PURE VANADIUM AND TITANIUM FOR LOW ACTIVATION ALLOYS

M.M. Pylypenko[1], S.D. Lavrinenko[1,2]

[1]National Science Center "Kharkov Institute of Physics and Technology",
Kharkov, Ukraine
E-mail: mpylypenko@kipt.kharkov.ua;
[2]V.N. Karazin Kharkov National University, Kharkov, Ukraine

The refining processes of vanadium and titanium from metal and gas impurities by physical methods in vacuum are considered. The effectiveness of using electron-beam melting, zone recrystallization and electrotransport for purification of these metals is shown. Vanadium and titanium in a purity of more than 99.99% have been produced.

INTRODUCTION

Modern tendencies of development of reactor technologies are aimed to further increase reliable and safe operation of power units and to provide efficiency and competitiveness of nuclear power. This requires an increase in power density, power of units, increasing the duration of campaigns, more efficient fuel burning, including by improving the quality of construction materials [1-4].

The progress achieved in the field of nuclear physics, reactor physics and reactor materials in recent years, led to the development of a number of advanced nuclear energy systems [1]. These projects have advantages in economy, security, reliability and non-proliferation of nuclear materials.

New structural materials must be pure. We know that high levels of impurities and gases in steels and alloys significantly worsen their mechanical, corrosion and radiation properties and, therefore, limit their use in operating and designing reactors. Use of high-purity metals as initial components of new structural materials will provide desired properties in the resulting products [5, 6]. Vanadium, titanium and chromium are metallic elements which are necessary components to produce low-activity alloys for nuclear energy of present and future.

Vanadium alloys are considered as a promising candidate structural material for fusion and fast-fission reactors applications because of their attractive properties such as superior high temperature thermal and physical properties, good resistance against neutron irradiation and low neutron activation level. It is well known that increased level of interstitial impurities such as C, N, O would result in loss of workability, weldability and irradiation resistance [7–8]. On the other hand, increased level of undesirable elements such as Co, Nb, Ag, Mo, Al, Na, Ni, Cu, Fe etc. would dominate the activation level of vanadium alloys which would substantially influence not only the recycling aspects of used reactor materials but also the waste management aspects of them. The required impurity levels for hands-on recycling of the low-activity vanadium alloys are around the magnitude concentrations of 0.01, 0.1, 0.01, 10, 0.5 and 30 wppm, respectively, for the elements Co, Nb, Ag, Mo, Cu, Ni and Al based on the neutron irradiation fluence of 15 (MW·year)/m^2 [7].

Impurities increase the strength of titanium, also greatly reduces it ductility, but interstitial impurities such as H, O, N, and C have the strongest negative action on properties of titanium. Titanium entirely loses its ability to plastic deformation and becomes brittle if it contains 0.003, 0.02, and 0.7 wt.% hydrogen, nitrogen and oxygen, respectively. Under neutron irradiation the embrittlement of titanium alloys increases with increasing contents of oxygen, nitrogen and hydrogen in the alloy.

The activation level of vanadium alloys will be depending on impurity contents in alloys. So obtaining of high-purity components (vanadium and titanium) for low-activity alloys is relevant today.

1. METHODS AND TECHNOLOGIES FOR REFINING OF METALS

To obtain pure metals at different stages of refining, the various chemical and physico-chemical methods are used, but usually the refining process comprises of physical methods – distillation, zone recrystallization, electrotransport and various combinations thereof. These methods are mainly physical processes: evaporation and condensation, crystallization, diffusion and electromigration, etc. The advantages of these methods over the others are the ability to yield high purity material, and the final product is obtained in a compact form including single crystals with a perfect crystal structure.

Electron beam melting (EBM) of metals is performed on an ultra-high vacuum installation. To pump installation, the two hetero-ion pumps were used with a pumping speed of 5000 l/s each, and the titanium sublimation pump was applied also. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6}$ Pa [9]. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals was carried out in vacuum $(1...5) \cdot 10^{-5}$ Pa. Refining was conducted in the regime: heating $\Rightarrow$ melting $\Rightarrow$ excerpt of metal in molten state $\Rightarrow$ crystallization $\Rightarrow$ pulling ingot. Zone recrystallization with an electron-beam heating is carried out, as a rule, in installations with combined pumping systems [9]. Diffusion pumps are equipped with sorption and condensation traps; sorption, cryogenic and ion-sorption pumps are used to give "oil-free" ultrahigh vacuum. Electron-beam zone recrystallization was carried out in vacuum

$1 \cdot 10^{-6} \ldots 1 \cdot 10^{-5}$ Pa. Choice of pumping system for different methods of refining was determined mainly by degree of interaction of metals with residual gases of the vacuum environment under refining conditions.

2. RESULTS AND DISCUSSION

Results of physical methods of refining of vanadium and titanium which are important components for the production of low-activity alloys for nuclear power are given below. The metals differing by initial degree of purity and method of preparation were used to research the purification processes.

2.1. Vanadium

The initial materials used for research: rods of technical vanadium, electrolytic vanadium VEL-1 and vanadium, which was received by iodide refining (IV). Studies have shown that carrying out EBM of electrolytic vanadium reduces the metallic impurities, for example, chromium concentration was reduced by two orders of magnitude, as well as potassium

concentration was reduced by about 75 times; but no reduction of silicon concentration. Carrying out electron beam melting of vanadium in vacuum $5 \cdot 10^{-4}$ Pa allowed to increase the purity of metal up to 99.95 wt.%. The impurity concentrations of that vanadium are given in Table 1.

Carrying out zone melting can effectively remove impurities of aluminum, iron, nickel, copper and chromium. Silicon is slightly removed while impurities of refractory metals (tungsten, molybdenum, tantalum and niobium) accumulated during long recrystallization of vanadium [10]. Table 2 compares the effectiveness of purification of technical vanadium rods by EBM methods and zone melting (ZM). ZM of vanadium is carried out at a speed of 4 cm/hour. The data in Table 2 show that ZM is more effective method for purification of vanadium samples than EBM. Silicon content in a technical metal is high, and it is the limiting impurity for ZM process.

Table 1

The impurity contents of vanadium, ppm

Metal	Al	Fe	Si	Cu	Cr	Na	K	Mn	Ni	Cl	P	O
Initial	120	70	17	100	850	3	130	1.5	8	42	70	590…800
After EBM	11	10	17	18	7	0.4	1.7	0.11	5	4	0.5	160…200

Table 2

The content of impurities in the technical vanadium after EBM and ZM

Type of metal	Content of impurities, ppm						
	Fe	Cr	Cu	Mo	Si	Mg	Al
Initial	1000	30	5	60	1500	16	200
After EBM in vacuum $5 \cdot 10^{-4}$ Pa	200	< 30	2.4	40	1500	5	20
After ZM in vacuum $2 \cdot 10^{-5}$ Pa	17	< 30	< 1.4	20	1300	< 0.5	< 10

For the study of ZM process IV was also used. The content of impurities in the IV after one pass of ZM is given in Table 3. The distribution of the relative residual resistivity (RRR = R (300 K)/R (4.2 K)) and microhardness of vanadium along the sample are shown in Fig. 1.

High efficiency of this method with respect to reduce concentration of gas-forming impurities was proved by study of thermal desorption of the initial samples and after refining. The dependence of total pressure on heating of vanadium samples in the temperature range 25…800 °C is given in Fig. 2. The degassing 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 correspond to H_2O, CO, N_2, CO_2 etc. The highest intensity of degassing took place in the temperature range 300…600 °C, peaking at about 500 °C [11].
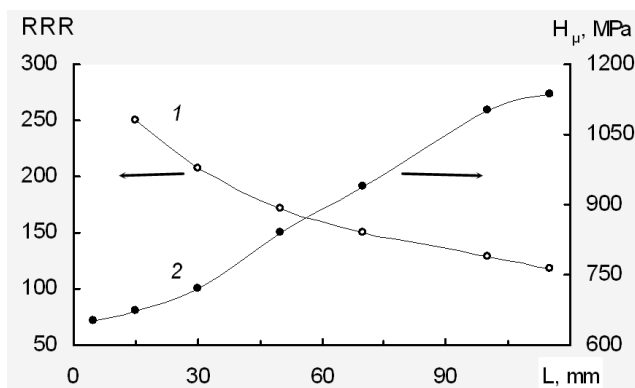

Fig. 1. Distribution of RRR (1) and microhardness (2) along the length of the sample of IV after one pass of molteng zone

Table 3

The content of impurities in the IV after ZM

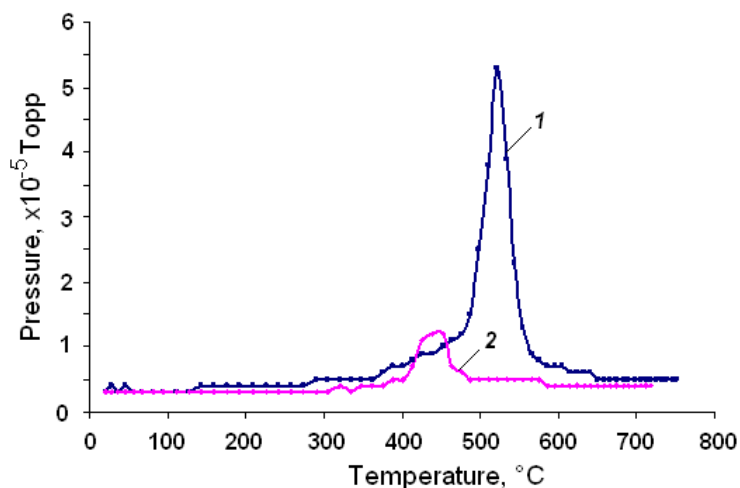| Type of metal		Content of impurities, ppm						
		Fe	Cu	Mo	Mn	Si	Mg	Al
Initial		920	9	13	6	40	1.5	80
After ZM	initial end of sample	150	4.8	16	1	40	<1	<10
	last end of sample	600	11	12	2	37	<1	<10

Fig. 2. The dependence of total pressure of vapors on heating of vanadium before (1) and after refining (2) in temperature range 25…800 °C

The results of metallographic measurements of vanadium samples before and after EBM under vacuum are given in Fig. 3. The initial samples of compacted powders were in tablets form. Refined sample has a relatively large grain with size of about 380 μm, which can be observed visually (see Fig. 3,b). The grains are equiaxial, the grain boundaries are clean. The microhardness of the initial vanadium is $H_\mu = 1090$ MPa, after electron-beam melting $H_\mu = 1440$ MPa. Increasing the microhardness of vanadium after EBM 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 microhardness value.
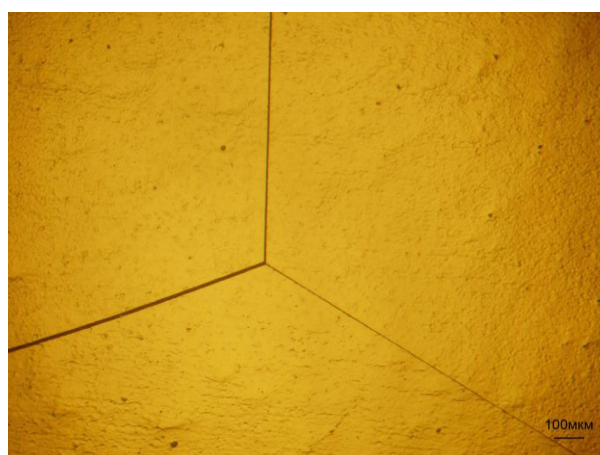
a   *b*

Fig. 3. Obtained samples of vanadium (a) and their microstructure (b)

The most pure vanadium was obtained using method of electrotransport or electromigration on wire samples produced from metal after double EBM of electrolytic powder vanadium. Solid state electrotransport is another technique useful particularly in the removal of interstitial impurities such as H, O, N, and C from refractory metals and has met with unprecedented success. Studies have shown that interstitial impurities are migrated to the cathode side of the vanadium sample when passing a constant electric current of high density,

i.e. effective charge of these impurities is positive. From the numerical solution of the equation for electrotransport follows that at 1650 °C for 200 hours at a current density of approximately $5 \cdot 10^3$ A/cm^2 the electrotransport will result in a significant reduction of oxygen, nitrogen and carbon. It is experimentally shown that under the above conditions the RRR of vanadium samples after purification by electrotransport increases from 50 up to 1600. The chemical composition of high-purity vanadium with RRR = 1200 and purity more than 99.99% wt.%, which was obtained by electrotransport, is as follows (mass spectral method, at.%): Na $< 1.0 \cdot 10^{-5}$; K $- 1.0 \cdot 10^{-5}$; Ca $- 4.0 \cdot 10^{-5}$; Cu $- 5.0 \cdot 10^{-5}$; Mg $< 1.0 \cdot 10^{-5}$; Zn $< 9.0 \cdot 10^{-5}$; Al $- 9.0 \cdot 10^{-5}$; Si $- 2.0 \cdot 10^{-3}$; Ti $- 4.0 \cdot 10^{-5}$; P $- 1.0 \cdot 10^{-4}$; As $- 3.0 \cdot 10^{-5}$; S $< 4.0 \cdot 10^{-5}$; Mn $< 1.0 \cdot 10^{-5}$; Fe $- 2.0 \cdot 10^{-5}$; Cl $- 7.0 \cdot 10^{-5}$; Nb $- 4.0 \cdot 10^{-5}$; Cr $- 1.0 \cdot 10^{-3}$; F $- 1.0 \cdot 10^{-3}$; Ni $- 3.0 \cdot 10^{-5}$; Ga $- 3.0 \cdot 10^{-5}$; Zr $- < 5.0 \cdot 10^{-5}$; Mo $- 2.0 \cdot 10^{-5}$; C $< 1.0 \cdot 10^{-2}$; N$_2 < 1.0 \cdot 10^{-2}$; O$_2 < 9.0 \cdot 10^{-3}$.

Analysis results indicates that for a higher degree of purification of vanadium it is necessary to use combination of different refining methods which would allow remove impurities such as silicon, refractory metals, carbon, nitrogen, oxygen from vanadium. Vacuum distillation of vanadium, which can reduce silicon content in the metal more than ten times as well as impurities of refractory metals, is worth exploring.

2.2. Titanium

Titanium sponge TG-90 and titanium produced by iodide refining (ITi) were used as starting materials for purification by electron-beam melting.

EBM of titanium sponge was carried out in two stages. In the first step the pieces of titanium sponge were heated to a high temperature and melted. Gaseous impurities intensively removed from the metal during heating and melting. During a second stage the obtained ingots were melted by drip melt method. Titanium ingots with diameter of 150 mm and 99.99 wt.% purity were produced by EBM method. The content of impurities in titanium after EBM is given in Table 4.

Analysis of the results of experimental melting of titanium sponge TG-90 showed that the hydrogen content of titanium after EBM decreased by 4.5 times compared to the initial concentration and the concentration of O and N was significantly decreased. The impurity content in the produced titanium ingots decreased much more than required by the standards for titanium.

Table 4

The content of impurities in titanium, ppm

Type of metal	Al	V	Fe	Si	Ni	O	N	H
Initial sponge TG-90	100	3	500	100	400	400	200	72
After EBM	7	1.5	400	5	50	70	15	16

More pure titanium was obtained after EBM of the initial iodide titanium. Impurity contents in the ITi after two electron-beam remelting are as follows: Al $- 8.0 \cdot 10^{-1}$; P $- 1.0$; S $- 8.0$; K $- 6.0 \cdot 10^{-1}$; Ca $- 2.0$; V $- 3.0$; Cr $- 3.0$; Mn $< 9.0 \cdot 10^{-1}$; Fe $- 15$; Ni $- 50$; Cu $- 3.0$; Zn $- 2.0$; As $- 8.0$; Sn < 8.0 ppm.

It should be noted that EBM of titanium favorably affects to the vacuum conditions of the installation due to the good getter abilities of titanium layers deposited on the chamber walls owing to evaporation at EBM [2].

CONCLUSIONS

Regularities refining of vanadium and titanium were investigated; it has allowed reaching a higher level of purity metals by applying methods of electron-beam melting, zone recrystallization and electrotransport in vacuum. These methods had demonstrated high efficiency of purification of vanadium and titanium from interstitial impurities and majority of metallic impurities. Vanadium and titanium in a purity of more than 99.99 % have been produced. Suggested methods for obtaining high-purity metals have created the necessary prerequisites for their use in improving existing and producing new structural materials.

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ЧИСТЫЕ ВАНАДИЙ И ТИТАН ДЛЯ МАЛОАКТИВИРУЕМЫХ СПЛАВОВ

Н.Н. Пилипенко, С.Д. Лавриненко

Рассмотрены процессы рафинирования ванадия и титана от металлических и газовых примесей физическими методами в вакууме. Показана эффективность использования электронно-лучевой плавки, зонной рекристаллизации и электропереноса для очистки этих металлов. Получены образцы титана и ванадия чистотой более 99,99 мас.%.

ЧИСТІ ВАНАДІЙ І ТИТАН ДЛЯ МАЛОАКТИВОВАНИХ СПЛАВІВ

М.М. Пилипенко, С.Д. Лавриненко

Розглянуто процеси рафінування ванадію і титану від металевих і газових домішок фізичними методами у вакуумі. Показана ефективність використання електронно-променевої плавки, зонної рекристалізації і електропереносу для очищення цих металів. Отримано зразки титану і ванадію чистотою понад 99,99 мас.%.