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TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

While there are many suitable topics for this quarter's President's Letter, it seems appropriate to defer comments on the current state of our industries until the General Assembly in Vienna. Plans for the meeting are now well developed and invitations have been sent to the T.I.C. membership.
Our technical program will include papers on a broad range of topics pertaining to the tantalum and niobium industries.
We have attempted, with success, to get a larger selection of presentations on niobium processing and applications.
Several papers on mineral activities and processing in Africa have also been promised.

The Executive Committee recognizes that summer time is a season for holidays and family affairs and not a time for thinking about meetings in the fall. However, early response to the invitations which you have received would be much appreciated. Vienna is a fine old historical city, an excellent venue for our meeting. We have a strong technical/commercial program and the promise of an interesting site visit courtesy of our host company, Treibacher Chemische Werke.

In closing this issue's very brief letter, I would like to express my sincere thanks for the special support which Treibacher Chemische Werke and its management have provided to the T.I.C. in organizing and implementing the Vienna Assembly.

Sincerely,

Peter Maden
President

SUMMARY

NEWS OF TANTALUM AND NIOBIUM : A REVIEW OF RECENT LITERATURE

TANTALUM

Two very different uses of colour changes in the oxide film on tantalum metal have recently been patented.

1. The first has application in routine medical diagnosis, for example by detection of antigens. The device consists of a substrate of glass or plastic on which is sputtered a layer of tantalum, followed by one of aluminium. This is then anodised at high voltage to convert all of the aluminium to a porous oxide film, and some of the tantalum to highly coloured oxide. A specific antibody is then applied to the porous layer, and the resulting structure generates a colour by a light interference and absorption effect : sensitivity may be increased by viewing at differing angles or under a different light source. When the device is immersed in a fluid sample containing the antigen for the antibody, they bond and effectively change the optical thickness of the alumina layer and so the colour.

Burrell et al (Alcan International)
U.S.P. 5124172 (23 June 92)

2. The second makes use of the fact that the colour of the oxide film on tantalum (and niobium) will change when the metal is bent. For this to work, the anodising must be carried out in the presence of an agent (e.g. a fluoride) which will weaken the bond between the anodic film and the underlying metal. Tantalum or niobium coated aluminium foil can be used for "tamper evident labels". A word such as OPEN may be printed on the foil before anodizing, and the label may then be laminated with a polyester film. The wine-coloured oxide film shows no trace of the message, but when it is bent, the oxide film colour changes to metallic grey leaving the message clearly visible in the original wine colour.

Smith et al (Alcan International)
U.S.P. 5135262 (4 August 92)

ELECTRONICS

1. Tantalum may have a use in one of its competing materials (aluminium) for capacitors. A good oxide film is formed by dipping etched aluminium foil into an organic solvent solution of an alkoxide (examples given include tantalum iso-butoxide and ethoxide). The foil is dried at 200- 400°C to

T.I.C. STATISTICS

TANTALUM

PRIMARY PRODUCTION

(quoted in lb Ta_2O_5 contained)	*2nd quarter 1993*
Tin slag (2 % Ta_2O_5 and over)	62 515
Tantalite (all grades), other	183 750
Total	246 265

Note : 14 companies were asked to report, 13 replied.
The companies which reported included the following, whose reports are essential before the data may be released :
Datuk Keramat Smelting, Gwalia/Greenbushes, Malaysia Smelting, Mamoré Mineraçao e Metalurgia, Metallurg group, Pan West Tantalum (Wodgina Mine production), Tantalum Mining Corporation of Canada, Thailand Smelting and Refining

QUARTERLY PRODUCTION ESTIMATES

(quoted in lb Ta_2O_5 contained)

LMB quotation :	*US $ 30*	*US $ 40*	*US $ 50*
3rd quarter 1993	234 000	317 000	377 000
4th quarter 1993	234 000	317 000	377 000
1st quarter 1994	232 000	315 000	375 000
2nd quarter 1994	232 500	315 000	375 000
3rd quarter 1994	232 500	315 000	375 000

Note : The quarterly production estimates are based on information available, and do not necessarily reflect total world production.

PROCESSORS' RECEIPTS

(quoted in lb Ta contained)	*2nd quarter 1993*
Primary raw materials (e.g. tantalite, columbite, struverite, tin slag, synthetic concentrates)	297 435
Secondary materials (e.g. Ta_2O_5, K_2TaF_7, scrap)	147 835
Total	445 270

Note : 18 companies were asked to report, 18 replied.

PROCESSORS' SHIPMENTS

(quoted in lb Ta contained)

Product category	*2nd quarter 1993*
Ta_2O_5, K_2TaF_7	30 543
Carbides	67 204
Powder/anodes	258 284
Mill products	103 198
Alloy additive, ingot, unworked metal, scrap, other	141 525
Total	600 754

equivalent to 811 018 lb Ta_2O_5.

Notes :
In accordance with the rules of confidentiality, categories have been combined as shown.

Response : April 18/18, May 18/18, June 17/18.
For both receipts and shipments by processors, reports by the following companies are essential before the data may be released :
Cabot Performance Materials, W.C. Heraeus, Kennametal, Metallurg group, Mitsui Mining and Smelting, H.C. Starck Inc. (NRC), Showa Cabot Supermetals, H.C. Starck, Thai Tantalum, Treibacher Chemische Werke, Vacuum Metallurgical Company, H.C. Starck - V Tech

NIOBIUM

PRIMARY PRODUCTION

(quoted in lb Nb_2O_5 contained)	*2nd quarter 1993*
Concentrates : columbite, pyrochlore	9 483 122
Occurring with tantalum : tin slag (over 2 % Ta_2O_5), tantalite, other	66 943
Total	9 550 065

Note :
15 companies were asked to report, 14 replied. The companies which reported included the following, whose reports are essential before the data may be released :
Cambior, Mineraçao Catalao de Goiás, Niobium Products Co. (CBMM)

PROCESSORS' SHIPMENTS

(quoted in lb Nb contained)	*2nd quarter 1993*
Compounds and alloy additive : chemical and unwrought forms (e.g. $NbCl_5$, Nb_2O_5, NiNb, FeNb [excluding HSLA grades])	508 240
Wrought niobium and its alloys in the form of mill products, powder, ingot and scrap	
(i) Pure niobium	36 906
(ii) Niobium alloys (such as NbZr, NbTi and NbCu)	98 730
HSLA grade FeNb	5 657 420
Total	6 301 296

Note :
19 companies were asked to report, 19 replied. Reports by the following companies are essential before the data may be released : Cabot Performance Materials, W.C. Heraeus, Kennametal, Metallurg group, Mitsui Mining and Smelting, Niobium Products Co. (CBMM), H.C. Starck Inc. (NRC), H.C. Starck, Teledyne Wah Chang Albany, Thai Tantalum, Treibacher Chemische Werke, Vacuum Metallurgical Company

CAPACITOR STATISTICS

CONSUMPTION BY AREA

(figures in millions of units)

	Average per quarter			
	1989	*1990*	*1991*	*1992*
North America	302	337	356	425
Europe	206	232	230	228
Japan	681	808	965	773
Rest of world	287	411	494	571
World	**1476**	**1788**	**2045**	**1997**

	1993			
Quarter :	*1st*	*2nd*	*3rd*	*4th*
North America	510			
Europe	266			
Japan	759			
Rest of World	626			
World	**2161**			

Source : Members' estimates

Note : Minor revisions have been made to the previously published figures for 1989-1992.

remove the solvent and to start hydrolysis of the alkoxide. It is then baked at 500- 650°C to form a high dielectric oxide film having excellent withstand voltage characteristics.

Toyo Aluminium K.K.
Japanese Patent 04-42519 (13 February 92)

2. A semiconductor can be given a high acid resistance by sputtering tantalum film on the device using a krypton/nitrogen carrier gas. The ratio of the flow rate of the reactive gas to that of the sputtering gas should be in the range 2-15 %. The tantalum film has the advantage of having low specific resistance.

Sharp Corporation
Japanese Patent 04-13861 (17 January 92)

3. A lithium tantalate wafer can be used to make a sensitive calorimeter (with chromium and gold films on its two faces to form electrodes). By adding an amine layer on one face, the device can be used to determine very small concentrations (down to 1 ppm) of hydrochloric acid (which generates heat as it reacts with the amine).

M. Foccio et al.
Sensors and Activators B7 (1992) 677-681

4. A chip-type solid electrolytic tantalum capacitor can be made in a parallel connection structure by having sintered tantalum powder contained in two or more tantalum foil boxes. The surfaces of the foil are anode-oxidised before final welding, and manganese dioxide, graphite and silver paste layers are formed on the foil to make the complete elements. Finally, an insulating resin is applied as an external cover.

NEC Corporation
Japanese patent 04-164308 (10 June 92)

NIOBIUM

1. A palladium-based alloy, containing 5-10 atomic percent niobium is particularly suited for electrical application such as coatings for electrical contacts or connectors. It has good oxidation resistance.

Cowie et al. (Olin Corporation)
U.S.P. 5139891 (18 August 92)

2. Niobium has the lowest density of the refractory metals so its alloys with aluminium are of great potential interest to makers of high-temperature aircraft engines. The aluminide Nb_2Al has a high melting point (1940°C) and high hardness, but it suffers, as do most intermetallics, from poor room-temperature fracture toughness. It is now known that brittle materials can be toughened by using ductile reinforcements, and in this case this has been attained by adding 3% boron to the original powder mixture. After this has been ignited (under argon "combustion synthesis"), the product is much tougher than straight Nb_2Al.

A.K. Bhattacharya
J. Amer. Ceram. Soc 75(6) 1678-81 (1992)

3. Niobium is most commonly used in the form of ferroniobium, and this is produced in large quantities by aluminothermic smelting of pyrochlore. The consumption of niobium either pure or alloyed with metals other than iron is increasing so much research has been devoted to developing its extraction from the ferroalloy. This paper describes a process in which the alloy is nitrided with ammonia at 950-1000°C, and then treated with a 9:1 mixture of nitric and hydrochloric acids to leach out the iron nitride. When the residue is heated under vacuum at 1825°C, a niobium metal results containing 0.2 % iron, which can be further refined by electron beam melting.

Suri et al.
Met. Trans. B 23B, 437-442 (August 92)

4. Niobium-titanium alloy scrap from the manufacture of super conducting wire may be recycled by heating it in a nonoxidising atmosphere at a temperature between the melting point of titanium and that of the alloy for more than five hours. This will bring the oxygen content of the material down to less then 500 ppm, and it can then be compacted and formed into a consumable electrode for arc melting.

Furukawa Electric Co. Ltd
Japanese Patent 04-276045 (1 October 92)

5. China has become the fourth largest steel producer in the world and the country has extensive resources of microalloying elements. Anshan Iron and Steel Complex (AISC), the largest and the first integrated steel company in China, has made an important contribution to the development of high strength low alloy steels (HSLA). The paper describes the development of HSLA steels at AISC, and gives reasoning for preference for niobium either alone or in combination with other microalloying elements in the design of new steels.

Long, Fu and Cao
Proceedings of the Conference of The Minerals, Metals & Materials Society on HSLA Steels, Beijing, Oct-Nov. 1990, pages 115-117.

6. Copper-niobium microcomposites are a new class of high-strength high-conductivity materials that have attractive properties for room- and elevated-temperature applications. Since niobium has little solid solubility in copper, addition of niobium to copper does not affect its conductivity. Cast Cu-Nb ingots consists of small dendrites of niobium uniformly distributed within the copper matrix. When such metal is drawn the niobium dendrites become fine filaments which impart a significant increase in strength. (In heavily drawn wires the tensile strength is distinctly greater than would be predicted by the rule of mixtures.) Simple cold rolling for the preparation of Cu-Nb sheet does not produce the same desirable structure but the authors report that the technique of multiple roll bonding enables the necessary high processing strains to be applied in order to refine the niobium particle size.

Jha, Delagi and Forster (Texas Instruments)
and Krotz (Rockwell International)
Metallurgical Transactions A, 24A, (1), 15-20. (January 1993)

7. Iron-based alloys with 25% chromium or 25% chromium + 20% nickel are used in many pieces of plant where high temperatures and stresses are met, but their resistance to attack is very much reduced in high-sulphur environments. Niobium (with or without the addition of zirconium), gives the necessary protection, and it is most economically added by ion implantation. The niobium ions are energised and accelerated, and made to strike the alloy surfaces used as a target in a vacuum chamber. The depth of niobium may extend to 800-1000 Ångstroms.

Krishnamurti/U.S. Dept. of Energy
USP 516470 (17 November 1992)

DLA PURCHASES AND DISPOSALS

At the beginning of June the DLA submitted to the U.S. Congress their Fiscal Year 1994 Annual Materials Plan. They estimate that $20.7 million will be required for acquisition, and that $508.2 million is the amount attainable from disposals. The largest value items include an acquisition of natural rubber (19 000 tons for material rotation - $19m) and in disposals, cobalt (4.6 million pounds contained), copper (200 000 short tons - $30m), silver (9 million ounces), metallurgical grade manganese (250 000 SDT) and tin (12 000 metric tons $60m). Tantalum and niobium products are not mentioned : purchases and upgrading were already provided for under the FY 1993 AMP for periods ranging over the next two-and-a-half years.

BELGIAN FEDERATION OF NON-FERROUS METALS

The Federation is celebrating the 75th anniversary of its foundation with an international symposium on the future of the non-ferrous metals industry, on November 22nd 1993 at the SAS Royal Hotel in Brussels.

Speakers will include Jean-Pierre Rodier, Administrateur délégué of Union Minière, Jean Gandois, Président Directeur Général of Pechiney, André Leysen, Président of Agfa-Gevaert and Rosolino Orlando, Président of Eurométaux. The proceedings will close with a panel discussion chaired by Luc Rivet, General Manager of Ogilvy Adams and Rinehart.

Further information, and invitations to attend, may be obtained from the Belgian Federation of Non-ferrous metals, 47 rue Montoyer, B-1040 Brussels, Belgium; telephone 32 2 506 41 11, fax 32 2 511 75 53.

STARCK : ELECTROCERAMICS

H.C. Starck GmbH & Co. KG, Goslar, a long-standing supplier of niobium oxides and tantalum oxides to the electroceramic sector (and member of the T.I.C.), has developed a new generation of precursors for the production of high-quality niobate and tantalate powders.

These complex perovskite oxides, including a variety of lead niobates and barium tantalates, are characterised by their homogeneity at a molecular level, high phase stability and narrow grain size distribution. The extremely fine powders are highly reactive and have a very good sintering behaviour, and dielectric and electrostrictive properties have been improved. For example, the lead magnesium niobate (PMN) produced shows a dielectric constant of more than 11 000 at room temperature when it has been sintered at 1000-1100°C.

The improved properties of these lead perovskites make it possible to produce even smaller capacitors with still better dielectric qualities and actuators with extraordinarily good electrostrictive properties. They also permit the use of silver electrodes in multilayer capacitors.

CABOT'S TANCO MINE

In February 1993, Cabot Corporation announced that it had acquired 100% ownership of the Tantalum Mining Corporation of Canada, Ltd. (Tanco) mine from its partners, Hudson Bay Mining and Smelting Co., Ltd. and Manitoba Minerals Resources, Ltd.

The Tanco mine, located under Bernic Lake in Manitoba, Canada, has the largest tantalum reserve in North America and is capable of supplying 25% of Cabot's requirements. Tanco also contains the world's greatest reserves of high-grade pollucite (a cesium ore), and is a major producer of spodumene (a lithium ore) and lepidolite (a rubidium ore).

In 1929, the main tin orebody was accidentally discovered by gold prospectors. Unfortunately, the mine did not contain economic grades of tin, but its lithium content was noted. The minesite was abandoned until the late 1950's when commercial markets for lithium developed. However, operations were short lived and by 1960, the site was again shut down. It was not until the late 1960's when the tantalum capacitor market was developed that the pegmatite was once again mined, this time for its tantalum.

Currently, Tanco is the only mine in the world which produces tantalum, lithium, quartz and high potassium feldspar. To date, some 90 different minerals have been identified in the orebody, including 15 tantalum bearing minerals, two which were first identified at Tanco – Tancoite and Cernyite.

The different ores are mined from separate areas of the orebody, which is situated some 60 meters below Bernic Lake. The mine is accessed by both a shaft and a 20 degree decline from the surface. Because Tanco is a flat lying orebody, mining is carried out using a "room and pillar" method. The large "rooms" permit the use of high capacity mining equipment such as two-boom "Jumbo" drilling machines, 7 yard scooptrams, and a 20 ton truck. The back (or roof) can extend up to 50 meters above working levels. To insure safety, the back is carefully monitored and regularly inspected from custom designed aerial lifting devices called "giraffes".

TANTALUM

In 1969, tantalum operations commenced at the rate of 500 tons per day, increasing over the years to 800 tpd. In 1982, poor markets forced a closure. During the late 1980's, market conditions improved and tantalum operations were restarted in 1988, with an annual capacity of 250 000 lbs of tantalum oxide containing concentrates.

Tantalum is recovered by gravity concentration, a process which makes use of the fact that tantalum minerals are much heavier than associated minerals.

As with other gravity separation mills, the process involves three main elements – liberation of the valuable material from the gangue; separation into different size fractions; and selective concentration of the products from the different fractions. At Tanco, the tantalum plant consists of three areas (Figure 1) – grinding/spiral circuit, sand circuit, and slime circuit.

The ore is first ground to minus 2mm. The minus 2mm ore is then processed with spirals to recover the coarse, free tantalum minerals. The amount of the tantalum recovered in this step is variable, depending on the mineralogy, but is typically about 40% of that in the feed to the mill.

Preparation of the feed prior to the shaking tables is critical for efficient operation. At Tanco, the tailings from the spirals are sized at 0.25 mm, deslimed with cyclones, followed by classification in Bartles-Stokes hydrosizers. The sand product from the hydrosizers is distributed to nine, triple-deck Concenco tables. Approximately 20% of the tantalum in the ore charged to the mill is recovered as a 40% Ta_2O_5 concentrate from tabling operations.

Overflows from the cyclones and hydrosizers constitute the feed to the slime circuit. The first stage consists of six Bartles-Mozley separators. The low grade rougher concentrate from the BM separators is further upgraded using two Bartles-Crossbelt concentrators.

The final concentrates produced at Tanco are a mixture of heavy minerals which, apart from the tantaliferous minerals, include small amounts of cassiterite and ilmenite. Overall recovery of tantalum ranges from about 70 to 72%, upgrading the ore from about 0.1% Ta_2O_5 in the feed to the mill to 38% Ta_2O_5 in the concentrate.

The plant has continuously improved process control and aggressively evaluates new equipment and processes, especially for the recovery of ultrafine particles. In fact, part of the development trials of the Crossbelt were carried out at Tanco. Tanco is also actively working with universities and industry, conducting studies on the relative merits of the new generation of centrifugal separators. This development will hopefully enable recovery of particles as fine as 2 μm.

Pilot studies have also confirmed the benefits of using statistical process control. This technique was first introduced into the lithium section in 1991, and is being incorporated into the tantalum mill in 1993.

LITHIUM

In the early 1980's, Tanco developed its spodumene (a lithium aluminium silicate) reserves, and started operation in 1984. Tanco rapidly became a major supplier of high quality spodumene concentrates.

Today, Tanco supplies high quality spodumene primarily to the pyroceramic industry. Spodumene is also used in other applications including frits and glazes, sanitaryware, black and white TV panels, pottery, and continuous steel casting. Currently, Tanco is carrying out market trials on a unique product, montebrasite, a lithium phosphate.

Spodumene processing incorporates heavy medium separation, flotation and magnetic separation. SPC is actively used for quality control. Tanco was the first, and is currently the only mining company to be awarded "Qualified" status by Corning Inc.

CESIUM

The Tanco mine contains the world's major economic source of pollucite, a principal cesium containing ore. Tanco's pollucite typically contains 24% Cs_2O.

Presently, Tanco supplies of 80% of the world's requirements. At current rates of usage, Tanco's pollucite reserves are sufficient for over 300 years.

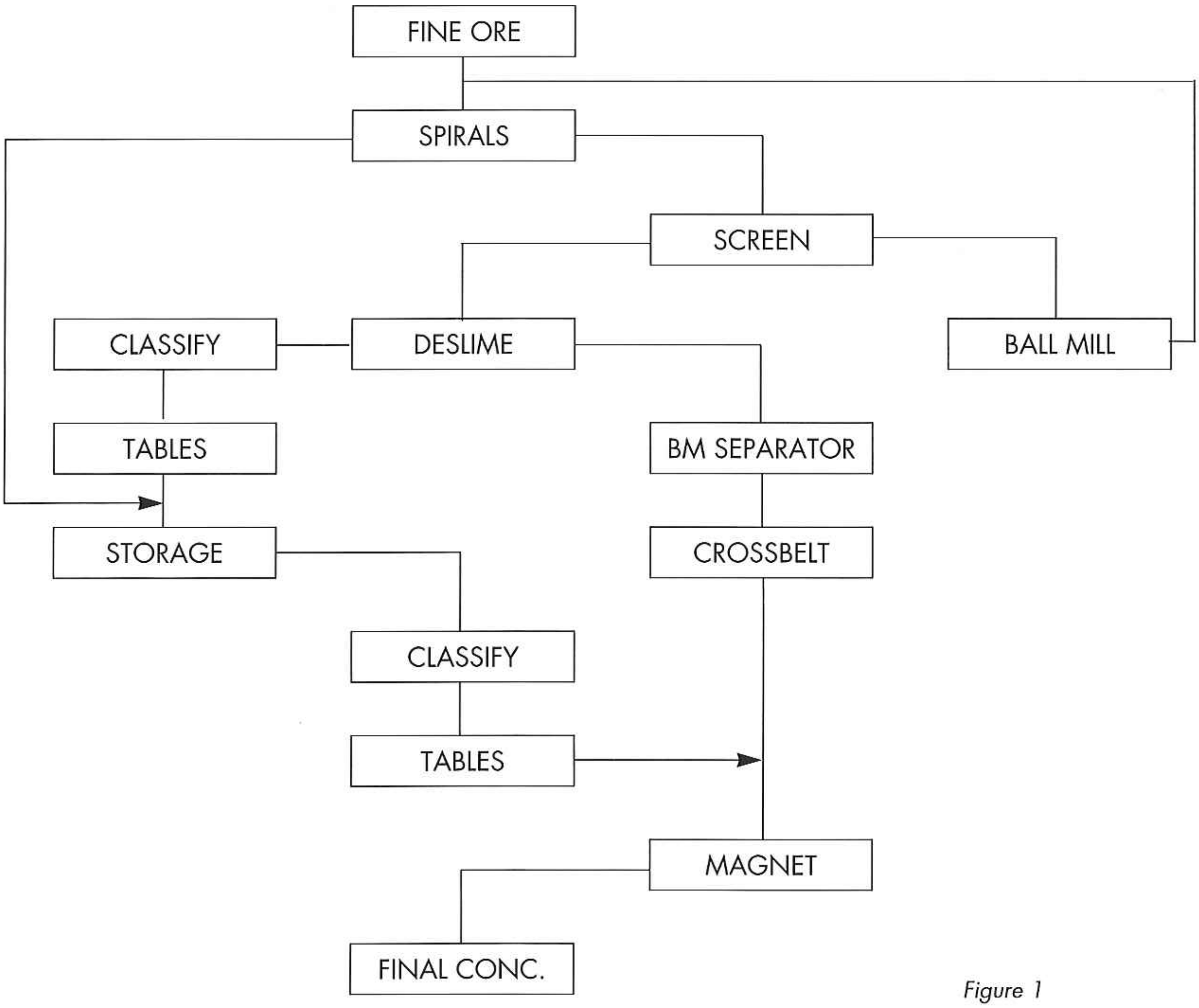

Figure 1

DATA SHEET

	TANTALUM	NIOBIUM
Physical Properties		
Atomic number	73	41
Atomic weight	180.95	92.91
Density @ 20°C	16.6 g/cm^3	8.57 g/cm^3
Melting point	2996°C	2467°C
Boiling point	5300°C	4734°C
Heat of fusion	28.5 kJ/g.atom	26.4 kJ/g.atom
Heat of vaporisation	781.0 kJ/g.atom	683.2 kJ/g.atom
Heat capacity @ 20°C	25.41 J/g.atomK	24.90 J/g.atomK
Coefficient of linear expansion @ 20°C	$6.5 \times 10^{-6} K^{-1}$	$7 \times 10^{-6} K^{-1}$
Electrical resistivity @ 20°C	12.5 $\mu\Omega cm$	16.0 $\mu\Omega cm$
Transition temperature	4.3°K	9.13°K
Mechanical Properties (Commercial metal)		
Tensile strength	390 N/mm^2	365 N/mm^2
Elongation	20 %	25 %
Modulus of elasticity	182 kN/mm^2	110 kN/mm^2
Vickers hardness	115	130
Chemical resistance	(I) High up to 100°C to all mineral acids except HF.	(I) High to all mineral acids except HF.
	(II) High to most organic compounds.	(II) Very high to oxidising agents (including HNO_3, aqua regia).
	(III) Very high to oxidising agents (including chlorine and bromine up to 150°C).	(III) Good to cold alkalies, but subject to hydrogen embrittlement if hot.
	(IV) High to many liquid metals (e.g. lead to 1000°C).	(IV)High to many liquid metals (e.g. Na to 1000°C).
Some current applications	(I) As the metal powder for the preparation of tantalum capacitors (dependent on the semiconducting property of the tantalum oxide film) and as metal wire for their connection to circuits.	(I) In structural steels (especially high strength low alloy - HSLA - steels with up to 1% Nb). In heat resisting steels and superalloys (iron, nickel or cobalt based).
	(II) As fabricated metal for the construction of chemical process plant, and heat exchangers.	II) As an alloy with titanium or tin for superconductive magnets.
	(III) As an ingredient of superalloys, principally for use in aircraft and spacecraft engines.	(III) As the oxide (Nb_2O_5) in high refractive index glass, as lead niobate in piezoelectric devices, and as single crystal lithium niobate in surface acoustic wave filters for e.g. television sets.
	(IV) As the carbide, in cutting tools, with tungsten and titanium carbides	(IV) With copper in powder metallurgy composites for components requiring high strength with conductivity.
		(V) As an alloying addition to zirconium for nuclear reactor fuel tubes.
		(VI) As the carbide, with tungsten and tantalum carbides, in cutting tools.
	The first item accounts for about 50% of current tantalum usage.	The first item accounts for about 90% of current niobium usage.

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