ELECTRON BEAM REFINING IN PRODUCTION OF PLATINUM AND PLATINUM-BASE ALLOYS

Information 1. Electron beam refining of platinum

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Commercial technology for production of platinum in ingots with content of the base element not less than 99.99 % was developed.

Keywords: electron beam remelting, platinum metals and alloys, impurity elements, melting conditions

Platinum metals (platinum, palladium, rhodium and iridium) and alloys on their bases are unique structural materials, capable of standing for many hundreds and thousands hours thermal and mechanical stresses in corrosive oxidizing media at extraordinary high homologous temperatures — $(0.70–0.95)T_m$ (1200–2300 °C).

Among known high-temperature metal and nonmetal materials platinum metals and alloys have no equivalent substitutes. That's why optimization of composition and increase of high-temperature strength of platinum metals and alloys for the purpose of achieving long service life and efficiency of application of the manufactured from them items is an extremely important task [1]. In majority of cases platinum is base of the materials for production of crucibles, vessels, and feeders for cooking and melting of glasses and manufacturing of different items from them, frequently operating at temperature above 1200 °C in air [2].

As production volumes of quality glasses, glass fibers, and single crystals grow, deficit of platinum metals and first of all platinum continuously increases because of their limited reserves in the earth crust.

According to requirements of GOST 12341–81, 12 impurity elements are regulated in platinum. Practice shows that certain impurities are permissible within certain limits, presence of some of them has to be strictly controlled in special application of the metal, while presence of others causes unsuitability of platinum for application. So, suitable for commodity application is platinum with total content of impurities less than 0.02 %, for work at high temperatures — less than 0.01 %, for thermoelectric converters platinum with total content of impurities less than 0.002 % and in production of optical fibers less than 0.001 %, is suitable. The most frequently impurity elements form solid solutions with platinum with melting point lower than that of platinum (copper, iron, nickel, etc.), or low-melting and brittle phases (silver, lead, stannum, silicon, antimony, barium, bismuth, arsenic, aluminium, magnesium, zinc, phosphorus, selenium, tellurium, etc.), which cause failure of platinum under load and high temperature conditions. At majority of enterprises of Ukraine control over content of oxygen and carbon in platinum is absent, which causes wrong estimation of the degree of platinum purity.

Impurity elements in platinum exert great influence on its physical and mechanical properties. That's why purity of platinum is one of important characteristics. Depending upon content of impurity elements platinum is conditionally divided into platinum of technical (99.80 %), chemical (99.90 %), physical (99.99 %), and spectral purity. Company «Johnson Mattie» produces platinum, having purity 99.999 %.

In this connection more and more actual become problems of rational and efficient application of platinum and platinum metals.

Goal of this work is development of the commercial technology for production of platinum in ingots with content of the base element not less than 99.99 %.

Technological scheme envisages hydrometallurgical refining of platinum with production of platinum sponge to be remelted in an induction furnace for production of platinum in ingots. Supplied scrap of platinum materials (platinum, rhodium, palladium) with content of platinum 70.0–99.5 % is subjected to hydrometallurgical refining with separation by elements of platinum metals and their simultaneous cleaning from impurities. The refining process finishes in production for further processing of platinum sponge with platinum content not less than 99.6 %.

Melting of titanium sponge was carried out in the induction high-frequency furnace in the rammed crucible from magnesium oxide that ensured high productivity of the process. However, in induction melting, carried out in air, contamination of platinum by oxygen, nitrogen, hydrogen and other gases, as well as by the crucible material — magnesium oxide, occurs.

Production of high-purity platinum (99.99 %) was carried out by its remelting after induction melting in the UE-178 commercial electron beam furnace, de-

Table 1. Chemical composition of platinum ingot before and after EBR, %

Chemical element	Before EBR	After EBR	*K*	Before EBR	After EBR	*K*
Pt	99.94	99.99	--	99.95	99.99	–
Pd	0.004	0.001	4	0.005	0.0013	4
Rh	0.005	0.004	1.25	0.003	0.003	1
Ir	<0.002	<0.002	1	<0.002	<0.002	1
Ru	<0.003	<0.003	1	<0.003	<0.003	1
Au	<0.002	0.0005	4	<0.0005	<0.0005	1
Pb	0.001	<0.0005	>2	0.001	<0.0005	>2
Fe	0.003	0.0025	1.2	0.002	0.001	2
Si	<0.005	<0.005	1	<0.005	<0.005	1
Sn	<0.0005	<0.0005	1	0.0008	<0.0005	>1.6
Al	<0.0005	<0.0005	1	<0.0005	<0.0005	1
Ag	0.001	<0.0005	>2	0.001	0.0001	10
Cu	0.0015	<0.0005	3	<0.0005	<0.0005	1
Ni	0.0008	<0.0005	>1.6	<0.0005	<0.0005	1
Mg	0.04	0.0005	80	0.009	0.001	9
Zn	<0.001	<0.001	1	0.001	0.0001	10
Sb	<0.0005	<0.0005	1	<0.0005	<0.0005	1
Î$_2$	0.002	0.0001	20	0.001	0.0001	10
Ñ	0.001	0.0001	10	0.002	0.0001	20

signed at the E.O. Paton Electric Welding Institute of the NAS of Ukraine (Figure 1).

In the process of development of melting conditions influence of specific power of electron beam and rate of melting on degree of refining and mass of the evaporated metal was considered.

In Figure 2 dependence of the platinum evaporation rate upon temperature, calculated according to Langmuir equation on basis of the data on pressure of saturated vapors of platinum under conditions of experimental electron beam remelting (EBR), is presented. Langmuir equation [3] describes interconnection between rate of sublimation k_s and pressure P of the substance vapor:

$$k_s = P\sqrt{M/2\pi RT},$$

where M is the atomic or the molecular weight; R is the gas constant; T is the absolute temperature, °C.

One can see from the Figure that the higher is temperature of platinum, the more intensive is process of its evaporation. Critical increase of the platinum evaporation rate was registered at the temperature above 2400 °C.

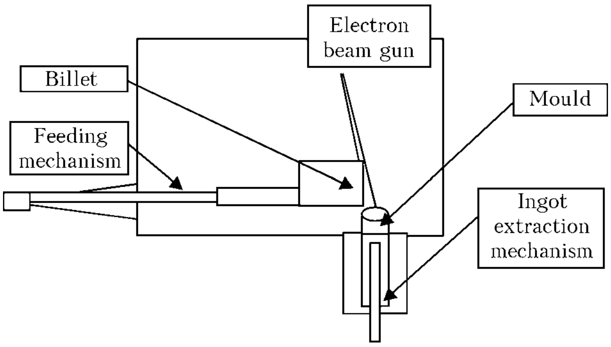

Figure 1. Technological block diagram of UE-178 electron beam installation

As a result of carried out works practical confirmation of the calculated data was obtained. Amount of evaporated and then condensed on screens and internal surfaces of the working chamber metal achieved in some melts 2–4 % of the alloy mass of the remelted metal. Content of platinum in the condensates constituted 92–98 %. That's why subsequent experimental works were directed at determination of optimal EBR conditions, which allow removing impurities at minimal evaporation of platinum.

Experiments in refining of platinum showed that low-melting non-ferrous metals (aluminium, copper, stannum, magnesium, zinc, antimony and lead) are subjected to deep refining (Table 1). Values of coefficient K of removal of mentioned metals vary from 125 to 80. Gas impurities reduce by one order.

Palladium is also volatile in refining remelting of platinum. Mean value of coefficient of its removal from platinum is, approximately, 5. Analysis of experimental melts showed that from the viewpoint of efficiency of cleaning of elements with high volatility it is necessary to overheat the melt to a lower degree. In this case it is rational to carry out EBR at specific power of electron beam 0.50–0.55 kW / cm^2.

Refining of platinum from iron turned out to be rather difficult task. Comparing pressure of platinum and iron vapors [4], one may assume that iron, pressure of vapors of which equals pressure of palladium vapors, may be removed from platinum by means of EBR. However, calculations of degree of separation of the metals, based on pressure of vapors of the ele-

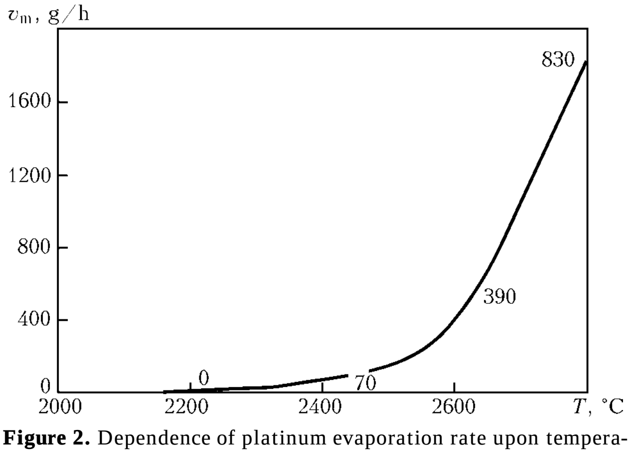

Figure 2. Dependence of platinum evaporation rate upon temperature of melt in EBR

Table 2. Chemical composition of platinum ingot after EBR, %

Chemical element	Platinum sponge	Ingot of induction melting	EBR ingot	GOST 12341–81 (Grade PlA-0)
Pt	99.6	99.95	99.9925	99.98
Pd	0.006	0.006	0.002	Σ 0.015
Rh	0.002	0.002	0.002	
Ir	0.002	0.002	<0.002	
Ru	0.001	0.001	<0.001	
Au	0.002	0.002	<0.001	0.002
Pb	0.003	0.002	<0.001	0.002
Fe	0.003	0.002	0.0015	0.003
Si	0.002	0.002	0.002	0.002
Sn	0.0045	0.004	<0.001	0.001
Al	0.001	0.001	<0.001	0.002
Ag	0.0033	0.003	<0.001	0.005
Cu	0.002	0.002	<0.001	0.002
Ni	0.001	0.002	<0.001	0.001
Mg	0.003	0.008	<0.001	0.002
Zn	0.002	0.002	<0.001	0.002
Ca	–	–	<0.001	Not regulated
Cr	–	–	<0.001	–
K	–	–	<0.001	–
Mn	–	–	<0.001	–
Mo		–	<0.001	–
Zr	–	–	<0.001	–
Sb	0.001	0.001	<0.001	0.001
Î$_2$	0.01	0.006	<0.001	Not regulated
Ñ	0.002	0.002	<0.001	–

ments, show only relative evaporation rate of the components [5]. Experimental data demonstrated that process of iron evaporation in the Pt–Fe system proceeds rather slowly. Triple refining remelting allowed reducing content of iron in platinum from 0.98 to 0.43 %, but evaporation of platinum in this case achieved 9.8 %, which may be explained by high chemical affinity of iron and platinum, unlimited solubility of platinum in γ-Fe, and high level of the interatomic bond strength in the melt.

Degree of platinum refining from impurities may be changed within wide limits by varying rate of remelting, corresponding to sufficient degree of refining at minimal sublimation of platinum. For determining optimal rate of remelting seven experimental melts were carried out at constant specific power 0.5 kW / h and rate from 2.5 to 9.0 kg / h. The investigations resulted in selection of optimal range of the melting rate — v_m = 4–5 kg / h [6].

Under optimal conditions of platinum refining more than 20 kg of platinum of not less than 99.99 % purity were produced (Table 2), which is confirmed by the data, obtained by the «Degussa-Huels» company.

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