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ALLOY Zr1Nb BASED ON MAGNESIUM-THERMAL ZIRCONIUM

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Refining processes of magnesium-thermal zirconium sponge by methods of electron beam and vacuum arc melting in laboratory conditions were investigated. Properties of obtained test samples of zirconium were studied. The works on optimization of melting of alloy Zr1Nb based on magnesium-thermal zirconium domestic production were made. Complex of research works on studying the properties of alloy ingots was made. Structure, chemical composition, thermal desorption, hardness and microhardness of samples of alloy Zr1Nb obtained by electron beam melting and vacuum arc melting under different conditions were investigated and compared.

The problem of increasing the technical resource of nuclear fuel and the term exploitation of the reactor core materials is one of the most topical today. Perspective direction of solving this problem is the use of alloy Zr1Nb based on magnesium-thermal zirconium for further production of zirconium products and its use in the constructions and production technique of the core elements of nuclear reactors [1–5]. The transition to the chloride-magnesium production scheme of zirconium sponge envisages the development of technology and commissioning of the production of zirconium alloys and products. The technology of obtaining zirconium sponge is developed at the Titanium Institute (Zaporozhe). The quality of zirconium sponge largely determines the technology of initial material preparation for the manufacture of constructional zirconium alloys and implementation of melting manufacture [6, 7].

Researches refining of test samples of magnesium-thermal zirconium sponge obtained at the Titanium Institute have shown that an increased content of impurities in all research sponge parties not allow effective use the method of electron beam melting (EBM) for obtaining high quality zirconium ingots nuclear grade. It was established that in some samples of magnesium-thermal zirconium sponge a content of certain impurities exceeds allowable their content, in particular titanium, iron and interstitial impurities.

The increased content of oxygen in almost all research sponge parties leads to spattering of starting materials during electron beam melting due to a significant amount of gas-forming impurities and the formation of refractory compounds which are not allowed to fully melt the sample and thereby obtain a high quality ingot both content of impurities and on structure. To reduce the gases and other easily volatile impurities a preliminary annealing of the initial sponge was carried out.

Initial sponge was annealed at a temperature of 700, 800, and 900 °C. Preliminary annealing of samples positively influences on the carrying out of electron beam melting: spattering of the sponge is reduced, warm-up time of initial materials decreases and, as a consequence, melting time is significantly less for the annealed sponge as compared with the sponge in the initial state.

The refining processes are actively occurring during electron beam melting. Evaporation of metallic impurities is determined by the melting temperature of zirconium. Therefore impurities whose melting temperature is lower melting temperature of zirconium (Al, Ti, Cr, Mn, Fe, Ni, Cu, Ca, etc.) during electron beam melting evaporate. The content of impurities in magnesium-thermal zirconium after double electron beam melting is given in the Table.

The content of impurities in the zirconium sponge after double electron beam melting, wt.%

Impurity	CTZ-110*	Zr after double EBM
Nb	0.9…1.1	< 0.00005
Hf	< 0.01	0.1
Cd	< 0.00003	< 0.00001
Si	< 0.02	0.0006
Al	< 0.008	0.0001
Ni	< 0.02	0.07
Cu	< 0.005	0.00002
Ca	< 0.03	< 0.0001
Mn	< 0.002	0.00002
Pb	< 0.005	< 0.0001
Ti	< 0.007	0.0092
B	< 0.00005	< 0.00001
Be	< 0.003	< 0.00001
Fe	< 0.05	0.035
Cr	< 0.02	0.00045
O	0.06…0.1	0.14
C	< 0.02	0.008
N	< 0.006	0.0009
F	< 0.003	0.00015
Mo	< 0.005	< 0.0005
Li	< 0.0002	< 0.00001
K	< 0.004	< 0.0001
Cl	< 0.003	< 0.0001

* *Alloy Zr1Nb based on calcium-thermal zirconium*

In order to investigate the influence of vacuum conditions and power of the electron beams on the content and distribution of impurities in the alloy ingots Zr1Nb and to optimize the electron beam melting the research melting at different parameters were carried out.

For specific melting conditions (diameter of crystallizer and melting temperature of metal)

parameters which are changing during melting are the power of the electron beam, vacuum in installation, melting rate. Melting was carried out by the following method: metal was placed on a pallet of crystallizer and was melted on one side and then metal was turned over and was melted on the other side. At such method the rate of melting has been a constant in all the experiments. Therefore the parameters of melting that were changed during electron beam melting were power of electron beam and vacuum in the installation chamber.

During warming up samples the pressure in chamber ranged $(6…8)\cdot10^{-4}$ Torr, in this case power density was 0.20…0.22 kW/cm^2. During melting the pressure in chamber changed in the range $(8.0…60)\cdot10^{-5}$ Torr, power density was 0.28…0.48 kW/cm^2.

Several alloy ingots Zr1Nb was obtained for research the influence of melting parameters on the properties of alloy Zr1Nb.

Research microhardness Zr1Nb of alloy samples showed the following results. Increasing the power at the electron beam melting under the same vacuum conditions leads to lower values of microhardness and the oxygen content in the samples (Fig. 1). For example, microhardness of the sample melted in vacuum $3\cdot10^{-4}$ Torr at power density 0.28 kW/cm^2 is 2310 MPa and at power density 0.48 kW/cm^2 is 2020 MPa.

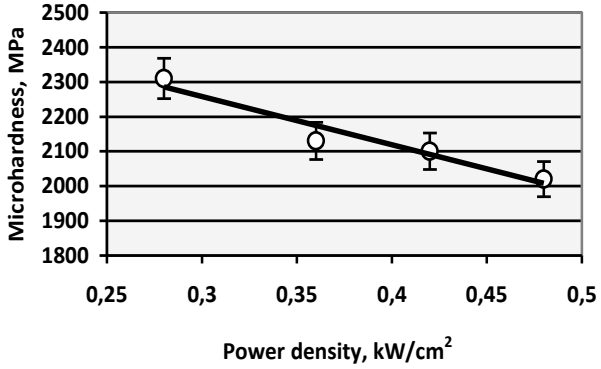

Fig. 1. Changing microhardness of zirconium samples after electron beam melting depending on the power density

Melting at the same capacity but at different vacuum conditions shows lower values of microhardness during melting at higher vacuum as shown in Fig. 2. Microhardness of alloy sample melted at vacuum $6\cdot10^{-4}$ Torr is 2290 MPa and at vacuum $8\cdot10^{-5}$ Torr is 2160 MPa. Both samples were melted with a beam power density 0.36 kW/cm^2.

The double electron beam melting favorably influence on improving the quality of alloy ingots Zr1Nb, i. e. decrease in the content impurities and reducing hardness of the samples. For example hardness of alloy sample after electron beam melting was 2250 MPa and after double electron beam melting was 1700 MPa that satisfies the requirements of technical specifications for zirconium alloy Zr1Nb (1500…1700 MPa).

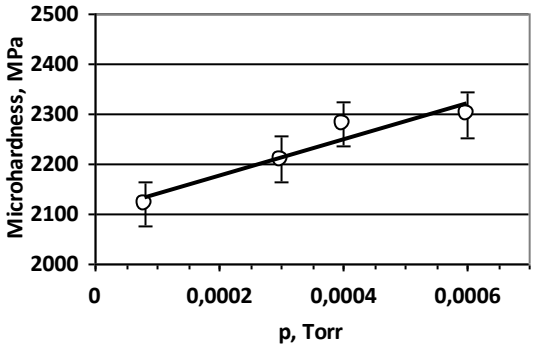

Fig. 2. Dependence microhardness of zirconium samples on the value of vacuum

The same occurs with the oxygen content in the alloy: oxygen content of initial sample was 0.22 wt.%, after electron beam melting oxygen content was 0.18 wt.% and after double electron beam melting oxygen content in the alloy Zr1Nb reduced to 0.14 wt.%. Fig. 3 shows the general data of dependence hardness of alloy samples Zr1Nb on the oxygen content. Using these data it is possible to determine oxygen content in the alloy according to the hardness.

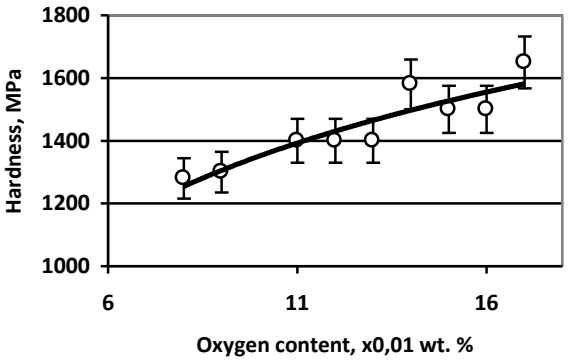

Fig. 3. Dependence hardness of alloy samples Zr1Nb on the oxygen content

Microstructure of magnesium-thermal zirconium after electron beam melting is shown in Fig. 4. As can be seen microstructure of magnesium-thermal zirconium is similar to microstructure of iodide zirconium. It is the same large grains, clean boundaries and set of colors when considering of zirconium grains in polarized light.

For microstructure of alloy Zr1Nb based on magnesium-thermal zirconium after electron beam melting a typical for zirconium alloy structure which resembles a wicker basket is observed. Basic field of grains and grain boundaries are clean, excretions of other phases are not observed.

Microhardness of magnesium-thermal zirconium is 900…1150 MPa. The value of hardness of magnesium-thermal zirconium after electron beam melting is 1350…1450 MPa. It is slightly higher than for electrolytic zirconium after electron beam melting. Apparently the high oxygen content in the initial sponge of magnesium-thermal zirconium is affected. Microhardness of the obtained alloy Zr1Nb is 2100…2250 MPa.

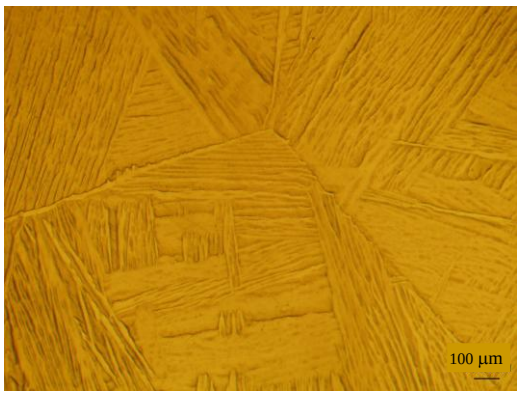

Fig. 4. Microstructure of magnesium-thermal zirconium after electron beam melting

Research of thermal desorption from zirconium sponge after electron beam melting showed that form of curves is similar to curves for initial materials only amount of evolved gases is significantly smaller [8]. Also the second peak (at 650 °C) which is associated with presence of residual amounts of magnesium chloride in zirconium sponge is absent on curve. After melting the second peak is not observed because melting conditions allow removing this impurity from metal what we see on thermal desorption curves (Fig. 5). Amount of evolved gases is 0.05% of the total samples for initial sponge and 0.001% for sponge after remelting.

Researches by gassing show that gassing process from alloys is similar gassing process from zirconium after electron beam melting. Similarity of process can be explained by the fact that alloys were melted under identical conditions from the same initial materials and in identical regimes.

During vacuum arc melting of alloy Zr1Nb the refining processes take place because evaporation of metallic impurities is determined by melting temperature of zirconium, alloy melt and pressure in the gap between electrodes. Thus the metal impurities with melting temperature below melting temperature of zirconium in the arc melting process will evaporate. But the rate of this process will be significantly underestimated due to the higher pressure in the arc gap.

At vacuum arc remelting a melting rate, temperatures of the molten metal and duration in the molten state are rigidly connected to each other. To increase duration of stay in the molten state it is necessary to reduce the power supplied for arc formation, and this leads to a decrease in temperature. The increase in power results in increased melting rate and only a slight increase in temperature. These conditions are not favorable to remove volatile impurities because to increase the evaporation rate is necessary to raise the temperature, and for complete evaporation is necessary a longer time. Evaporation of volatile impurities is also decelerated by relatively high pressure in the zone of the arc discharge which can be on two-three orders of magnitude higher than in the cold upper part of the melting chamber.

Investigation showed that microstructure of magnesium-thermal zirconium after vacuum arc melting is similar to microstructure of iodide zirconium and microstructure of magnesium-thermal zirconium remelted by electron-beam melting. It is the same large crystals with clean boundaries.

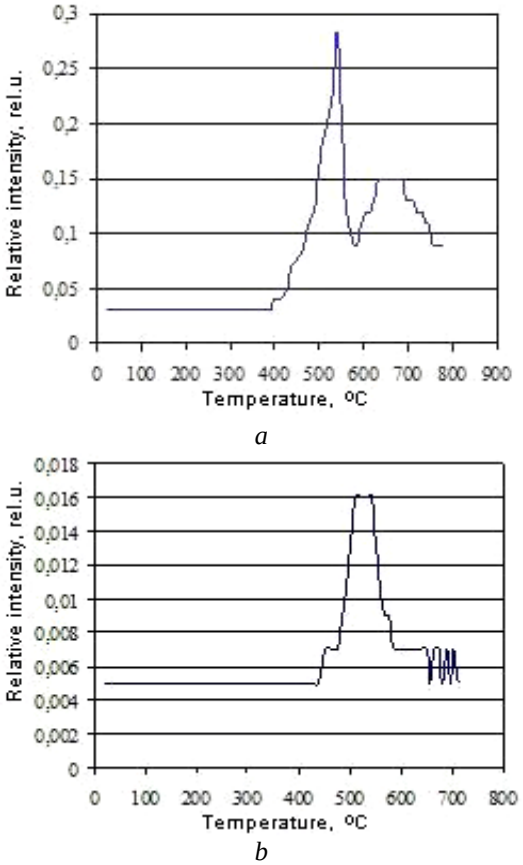

Fig. 5. Thermal desorption of zirconium sponge in initial state (a) and after melting (b)

Measurement showed that microhardness and hardness of magnesium-thermal zirconium after vacuum arc melting is comparable to microhardness and hardness of electrolytic and calcium-thermal remelted metals. Microhardness (H_μ) of magnesium-thermal zirconium is 2100…2200 MPa, for the alloy E-110 microhardness is 2040…2100 MPa and for calcium-thermal zirconium H_μ is 2060…2130 MPa. This slight difference in the values of microhardness is explained by the different content of oxygen in metals as a result of a variety of technologies of the production of initial material.

Research alloy ingots Zr1Nb obtained after vacuum-arc melting on the content of metal impurities satisfy the requirements of the standard ASTM B350 on this alloy. Investigation of the structure of ingots showed that for alloy the characteristic structure which resembles a wicker basket is observed. Basic field of grains is clean, excretions of other phases are not observed. Microhardness and hardness of alloy Zr1Nb corresponds to the hardness and microhardness of alloy E-110.

CONCLUSIONS

Research on obtaining an alloy Zr1Nb based on magnesium-thermal zirconium domestic production at the stages of metallurgical processing has been carried out. The tests of alloys Zr1Nb made by different techniques showed that at obtaining of the alloy ingots

on their quality greatly affect parameters of melting. The results of the studies have shown that for obtaining qualitative alloy ingots it is necessary to carry out electron beam melting under high vacuum conditions, apply the double electron beam melting, carry out control spectra of residual gases in the chamber during the melting, increase power density to reduce interstitial impurities.

The optimal parameters of vacuum arc melting that should be considered at obtaining the alloy Zr1Nb have been determined.

When carrying out vacuum arc remelting a melting rate, temperature of the molten metal and the duration of its stay in the molten state are rigidly connected to each other. Therefore to obtain by vacuum arc melting alloy ingots Zr1Nb required quality is necessary to choose a regime favorable both to maintain power supplied to form an arc and evaporation of impurities. The uniformity of the composition of the ingot at the vacuum arc melting is achieved by repeated remelting.

It is shown that carrying out the meltings with optimal parameters allows obtaining samples of the alloy Zr1Nb which by chemical composition, structure, hardness and microhardness meet the modern requirements of the reactor production.

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СПЛАВ Zr1Nb НА ОСНОВЕ МАГНИЕТЕРМИЧЕСКОГО ЦИРКОНИЯ

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Исследованы процессы рафинирования губки магниетермического циркония методами электронно-лучевой и вакуумно-дуговой плавок в лабораторных условиях. Получены опытные образцы циркония и исследованы их свойства. Проведены работы по оптимизации процессов выплавки сплава ZrNb на основе магниетермического циркония отечественного производства. Выполнен комплекс исследовательских работ по изучению свойств слитков сплава Zr1Nb. Исследованы структура, химический состав, термодесорбция, твердость и микротвердость образцов сплава Zr1Nb, полученных методами электронно-лучевой и вакуумно-дуговой плавок при разных режимах, и проведено их сравнение.

СПЛАВ Zr1Nb НА ОСНОВІ МАГНІЄТЕРМІЧНОГО ЦИРКОНІЮ

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Досліджено процеси рафінування губки магнієтермічного цирконію методами електронно-променевої та вакуумно-дугової плавок у лабораторних умовах. Одержано дослідні зразки цирконію та досліджено їх властивості. Проведено роботи з оптимізації процесів виплавки сплаву Zr1Nb на основі магнієтермічного цирконію вітчизняного виробництва. Виконано комплекс дослідницьких робіт з вивчення властивостей злитків сплаву Zr1Nb. Досліджено структуру, хімічний склад, термодесорбцію, твердість та мікротвердість зразків сплаву Zr1Nb, які отримано методами електронно-променевої і вакуумно-дугової плавок при різних режимах, та проведено їх порівняння.