High Temperature Materials and Processes, Vol. 9, Nos. 2-4, 1990

Purification of Refractory Metals by Solid-State Refining

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CONTENTS

ABSTRACT

Different solid-state refining techniques can be used to decrease the interstitial impurity level of refractory and other high melting metals. Purification by external gettering is particularly effective for carbon, oxygen and nitrogen in vanadium and niobium. Oxygen and nitrogen can also be readily removed from niobium and tantalum by degassing in ultra-high vacuum. The advantages and limitations of electrotransport purification are discussed, and the degree of purity attainable by this technique is summarized for various metals. The potential of thermotransport purification is also evaluated.

1. INTRODUCTION

Some of the purest metals in the world have been prepared by solid-state refining techniques. Since these techniques involve diffusion in the solid, long times at high temperatures are required. This limits the size of the specimens (at least in one dimension) to small rods, wires, thin plates or sheets.

The most widely used solid-state refining processes are: external gettering, vacuum degassing and electrotransport. Purification by one or more of these techniques has found increasing usage in the preparation of high purity refractory and reactive metals in recent years. It is the purpose of this paper to evaluate the efficacy of these processes and to review the underlying principles of each.

2. EXTERNAL GETTERING

Interstitial impurities can often be removed rather completely by reaction with a chemically active solid, liquid or gaseous element in contact with the surfaces of the solid. This is referred to as external gettering.

2.1. By Gases

A familiar example of external gettering of a metal by a gas is the decarburization of steel during heating in an oxygen-containing atmosphere. A similar technique has been used to decarburize niobium and tantalum. According to Schulze /1/, carbon can be reduced to extremely low levels (<1 atm ppm) in niobium by heating at 2000°C in an oxygen partial pressure of 10^{-3} Pa. The residual oxygen is then removed by annealing in an ultra-high vacuum, details of which are given in a later section.

Stein *et al.* /2/ used a somewhat similar technique to decarburize iron in a continuously recycled hydrogen atmosphere by the reaction:

$$Fe[C](s) + 2H_2(g) \xrightarrow{850°C} Fe(s) + CH_4$$

The methane was removed from the flowing gas by recirculating it over zirconium turnings. The free energy change for the reaction

$$Zr + CH_4 \xrightarrow{850°C} + 2H_2$$

is -173.4 kJ, and the calculated equilibrium concentration of carbon is extremely low (10^{-6} atm ppm). Carbon concentrations reportedly as low as 0.02 atm ppm in iron were obtained experimentally by this method.

The deoxygenation of molybdenum or tungsten by hydrogen has not actually been reported, but it is certainly thermodynamically feasible for these metals. They are both prepared commercially in powder form by the reduction of their respective oxides with oxygen. Thus under conditions at which oxygen can diffuse readily, it should react with hydrogen at the surface to form H_2O gas.

2.2. By Alkaline Earth Metals

A method that has found increasing application as a deoxygenation technique during the past decade is external gettering by one of the alkaline earth metals.

The base metal is heated in direct contact with the more active metal in liquid or vapor form. The oxygen atoms diffuse to the surface and react with the getter to form a stable oxide that can be removed either chemically or mechanically. The deoxygenation of a metal by one of the alkaline earth metals was first demonstrated by Allen *et al.* /3/, who showed that it is possible to predict the degree of purification from thermodynamic data. Peterson and coworkers /4/ calculated the equilibrium oxygen concentration in vanadium after equilibration with calcium, barium and magnesium, assuming Henry's law of behavior in the low oxygen range (see Table 1). Deoxygenation occurs by the reaction

$$V[O](s) + Ca(\ell) \xrightarrow{1200°C} CaO(s) + V(s)$$

and the oxygen content of the base metal is decreased until its partial pressure equals the dissociation pressure of CaO. From the standard free energy data the equilibrium O_2 pressure of CaO at 1200°C can be shown to be 7.4 x 10^{-33} Pa. The solubility of oxygen in vanadium obeys Henry's law /5/ and is described by the equation

$$\log c_o(\text{atm\% O}) = \tfrac{1}{2}\log PO_2(\text{MPa}) - 2.75 + 22{,}050/T$$

Hence at 1200°C, c_o = 4.7 x 20^{-6} atm% O = ~0.05 atm ppm. Note that this calculated value is more than 2 orders of magnitude lower than the experimentally observed value of 8 atm ppm. Peterson *et al.* /4/ attributed this failure to reach the calculated oxygen level to a slow approach to equilibrium. Yoshinari *et al.* /6/, on the other hand, ascribed it to trapping of oxygen by calcium that had diffused into the vanadium.

2.3. By Reactive Metals

A major drawback to gettering with calcium or magnesium is the lack of any significant change in the carbon or nitrogen contents of the base metal, as is seen from the data in Table 1. For this reason metals with a greater affinity for these interstitial impurities (e.g., titanium, zirconium or yttrium) are used as getters. Table 1 shows that vanadium coated with a thin layer of titanium and heated to 1000°C exhibits a dramatic decrease in the carbon and nitrogen contents to below analyzable limits, i.e., <9 and <4 atm ppm, respectively. The experimentally

TABLE 1
Purification of Vanadium by External Gettering with Different Metals

Getter	Temp. °C	Atm. ppm O			Atm. ppm C		Atm. ppm N		Ref.
		Init.	Calc.	Expt.	Init.	Expt.	Init.	Expt.	
Ca	1200	225	0.05	8	-	-	-	-	4
Ca	900	5000		45	-	-	-	-	6
Ca	1000	1.6%		110	85	65	235	125	7
Mg	1200	225	0.7	6	-	-	-	-	4
Ba	1200	225	0.5	14	-	-	-	-	4
Ti[a]	1000	925	20.0	65	210	10	7	4	8
Ti[b]	1170	5000		25	-	-	-	10	6
Zr[b]	1070	735		6	-	-	-	-	9

[a]Vapor deposited layer

[b]Foil wrapper

determined oxygen content is only slightly higher than the calculated equilibrium value (60 vs 20 atm ppm). Yoshinari and coworkers /6/ demonstrated that titanium foil wrapped around a vanadium rod and sealed in a quartz capsule is equally effective in reducing the oxygen level (from 5000 to 25 atm ppm), but no results were reported for carbon or nitrogen.

Zirconium foil is also effective as an oxygen getter, as is shown in Table 1. Vanadium containing 735 atm ppm oxygen is deoxidized to a level of 6 atm ppm by zirconium at 1070°C /8/. Uz and Carlson /10/ decreased the carbon content of a V-20% Ti alloy from 1340 to 250 atm ppm by the zirconium foil technique.

External gettering with a reactive metal has also been applied extensively to niobium. The use of niobium for superconducting accelerator microwave cavities has resulted in a major emphasis on obtaining large quantities of the metal in high purity. Interstitially dissolved impurities, particularly oxygen, adversely affect the thermal conductivity of niobium in the superconducting temperature range /11,12/. It is, therefore, extremely critical that these impurities be held to the low ppm range for this application. A residual resisitivity ratio (RRR) of 200, corresponding to a total O+C+N content of ~185 atm ppm /1/, is the minimum specification for use as a cavity material.

Shibiata and Koiwa /13/ report that both oxygen and hydrogen can be reduced to very low levels by annealing niobium wires wrapped with zirconium foils at 1070°C. By this treatment the RRR was increased from 166 to 630 (see Table 2), which corresponds to a decrease in oxygen content from 600 to 20 atm ppm.

Padamsee /14/ has developed a solid-state gettering technique that is applicable to niobium microwave cavity production using yttrium foils as the getter. During heating, yttrium vapor is deposited on the niobium surface, forming a layer of several micrometers thick. The data in Table 2 show an increase in the RRR from 68 to 175. This corresponds to a decrease in oxygen from 255 to 100 atm ppm and in nitrogen from 115 to 80 atm ppm. Padamsee obtained niobium with an RRR as high as 540 starting with metal with an RRR of 165. This corresponds to a total interstitial content of ~60 atm ppm.

Kneisel /15/ purified niobium by heating it for 10 hr at 1300°C in titanium foil. Following this treatment the TiO_2/TiN and Ti-rich diffusion layers were removed by chemical etching. Studies were conducted on niobium from different commercial sources, the results of which are given in Table 2. RRR values consistently greater than 300 were obtained for the different materials with the exception of the metal obtained from Kawecki. A com-

TABLE 2
Effects of Gettering with Zr or Y on Resistivity Ratio and Thermal Conductivity of Nb

Getter	Nb Source	Temp °C	RRR[c] Before	RRR[c] After	k, $W \cdot m^{-1}K^{-1}$ Before	k, $W \cdot m^{-1}K^{-1}$ After	Ref.
Ti	Herreaus	1300	160	300	40	140	14
Ti	Fansteel	1300	45	350	19	160	14
Ti	Wah Chang	1300	200	-	51	150	14
Ti	Kawecki	1300	30	75	-	-	14
Zr	S-K[a]	1070	166	630	-	-	11
Y	Fansteel	1300	68	175	-	-	13
Y	Fansteel[b]	1300	70	335	-	-	13
Y	Ames	1300	165	540	-	-	13

[a]Shin-etsus Kaga Co. Ltd., EB-melted and EBFZR

[b]EB-melted

[c] $\rho_{300}/\rho_{4.2K}$

parison of the crucial thermal conductivity, k, before and after treatment, can also be made from the data in Table 2. It will be noted that k is increased by a factor of anywhere from 3 to 8 by this gettering treatment, depending on the original material.

3. VACUUM DEGASSING

Another commonly used technique for removing impurities from refractory metals is vacuum degassing (or outgassing) at high temperatures. Deoxygenation by this method depends on the formation of a volatile oxide or suboxide. The impurities diffuse to the surface of the solid where they congregate at active sites. Here they combine with other atoms to form a volatile species such as H_2, N_2 or CO and are desorbed. The impurity atoms may also react with the matrix metal at the surface to form a volatile oxide such as NbO, TaO or VO.

3.1. Deoxygenation

Deoxygenation of a solid metal occurs primarily by the formation of a volatile oxide or suboxide. The commercial processes for producing niobium and vanadium depend on the tendency for oxygen and aluminum to form the volatile suboxide Al_2O /16, 17/. During the reduction of their oxides by aluminum, a V-Al alloy containing ~1 atm% oxygen is obtained. Most of the oxygen and some of the aluminum are subsequently removed as Al_2O by heating in vacuum at high temperatures. This yields a metal sponge containing about 0.03 atm% oxygen. The residual aluminum and most of the oxygen are then removed by electron beam melting.

Horz /18/ has shown that oxygen can be desorbed from the group VA metals by the diffusion of oxygen atoms to active sites on the surfaces during heating in high vacuum. Here the oxygen reacts with the matrix atoms to form the monoxides VO, NbO or TaO that evaporate and condense on the walls of the vacuum system. As in seen from Table 3, the desorption rate for oxygen in niobium, tantalum and vanadium is primarily first order, and the formation and evaporation of the monoxide are rate determining. The method is more successful for niobium and tantalum than for vanadium. At the deoxygenation temperature of vanadium (i.e., 1450-1600°C under a pressure of 9×10^{-8} Pa), the vapor pressure of vanadium is so high that large metal losses are encountered. Because of the higher melting points of niobium and tantalum and their relatively low vapor pressures at the deoxygenation temperature (1700 to 2100°C), the metal losses are quite low.

3.2. Denitrification

In a classic paper, Horz /18/ has shown that denitrification of group VA metals occurs by diffusion of nitrogen atoms to active sites on the surface, where they form a chemisorbed layer and are then desorbed as N_2 molecules. The desorption energy Q_{des} is the negative sum of the heat of solution ΔH_s and the heat of absorption Q_{ab}, i.e., $Q_{des} = -(\Delta H_s - Q_{ab})$. From Table 3 it will be noted that the activation energies for desorption of N_2 from Ta and Nb are large positive values inasmuch as ΔH_s and Q_{ab} are large negative quantities for these metals. For example, for Ta-N ΔH_s = -364 kJ/mol, Q_{ab} = -197 kJ/mol and Q_{des} = -(-364-197) = 561 kJ/mol, and the recombination step is rate determining—hence, second order. On the other hand, for the VIA metals Mo and W, the ΔH_s values for N_2 are large positive quantities, e.g., ΔH_s = 389 kJ/mol for W-N. Thus, Q_{des} is a small value equal to the activation energy for diffusion, and the diffusion of nitrogen through the bulk is the rate-determining process.

3.3. Dehydrogenation

Hydrogen is readily removed from most refractory or reactive metals by vacuum degassing. Metal groups IVA, VA and VIA, for example, are readily dehydrogenated by heating in vacuum at 800-900°C.

3.4. Decarburization

Carbon can be removed by vacuum degassing of solids only if adsorbed oxygen or oxides are present at the surface. Horz /18/ describes the decarburization of niobium that takes place between 1600 and 2120°C at oxygen pressures on the order of 10^{-4} Pa as occurring in several steps. Oxygen molecules adsorbed at the metal surface undergo dissociation, chemisorption and finally dissolution. Meanwhile carbon atoms in the matrix diffuse to the surface where they combine with oxygen atoms and evaporate as CO molecules. In Table 3 it will be noted that Q_{des} for Nb is 159 kJ/mol, which is the same as Q_{diff} for carbon in niobium, indicating that the kinetics for decarburization are controlled by diffusion. The decarburization of tantalum and vanadium occurs by a very similar process.

As was noted above, the residual oxygen must be removed by one of the deoxygenation processes herein described.

4. ELECTROTRANSPORT PURIFICATION

Electrotransport, also referred to as electromigration or electric field transport, was first used to

TABLE 3
Kinetics of Degassing of Group VA and VIA Metals /18/

System	Lowest Desorption Temp., °C	Desorbed Product	Rate Law	Q_{des} kJ/mol	Rate Determing Process
V-O	1400	VO	kc	569	Oxide formation and evaporation
Nb-O	1600	NbO	kc	544	Oxide formation and evaporation
Nb-O	1600	NbO_2	kc^2	464	Evaporation
Ta-O	1600	TaO	kc	552	Evaporation
	1600	TaO_2	kc^2	460	Evaporation
V-N	> 1600	H_2	kc^2	-	No degassing
Nb-N	1600	N_2	kc^2	519	Recombination and desorption
Ta-N	1600	N_2	kc^2	562	Recombination and desorption
Mo-N	1200	N_2	kc	109	Diffusion
W-N	1300	N_2	kc	117	Diffusion
Nb-C	1600	CO	kc	159	Diffusion

deoxygenate zirconium metal by DeBoer and Fast /16/ in 1940. Since then the technique has been successfully applied to a number of metals, particularly the refractory and reactive metals and some of the rare earth and actinide metals. All of these show a high affinity for oxygen, nitrogen and carbon; and the hardness and mechanical and physical properties are quite sensitive to small amounts of these impurities.

The principles of electrotransport purification are described in papers by Peterson /19,20/, Verhoeven /21/ and Carlson *et al.* /22/, and therefore are not presented in detail here. Briefly, solute atoms migrate toward either the positive or negative electrode in the presence of an electric field at elevated temperatures. It is generally observed /23/ that interstitial solutes, notably carbon, oxygen and nitrogen, migrate toward the anode in refractory Group VA and VIA metals, whereas they migrate toward the cathode in the rare earth, actinide and Group IVA reactive metals. The technique is limited to relatively small specimens in rod or strip form and is useful for preparing small quantities of ultra-pure metals for use in research or similar applications. As the length of the specimen increases, the time required to achieve steady state increases proportionately. Likewise, the sample diameter is limited by its ability to radiate the Joule heat as the radiating surface of a rod relative to its volume decreases as $2\pi r \ell / \pi r^2 \ell = 2/r$. Another limitation is the long turn-around time associated with the prolonged bakeout and pump-down periods required for an ultra-purification run. Schmidt /24/ has overcome some of this difficulty by using a large vacuum chamber equipped with multiple electrodes. Up to three samples 30 x 1.25 x 0.3 cm in dimension can be run consecutively in this system without intervening bakeout steps. Triplicate specimens of the same or different metals (e.g., zirconium, niobium and yttrium) have been purified in this apparatus.

4.1. Environmental Contamination

Since electrotransport purification involves long times at high temperatures, the more reactive metals tend to pick up gaseous impurities from the surroundings. The chief sources are the chamber atmosphere and the electrodes. Experience has shown that pressures as low at 10^{-8} Pa are desirable for reducing the level of interstitial impurities to the low ppm range. Schmidt *et al.* /25/ have shown that the RRR, $\rho_{300}/\rho_{4.2K}$ of thorium is dependent on the pressure in the vacuum chamber during purification. As is seen from Fig. 1, the ratio increases monotonically from 100 for thorium purified at 3 x 10^{-3} Pa to 2200 purified at 3 x 10^{-9} Pa.

The other major source of contamination is the electrodes that support the specimen during the transport process. Interstitial impurities either diffuse or are electrotransported from the electrodes into the sample. This problem can be minimized by use of high-purity electrodes or by a judicious choice of the electrode material. For example, C, N and O migrate in the direction of the cathode in tantalum, whereas they migrate in the opposite direction in thorium. Hence the use of high-purity tantalum as the cathode in such a case can alleviate most of this problem.

4.2. Application of Electrotransport Purification

The most suitable metals for electrotransport purification are those with high melting points and low vapor pressures and in which the impurities have high mobilities. Some metals that fall into this category and to which the technique has been most successfully applied are: Th, U, Zr, V, Nb, Ta, Mo, Y, Sc, Gd and Lu. The highest purities and also the highest RRRs attained for these metals are listed in Table 4. Thorium metal, which has been prepared with a purity of 99.9999%, is nearly an ideal metal for electrotransport purification. It has a very low vapor pressure at its melting point, and most of the impurities commonly associated with it,

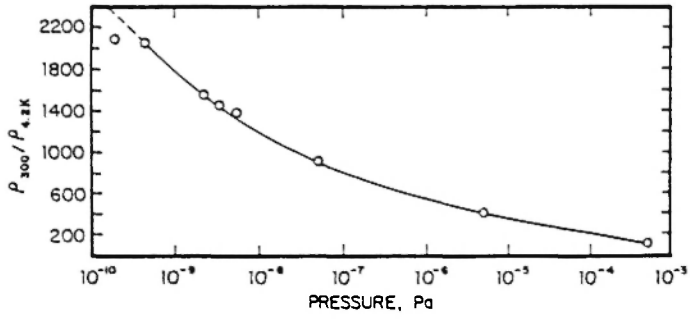

Fig. 1: Residual resistivity ratio vs pressure inside the vacuum chamber during electrotransport processing of thorium at 1600°C for 144 hr. Original RRR=35.

TABLE 4
Residual Resistivity Ratios and Purities of Metals Purified by Electrotransport

Metal	Temp. °C	Pressure Pa	RRR		Analyzed Purity wt%	Ref.
			Original	As-purified		
Thorium	1575	6.7×10^{-8}	33	1300	99.995	26
Thorium	1500	2.7×10^{-9}	35	4200	99.9999	25
Vanadium	1400	1.7×10^{4} He	130	1800	99.999	27
Yttrium	1175	2.7×10^{-5}	30	127	99.97	28
Scandium	1360	1.7×10^{4} He	32	520	-	29
Lutetium	1150	2.7×10^{-8}	21	150	99.98	30
Gadolinium	1190	1.7×10^{4} He	40	370	99.99	31
Zirconium	1600	1.3×10^{-7}	100	650	-	32
Hafnium	2000	1.3×10^{-5}	6	15	99.98	33
Uranium	960	1.3×10^{-4}	-	-	99.99	24
Niobium[a]	1900	1.3×10^{-8}	35	7200	-	24
Tantalum	2200	1.3×10^{-8}	30-40	<1200	-	24
Molybdenum	2200	1.7×10^{4} He	-	3830	-	24

[a]Single crystal

including both interstitial and metallic, have high mobilities and therefore readily migrate in the material. Uranium also appears to fall in this category, although much less work of this type has been done with this metal.

Vanadium is another metal to which electrotransport purification has been applied extensively. Because of its comparatively high vapor pressure, the runs were performed under a partial pressure of purified helium. Inasmuch as the common metallic impurities, notably iron, aluminum and silicon, are relatively immobile, electrorefined vanadium that is very low in these impurities is used as the starting material. Carbon, nitrogen and oxygen are readily transported toward the anode in vanadium, and thus are decreased to less than 5 wt ppm (15 atm ppm) total /27/.

Schmidt /24/ has successfully purified niobium, tantalum and molybdenum by electrotransport. The RRR of a niobium single crystal was increased from 35 to 7200 by passage of a high-density direct current through a rod-like specimen at 1900°C under a pressure of 10^{-8} Pa. In the case of niobium and tantalum, purification is obviously the combined result of vacuum degassing and electrotransport. Because of its high vapor pressure at temperatures near its melting point, molybdenum was electrotransport purified under a partial pressure of helium to yield metal with an RRR of 3830.

5. PURIFICATION BY THERMOTRANSPORT

Solute atoms migrate in materials under the influence of a temperature gradient, a phenomenon referred to as thermotransport. Although it is a potential method for purifying materials, no such application has been reported to date. As a general rule the redistribution of solutes by thermotransport in a homogeneous solid is not great enough to affect a high degree of purification. For example, vanadium containing 0.5 atm% oxygen held in a temperature gradient between 1650 and 1850°C for 6.5 hr undergoes a decrease in the oxygen content in the higher temperature portion to only 0.35

atm% hardly a significant degree of purification /34/. Uz *et al.* /35/ obtained similar results for carbon in vanadium and niobium, although carbon migrates toward the higher temperature in these metals.

A somewhat greater redistribution occurs in two-phase alloys, however, as has been found for the V-C and Nb-C systems. This is illustrated in Fig. 2 for a V-2.39 atm% C alloy held between 1285 and 1630°C for 80 hr and for an Nb-1.94 atm% C alloy held between 1640 and 2045°C for 175 hr. As is seen in the figure, there is a large build-up of carbon at the colder ends of both specimens and a decrease of greater than one-half and one-quarter, respectively, in the higher temperature mid-section of the vanadium and niobium rods.

Recently Axtell /36/ has investigated the thermotransport of cobalt, a fast diffusing solute in a two-phase Th-Co alloy. He found a decrease from 0.56 atm% Co in the original alloy to <0.03 atm% Co in the higher temperature region after heating between 900 and 1200°C for 120 hr (see Fig. 3).

The above results suggest that, at least for some

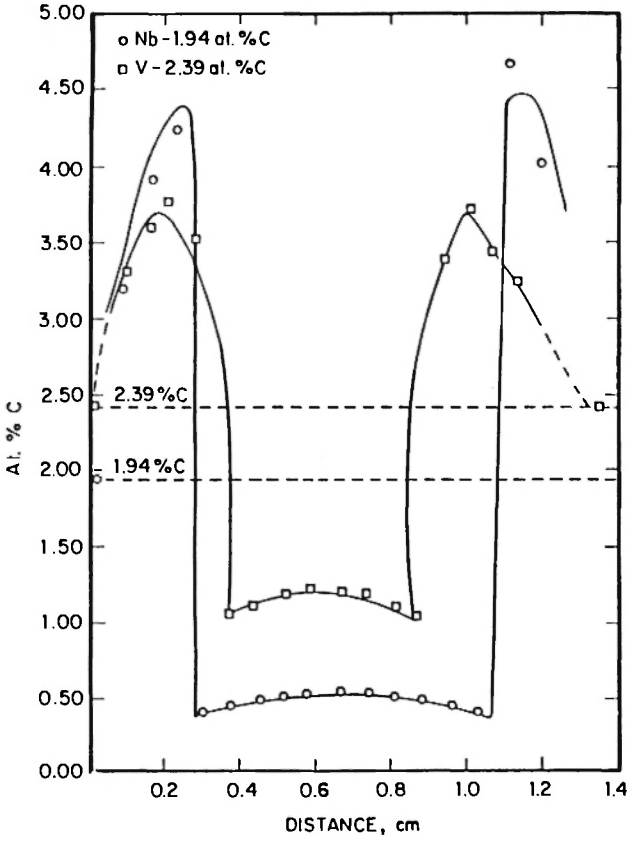

Fig. 2: Carbon distribution in two-phase V-2.39 and Nb-1.94 atm% C alloys after thermotransport for 80 and 175 hr, respectively.

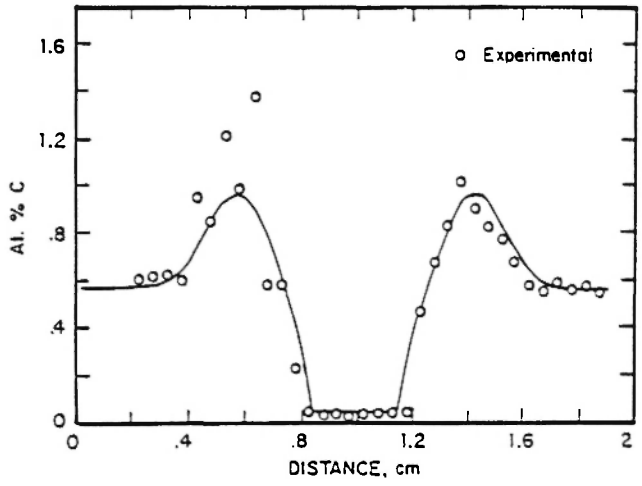

Fig. 3: Cobalt concentration vs distance in a Th-0.56 atm percent Co rod after thermotransport for 120 hr at 900-1200°C.

systems, thermotransport may be applicable as a purification method. This is particularly so for systems in which there is an appreciable amount of second-phase impurities, and the solid solubility of the matrix metal for those impurities is quite low.

6. CONCLUSIONS

Several methods for purifying metals by solid-state refining, all of which are applicable to refractory metals, have been described in this paper. External gettering by reactive metals such as Ti, Zr or Y is finding increased usage for removing interstitial impurities from niobium and vanadium. Likewise, degassing at high temperatures under ultra-high vacuum conditions is particularly effective for removing oxygen and nitrogen from niobium and tantalum.

Electrotransport ultra-purification in either a partial atmosphere of purified helium or an ultra-high vacuum has been successfully demonstrated for a number of metals. These include not only the refractory metals of Groups VA and VIA, but also the Group IVA reactive metals, the higher melting rare earths and the actinide metals, thorium and uranium. Some of the highest purity thorium, vanadium, gadolinium and scandium in the world have been prepared in this way.

Thermotransport is not generally considered to be a very promising method of ultra-purification, but some results are presented that indicate that it

may have such an application under special conditions.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of F.A. Schmidt in supplying some of the ultra-high purity information used in this paper, and also to thank M. Uz and S.C. Axtell for their computer calculations. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract No. W-7405-Eng-82.

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