Obtaining and application of high-pure tantalum and ruthenium

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Abstract.
The results of systematic research on the complex refining of refractory metals Ta and Ru, and some applications of these are represented. Methods of electron beam melting, zone recrystallization and zone recrystallization in combination with electrotransport in high vacuum were mainly used for the refining of these metals. Refining of tantalum and ruthenium based on the use of complementary physical methods and use high vacuum technology, achieves the high degrees of purification and obtaining metals in its pure form: Ta – 99,999 wt.%; Ru > 99.99 wt.%.

Keywords:
tantalum
ruthenium
purification
electron beam melting
zone recrystallization
electrotransport
vacuum
High-purity metals are widely used in modern technology and the national economy: nuclear power, electronic, aerospace, medicine, defense, and military industries, as well as in fundamental scientific research. The fields of application of high-purity rare metals are constantly expanding. The development trend of modern science and technology requires high-purity or ultra-high-purity of metals, because some important characteristics of metals are affected by the type and amount of impurities in the matrix, and some characteristics are even masked by trace elements. Therefore, existing methods of refining metals are being improved all the time and new ones are being developed.

For obtaining pure metals at different stages of refining use various chemical and physical-chemical methods, but usually the refining process completes physical methods – distillation, zone recrystallization, electrotransport, and various combinations thereof. These methods are based mainly on physical processes: evaporation and condensation, crystallisation, diffusion and electromigration, etc. The advantages of these methods over the other are associated with the ability to achieve high purity and obtain the final product in a compact form, including single crystals with a perfect crystal structure [1].

This paper summarises the results of research on the purification and obtaining of high-purity Ta and Ru metals and presents some areas of their application.

**Materials and methods**

Electron beam melting, zone melting and electrotransport methods were used for obtaining pure Ta and Ru metals.

Electron beam melting (EBM) of metals is performed on an ultra-high vacuum installation. For pumping of installation used two hetero-ion pumps with a pumping speed of 5000 l/s each, and a titanium sublimation pump. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6} \text{ Pa}$ [1, 2]. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals is carried out in vacuum $(1-5) \cdot 10^{-5} \text{ Pa}$. Refining is conducted in the regime: heating → melting → excerpt of metal in molten state → crystallisation → pulling ingot.
Zone melting (recrystallization) with an electron-beam heating is carried out, as a rule, in installations with combined pumping systems \[1, 3\]. Diffusion pumps are equipped with sorption and condensation traps. Sorption, cryogenic and ion-sorption pumps which are used to give "oil-free" ultrahigh vacuum. Crucibleless electron-beam zone melting (ZM) is carried out in vacuum \(1 \times 10^{-6} - 1 \times 10^{-5}\) Pa. There are two purification mechanisms during the vacuum zone melting: zone recrystallization (distribution of impurities along the length of the ingot) and evaporation of impurities. An optimal zone melting speed and a number of zone refining times make the zone purification efficiency higher.

Electron-beam zone melting in an ultra-high vacuum and controlled environment in combination with electrotransport was used to improve purity of Ta.

The impurities concentration in metal samples has been determined by the Laser Mass Spectrometry measurements on EMAL-2 mass-spectrometer with a laser-plasma ion source. The limiting sensitivity of the analysis method for the metal impurities was \(\sim 10^{-5} - 10^{-6}\) at. %.

The purity level of some metals was detected by the values of residual resistivity ratio measurements. Residual resistivity ratio or residual resistance ratio (RRR) is defined as the ratio of a metal’s electrical resistance at room temperature to that at 0 K, which is usually replaced by liquid helium temperature (4.2 K).

The structure of the metal samples has been investigated by a metallographic method. The thin sections were prepared by electro-polishing method, and further were examined by optical microscopes at different magnifications. The microhardness of those samples was measured by PMT-3 apparatus.

**Results and discussion**

**Application of tantalum and ruthenium.** Tantalum features several unique properties that have led to its increasing use in a range of modern industrial applications. The metal’s many unique properties – such as high melting point, corrosion resistance, hardness, and resistance to chemical attack – make it ideal for a wide range of industrial applications. Tantalum is used for manufacturing electronics, tools, and
other types of industrial equipment.

Tantalum is used for the production of electrical capacitors and resistors, while the ability to hold substantial amounts of charge in a small component has made it possible for electronics manufacturers to miniaturise electrical parts and devices. With over 75% of electronics and components — such as mobile phones, computers, DVD players and video game systems — contain Ta in some format. Tantalum is also well known for its biocompatibility and this makes tantalum ideal for pairing with living tissue in medical implants and prosthetics. Ta and its alloy are used in nuclear reactors, missile parts, chemical processing equipment, heat exchangers, and storage tanks. Impurities in the metal can have an undesirable effect on the properties of the articles formed from the Ta. Decrease of total impurities or increase in purity in tantalum has resulted in the decrease of its hardness [4].

Many new uses are emerging for ruthenium. Most is used in the electronics industry for chip resistors and electrical contacts. Ru alloys also find application in manufacturing of turbines of jet engines. Ru has also applications in therapy. For instance, 106 isotope of ruthenium has application in radiotherapy of malignant cells of the eye. Ru finds application in manufacturing solar cells for production of solar energy. Ru oxide is used in the chemical industry to coat the anodes of electrochemical cells for chlorine production. Ru is also used in catalysts for ammonia and acetic acid production [5].

Ruthenium is one of the elements used for carrying out low-background experiments for recording double β-decay. An increase in the sensitivity of the experiment is directly related to a decrease in the level of the internal background of the samples. The main sources of the internal background in the metal can be α- and β-active isotopes of natural origin. These are $^{40}$K, as well as radionuclides of uranium ($^{238}$U and $^{235}$U) and thorium ($^{232}$Th) series. Therefore, additional purification of Ru from these and other elements is necessary, which should also lead to a decrease in the level of background radionuclides [6].

**Purification of tantalum and ruthenium.** Powder and rods of Ta with purity of 99.8 wt.% were used for purification.
Vacuum electron beam melting reduces metallic impurities in Ta samples and significantly reduces the interstitial impurities ($\times 10^{-4}$ wt.%): Al – 3-20; Si – 3-20; Cr <5; Fe – 5-10; Cu < 1; H2 – 1-6; C – 3-20; N2 – 1-10; O2 – 5-50. Main consideration is given for behaviour of metal impurities and interstitial impurities during EBM. Degassing and evaporation of volatile impurities are the main purification processes of tantalum by electron beam melting [7]. The impurities which lower the contents in initial metal will allow obtaining necessary purity of Ta are determined, this is W, Re, Os, Nb [8].

The physical substantiation and experimental study of the Ta refining by crucibleless electron beam zone melting method in vacuum were carried out. It was found that for the refining of Ta, the zone melting method will be most efficiently applied when several stages of experiments are carried out sequentially, namely: high-temperature heating, zone melting at a big speed (16 or 8 mm/min) to remove highly volatile metallic impurities, melting at a low speed (2 or 1 mm/min) for the display of the effect of impurity displacement of together with the movement of the liquid zone. Experimental results of tantalum refining by the zone melting method from various starting materials (powder and rod) are given in Table 1. These data confirm the existence of two purification mechanisms: zone recrystallization (distribution of impurities along the length of the ingot) and evaporation of impurities. For example, the content of copper in the beginning part of the ingot is $1 \cdot 10^{-5}$, and in the end part it is $1 \cdot 10^{-4}$ wt.%, silicon $7 \cdot 10^{-5}$ and $5 \cdot 10^{-4}$ wt.%, respectively. Table 1 also clearly shows the influence of the movement velocity of the molten zone during the refining of tantalum by this method on the distribution of impurities in the ingot. Elemental analysis of the obtained samples showed that the main impurity elements that hinder the purity of tantalum are niobium (the content after zone melting is $8 \cdot 10^{-2}$ wt. %), tungsten ($4 \cdot 10^{-3}$ wt. %), carbon ($4 \cdot 10^{-1}$ wt. %) and oxygen ($< 3 \cdot 10^{-3}$ wt. %) [9].

The efficiency of zone melting increases in case of its combination with the method of electrotransport. In this case, the effective distribution coefficient changes due to additional electrodiffusion flows, and an increase in the
The degree of purification of metals is achieved as a result of the electromigration of impurities. As a result of ZM with electrotransport, carried out under cryogenic pumping conditions, there was a redistribution of impurities along the length of the samples. For example, the carbon concentration was 0.002 and $5 \cdot 10^{-4}$ wt. %, iron $0.7 \cdot 10^{-4}$ and $<0.1 \cdot 10^{-4}$ wt. %, niobium 0.015 and 0.004 wt. % in the cathode and anode parts of the samples. Studies have shown that electrotransport achieves the distribution of impurity elements (niobium, carbon and oxygen) which limit the purification of tantalum by zone melting; therefore, the combination of zone melting with electrotransport provides a higher degree of refining [10].

### Table 1

<table>
<thead>
<tr>
<th>Metal</th>
<th>RRR of the samples</th>
<th>Parameters of ZM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Starting part</td>
</tr>
<tr>
<td>Rod</td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>160</td>
</tr>
<tr>
<td>Powder</td>
<td>–</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>154</td>
</tr>
</tbody>
</table>

$n$ - number of zone passes, $f$ - zone movement velocity, mm/min.

The physical grounds and an experimental study of the efficiency of applying the zone recrystallization method in an electric field for tantalum refining from metal and gas-forming impurities were carried out. The changes in the elemental composition, microhardness, and structure of the obtained ingots were investigated. It is shown that the application of the method can significantly reduce the content of interstitial impurities.

Float-zone melting in an ultra-high vacuum and controlled environment in combination with electrotransport was used to improve purity of tantalum to grow single crystals. Single crystals of tantalum obtained by zone melting in a controlled environment of oxygen had 99.999 wt. %.

The content of impurity elements in the tantalum such purity was as follows:
Ag <7.0·10^{-6}; In <1.0·10^{-5}; Rh <1.0·10^{-5}; As <1.0·10^{-5}; K <3.0·10^{-6}; Ru <1.0·10^{-4};
B = 3.0·10^{-5}; Mg <1.7·10^{-6}; S <2·10^{-6}; Ba <2.0·10^{-5};
Mn <1.0·10^{-5}; Sb <7.0·10^{-5};
Bi <5.0·10^{-4}; Mo <2.0·10^{-4}; Se <5.0·10^{-5}; Br <2.0·10^{-5};
Na <1.0·10^{-6}; Si – 6.6·10^{-6};
C – 4.0·10^{-3}; Nb – 2.4·10^{-4}; Sn <1.0·10^{-4}; Cl – 2.0·10^{-5};
Ca <3.0·10^{-6}; Sr <1.0·10^{-4};
Co <3.0·10^{-5}; Ni <4.0·10^{-5}; Th <6.0·10^{-5}; Cr <1·10^{-5};
O <3.0·10^{-3}; Ti <1.0·10^{-3};
Cs <1.0·10^{-5}; Os <7.0·10^{-5}; Tl <2.0·10^{-4}; Cu <1.0·10^{-5};
P <1.0·10^{-5}; V <9.0·10^{-6};
Fe – 1.2·10^{-5}; Pb <6.0·10^{-5}; W <4.0·10^{-4}; Ga <1.0·10^{-5};
Pd <5.0·10^{-5}; Zn <1.0·10^{-4}; Ge <1.0·10^{-5}; Rb <2.0·10^{-5};
F <1.0·10^{-6}; I <4.0·10^{-5}; Re <3.0·10^{-4} mas.%.

The content of metallic impurities in the resulting tantalum is below the sensitivity of analysis methods: for easily volatile <10^{-5} %, for hardly volatile <10^{-4} %. Zone refining were gave oriented single crystals of Ta with diameter 7-10 mm and length 150-180 mm and disorientation elements of substructure <0,01° and the microhardness value of 750 MPa [9-11]. Zone recrystallization in a rarefied oxygen medium and in combination with electrotransport is an effective process that makes it possible to obtain single-crystal samples of tantalum of a high degree of purity and high structural perfection. The calculations of the optimal parameters of the EBM for the refining of ruthenium from metal impurities are made. The main parameters of refining conditions were obtained: the number of remeltings, melting time and material loss. The obtained parameters were used to optimise the EBM of ruthenium.

Powdered ruthenium with a purity of 99.85 wt.% was used as the starting material for refining. Purification of the initial ruthenium was carried out by the electron beam melting method in high vacuum. Samples of high purity ruthenium were obtained by refining this method. The content of the main impurity elements in the ruthenium samples before and after the electron beam melting is given in Table 2. The multiple electron beam melting method made it possible to obtain
ruthenium with a purity of > 99.99 wt.%, primarily due to purification from interstitial impurities and most metal impurities, including potassium. When compared with the impurity composition of the original metal, the high efficiency of using this method for refining ruthenium is confirmed. As can be seen from Table 2, as a result of refining, all the analysed impurities are purified by an average of two to three orders of magnitude, including potassium — by more than 50 times.

The results of studies of thermal desorption of gases from ruthenium samples showed a significant decrease in the intensity of gas evolution of their purified metal in comparison with the original one. Metallographic studies showed the high purity of the obtained samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>B (wt.%)</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Na</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ru</td>
<td>0.00004</td>
<td>0.12</td>
<td>0.0001</td>
<td>0.004</td>
<td>0.00001</td>
<td>0.00006</td>
<td>0.00004</td>
</tr>
<tr>
<td>After EBM</td>
<td>&lt;0.00002</td>
<td>0.005</td>
<td>0.00008</td>
<td>0.0006</td>
<td>&lt;0.000003</td>
<td>0.000005</td>
<td>0.000001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>P</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ru</td>
<td>0.0005</td>
<td>0.00002</td>
<td>0.0002</td>
<td>0.0008</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.004</td>
</tr>
<tr>
<td>After EBM</td>
<td>0.00003</td>
<td>&lt;0.000003</td>
<td>&lt;0.000005</td>
<td>0.00015</td>
<td>0.00002</td>
<td>&lt;0.000008</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>Cu</th>
<th>Ga</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ru</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.001</td>
<td>0.0002</td>
<td>0.012</td>
<td>0.007</td>
<td>0.002</td>
</tr>
<tr>
<td>After EBM</td>
<td>0.00005</td>
<td>&lt;0.000009</td>
<td>0.0004</td>
<td>&lt;0.000002</td>
<td>0.0005</td>
<td>0.0008</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

The structure of the ruthenium samples before and after EBM is shown in Fig. 1. The initial sample is presented in the form of a tablet pressed from very fine Ru powder (Fig. 1, a). The remelted sample has fairly large grains approximately 1-5 mm in size, which can be observed visually (Fig. 1, b). Ru after EBM is characterized by a step (layered) structure (Fig. 1, c). Etching figures of various shapes and sizes are
also observed. The value of the microhardness of ruthenium after electron beam melting is 6420 MPa. The resulting ruthenium ingots meet the requirements for the material necessary for carrying out low-background experiments for recording double $\beta$-decay of ruthenium.

![Figure 1](image1.png)

**Figure 1**

Structure of ruthenium samples: a – initial; b and c – after EBM

**Conclusions**

The high purity levels of Ta and Ru metals can be achieved by conventional purification processes such as zone melting, electron beam melting in high vacuum. Zone refining and electron beam melting for high melting point metals and chemically active metals tantalum and ruthenium are very much useful. Combinations of purification processes are necessary to improve the efficiency of metal purification from...
impurities. The purity of the obtained metals is: Ta - 99.999 wt.%, Ru > 99.99 wt.%. The high purity Ta and Ru metals are crucial materials for fundamental scientific research and development, and production of advanced materials technologies, which generally require optimum properties, performance, quality and efficiency.

References:


