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Electrorefining in molten salts – an effective method of high purity tantalum, hafnium and scandium metal production

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Abstract

The purity of tantalum, hafnium and scandium metals obtained by electrolysis in molten salts is compared with literature data on the purity of these metals produced by other methods. The advantage of electrorefining in high temperature electrolytes for high purity rare metal production is shown.

Keywords: Tantalum; Hafnium; Scandium; High-purity; Molten salt electrolysis

1. Introduction

The steady advances in science and technology necessitate the development of still better technologies for obtaining high purity materials. Even the notion of "high purity" itself has altered over the past 50 years. Whereas in the 1940s the attained level of total concentration of the limiting impurities was 10^{-3}–10^{-4} at.%, in modern times the total content of impurities in the purest substances is only 10^{-5}–10^{-6} at.%. In future years it will be realistic to anticipate producing and analysing substances with total impurity contents of 10^{-6}–10^{-7} at.% and individual impurity concentrations of 10^{-10}–10^{-12} at.% [1]. An analysis of the level of purity of 70 simple solid substances has shown that the least pure are metals of the III and IV side subgroups, with maximum total impurity contents of 0.33 and 0.32 at.% respectively. These are the rare earth metals, titanium, zirconium and hafnium. The most contaminated specimens of s-, p-, d- and f-elements appear to be the same transition metals (d and f elements). The level of chemically analogous impurities within the materials is relatively high because of the similarity of the melting temperatures of the components (often refractory ones) and the broad regions of liquid and solid solution homogeneity. This is true, for instance, for systems based on rare earth elements and for Nb–Ta and Zr–Hf systems. In addition, the interstitial impurity level (carbon, oxygen, nitrogen) in transition element samples is considerable. The reason for this is the large bonding energy generated by spd-hybridization of electron shells of metal atom s- and d- electrons and interstitial impurity atom p- electrons.

The current methods for producing high purity substances may be conventionally classified into chemical and physicochemical ones. The chemical methods are based on the difference in reaction rate constants or reaction equilibrium constants between the matrix and the impurity. In this case refining occurs when chemical or electrochemical reactions take place. The basis of the physicochemical methods is the difference between the matrix and impurity element intermolecular interactions. Among this group are distillation, sorption and crystallization methods as well as thermodiffusion. For instance, a difference in the matrix and impurity metal redox potentials allows application of the electrochemical method. A varied ability to form volatile halides provides the basis of the method of chemical transport reactions. Refining by distillation or sublimation is possible if the saturated vapour pressure over the liquid or solid phase varies between the matrix element and the impurity. Each purification method ensures removal of a certain group of impurities, but if a high purity substance is needed, various methods can be used in combination. High purity rare earth metals are produced both by a multistep distillation or sublimation and zone melting with solid state electrolysis. High purity rare refractory metals are obtained by a combination of electron beam zone melting in a high vacuum with subsequent treatment by solid state electrolysis [1]. Unfortunately, both in the practice of high purity metal

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production and in the literature covering this problem, the method of electrochemical refining in molten salts is often undeservedly disregarded. Electrolysis of aqueous solutions, widely used for electropositive metal refining, is inapplicable for electronegative metals such as rare earth metals, hafnium, titanium, zirconium, niobium and tantalum owing to the low overvoltage of hydrogen evolution. For these metals the only acceptable method is electrorefining in molten salts. In its capabilities this method at least does not rank below the above methods.

In the present work the purity of tantalum, hafnium and scandium metals obtained by electrolysis in molten salts in our laboratory at the Institute of Chemistry KSC RAS is compared with literature data on the purity of these metals obtained by other methods. It should be noted that Ta, Hf and Sc are classed among the transition d-metals, which are the least pure of high purity metals as was stated above. Consequently, in their refining, a problem arises of purification from chemical analogues (tantalum from niobium; hafnium from zirconium; scandium from rare earth elements) as well as from interstitial impurities (carbon, oxygen, nitrogen). Nevertheless, the attained purity, as will be shown below, allows us to suggest the ample possibilities of electrolytical refining from halide melts.

2. Results

2.1. Tantalum

Table 1 collates the data on tantalum purity obtained by various methods. As a result of electrorefining in K_2TaF_7–NaCl–NaF melt, most of the impurities are observed to decrease. More electropositive W, Mo, Mn, Ni and Fe as compared with tantalum in the given melt do not dissolve from the anodic material. Impurities with a greater negative potential (Al, Zr, Ti, Cr, Si) pass into the electrolyte, but up to a certain level of concentration they are not reduced at the cathode. Even the content of tantalum's chemical analogue niobium decreases, which does not occur e.g. with high vacuum sintering of pressed tantalum powder by direct passage of current. At the same time the material is observed to be considerably purified of alkaline metals and interstitial impurities. By heating tantalum to 2300 °C under vacuum, SiO, CO and gas-forming impurities present in the form of solid solutions are withdrawn

Table 1
Data on purity ($\times 10^4$ at.%) of tantalum metal produced by various methods

Element	Electrorefining				Sintering [2]		Electron beam melting [2]	Our data [e]	Goodfellow catalogue [f]
	Init. [a]	End [b]	Init. [c]	End [d]	Init.	End			
Fe	970	970	650	320	650	320		15	130
Nb	3900	780	58400	9700	1950	1950		300	<50–700
Cu	1400	850	850	280				5	<2
Mn	330		330	330				7	<3
Ti	380		380		380	380		40	<20
Al	1340		670					13	<70
Mo	380	570	190	190				9	<20
Ni	310		310					6	380
C	45250	2700	3620	750	7500	1500	30–200	450	450
O					11300	570	20–300	500	6700
Si					3230	650		30	100
Na					790	160			550
K					460	93			
N					6460	390	10–60	380	120
H					18100	1800	1	5400	1800
Co								6	
Mg								15	<7
V								7	
Sn								8	
W								5	<40
Cr								35	120
Ca								45	

[a] Sodium–thermal tantalum powder bricks [2];
[b] tantalum after electrorefining in K_2TaF_7(20wt.%)–NaCl(65–wt.%)–NaF(15wt.%) melt, $T=940$ °C [2];
[c] tantalum alloy sheet (3% Nb) [2];
[d] tantalum after electrorefining in K_2TaF_7(20wt.%)–NaCl(50wt.%)–NaF(30wt.%) melt, $T=940$ °C [2];
[e] tantalum of sodium-thermal reduction [a] after electrorefining in (NaCl–KCl–CsCl)(80wt.%)–K_2TaF_7(10wt.%)–NaF(10wt.%) melt;
[f] tantalum powder with maximum particle size 250 μm, method of purification unknown.

from the refined metal [2]. A lower level of interstitial impurity content is attained by subsequent electron beam or arc melting under vacuum. The particular attention focused on these impurities is due to the fact that an increase in their concentration results in an abrupt worsening of the physicomechanical properties of tantalum [2]. Table 1 also gives data on the purity of tantalum obtained by the authors by electrorefining in NaCl–KCl–CsCl–K_2TaF_7–NaF melt as well as data on tantalum powder purity taken from the Goodfellow catalogue for the years 1993–1994. In terms of metallic impurities the metal electrorefined in our laboratory turns out to be better than that produced by other methods or by electrorefining under a different set of conditions, whereas it compares well with the Goodfellow catalogue powders in terms of interstitial impurities.

2.2. *Hafnium*

Table 2 presents the literature data on the purity of hafnium produced by the method of iodide refining and solid state electrolysis as compared with hafnium obtained in our laboratory by electrorefining in molten electrolyte. Iodide refining has proved to be an effective method of purification from metallic impurities and especially from interstitial impurities. However, a markedly lower impurity level can be attained by the method of solid state electrolysis. It is also possible to decrease the interstitial impurity concentration in hafnium by zone melting [3]. Carbon and oxygen are withdrawn in the form of CH_4, CO and CO_2. The hardest impurities to eliminate are gas-generating impurities and zirconium. In terms of the majority of the elements the electrorefined hafnium is as pure as or purer than hafnium obtained by the Van Arkel method. It should be noted that the purification from hafnium's chemical analogue zirconium is also hampered with electrorefining in the melt. Comparison with the data from the Goodfellow catalogue allows us to conclude that our method makes possible the production of metallic hafnium comparing in purity more than favourably with the known analogues.

Table 2
Data on purity ($\times 10^4$ at.%) of hafnium metal produced by various methods

Element	Iodide refining [1]		Electrolysis in solid state [1]		Electrorefining, our data		Goodfellow catalogue [a]
	Init.	End	Init.	End	Init.	End	
O	11100	750	830	460	1110	550	22200
N	5230	260	1140	700	640	<100	2500
C	40300	600	2970		1480	60	3700
Si	1910	450			1910	40	
Mo	56	18			930	<40	37
Pb	86	86					
Fe	640	640			640	40	2400
Al	5960	6610			130	<60	660
Zr	16600	15600			7820	7820	<87000
Mn					3	<3	
Cr					34	<7	
Ca					445	20	
Ni					600	40	
H							178000
Cu							1400
Ti					185		370
U							7
W							150

[a] Hafnium powder with maximum particle size 40 μm, method of refining unknown.

2.3. *Scandium*

Table 3 gives the data on the purity of metallic scandium produced at each step of the process developed at the Institute of Chemistry KSC RAS. The process involves calcium–thermal reduction and electrorefining in molten salts. Here are also cited data on distilled scandium purity and on the purity of scandium produced abroad. Electrorefining allows us to significantly purify scandium from most metals. For instance, the content of tantalum, molybdenum, tungsten, copper and metals of the iron group decreases by three to four orders of magnitude per cycle. Less effective is the removal of rare earth metals owing to the similarity of their electrochemical properties and those of scandium. A high degree of refining can also be attained with interstitial impurities. It follows from Table 3 that distilled scandium is inferior to electrolytical scandium in terms of purity. Azhazha et al. [3] provide data on scandium ScM-1 vacuum melting. The nitrogen content is shown to diminish two-fold and carbon, hydrogen and fluorine 1.5, 50 and 1000 times respectively. The oxygen content increased 1.8-fold, which is explained by the authors in terms of scandium interaction with residual gases. On correlating these data with the results of electrorefining, the advantage of the latter is evident. It should also be noted that electrorefined scandium has a quality superior to that of other sources.

3. Discussion

From the data on Ta, Hf and Sc purity presented above, it can be inferred that the method of electrorefining in molten electrolytes is quite competitive in high purity metal production. Owing to the noticeable interaction of transition metals with interstitial impurities, the gas atmosphere over the melt must be particularly pure. Another necessary condition is the selection of structural materials indifferent to the metal being refined, with a view to ruling out the latter's

Table 3
Data on purity ($\times 10^4$ at.%) of scandium metal produced by various methods

Element	Our data		Vacuum distillation			Sublimated scandium [4]		Goodfellow catalogue [c]
	After calcium–thermal reduction	After electrorefining	[1]	[3]		[a]	[b]	
				Init.	End			
O	6980	<840	84	3100	2300	1820	270	
Ta	9450	<1				4000	1	
F	1200	240		30	0.05	300	37	
C	2100	<20	486	86	13	100	56	
N	200	<5	64			48	26	
Mg	20	2						2
Al	25	<0.7		25	8			33
Si	50	3		20	11			3
Cl	25	190						
K	<5	0.5						
Na	<10	140						
Ca	300	3	1	12	3			110
Cr	70	<1						5
Fe	1600	2	1	110	2			8
Ni	150	<1		14	2			40
Cu	14	1						1
Zr	20	<2						
Nb	10	1						
Mo	980	<2						
ΣREM	14	<2						
P		<0.5						
S		4						
Ti		<1						
V		<2						
Mn		<1		90	2			<1
Co		<1						
Zn		2						
Y		<1						
H		500	449			4900	360	
		Sum of transition metals				77	16	
		Sum of rare metals				10	10	

[a] Commercial scandium;
[b] scandium refined at the Materials Preparation Center, Ames Laboratory;
[c] scandium powder with maximum particle size 250 μm, method of refining unknown.

contamination. These requirements are common for all the methods. A characteristic peculiarity of electrorefining in melts is the possibility of controlling the process and hence the quality of metal produced by changing the main process parameters. For example, by varying the electrolyte composition, one can change via complexation, both the matrix and impurity metal redox potentials and improve the purification degree. The same objective is achieved by changing both the cathode and anode current densities. By harnessing the temperature dependence of the metal redox potentials and presetting the required temperature of the melt, it is possible to influence the quality of metal obtained.

To summarize the above factual evidence on metal purity and data on the feasibility of electrorefining in halide melts, it must be emphasized that the described method is preferable for high purity material production, whereas when used in combination with other methods, it allows one to obtain materials of the highest purity attainable at the present time.

References

[1] G.G. Devyatykh and G.S. Burkhanov, *High-Purity Refractory and Rare Metals,* Nauka, Moscow, 1993.
[2] A.N. Zelikman, B.G. Korshunov, A.V. Elyutin and A.M. Zakharov, *Niobium and Tantalum,* Metallurgiya, Moscow, 1990.
[3] V.M. Azhazha, P.N. Vjugov, S.D. Lavrinenko, V.S. Pavlov, N.N. Pilipenko and G.F. Tikhinskiy, Refining of the rare-earth metals by the physical methods, *Vysokochistye Veshestva,* (2) (1993) 5–12.
[4] K.A. Gschneidner, Metals, alloys and compounds — high purities do make a difference!, *J. Alloys Comp., 193* (1993) 1–6.