ELECTRON BEAM MELTING AND REFINING – ANOTHER POSSIBILITY FOR RECYCLING OF METAL SCRAP

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Abstract: *Electron beam melting and refining (EBMR) is one of the modern and widely used technologies which is employed industrially for melting and metal purification. Experimental investigations, computational modeling and optimization approaches are indispensable tools in the study of this ecological technology, for the development and optimization of effective technological schemes and their application to different materials as well as for reducing the price of the pure metals produced. On the basis of experimental and theoretical studies performed, data and results of practical importance for various applications of EBMR are obtained and summarized (for Cu, Ta, Hf, Ti, Au, etc.). The obtained results allow us to formulate requirements on the process parameters and are important and useful in view of studying, controlling and optimizing the quality and purity of the new materials obtained by recycling of metal scrap by EBM.*

Keywords: ELECTRON BEAM MELTING, REFINING, REFRACTORY METALS, REACTIVE METALS, ALLOYS, RECYCLING OF SCRAP, IMPURITIES

1. Introduction

Electron beam melting (EBM) in vacuum has played an important role for production of ultrapure materials and alloys, for recycling of metal wastes (including refractory and reactive metals), for purification of metallurgical-grade silicon to solar-grade silicon, etc. [1-14]. Due to a high vacuum level and superheating, the EBM provides efficient refining processes and superior refining level of gases, metals and non-metals inclusions [2]. The use of water-cooled copper crucible, where the raw material is melted, refined and solidified leads to absence of additional pollution due to the contact between the material and the refractory oxide ceramic pot, typically used in the conventional metallurgy. There are no special requirements concerning the kind of the raw (started) material which is an additional advantage of the e-beam melting method. The produced metal ingots are with homogeneous microstructure, have better performance characteristics and their weight varies from a few grams (pure metal tablets) to a few tons (large component production in airspace industry, nuclear reactors, etc.). The production of each metal requires a successful process control, leading to decreasing the quantity of the unwanted impurities so the refined metal has to meet requirements for quality and composition, depending on the intended new applications.

The EBMR method has gained wide application in production of metals with high purity such as Cu, W, Zr, Ti, Mo, etc., and it has also an important role in recycling of metal wastes [1,12,15] containing valuable metals that have been oxidized or polluted (enriched with impurities) in their previous processing or applications. It is important to find optimal process conditions for achieving maximal level of impurities removal and minimal weight and energy losses.

There is dynamic increase in construction, implementation, and exploitation of equipment for obtaining pure metals and special alloys by EB melting in the recent years in countries like the USA - a certain leader in e-beam melting as well as in countries with developing nuclear power and space industry (China, India, etc.) which are definitely interested in this technological method. Manufacturers of refractory metals and their alloys (in the USA and in EU countries such as France, Germany, UK as well as manufacturers in Ukraine, Russia, China, India, etc.) are highly interested in developing such technologies concerning the production of wide variety of metals and alloys.

The world's recourses of many valuable metals are exceedingly limited. At the same time there are some large amounts of metal wastes collected in the country from different productions and after the laying-off of many metallurgical and metal-working manufacturing plants. Metal scrap is also collected as a result of wearing out of equipment in plants.

For countries (e.g. Bulgaria) that do not produce many metals due to the lack of ore products, the recycling of wastes of industrial use is important. As a result of studying, realized by asking the biggest industrial factories it was found that in Bulgaria there are some large amounts of metal wastes, including refractory and reactive metals and their alloys [15]. The scrap materials are mainly used catalysts, containing V_2O_5, Mo; used capacitors, containing Ta, and chips and small pieces of Ti, Hf, W and Mo, broken knifes, stale bearings and other used components from different kinds of alloyed steels. Their quantities vary from 100 tons to 10 000 tons.

The reuse of the refined metals needs to satisfy certain requirements for quality and composition that are set by the companies using these metals depending on their new applications. A major requirement to the developed refining technology is the high quality and reproducibility of the metal compliant to the corresponding standards (ASTM, BDS, etc.). The production of each metal is unique and the selective removal of impurities from the metal wastes is important. These impose the need to search for specific technological schemes and development of process regimes for different raw (initial) materials and for specific e-beam equipment [16-19].

Investigations and experiments dealing with the relations of EBM process parameters and impurities removal at EBMR of different metals, including refractory, reactive and precious ones, special alloys and scrap recycling are performed. Obtained data and results for various applications of EBMR are summarized and presented in the paper.

2. Results and discussion

Investigation was performed in the laboratory "Physical problems of electron beam technologies" at the Institute of electronics of the Bulgarian Academy of Sciences (IE-BAS). Experiments were carried out using 60 kW e-beam installation ELIT 60 (Fig. 1) with one electron gun (1), horizontal feeder (2), water-cooled copper crucible (3), and extraction system (pulled mechanism) (4).

In electron beam melting the refining processes take place mainly at the interface molten metal/vacuum [2] in three zones (Fig. 1): zone I – the front part of the started material (feeding rod), zone II – generated droplets and zone III – liquid pool (in the water-cooled crucible).

At right choice of EBM process parameters, proper thermodynamic, hydrodynamic and kinetic conditions for taking place of refining processes, concerning various impurities in each reaction zone, can be created. During the process, by changing the e-beam power and the casting velocity it is possible to control the geometry of the liquid pool, the temperature distribution in the reaction zone and the duration of the thermal influence on the metal, which influence on the refining processes and on the quality of the obtained metal (after EBMR).

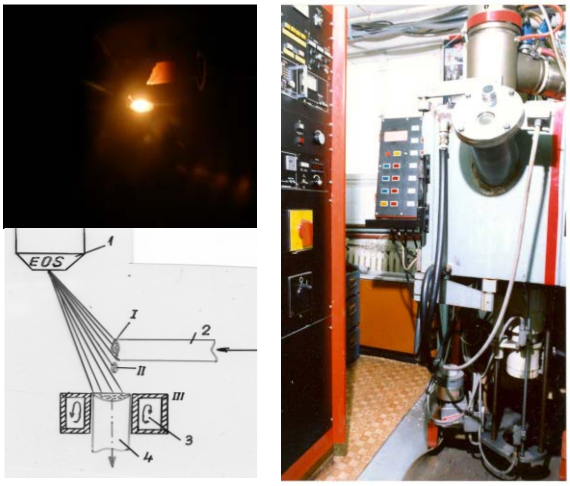

Fig. 1 *ELIT 60 equipment and principal scheme of e-beam melting and refining drip process.*

For development of particular technology for electron beam refining of metals it is necessary to study in details the thermodynamic limits for each chemical reaction and its rate, namely refining kinetics. Knowledge referred to the process mechanisms at e-beam refining allows more precise control the chemical composition of the obtained metals and alloys and allows obtaining alloys with given composition. This requires study of the limiting processes and factors determining the liquid pool geometry and behavior of the metals and their compounds during the refining as well as precise evaluation of the temperature field distribution.

Experimental and theoretical investigations of the processes at EBMR of various metals, including refractory, reactive and noble ones (Ti, Mo, Zr, Ta, Hf, Ni, Cu, Al, Au, Pt, etc.) and special alloys were performed and the corresponding technologies were developed. The obtained results and the various applications of EBMR method can be summarized and systemized as follows:

2.1. EBMR as a final step of the conventional metallurgical methods for production of pure metals

In many cases it is possible to involve the EBMR at an earlier stage of the conventional metallurgical process. In this way, resources such as time, funds, etc. for obtaining metals with high purity and without defects, with geometry and dimensions near to the desired ones for their application, can be reduced. In Table 1 obtained results for EBMR of titanium, zirconium, copper, molybdenum and nickel are presented. The initial material for each of these metals was material with high level of impurities' concentrations – gases, metal and non-metal inclusions (C_0 is the initial concentration, i.e. before EBM, C is the concentration after EBM, P is the e-beam power, η_i is removal efficiency of the specific impurity, Φ is the diameter of the obtained ingot after EBM).

Table 1: *EBMR of metals.*

Me	C_o, %	$C_{o[O]}$, ppm	P, kW	C, %	$C_{[O]}$, ppm	η_i, %
Ti	99,86	1000	15	99,97	150	78,6
Cu	99,5	500	15	99,994	10	98,8
Zr	99,73	900	15	99,95	144	81,5
Mo	99,2		30	99,95		93,7
Ni	99,4		15	99,97		95
Φ = 60 mm						

For example, in the case of EBMR of titanium and zirconium the initial material was compacted powder concentrate (titanium and zirconium sponge); the used raw material for EBMR of copper was anode copper in which the concentrations of oxygen ($C_{o[O]}$) and of metal impurities were high. Due to the fact that there are no special requirements for the kind and the characteristics of the started (raw) material, copper from the various stages of the conventional electrolyte production – anode, cathode capper, etc. can be used as initial material. During the refining a lot of impurities serve as a gather that pulls up and combines the oxygen from the copper oxides in stable oxides, which are removed from the liquid copper through distillation. Thus both the oxygen concentration and the concentration of the metal impurities in the refined material decrease and the purity of the obtained copper (after EBMR) is higher than the purity of the electrolyte copper. For EBMR of molybdenum and nickel the initial material was concentrate or compound.

The produced metal after refining solidifies (crystallizes) in the water-cooled crucible and the ELIT 60 installation allows to obtain ingots with diameters Φ = 50 mm, 60 mm, 80 mm or 100 mm and the ingot length – up to 25 cm (Figs. 1-3).

Fig. 2 *Zirconium ingot obtained by EBMR of zirconium sponge.*

Fig. 3 *Pure metal sample obtained after EBMR.*

2.2. EBMR for recycling of targets: Al, Au, Ag, Pt, Ti, Cu, Co

In many recent methods for layer deposition such as magnetron sputtering, electron beam, ion and laser evaporation etc., metal targets with high purity and strict requirements concerning the shape and the composition are used. During the process some parts of the targets are partially spent and the bigger part remains unused as expensive metal scrap with high purity.

At recycling of these used targets it is important to achieve desired geometry without changes in the chemical composition. Usually, the requirements concerning the chemical composition are connected with the concentration of gases and especially the oxygen concentration. Sometimes there are requirements about other impurities – for example at recycling of rectangular aluminum targets the requirements were connected with the removal of the alkali metal elements and their concentrations had to be less than 0,1 ppm. After EB recycling the concentration of the alkali metals decreases 10 times (Table 2).

Table 2: *EBM of used metal targets with high purity.*

Me	dimens., mm	P, kW	C_{i0}, ppm	$C_{0\,[O]}$ ppm	C, %	C_i, ppm	$C_{[O]}$, ppm
Al	285 x 160 x 15	7,5	alk Me 0,1	1	99,9	alk Me 0,01	1
Au	Φ 60	7,5		1	99,97		1
Ag	Φ 60	7,5		1	99,97		1
Pt	Φ 80	10		1	99,97		1
Ti	285 x 160	11		15	99,94		10
Cu	Φ240 x 15	25		10	99,97		10
Co	Φ 60	20		10	99,9		10

EBMR method offers various possibilities concerning the geometry of the obtained materials – their shape and dimensions. Using proper equipment elements – crucibles, made with desired shape and dimensions – the obtained targets after EBMR do not need additional processing and can be used for their applications (Fig. 4).

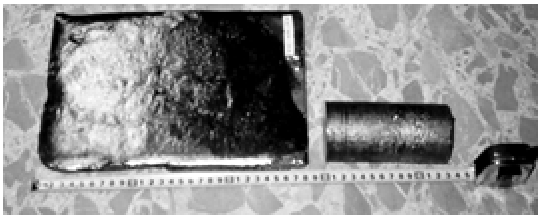

Fig. 4 *Titanium targets regenerated by EBMR.*

The application of EB method in the case of precious metals recycling is especially valuable due to the fact that it is possible to minimize the material losses.

2.3. EBMR for recycling of used metals (Ta, Hf, Ti, Ni) enriched with gases

Bulgaria is not a traditional producer of many metals that are active toward the oxygen at high temperatures (such as titanium, hafnium, tantalum, nickel, etc.) due to the lack of ore products. These metals have unique physicochemical and chemical properties and that is why they are of present interest to various productions such as medical implants, artificial joints, materials for vacuum components and special equipment, electronic components, etc. (Fig. 5). At their use and processing considerable quantities of high quality metal scrap are obtained. These pure metals with unique properties were oxidized and their reuse is possible after treatment aiming to remove the oxygen and to decrease the oxygen concentration in the composition. The EBM is a proper refining method for this purpose [1,4,5,12]. The oxygen is in the solid metal scrap as oxides that pass to the liquid pool at heating. Part of them dissolves or dissociates in the liquid pool volume and another part moves and reaches the top surface (the interface molten pool / vacuum) and also dissociates due to the low relative weight. Due to the higher temperatures at the surface and the contact with the vacuum environmental, the level of dissociation of the oxides and the efficiency of the refining processes are higher (Table 3).

Ta

Hf

Fig. 5 *Initial material (metal scrap) and ingots obtained after EBMR of tantalum and hafnium.*

Table 3: *EBMR of oxidized pure metals.*

Me	C_o, %	$C_{o[O]}$, ppm	Φ, mm	P, kW	C, %	$C_{[O]}$, ppm
Ti	99,5	1500	100	25	99,9	400
Ni	99,7		60	16	99,9	
Ta	98,9	800	100	35	99,9	400
Hf	99,6	1000	60	25	99,9	500

The obtained results show that after EB refining the oxygen concentration in hafnium can decrease up to 4 times, in zirconium – 7 times and in titanium – 10 times. Additional removal of other volatile metal impurities (such as aluminum, calcium, nickel, copper, etc.) is also possible and their concentration also decreases (up to 30 times).

2.4. EBMR for recycling of used alloys where unwanted inclusions have to be removed – Co-alloy, Cu-Ag-Ni alloy, high-speed steel and bearing tool steel

Usually, the properties of special alloys strongly depend on the proportion and the quantity of the alloyed components in the obtained composition after EBMR. Some results for recycling of: Cu-Ag-Ni alloy intended for high temperature vacuum solders, Co-alloy with low fraction of nonmetal impurities, dedicated for producing heart implants and high-speed steel and bearing tool steel are presented in Table 4.

Table 4: *EBMR of alloys with spatial purpose.*

Me	alloy comp.	$C_{o\,[O]}$	impur	ΔG,	P,	alloy comp	$C_{[O]}$	impurities
	C_o, %	ppm	ppm	%	kW	C, %	ppm	η_i, %
Cu/Ag/Ni	84,9/11,7/ 1,5	290				86,5/10,3/ 2,0	10	
P6M5	W, Mo/C, Cr, V, Co			1%	12	C = Co		
P18	W, Mo/C, Cr, V, Co		N, S	4%	12	C = Co		N=100% S=76,2%
ШХ15	Cr, Mn, Ni, Si, V				14	C = Co		
Co-alloy	Mn = 4,31 ppm	104	S=40			Mn=2,4 ppm	4	S=28ppm

The main problem at recycling of alloys is the selection of proper conditions at which the removal of the unwanted impurities takes place while keeping the proportion of the alloyed components unchanged at minimal material losses. This is very important especially in the case of alloys with special purpose and it requires process investigation leading to finding optimal conditions (process parameters) ensuring maximal level of unwanted impurities removal and creation of desired structure at minimal losses of the alloyed elements. The obtained ingots are without defects and the alloyed components are uniformly distributed in radial direction and along the sample.

2.5. EBMR for obtaining multiple metals through recycling of metal scrap

Another important application of EBMR is separation of valuable metals at recycling of wastes in which the metals present as compounds – carbides, oxides, sulfides, etc. or as impurities with high concentrations. The possibility for influencing the thermodynamic and kinetic conditions for EB refining allows pure metal obtaining from these compounds through chemical decomposition and their collection in the condensate.

When the main impurities are valuable metals with high concentrations in the raw material and have high removal efficiency, their complete removal can take place for technological conditions which are also optimal process conditions for the base metal purification. For example, at EB recycling of tungsten scrap with high level of cobalt (3,5 %) and molybdenum (1,1 %) in the initial material, high removal efficiency is seen: η_{Co} = 97,1 % and η_{Mo} = 99,6 %. The provided evaluations show that the cobalt quantity generated in the condensate is more than a half of the condensate mass and the molybdenum mass is about a quarter of the condensate. In this case additional processing of the generated condensate aiming to obtain molybdenum and cobalt as pure metals is recommended and justified taking into account their characteristics and applications.

3. Conclusion

Research is conducted and technologies are being developed as the obtained applications of the electron beam method for melting and refining of various metals and alloys with special purpose are summarized and systemized. The obtained results show a wide variety of possible applications of the e-beam method for melting, refining, and recycling of materials that contain refractory, reactive and precious metals. All of these applications are technically possible, economically reasonable, and environmentally friendly. Through each of them the most suitable and up-to-date approach is developed for processing an important category of waste materials - obtaining valuable metals, which can be used by the local economy; increasing their exploitation characteristics through refining/ homogenizing of the metals/metal alloys, as well as optimizing their price when selling these materials on a local, European, or international level.

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