UDC 621.039; 669.11; 669.24

PURE IRON AND NICKEL FOR NEW STRUCTURAL REACTOR MATERIALS

M.M. Pylypenko[1,2], Yu.S. Stadnik[1], A.O. Drobyshevska[1]
[1]National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
E-mail: mpylypenko@kipt.kharkov.ua;
[2]V.N. Karazin Kharkiv National University, Kharkov, Ukraine

The refining processes of iron and nickel from metal and gas impurities by physical methods in vacuum are considered. The effectiveness of using electron-beam melting for purification of these metals is shown. Iron and nickel in a purity of more than 99.98 and 99.994 wt.% respectively have been produced.

INTRODUCTION

Further development of nuclear energy is associated with the development of the following directions: improvement of the nuclear fuel cycle with minimization of radioactive waste; economical use of uranium resources; reducing the risk of proliferation of nuclear materials; economic competitiveness with other energy sources; safety of operation of nuclear facilities; generation of promising nuclear energy technologies.

The international community collaboration in the development of Generation IV nuclear energy systems has identified a list of robust reactor systems and concepts that can help meet the world's future energy needs [1]. These conceptual reactor systems have advantages in the economy, security, reliability and nonproliferation of nuclear materials. The core temperature of these systems is 600...1200 °C, and the energy spectrum of the neutrons is fast and in some cases is thermal. The implementation of these concepts should be ensured by the development of new structural materials: ferrite-martensitic and austenitic grade steels, nickel alloys and other new alloys.

New structural materials must be pure. We know that high levels of impurities and gases in steels and alloys significantly reduce 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 [2–5]. Iron and nickel are metallic elements which are necessary components to produce new alloys for advanced nuclear energy of present and future.

Steel is considered today as one of the main structural materials for future reactors. Given the complex conditions of operation of various parts and units of nuclear and thermonuclear reactors, increased requirements are set for steels and alloys. Harmful impurities in structural materials significantly affect the strength, corrosion and radiation properties. It is known that the presences of phosphorus, copper, sulfur, lead, bismuth and arsenic in steels greatly affect the low-temperature radiation embrittlement of steels. The negative role of these impurities is the formation of grain boundary segregations and the reduction of grain boundary energy. As a result, conditions for the formation and development of grain-boundary cracks, the main cause of the low-temperature radiation embrittlement, are facilitated [6]. To avoid the low-temperature radiation embrittlement of steels need to reduce the content of harmful impurities in steel by using high-purity metals in the production of steel.

Nickel alloys have good technological, corrosion and radiation properties, which allows them to be considered as promising structural materials for core of fast reactors, thermonuclear reactors and reactors that use molten metals and salts as a coolant. Various nickel-based alloys are manufactured: structural, heat-resistant, corrosion-resistant and other types of alloys.

The impurities in nickel have a significant effect on its structure and properties. Particularly harmful impurities in nickel are sulfur, oxygen, carbon, and some metals that form nickel fusible eutectics (Pb, Se, Bi). Such impurities like lead, tin, antimony, sulfur have harmful effects on the heat-resistant properties of nickel alloys. These fusible impurities are usually located along the grain boundaries and have a negative effect on nickel structural materials in the operating temperature range (600…900 °C) [7].

The basic physical and mechanical properties of nickel and iron are given in Tabl. 1.

Table 1

Basic properties of nickel and iron [8]

Properties	Nickel	Iron
Melting temperature, °C	1453	1539
The coefficient of linear expansion $\alpha \cdot 10^6$, K^{-1} (0…100 °C)	13.5	11.7
Coefficient of thermal conductivity λ, W/(m·K)	0.61	0.71
Resistivity $\rho \cdot 10^6$, Ω·cm	7.2	10.0
Density, g/cm^3	8.9	7.86
Hardness HB, MPa	730	700
Tensile strength $\sigma_в$, MPa	450	200

To reduce the influence of harmful impurities on the operational properties of materials, it is necessary to use pure metals as components of new structural materials with specified properties, as well as to apply modern metallurgical methods for the creation of new alloys. With the industrial production of iron and nickel, it is not possible to achieve a high degree of purity of metals, which is necessary in some cases, so it is very important to investigate the processes of obtaining iron and nickel with low content of impurities.

Iron and nickel are the main components for creating new and promising alloys for the nuclear power industry [9]. Therefore, the study of the processes of refining and obtaining high-purity iron and nickel, as the basis of steels and alloys, from impurities are relevant and of interest when creating steels and new alloys with desired properties for reactors of the future.

1. METHODS AND TECHNOLOGIES FOR REFINING OF 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 the titanium sublimation pump. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6}$ Pa [10]. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals is carried out in vacuum $(1 \ldots 5) \cdot 10^{-5}$ Pa. Refining is conducted in the regime: heating ⇒ melting ⇒ excerpt of metal in molten state ⇒ crystallization ⇒ pulling ingot.

Distillation of iron is carried out on the vacuum installation. The vacuum system of installation provide the pumping speed of 0.5 m^3/s, and the residual pressure of $7 \cdot 10^{-7}$ mm Hg. The crucible filled with the metal was placed in a resistance furnace. On the crucible was put on the condensation column, made from carbonyl iron after EBM of 0.2 mm thickness. 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.

The initial material used Armco-iron rods, sponge of carbonyl iron and electrolytic nickel.

The structure of iron and nickel samples “before” and “after” electron-beam melting has been investigated by metal-graphic method. The samples were examined by optical microscope MMP-4 at different magnifications. The micro-hardness of those samples was measured by PMT-3 apparatus at 50 g loading. In order to determine the impurities concentration in iron and nickel samples the 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 metals samples “before” and “after” electron-beam melting has been studied using experimental set-up with MX7203 mass-spectrometer under vacuum, in temperature range from room temperature up to 800 °C.

2. RESULTS AND DISCUSSION

Results of refining of iron and nickel which are important components for the production of new 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. IRON

For the study the influence of oxygen on purification of Armco-iron, smelts were made at various oxygen partial pressures in the chamber unit. Preliminary experiments have found that the addition of oxygen in the chamber up to pressure of $2 \cdot 10^{-4}$ mm Hg is optimal for removal of carbon. The partial pressure of CO was significantly increased in spectrum of residual gases during meltings with additives oxygen in chamber, indicating that there is intensive purification of iron from carbon on the reaction of formation of carbon monoxide gas.

To determine the optimum time of melt processing of iron by oxygen were carried out smelting at different rates of melting. Melting of iron a rate of 3 mm/min in oxygen at a pressure of $2 \cdot 10^{-4}$ mm Hg in chamber reduces the carbon content from 0.043 to 0.01 wt.%. Decrease the rate of smelting to 1 mm/min reduces the carbon content of the iron to 0.005 wt.% after the first remelting. Furthermore, for efficient removal of carbon requires a considerable overheating of iron.

As a result of experimental meltings optimal parameters for refining Armco-iron were selected: rate of melting – 1 mm/min, vacuum in chamber after adding of oxygen – $2 \cdot 10^{-4}$ mm Hg.

In Tables 2 and 3 present data on the change in the content of impurities in the Armco-iron as a result of the successive electron-beam meltings in vacuum and after adding of oxygen into chamber. As seen from Tabl. 2 EBM of iron in vacuum decreases the content carbon to 0.015 and oxygen to 0.001 wt.%. Subsequent remelting not gives any perceptible change in the content of oxygen and carbon. It should be noted that in EBM process takes place good purification from nitrogen and hydrogen. Carrying out EBM in a vacuum with an increased partial pressure of oxygen leads to a more intensive purification of the iron from carbon. Even the first remelting decreases carbon content up to 0.005 wt.%, there is a decrease of oxygen content up to 0.0008 wt.% too. The second remelting reduces the carbon content to 0.003 wt.%, but happens a slight increase of the oxygen content in iron. The third remelting in oxygen does not give significant change in the carbon content, but the oxygen content increases. Therefore, the third remelting of iron in vacuum with an increased partial pressure of oxygen is undesirable.

The oxygen environment was also useful for refining iron from silicon, although the EBM in a vacuum practically does not reduce the silicon content (see Tabl. 3). Vapor pressure of silicon is low when iron the melting point and therefore the evaporation of silicon at vacuum melting not occur. Carrying out three consecutive EBM in oxygen leads to a substantial reduction of the silicon content in the iron to 0.02 wt.% (see Tabl. 3), obviously, due to the formation of gaseous compound SiO, because SiO_2 have low volatility. Substantial reduction of content of the copper, tin and manganese also occurs, but content of nickel and chromium in the iron after EBM is practically not changed. Brinell hardness of the initial samples of Armco-iron was 830 MPa, after refining – 624 MPa.

Table 2

Changing the content of interstitial impurities in Armco-iron after EBM, wt.%

Material	Vacuum at the EBM, mm Hg	Carbon	Oxygen	Nitrogen	Hydrogen
Initial	–	0.043	0.02…0.008	0.010	0.0001
1 EBM	$(14…8)\cdot10^{-6}$	0.015	0.001	0.0008	0.0001
2 EBM	$(10…8)\cdot10^{-6}$	0.015	0.001	0.0003	<0.0001
3 EBM	$(8…6)\cdot10^{-6}$	0.014	0.001	0.0003	<0.0001
1 EBM	After adding of oxygen to $2\cdot10^{-4}$	0.005	0.0008	0.0008	<0.0001
2 EBM		0.003	0.0010	0.0007	<0.0001
3 EBM		0.003	0.0040	0.0040	<0.0001

Table 3

Changing the content of metallic impurities in the Armco-iron after EBM, wt.%

Material	Vacuum at the EBM, mm Hg	Si	Al	Cu	Ni	Cr	Sn	Mn	Mg	Pb
Initial	–	0.14	0.003	>0.10	0.30	0.055	0.026	>0.02	0.0002	0.0006
1 EBM	$(14…8)\cdot10^{-6}$	0.13	0.003	0.03	0.30	0.040	0.0014	0.0026	0.0002	0.0006
2 EBM	$(10…8)\cdot10^{-6}$	0.15	0.003	0.016	0.30	0.035	0.0006	0.0006	0.0002	0.0006
3 EBM	$(8…6)\cdot10^{-6}$	0.12	0.003	0.007	0.30	0.024	0.0006	0.0009	0.0002	0.0006
1 EBM	After adding of oxygen to $2\cdot10^{-4}$	0.12	0.003	0.011	0.28	0.040	0.0037	0.0016	0.0002	0.0006
2 EBM		0.05	0.003	0.007	0.24	0.040	0.0006	0.0010	0.0002	0.0006
3 EBM		0.02	0.002	0.006	0.25	0.036	0.0006	0.0006	0.0002	0.0006

The impurity contents in carbonyl iron after EBM are shown in Tabl. 4. It is evident that the most difficult impurities to remove in vacuum are cobalt and nickel. The Brinell hardness of samples of carbonyl iron after EBM was 558 MPa.

Table 4

Content of impurities in carbonyl iron

Impurity	Content of impurities $\mathbf{x}10^3$, wt.%		
	Initial	After EBM	Distillate
Mn	120	2	0.1
Al	20	10	0.3
Cu	150	10	4
Co	17	17	8
Ni	150	100	20
Si	200	50	2
C	50	10	1
O	30	20	2
N	6	3	<1

To further reduce the content of impurities distillation method was adopted. Impurity content in iron after distillation (bottom of distillation column, T = 1500 °C) are shown in Tabl. 4. It is possible to obtain metal purity more than 99.98 wt.% by distillation of the carbonyl iron remelted by EBM. The purity level of iron is largely determined by the content of nickel and cobalt.

2.2. NICKEL

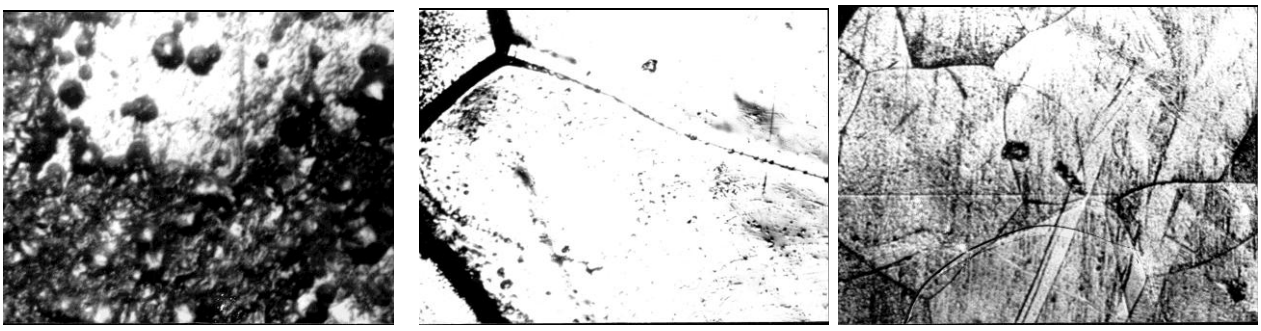
Double EBM in a high vacuum of initial electrolytic nickel with purity 99.987 wt.%, allowed to obtain metal with purity 99.994 wt.%. The refining resulted in reduction of Fe, Co, P, Al, Mg while the concentration of As, Zn, Se, Cl decreased significantly. The impurity contents in nickel after EBM are shown in Tabl. 5. Purification of nickel by EBM from metallic impurities and interstitial impurities has been experimentally demonstrated. Electron beam remelting of nickel leads to reduction of the content of interstitial impurities – oxygen, nitrogen, carbon up to 0.0005, 0.00006, and 0.002 wt.%, respectively. Such interstitial impurities content has practically no effect on the properties of nickel. If purity of nickel is increases then the hardness decreases, for hardness HB = 1690 MPa, and for nickel after two EBM – 800…900 MPa. Microhardness values also decrease for nickel after refining. For the initial nickel microhardness H_μ = 1610 MPa, and for nickel after two EBM – 1100…1270 MPa, which indicates an increase in the purity of the metal.

Table 5

The content of impurities in nickel

Impurity	Initial	After two EBM	Impurity	Initial	After two EBM	Impurity	Initial	After two EBM
Al	0.00009	0.00006	Pb	0.00007	0.00007	Zn	0.0041	0.0008
As	0.00004	0.00001	Mg	0.00005	0.00004	Sn	0.00005	0.00005
Cd	0.00005	0.00005	Co	0.0026	0.0009	Si	0.00003	0.00003
Fe	0.002	0.0017	Bi	0.00004	0.00004	Cu	0.0017	0.0017
P	0.0001	0.00007	Cl	0.0005	0.0002	Se	0.0014	0.00027

Studies of the nickel microstructure showed that the structure of nickel after EBM is significantly different from the structure of the initial metal (Figure). The nature of the grain structure of the samples after EBM is as follows: in the central part of the ingot there are large equiaxed grains ~ 3.2 mm in size, in the peripheral part - small, elongated ~ 0.13 mm in size. There are accumulations of impurities along the grain boundaries in nickel after the first remelting (see Figure), and the grain boundaries are clean after the second remelting, there are no accumulations of impurities along them, and the number of inclusions significantly decreased (see Figure), indicating that efficiency of refining nickel by method EBM.



a *b* *c*

The microstructure of nickel:
a – initial (x110); b – after the first EBM (x100); c – after the second EBM (x145)

CONCLUSIONS

Application of pure and high-purity metals as initial materials for components of construction of nuclear power plants largely determines the further development of nuclear energy: high purity steel for reactor vessel provides increased service life, reliability and safety of the reactor pressure vessels; new high-temperature, corrosion-resistant and radiation-resistant materials of construction – the basis of the elements of a new generation of reactors to ensure their high performance.

The electron beam melting had demonstrated high efficiency of purification of iron and nickel from interstitial impurities and majority of metallic impurities. Studies have shown a significant improvement in the quality of the metals after refining. Iron and nickel in a purity of more than 99.98 and 99.994 wt.% respectively 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.

REFERENCES

1. *A technology roadmap for generation IV nuclear energy systems, issued by U.S. DOE nuclear energy research advisory committee and the Generation IV international forum (GIF – 002-00).* Washington, 2002, 91 p.

2. V.M. Azhazha, S.D. Lavrynenko, M.M. Pylypen-ko. Pure and super pure metals in atomic energy // *Problems of Atomic Science and Technology. Ser. "Vacuum, pure materials, superconductors"*. 2007, N 4, p. 3-12.

3. M.M. Pylypenko. Construction materials for the elements of equipment of nuclear-power plants // *The Journal of Kharkiv National University. Physical series: Nuclei, Particles, Fields.* 2009, N 859, issue 2(42), p. 44-50.

4. V.N. Voyevodin. Actual problems of scientific and technical support of safe operation and development of the nuclear power complex of Ukraine // *Herald of the National Academy of Sciences of Ukraine*. 2014, N 8, p. 25-32.

5. S.D. Lavrynenko, M.M. Pylypenko. Pure Metals for Nuclear Power // *SMC Bulletin*. 2015, v. 6, N 1, p. 19-24.

6. Н.М. Бескоровайный, Б.А. Калин, П.А. Платонов, И.И. Чернов. *Конструкционные материалы ядерных реакторов*. М.: «Энергоатомиздат», 1975, 704 с.

7. Б.А. Калин, П.А. Платонов, Ю.В. Тузов и др. *Конструкционные материалы ядерной техники*. М.: НИЯУ МИФИ, 2012, 736 с.

8. Е.А. Ульянин, Т.В. Свистунова, Ф.Л. Левин. *Высоколегированные коррозионно-стойкие сплавы*. М.: «Металлургия», 1987, 88 с.

9. M.M. Pylypenko. The role of high-purity metals in the creation of new materials for structural elements NPP // *Problems of Atomic Science and Technology. Ser. "Vacuum, pure materials, superconductors"*. 2008, N 1, p. 10-17.

10. G.F. Tihinsky, G.P. Kovtun, V.M. Azhazha. *Obtaining of ultrapure rare metals.* M.: "Metallurgy", 1986, 160 p.

Article received 21.03.2019

ЧИСТЫЕ ЖЕЛЕЗО И НИКЕЛЬ ДЛЯ НОВЫХ КОНСТРУКЦИОННЫХ РЕАКТОРНЫХ МАТЕРИАЛОВ

Н.Н. Пилипенко, Ю.С. Стадник, А.А. Дробышевская

Рассмотрены процессы рафинирования железа и никеля от металлических и газовых примесей физическими методами в вакууме. Показана эффективность использования электронно-лучевой плавки для очистки этих металлов. Получены образцы железа и никеля чистотой более 99,98 и 99,994 мас.% соответственно.

ЧИСТІ ЗАЛІЗО І НІКЕЛЬ ДЛЯ НОВИХ КОНСТРУКЦІЙНИХ РЕАКТОРНИХ МАТЕРІАЛІВ

М.М. Пилипенко, Ю.С. Стаднік, А.О. Дробишевська

Розглянуто процеси рафінування заліза і нікелю від металевих і газових домішок фізичними методами у вакуумі. Показана ефективність використання електронно-променевої плавки для очищення цих металів. Отримано зразки заліза і нікелю чистотою понад 99,98 і 99,994 мас.% відповідно.