utilized in separation processes. Niobium and, to a lesser extent, titanium are very inert metals which are not attacked by strong acids or alkalis, whereas copper can readily be dissolved in oxidizing acids.

5 USES FOR RECOVERED NIOBIUM

The main uses of niobium is in high strength steel alloys and superalloys. These uses account for over 90% of uses of niobium whereas only 3% is used to make superconductors. Standards for these alloys have been reviewed and there are many alloys that contain both niobium and titanium which would remove the need to separate niobium from titanium.

NbTi superconductor is 1:1 atomic ratio = 66:34 weight percent ratio.

Niobium-titanium alloy, reported to be of similar composition to the superconducting alloy, is used for rivets in the aerospace industry and may also be used by other industries due to its corrosion resistance[1].

The following table is a list of high alloy steel alloys and superalloys that contain niobium.

EN steel number	Short name	Nb content
1.4509	X2CrTiNb18[2]	(3 × C) + 0.30% up to 1.00% (C ⩽ 0.03%)
1.4511	X3CrNb17	12 × C up to 1.00% (C ⩽ 0.05%)
1.4526	X6CrMoNb17-1	7 × (C + N) + 0.10% up to 1.00% (C ⩽ 0.08%; N ⩽ 0.04%)
1.4542	X5CrNiCuNb16-4	5 × C up to 0.70% (C ⩽ 0.07%)
1.4550	X6CrNiNb18-10	10 × C up to 1.00% (C ⩽ 0.08%)
1.4565	X2CrNiMnMoNbN25-18-5-4	Up to 0.15%
1.4580	X6CrNiMoNb17-12-2	10 × C up to 1.00% (C ⩽ 0.08%)
1.4590	X2CrNbZr17	0.35%–0.55%
1.4595	X1CrNb15	0.20%–0.60%
1.4607	X2CrNbTi20	Up to 1.00%
1.4621	X2CrNbCu21	0.20%–1.00%
1.4634	X2CrAlSiNb18	(3 × C) + 0.30% up to 1.00% (C ⩽ 0.03%)
2.4600	NiMo29Cr Nicrofer® 6629, Hastelloy® B-3	Up to 0.40%
2.4619	NiCr22Mo7Cu Inconel® G-3, Nicrofer® 4823hMo	Up to 0.50%
2.4660	Nicrofer® 3620, Incoloy® alloy 20	NiCr20CuMo 8 × C up to 1.00% (C ⩽ 0.07%)
2.4856	NiCr22Mo9Nb Inconel® 625, Nicrofer® 6020	3.15%–4.15%
2.4868	NiCr19Fe19Nb5Mo3 Inconel® 718, Nicrofer® 5219	4.7%–5.5%
Superalloy	Inconel 713C	contains 0.8Ti and 2Nb
Superalloys	Inconel 738LC, Inconel 939, Mar 200, Rene 220, Rene N4, all contain Ti and Nb[3].	
Nickel based superalloy	CMSX-10	Contains 0.2Ti and 0.1Nb

Other alloys:

C-103, which is 89% Nb, 10% Hf and 1% Ti (a medium strength alloy)[4].

IMI834: Ti-5.5Al-4Sn-4Zr-1Nb-0.3Mo-0.5Si – a titanium based superalloy used in aeroengines.

6 COMMERCIAL NIOBIUM RECYCLERS

An Internet search was carried out to identify companies that recycle niobium scrap. The following were identified:

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1 https://www.atimetals.com/Products/Documents/datasheets/titanium/alloyed/ti-45nb_tds_en_v1.pdf

2 http://www.worldstainless.org/Files/issf/non-image-files/PDF/Euro_Inox/Tables_TechnicalProperties_EN.pdf

3 https://www.tms.org/communities/ftattachments/superalloystable_castcomp.pdf

4 https://www.hcstarck.com/niobium_for_space_exploration

- Kuusakoski, Finland has developed a process for recycling superconductor scrap that contains NbTi or Nb3Sn[5]. The process involves heating the cables to decompose resins and then using electrochemical dissolution to dissolve copper, but leaves NbTi wires which can then potentially be used as a superalloy feedstock. The process is similar to one developed in Japan by Nanjo, et.al.[6] but their process is based on a research for a master's thesis by Matti Vaajamo[7]. Further details are given below in section 6.1.
- H. C. Starck, Germany. Processes available not published, but reported to include electron beam melting and oxidation (to niobium oxide), purification using leaching with acids and bases and mechanical sorting.
- Telix metals, USA (metals recycling).
- Monico Alloy, USA (metals recycling).
- Exotech USA (metals recycling).
- A&R Metal Recycling USA (metals recycling).
- MM&A, Canada (metals recycling).
- Buss&Buss Spezialmetalle GmbH, Germany (metals recycling).
- Hydrometal, Belgium (materials recycler).
- ELG Utica Alloys Ltd, global (metals recycler).

6.1 Discussion of Kuusakoski process

Kuusakoski[8] has developed a pilot scale process in Finland to recover NbTi wire from superconductor cables and has not yet delivered any NbTi product that can be reused. The NbTi wires from MRI cables are extremely thin and as a result are prone to contamination. Kuusakoski is planning to deliver NbTi wire mostly into superalloy production. At the moment their annual capacity is roughly 200 metric tons of copper and ca. 20 tons of NbTi, depending on the source material. This is sufficient capacity for the current EU supply from end of life MRI as calculated by COCIR (see section3). Kuusakoski is prepared to double or triple their capacity if there is enough material available on the market.

Kuusakoski dismantles MRI at their recycling facility and remove the superconductor cables which are recycled in batches when sufficient material is available. The cable is first heated at their pyrolysis plant to remove resins. Next the Cu-NbTi is treated at their hydometallurgy plant along with other similar materials if these are available to separate copper from the NbTi wire.

7 REVIEW OF RECYCLING PROCESSES PUBLICATIONS

The scientific and technical literature were searched for information on processes for the extraction and recovery of niobium, especially those processes suitable for secondary (scrap) materials. The following summarises the types of processes that are either being used commercially or are the topics of research:

7.1 SUPERCONDUCTOR CABLE RECYCLING

Only one publication and commercial process, which anyway appears to be based on the publication, were identified[6]. Based on the available publications, the process appears to be as follows:

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5 https://www.recyclingproductnews.com/article/27381/kuusakoski-unveils-recycling-technology-for-separating-copper-and-niobium-titanium-from-superconducting-wires

6 Fundamental Studies of Municipal Waste Treatment and Utilization. VII. Copper-Elimination Step of Recycling Process for Niobium in Nb--Ti and Nb sub 3 Sn Superconductor Wire Scraps, by Nanjo, M; Ito, Y; Sato and Y; Sato, T, Bull. Res. Inst. Miner. Dressing Metall 43.2 (Dec. 1987): 215-226. 1987.

7 Written in Finnish "LTS-romun elektrolyyttinen talteenotto".

8 Email to RINA from Mr Arsi Saukkola, R&D Manager, Kuusakoski Oy.

1. Superconducting magnets used for MRI and other applications (particle accelerators, NMR, etc.) contain a resin used to prevent damage due to vibration and forces induced by the magnetic field. This must first be removed, as it would prevent the next stage from being carried out, by heating at a temperature that causes the resin to decompose to a friable powder but below the oxidation temperature of copper, niobium and titanium.
2. Copper is selectively dissolved by electrochemical dissolution in acid (probably sulphuric acid). This yields a solution of copper sulphate with sulphuric acid from which copper metal can be electrowon leaving sulphuric acid for reuse. It may be possible to carry out electro-dissolution and electrowinning simultaneously so that as copper dissolves at the anode, metal is simultaneously electrodeposited onto the cathode.
3. Although recycling of separated copper-free NbTi into new superconductor or its use to make superalloys is probably the preferred route, other options are considered in this publication to separate niobium from titanium. The method proposed has been used commercially to purify niobium by separating it from tantalum, tungsten and other metals, as follows:

   NbTi alloy is heated in chlorine gas. This produces niobium pentachloride and titanium tetrachloride which are separated by their differing boiling temperatures ($NbCl_5$ boils at 248°C and $TiCl_4$ at 136°C).

   $NbCl_5$ is then heated with sodium metal to form niobium metal and sodium chloride (NaCl).

7.2 METALS

Niobium metal does not react with hydrochloric, sulphuric or nitric acids at room temperature, but it is dissolved in these acids and also by phosphoric acid when hot. Due to the issues described in section 7.4, niobium metal and its compounds are usually dissolved in hydrofluoric acid for refining processes. This acid is very toxic and dangerous to use and so research into alternatives has been carried out but with little success. However, one publication describes replacement of hydrofluoric acid by ammonium bifluoride, which is less dangerous, although is also classified as toxic.

Steel scrap melting

The metal is stable in air but oxidises when heated at >200°C to form Nb_2O_5. When high alloy steel and superalloy scrap is recycled, this is usually carried out in a basic oxygen furnace or electric arc furnace. Usually, niobium-containing alloys are not segregated and so the mixed scrap metal is melted to make lower grade steels and the niobium content is diluted or oxidised and lost. One publication states that when the alloys contain <1% niobium, when melted under oxidising conditions, all of the niobium is oxidised and separates into the slag layer.

High strength alloys and superalloys such as those listed in section 5 are usually made by addition of primary ferroniobium (FeNb) to the melt under reducing conditions to prevent oxidation of niobium. Scrap alloys with a high niobium content are used to provide the niobium content but is usually “new scrap” which is a single alloy of known composition. There is no technical reason, though, why NbTi superconductor wire could not be used as a feedstock. This is proposed as an option by Kuusakoski[9] (unless it becomes heavily oxidised).

Superalloy recycling

Several methods have been described and may be used commercially to separate components, although niobium is often not recovered. Superalloy scrap can be melted using an electric arc followed by vacuum refining which removes volatile impurities.

Hydrometallurgical processes are also proposed[10]. One process uses electrodissolution with reverse polarity in acid which makes a solution of mixed metals which can then be separated by various methods. This is used to recover cobalt, nickel, molybdenum, chromium, etc., but not niobium.

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9 https://www.recyclingproductnews.com/article/27381/kuusakoski-unveils-recycling-technology-for- separating-copper-and-niobium-titanium-from-superconducting-wires

10 Innovation potential in the recovery of refractory metals from urban mines, Author : Mr. Witold KURYLAK, MSP-REFRAM - D4.3 - Issued 2016-by IMN for the European Commission

Scrap alloy refining is also carried out by addition of sulphur to molten metal at 1450°C[11], which reacts to produce sulphides in the slag layer. The slag is ground then leached with a mixture of hydrochloric acid and chlorine. This dissolves most metals but leaves insoluble niobium with tungsten and titanium.

Cutting tools

These use hard steels and carbides including niobium carbide. One process used is to heat in hydrogen gas which causes embrittlement so that the metal can be pulverised to a powder. Iron is then dissolved with acid to leave niobium and other additives. Another commercial process for separation of carbides from tool steels is to use a bath of liquid zinc.

7.3 OTHER MATERIALS

Electronic scrap

Research into separation of metals including niobium from electronic scrap has been published[12]. Scrap containing 36 grams niobium per tonne is pulverised to small particles which are then leached in a column with a solution of alkali sodium cyanide for 15 days. This extracted 48.1% of the niobium content. The concentration of niobium in the leach solution is very low, but can be absorbed by active carbon with a recovery rate of 98.2%. Most electronics scrap contains very little niobium so its recovery is uneconomic. However, scrap from MRI including the superconductor cables may have sufficient niobium to make this process economically viable for niobium recovery. The authors estimate that a small-scale plant suitable for 1 tonne per month, operating for 10 years would give a financial yield of 27% and NPV (net present value) of US$ 105,925, although most of this value is from the precious metals content of electronics scrap.

Oxides

Steel refinery slags and residues from other processes may contain niobium as its oxide mixed with other metal oxides. One process that is used is the carbothermic process in which the material is heated in a mixture of carbon monoxide and chlorine gases. Carbon monoxide is a reducing agent and the ratio of gases affects the product. With excess carbon monoxide, carbides can be produced, but with lower concentrations, volatile chlorides are produced, including the chlorides of niobium, tantalum and titanium. This process is an option if NbTi wires if they become heavily oxidised after separation from copper.

Tin refinery slags sometimes contain economically viable amounts of niobium. These can be recovered from the tin slag by leaching with a mixture of hydrofluoric and sulphuric acids. This gives a mixed fluoride solution from which niobium can be separated by the processes described in section 7.4.

7.4 SEPARATION OF NIOBIUM FROM TITANIUM AND OTHER METALS

It is possible to reuse recovered NbTi alloy to make superalloys or possibly to make new superconductors, however, if neither of these are viable, then separation of the two metals is possible, as is now discussed.

Titanium and niobium are attacked and dissolved by leaching in strong hot acid, but it is claimed that titanium dissolution can be suppressed by adding ammonium sulphate to the leach liquor.

Niobium and the similar tantalum form a variety of polymeric complexes in solution when the metals are dissolved in sulphuric or hydrochloric acids and this makes their separation very difficult. As a result, hydrofluoric acid has to be used to dissolve the mixtures of metals so that polymeric complexes do not form. Various separation methods are possible from fluoride solutions:

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[11] Recovery of Critical Metals From Superalloy Scrap by Matte Smelting and Hydrometallurgical Processing, by Gary L. Hundley and D. L. Davis. US Bureau of Mines, Report of Investigations 9390, 1991.

[12] Recovery of Gold, Silver, Copper and Niobium from Printed Circuit Boards Using Leaching Column Technique, Ricardo Montero, Alicia Guevara and Ernesto de la Torre, Journal of Earth Science and Engineering 2 (2012) 590-595.

Fractional crystallisation

This is a relatively old process that relies on differences in solubility of fluoro-compounds. This is used in commercial refining processes to separate titanium from niobium and tantalum[13] as well as to partially separate niobium from tantalum. In solutions of hydrofluoric acid, niobium has a solubility of at least ten times higher than tantalum[14]. The solubility of potassium fluorotantalate (K_2TaF_7) is much lower than potassium fluoroniobate (K_2NbF_7) and so it crystallizes out leaving niobium in solution, with only a small amount of tantalum. Under appropriate conditions, titanium can be made to hydrolyse to its oxide and separate from niobium which remains in solution.

Solvent extraction

As the chemistries of niobium and tantalum are very similar, solvent extraction is used to separate these metals completely and this is carried out after removal of other metals including titanium[13].

8 ECONOMICS

The market price of niobium metal between 2010 and 2018 has been $40,000 to $42,000 per tonne (metric ton)[15]. According to COCIR, 212.7kg of niobium is present in EU MRI superconductor cable scrap per unit for a total value of €8,500 to €9000. In addition copper metal would also be recovered by a recycling process which currently has a metal price of $5,900 (€5,190) per tonne. COCIR estimate that 4.2 tonnes of copper is present in EU MRI superconductor cable scrap per unit and so the value of copper would be around €22,000 per unit. The total value of niobium and copper from a MRI superconductor cable scrap is therefore $31,000 per MRI. However, the total value depends on the MRI reaching end of life each year.

It is not easy to determine how many MRIs are scrapped every year in EU as not all units are given back to manufactures as they may be sold outside Europe or sent to recyclers directly by the user or through brokers. Moreover, quantities collected and treated are reported under the single voice “Medical devices” according to the WEEE Directive.

Considering 50 MRI sent to recycling every year a good estimation, the following values can be calculated for EU and globally

	EU (Tons/y – 50 MRI/year)	**Value of metals from EU EOL MRI EU (€)**	**Global(Tons/y) – ca. 192 MRI/year**	**Value of metals Global (€/y)**
Niobium	10,6	447,000	40,7	1,709,000
Copper	210	1,090,000	808	4,194,000
TOTAL		1,537,000		5,903,.000

The total value of metals at €5,903,000 from superconductor scrap available from MRI production and at end of life per year is a reasonably large sum. It would not support investment in a large-scale dedicated recycling process for niobium-based scrap unless the process were to be relatively simple (i.e few process steps) and with a high process efficiency and it is clearly sufficient for Kuusakoski to have set up a recycling plant in Finland for MRI

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13 A Review of Niobium-Tantalum Separation in Hydrometallurgy, Olushola S. Ayanda and Folahan A and Adekola, Journal of Minerals & Materials Characterization & Engineering, Vol. 10, No.3, pp.245-256, 2011.

14 Multi-Stakeholder Platform for a Secure Supply of Refractory Metals in Europe, Factsheet. http://prometia.eu/msp-refram

15 https://www.metalary.com/niobium-price/

superconductors. Increasing scale (and so value of products) by inclusion of a capability to treat other types of scrap that contain niobium may necessitate increased process complexity to separate other metals from the mixture and this would significant raise the cost of the recycling plant and of the process.

The Kuusakoski process produces copper metal which will always have a market and fine niobium-titanium wire may be used as a feedstock in superalloy and hard steel production if not heavily oxidised. There are many types of superalloys that contain both titanium and niobium.

Conversion of recovered niobium-titanium wire back into superconductor cables (or into alloy for aerospace rivets) may also be feasible but will require vacuum melting. This is a process, reported to be used by H. C. Starck to obtain the thickness for rivets and material that is used to manufacture new superconducting cables (these are produced from thick NbTi rods embedded in copper by drawing this down into cables that contain the fine NbTi strands.

All recycling processes will result from some losses as niobium readily oxidises, especially when heated in air, and this will reduce the quantity of free metal and so the market value of niobium-titanium wire that is recovered from superconductor cables.

8.1 Kuusakoski Oy - Economics

The email from Kuusakoski Oy explains the economics of the process and so this section is reproduced below:

- *At domestic market (Finland) we co-operate with the major MRI distributors. The big issue usually is the quick hauling and partial dismantling of the old MRI, inside clean hospital circumstances, which is intensive work with strict time schedule. Often the cost of hauling overrides the metal value of the MRI unit.*

- *We can also buy the MRI units, where the main value lies in ordinary aluminum and stainless steel structures, and the transmit coil, those contents being recyclable using ordinary scrap treatment methods. It might be impractical to ship the whole units over very long distances, but we can calculate prices including the shipping costs. Inside USA and Europe, the net price would still become slightly positive, meaning, we will pay money to the customer.*

- *Or, we can buy the superconductive coil which calls for our special treatment technology. The coil is heavy, thus the transport cost is not so crucial. There is a positive price on the coil alone, including all the resin and fibre glass reinforcement.*

- *The pricing differs from MRI to MRI. We prefer negotiating with the customer to reach a basic understanding of content values. Since there seem to be dozens of different MRI designs of different ages, we will often have to make the pricing case by case, and even better, after weighing and calculating the total material balance of that particular unit.*

Kuusakoski also state:

> *We wish to be part of this recycling market. Kuusakoski Oy is nowadays an important player in WEEE recycling. We have local dismantling and mechanical separation plants in Finland, Sweden, Estonia, UK, Russia and USA. Furthermore, we buy a lot of dismantled WEEE fractions to our processing routes. Mostly this is printed circuit boards, cables and the like.*

The economics of WEEE recycling is usually based on sales of copper, aluminium and steel, but especially precious metals from PCB scrap. NbTi is not currently recovered commercially but the Kuusakoski process shows that this can potentially be economically viable with NbTi wire having a value as superalloy feedstock.

9 CONCLUSIONS

The options for recycling of MRI superconductor cables and recovery of metals; copper and NbTi has been investigated.

Currently this material is not recycled but a Finnish recycler, Kuusakoski, has set up a pilot plant which appears to show that separation of copper from the very thin NbTi wires is technically possible and should also be economically viable. This could be scaled up to treat 100% of global MRI WEEE. What is still uncertain though is the value of recovered NbTi wire. If it has a low oxide content then it can be used to make alloys such as superalloys as many types exist that contain both Nb and Ti. If however the hydrometallurgical process results in the very thin wire being significantly oxidised, other options may need to be considered.

There is an EU recycler, H.C. Starck, that claims to be able to recycle niobium in the form of oxides and there are many publications on the separation of niobium from other metals including titanium as well as treatment of oxides and production of metal from oxides.

For MRI manufacturers, disposal at end of life should earn a small profit because of the large quantity of valuable metals which includes copper and niobium from the superconductor cables.

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