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PURIFICATION OF VANADIUM BY ELECTRON-BEAM MELTING

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In this paper we are reported about theoretical calculation and experimental investigation of Vanadium purification by electron-beam melting. This method has demonstrated high efficiency of Vanadium purification from interstitial impurities and majority of metallic impurities, including Potassium. The Vanadium metal with purity of 99.7 wt.% have been obtained. The thermal desorption from Vanadium metal samples "before" and "after" electron-beam melting has been studied. The purified in such way Vanadium have satisfied all the requirements of low background experiment for search of rare decay of ^{50}V, especially concerning of Potassium contamination.

INTRODUCTION

In Nature there are a number of isotopes, which are accepted to consider as "stable", but for which the radioactive decay is energetically allowed. These, conditionally "stable", the nuclei can be attributed nuclides with half-lives greater than the life-time of Universe, i.e. more than 12.5 billion years ($1.25 \cdot 10^{10}$ years) [1]. Unless take into account the "exotic" processes beyond the Standard Model, such as the neutrinoless double beta decay with a half-life of more than $10^{23} \ldots 10^{25}$ years [2-4], there are allowed by all conservation laws, well described the Standard Model, and the "usual" nuclear processes such as alpha decay or beta decay, which have the expected half-life of many orders of magnitude longer than the life-time of Universe.

Among these processes, with an extremely long half-life could be attributed also beta decay with a high degree of prohibition – beta decay, in which the level of the parent nucleus from which decay occurs, has a very different angular momentum and parity in comparison to final level of the daughter nucleus. In general, the wide studied beta decays are permitted or 1-fold prohibited decays (i.e. $\Delta I^{\Delta\pi} = 0, 1^{+/-}$). However, there are several nuclei even with 4-fold forbidden beta decay, with half-life more than 10^{13} years. There are only three isotopes, for which may occur 4-fold forbidden non-unique (i.e. the parity of the decay does not change, $\Delta I^{\Delta\pi} = 4^+$) beta decay – ^{50}V, ^{113}Cd and ^{115}In. Theoretical half-lives estimation for these nuclei exceeds 10^{14} years, and respectively, when you try to detect such decays, they will produce a very weak counting rate for the desired effect. The experiments dedicated to search for such rare decays should be performed in underground laboratory well-shielded from external factors using a low-background detectors and sample with high chemical and radioactive purity.

Despite more than 40 years history of research, the value of half-life for a 4-fold forbidden beta decay of ^{50}V still raises questions [5-13]. This isotope is unique since the beta decay to the ground state of daughter nucleus has an even higher degree prohibition (6-fold forbidden decay), leaving the possibility or for a 4-fold forbidden non-unique beta decay to the first excited level of the ^{50}Cr or for the electron capture with the transformation in ^{50}Ti. For both branches of the decay, there is only one excited level, which can be occupied at a given decay energy: (2^+, 783.29 keV) for beta decay and (2^+, 1553.77 keV) for electron capture [14]. So, in the low-background experiments in which sample of Vanadium metal is placed on HPGe detector, those energies gammas should be sure detected. But, seeing energies of both de-excitation gammas are below the cut-off energy of the 2615 keV of natural radioactivity of ^{208}Tl nuclide (daughter nucleus of ^{232}Th chain), is necessary to use Vanadium with the lowest concentration of natural (^{40}K, ^{232}Th, and ^{238}U), as well as anthropogenic (^{90}Sr, ^{137}Cs) radionuclides, to reach required level of experiment sensitivity.

We report here the results of development of deep purification of Vanadium by vacuum electron-beam melting in order to obtain the lowest possible contamination by radioactive impurities, that allow to achieve high sensitivity of low-background measurements to find the 4-fold forbidden beta decay of ^{50}V.

EXPERIMENTAL TECHNICS

The pure electrolytic vanadium with initial purity grade of 97.7 wt.% was used as a starting material. The small pieces of vanadium were compressed into tablets with dimensions $\varnothing 30 \times 10$ mm and 35 g of mass. The purification processes was performed by electron-beam melting under high vacuum in UPM-1 set-up, described in details in [15]. This set-up was designed for electron-beam melting under high vacuum ($10^{-2} \ldots 10^{-4}$ Pa) of infusible, rare or dispersed metals, such as niobium, zirconium, vanadium, tantalum, etc, and also to produce the alloys based on these metals. After purification were obtained ingots with diameter about 45 mm.

The structure of Vanadium metal samples "before" and "after" electron-beam melting has been investigated by metal-graphic method. The thin sections were prepared by electro-polishing method, and further were examined by optical microscope MMP-4 at different magnifications. The pictures were taken by digital camera Olympus. The micro-hardness of those samples was measured by PMT-3 apparatus at 50 g loading.

In order to determine the impurities concentration in Vanadium samples the LMS (Laser Mass Spectrometry)

measurements have been performed on EMAL-2 mass-spectrometer with a laser-plasma ion source. The uncertainties can be estimated as about 15…30% of the given concentration value.

The thermal desorption from Vanadium metal samples "before" and "after" electron-beam melting has been studied using experimental set-up with MX7203 mass spectrometer [16] under vacuum, in temperature range from room temperature up to 800 °C.

RESULTS AND DISCUSSION

During the refining process of Vanadium by electron-beam melting the metal is melting and is maintained in a liquid state a certain time in water-cooled copper crystallizer under high vacuum. The main refining factor is exposure of metal in a liquid state. Due to difference of the relative volatility α of separable component (so-called, factor of separation), the chemical composition in vapors and in a liquid state is difference. What a large factor of separation is different from unity, the more effective separation of the components. In the case of a diluted ideal solution, when the activity coeffi-

cients of the main and impurity elements $\gamma_A = \gamma_V = 1$, the ideal factor of separation α_i during molecular evaporation is defined as [17]:

$$\alpha_i = \frac{p_A^0 \sqrt{M_B}}{p_B^0 \sqrt{M_A}}, \qquad (1)$$

wherein p_A^0, p_B^0 – the vapor pressure of the pure components A and B, respectively; M_A, M_B – molecular weight the basic and impurity elements, respectively.

The ideal values of separation factor could provide an estimation of the effectiveness metal refining by electron-beam melting under vacuum. For this reason, the values α_i for main impurity elements have been determined at temperature 2400 K, which is typical for vanadium refining process. The computed values of separation factor are listed in Table 1, together with the melting points and vapor pressure of corresponding impurity element at T = 2400 K [18].

Table 1

Computed values of separation factor α_i for main impurity elements determined for temperature 2400 K

Element	T_m, K	Molecular weight	Vapor pressure, mm Hg	Separation factor, α_i
Na, K, Mg, Ag, Zn, Cd, Hg, Ga, S, Te	–	–	$\gg 1000$	$\ll 1\cdot10^{-3}$
Cu	1356	29	35.2	$7.52\cdot10^{-3}$
Cr	2130	24	47.8	$5.0\ 10^{-3}$
Sc	1673	21	141	$1.59\cdot10^{-3}$
Be	1556	4	63.2	$1.55\cdot10^{-3}$
Al	700	13	123	$1.44\cdot10^{-3}$
Co	1768	27	189	$1.352\cdot10^{-3}$
Pd	1823	46	3.50	$9.536\cdot10^{-2}$
Si	1683	14	24.2	$7.60\cdot10^{-2}$
Ge	1210	32	7.04	$3.95\cdot10^{-2}$
Nd	1297	60	12.4	$3.074\cdot10^{-2}$
Fe	1812	26	8.75	$2.86\cdot10^{-2}$
Y	1773	39	19.6	$1.567\cdot10^{-2}$
Sn	505	50	26	$1.38\cdot10^{-2}$
La	1193	57	$7.87\cdot10^{-1}$	$4.72\cdot10^{-1}$
Ti	1980	22	$5.63\cdot10^{-1}$	$4.099\cdot10^{-1}$
V	**2190**	**23**	**$2.36\cdot10^{-1}$**	**1**
Rh	2239	45	$3.35\cdot10^{-2}$	9.85
B	2300	5	$8.96\cdot10^{-3}$	12.28
Pt	2043	78	$2.39\cdot10^{-2}$	18.1
Ir	2727	77	$1.32\cdot10^{-3}$	327.1
Zr	2125	40	$5.71\cdot10^{-4}$	545
Ru	2520	44	$2.79\cdot10^{-4}$	1169
Mo	2890	42	$1.16\cdot10^{-1}$	2750
C	–	6	$2.82\cdot10^{-3}$	4275
Hf	2250	72	$7.10\cdot10^{-5}$	5880
Nb	2770	41	$1.10\cdot10^{-5}$	$2.864\cdot10^{4}$
Os	3000	76	$1.47\cdot10^{-5}$	$2.922\cdot10^{4}$
Re	3453	75	$5.88\cdot10^{-8}$	$7.247\cdot10^{6}$
Ta	2270	73	$1.76\cdot10^{-7}$	$2.389\cdot10^{6}$
W	3650	74	$1.34\cdot10^{-8}$	$3.16\cdot10^{7}$

As you could see from Table 1, the values of ideal separation factor α_i are varying in wide range. It is highly volatile impurities with $\alpha_i \ll 1$ (top part of the table), purification from which will be effective. The nonvola-
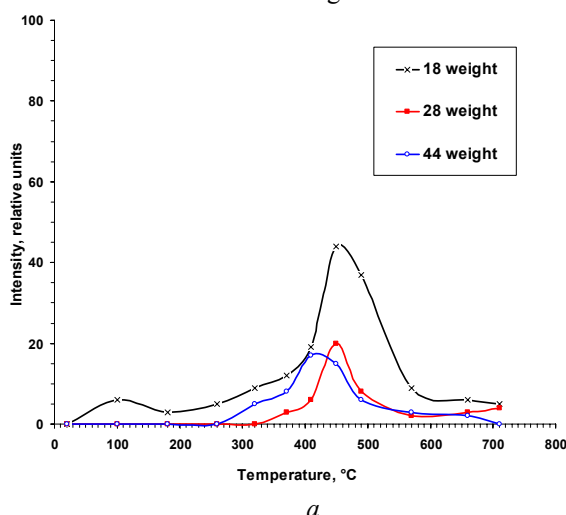
tile impurities with $\alpha_i \gg 1$ (bottom part of the table), purification from which will not occur. There are also several impurities (Mo, C, Hf, Ir, Zr) with α_i close to unity, purification from which will be rather difficult.

In case, if you should deal with samples of compacted powders, you should take into account that exploiting a high speeds of melting at the first stage of process leads to intensive spraying of initial material, through a presence of significant amount gas forming impurities. In order to avoid these unwanted losses of initial material it is required the gradual melting of samples, which increases the duration of melting and, consequently, increases losses of metal due to its evaporation. Therefore, the total loss of initial Vanadium metal is a few percent.

Table 2

Impurities concentration in Vanadium metal sample before and after multifold electron-beam melting

Element	Before, ppm	After, ppm
Cr	850	7
K	130	1.7
Al	120	11
Cu	100	18
Fe	70	10
P	70	0.5
Cl	42	4
Si	17	17
Ca	13	5
Ni	8	5
Mg	4	0.7
Ti	3,5	1
Na	3	0.4
Zn	1.6	1
Mn	1.5	0.11
O	600…800	160…200

The high purity Vanadium metal samples with purity 99.7 wt. % have been obtained using multifold electron-beam melting under vacuum. In Table 2 is presented in comparison purity of initial metal and Vanadium after refining. Indeed, this refining method is very effective for all analyzed elements, for example, we have reduced Cr contamination by two orders of magnitude, as well as Potassium contamination was reduced by about 75 times.

High efficiency of this method with respect to elimination also gas-forming impurities was proved by measurements of thermal desorption of the initial samples and after refining. On Fig. 1 present dependence of total pressure on heating of metal sample in the temperature range 25…800 °C. The outgassing intensity for the sample after refining is five times less than for initial metal. The mass-spectra of gases released from Vanadium sample during the thermal desorption are shown in Fig. 2, and correspond to H_2O (mass 18), $CO+N_2$ (mass 28), CO_2 (mass 44), etc. The main gas components are emanate in the temperature range 300…600 °C, peaking at about 500 °C.
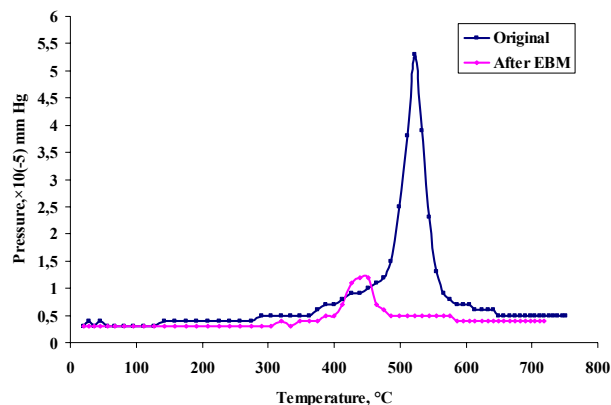

Fig. 1. The dependence of total pressure of vapors on heating of metal sample before and after refining in temperature range 25...800 °C
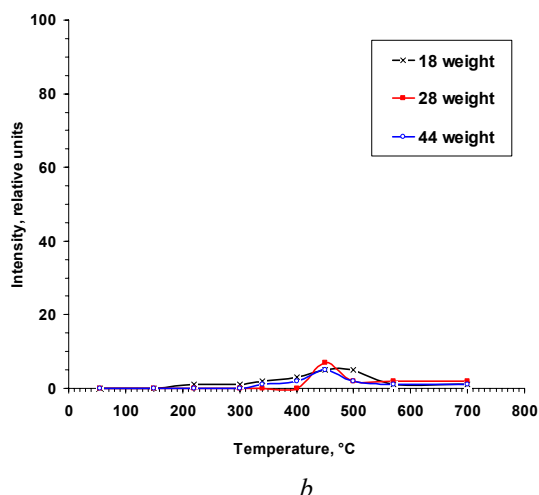

a

b

Fig. 2. The mass-spectra of gases released from Vanadium sample during the thermal desorption: before refining(a); after refining (b)

On Fig. 3 the results of metallographic measurements of Vanadium samples before and after by electron-beam melting under vacuum are presented. The initial samples of compacted powders were in tablets form (see Fig. 3,a). Refined sample has a relatively large grain with size of about 380 microns, which can be observed visually (see Fig. 3,d). The grains are equiaxial, the grain boundaries are clean. The microhardness of the initial vanadium metal is $N_\mu = 1090$ MPa, after electron-beam melting

N_μ = 1440 MPa. Increasing the micro-hardness of vanadium after electron-beam melting can be explained by the fact that the initial samples of compacted powders were produced from flakes of electrolytic vanadium. Consequently, these samples have a higher porosity and, correspondingly, less micro-hardness value.
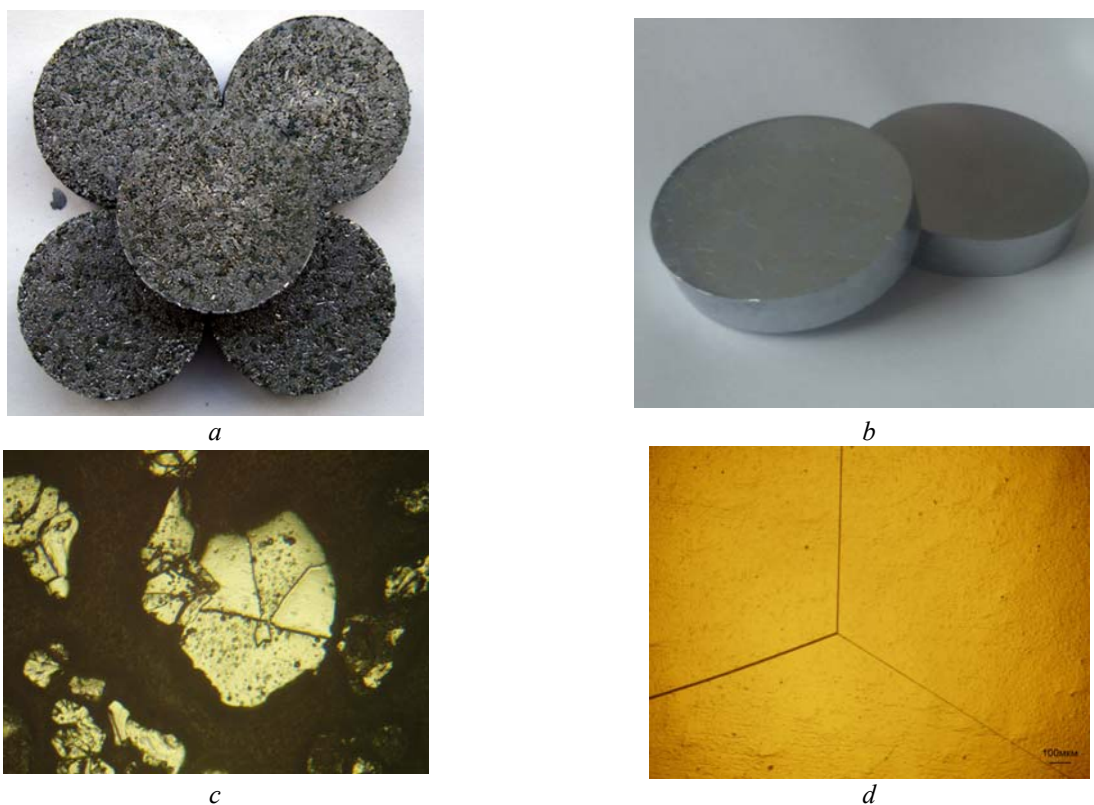

Fig. 3. Outward (a, b) and microstructure (c, d) the Vanadium metal samples before (a, b) and after electron-beam melting under vacuum (b, d)

CONCLUSIONS

In this paper we are reported about theoretical calculation and experimental investigation of Vanadium purification by electron-beam melting. The α_i separation factor values for main impurity elements have been determined at the temperature 2400 K, temperature of Vanadium refining. The separation efficiencies for main impurity elements were also evaluated. The electron-beam melting under high vacuum has demonstrated high efficiency of Vanadium purification from interstitial impurities and majority of metallic impurities, including Potassium. The Vanadium metal with purity of 99.7 wt.% have been obtained. The thermal desorption from Vanadium metal samples "before" and "after" electron-beam melting has been studied. The outgassing intensity for the sample after refining is five times less than for initial raw metal. The metallographic measurements also have demonstrated a high purity of refining metal sample. The purified in such way Vanadium have satisfied all the requirements of low background experiment for search of rare decay of ^{50}V, especially concerning of Potassium contamination.

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ЭЛЕКТРОННО-ЛУЧЕВАЯ ПЛАВКА ВАНАДИЯ

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Проведены расчетные и экспериментальные исследования процесса рафинирования ванадия методом электронно-лучевой плавки. Показано, что электронно-лучевая плавка является эффективным методом рафинирования ванадия от примесей внедрения и большинства металлических примесей, в том числе от калия. Получены образцы ванадия с чистотой 99,7 мас.%. Исследована термодесорбция из образцов ванадия до и после электронно-лучевого переплава. Приведены результаты микроструктурных исследований и измерения твёрдости. Установлено, что полученный ванадий удовлетворяет всем необходимым условиям, в первую очередь по содержанию примеси калия, для проведения исследований поиска 2β-распадов на ядрах изотопов ванадия, а также для применения в качестве компонента перспективных, малоактивируемых сплавов.

ЕЛЕКТРОННО-ПРОМЕНЕВА ПЛАВКА ВАНАДІЮ

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Проведені розрахункові та експериментальні дослідження процесу рафінування ванадію методом електронно-променевої плавки. Показано, що електронно-променева плавка є ефективним методом рафінування ванадію від домішок проникнення і більшості металевих домішок, у тому числі від калію. Отримано зразки ванадію чистотою 99,7 мас.%. Досліджено термодесорбцію із зразків ванадію до і після електронно-променевого переплаву. Наведено результати мікроструктурних досліджень і вимірювання твердості. Встановлено, що отриманий ванадій задовольняє всім необхідним умовам, в першу чергу за вмістом домішки калію, для проведення досліджень пошуку 2β-розпадів на ядрах ізотопів ванадію, а також для застосування в якості компонента перспективних малоактивованих сплавів.