Obtaining of pure molybdenum through electron beam melting of scrap materials

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Investigations are carried out applying electron beam melting method for obtaining of pure molybdenum from waste materials. The obtained results are presented and factors controlling the refining processes of metal impurities have been also studied. Effective technological schemes for obtaining of pure molybdenum with good structure are proposed.

Получаване на чист молибден чрез електроннолъчево топене на материали, съдържащи молибден (Ваня Василева, Катя Вутова, Мария Наплатанова, Негеговнивари Муниратнам, Динеш Амалнеркар). *Представени и анализирани са резултати от проведени изследвания за получаване на чист молибден чрез електроннолъчево топене и рафиниране на молибденов концентрат и чрез рециклиране по електроннолъчев метод на отработени материали, съдържащи молибден. Предложени са ефективни технологични схеми за получаване на молибден с висока чистота и качествена структура.*

Introduction

Electron beam melting and refining of materials is a widely used physics method [1-8]. Initially, in metallurgy the Electron Beam Melting and Refining (EBMR) applications have been mainly exploited for melting and refining of refractory metals such as molybdenum, tungsten, niobium, tantalum, vanadium, and their alloys. That it is justified by the specific properties of these metals (high melting temperature and high chemical activity to gases), which make them resistant to treatment with the conventional metallurgical methods. EBMR remains a preferred method (sometimes it is even the only possible method) in special electrometallurgy irrespective of the experience acquired over the years and the extended set of applications.

The EBMR method does not have special requirements to the type of initial (raw) material but it still ensures a good refinement level of gases, non-metal, and metal impurities with higher volatility than that of the metal being refined (the base metal). In addition to the metallurgy of refractory metals, the electron beam melting method is also suitable for recycling of waste materials consisting of such metals, their compounds, and their alloys.

The present paper is part of a series of studies related to the application of EBMR for recycling of waste materials that contain refractory metals such as tantalum, vanadium, tungsten, molybdenum, etc. and their alloys and compounds. The results in the paper are obtained at electron beam recycling of waste materials containing molybdenum.

Molybdenum is a refractory metal with unique properties that is used in variety of industrial sectors such as metallurgy – for alloying of steels and manufacturing of high temperature and corrosion-resisting alloys, manufacturing of vacuum tubes – as a main constitutive material in light sources, manufacturing of mirrors for gas dynamic lasers, molybdenum compounds (molybdates, oxides, sulfides) are good catalysts, coloring pigments, and components of glazes and mixtures.

After the suspension of Bulgarian metal processing industries and closing of plants such as Kremikovtzi Metallurgical Works, Non-ferrous Metal Works, Svetlina Works, etc., lot of unused wastes containing refractory metals and their alloys remained in the territory of Bulgaria, and in particular molybdenum and its compounds. Recently conducted survey [9] showed that these wastes consist mainly of particles and castings of molybdenum concentrates, turnings, cuttings and wasted hard metal strips containing molybdenum, and other wastes of the metallurgy and electronic industries.

Data of EBMR experiments for obtaining high purity molybdenum that is fit for re-use are analyzed and presented in the paper. The experiments have been performed with waste metals and alloys containing molybdenum – cuttings of molybdenum strips, molybdenum turnings, pieces and mouldings of molybdenum concentrates.

Factors controlling the refining processes of metal impurities in the refined molybdenum for each particular raw material and technological regime (process conditions) have been also studied in the paper. The removal efficiency of the impurities for each studied technology process (conditions) has been used as a criterion for evaluation of efficiency at EBM.

Experiments, results and discussion

The experiments have been carried out using an electron beam installation for melting and refining ELIT-60 in the Laboratory “Physical problems of electron beam technologies” in the Institute of electronics at the Bulgarian Academy of Sciences (IE-BAS). The maximum power of the electron gun is 60 kW. The initial (raw) material has been horizontally fed into the melting zone [4,10].

Samples of waste materials containing molybdenum with different concentration and containing tungsten, niobium, iron and other metal impurities are used as initial materials. For the experiments the materials have been pre-processed and prepared – oil removal treatment and they have undergone chemical and metallographic analysis. Appropriate technological regimes (EBMR process parameters) for which the thermodynamic and kinetic limitations are taken into consideration, that depend on the chemical composition, have been realized for each particular raw material. The chemical composition of the samples before and after EBMR has been defined by emission spectral analysis.

Extraction of pure molybdenum through electron beam melting and refining (EBMR) of molybdenum concentrate

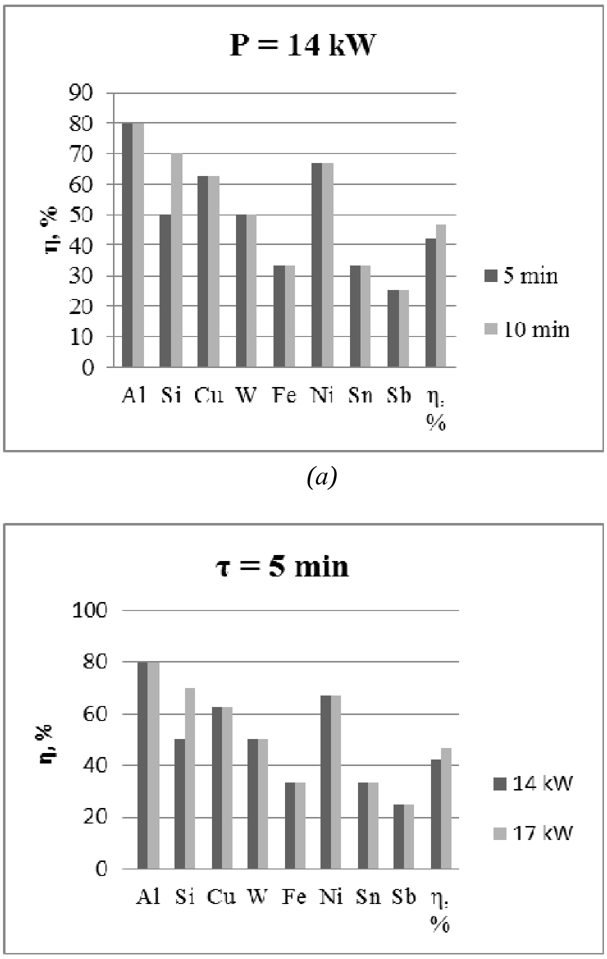
The concentration of molybdenum in the initial material has been 95.4 %. The main impurities with concentrations above 1 % have been Sb – 2 % and Si – 1 %. A concentration between 5000 ppm and 100 ppm in the raw material has been measured for the rest of the metal impurities (Al, Ni, Sn, W, etc.). After oil-removal treatment, well dried pieces of the initial material have been refined once (single melting) under the following process conditions: electron beam power 14 – 17 kW and duration of the refinement process 5 – 10 min. A chemical analysis of the initial material and the samples after each e-beam melting process has been performed. The results obtained are shown in Table 1 (Σ_i - total concentration of the studied impurities, [%]; P_b - electron beam power [kW]; τ - melting time, [min]).

Table 1

Impurities concentrations at EBMR of molybdenum concentrate

P = 14 kW					**Concentration, %**									
	τ, *min*	**Al**	**Si**	**P**	**Ti**	**Cu**	**W**	**Fe**	**Ni**	**Rh**	**Sn**	**Sb**	**Σ i**	**Mo**
M-0	**0**	0,5	1	0,1	0,01	0,08	0,2	0,03	0,3	0,08	0,3	2	4,6	95,4
M-11	**5**	0,1	1	0,1	0,01	0,03	0,1	0,02	0,1	--	0,2	1,5	2,7	97,34
M-21	**10**	0,1	0	0,1	0,01	0,03	0,1	0,02	0,1	--	0,2	1,5	2,5	97,54
τ = 5 kW					**Concentration, %**									
	P , *kW*	**Al**	**Si**	**P**	**Ti**	**Cu**	**W**	**Fe**	**Ni**	**Rh**	**Sn**	**Sb**	**Σ i**	**Mo**
M-0	**0**	0,5	1	0,1	0,01	0,08	0,2	0,03	0,3	0,08	0,3	2	4,6	95,4
M-11	**14**	0,1	1	0,1	0,01	0,03	0,1	0,02	0,1	--	0,2	1,5	2,7	97,34
M-32	**17**	0,1	0	0,1	0,01	0,03	0,1	0,02	0,1	--	0,2	1,5	2,5	97,54

In Fig.1 the charts of the removal efficiency of the controlled impurities after EBMR of molybdenum concentrate are given: (a) removal efficiency vs. melting time τ at a constant electron beam power P_b = 14 kW; (b) removal efficiency vs. e-beam power P_b at melting time τ = 5 min.



(a)

(b)

Fig.1. Removal efficiency η_i=(C_0-C)/C_0.100% of metal impurities at EBM of molibdate.

The maximum overall removal efficiency η = 46.7 % is obtained at duration of τ = 10 min and P_b = 14 kW as well as at τ = 5 min and beam power of P_b = 17 kW. A removal efficiency of the main impurities between 80 % for Al and 25 % for Sb has been achieved under these process conditions; the concentration of Mo after the EBMR is 97.54 %.

The results show that there are no thermodynamic limitations for the removal of impurities from the initial material at EBMR of molybdate under the studied proportion of impurities in the raw material. The increase of electron beam power over 14 kW and the increase of refinement time over 5 min do not significantly increase the purity of the metal being refined. For EBMR at P_b = 14 kW and τ = 5 min the removal efficiency is 42.17 % and at P_b = 17 kW (τ = 5 min) or τ = 10 min (P_b = 14 kW) – it is 46.7 %. Hence, the overall removal efficiency *(η)* does not significantly increase with the increase of e-beam power or the duration of melting process.

Metallographic studies of samples of Mo concentrate have been performed before and after EMBR. It is found that the dendritic metal structure of the raw material after EMBR at P_b = 14 kW changes to coarse grain texture. With the increase of electron beam power to 17 kW the grains' size reduces. Figure 2 shows metallographic photos of Mo before and after EMBR.

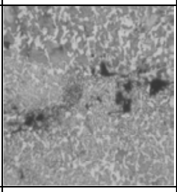
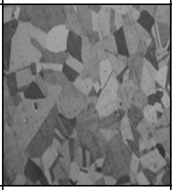
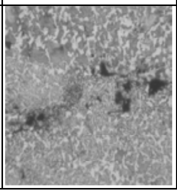
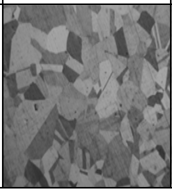
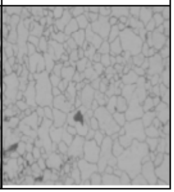
	0	**5 min**	**10min**
14 kW			
	0	**14 kW**	**17 kW**
5 min			

Fig.2. Structure of molybdenum before and after EBMR.

EBMR of molybdenum scrap (strip and chips)

Two series of experiments have been conducted with Mo scrap with different concentration of the molybdenum in the initial material.

<u>Series 1</u>: The raw material consists of Mo strips cuttings with purity of ≈ 98.4 %; the main impurities are Fe – 1.3 %, Nb – 0.2 % and Zr – 0.1 %. The other controlled impurities are W, Mn, V, Al, and Ti and their concentration is under 650 ppm.

Experiments were performed in single melting for 5 min with beam power P_b = 19 kW and in double-melting (in two operations) for 5 min with P_b = 17 kW at the first EBM process and P_b = 22 kW at the second melting, respectively. Figure 3 presents the chart of chemical composition and structures of the samples before and after EBMR. The charts show concentration of impurities with the highest content in the initial material (Fe, Nb, Zr), the total concentration of all other impurities existing in the raw material (Σ_i , %), and the total concentration of all controlled impurities (Σ_I , %).

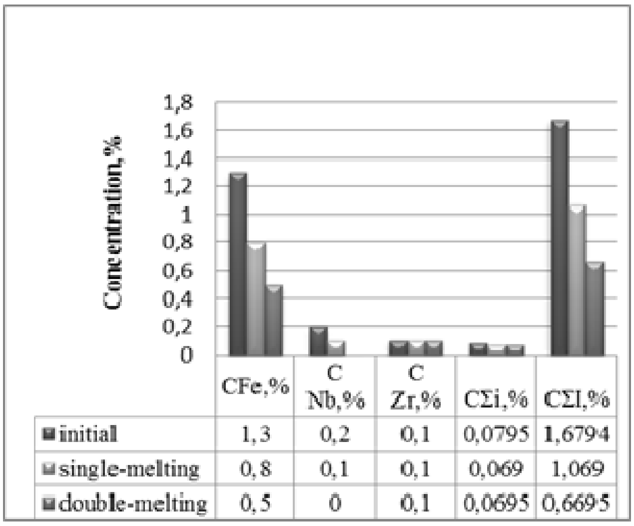


Fig.3a. Concentration of impurities in molybdenum after single and double-melting operation.

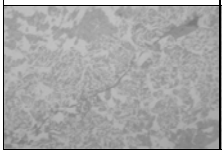
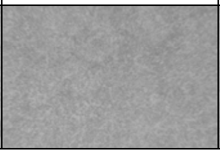
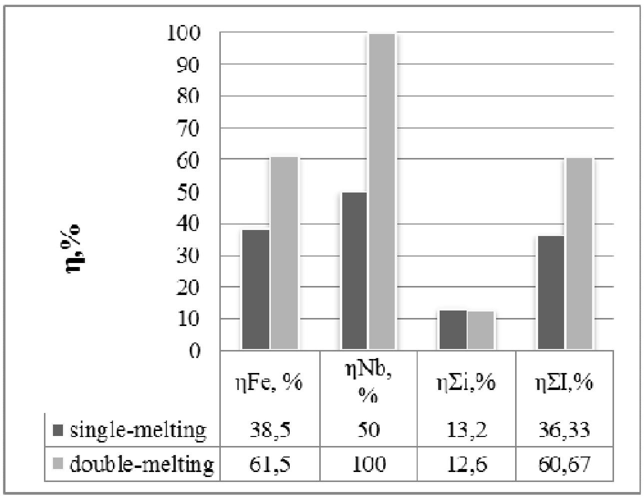
initial material	**Single-melting** P_b=19kW, τ=5min	**Single-melting** P_b=17kW, τ=5min **Double-melting** P_b=22kW, τ=5min
		

Fig.3b. Structure of molybdenum after single and double-melting operation.

The removal efficiency η for each technological regime has been evaluated and this is the key indicator for selection of refinement process conditions. The results are given in Fig.4. The analysis has revealed that the removal efficiency of impurities with high concentrations in the initial material (and respectively the overall removal efficiency) during double EB melting of molybdenum scrap (strips) is high – over 60 %; and the purity of the obtained Mo increases with one order – to Mo 99.34 %.



	ηFe, %	ηNb, %	ηΣi,%	ηΣI,%
■ single-melting	38,5	50	13,2	36,33
■ double-melting	61,5	100	12,6	60,67

Fig.4. Removal efficiency at single and double-melting operation of molybdenum scrap.

Series 2: The initial material consists of a mixture of high purity chips – Mo (75 %) and W (25 %). The concentration of each of the other controlled impurities, namely – Mn, Zr, Si, and Cu – is less than 60 ppm excepting Ti – 0.9 % and Ta – 0.1 %.

The raw material is refined in single melting and in double-melting. During the single melting process the electron beam power was P_b =10 kW and melting time τ = 5 min. At the double-melting the duration of each of the refining operations was τ = 5 min, at P_b = 20 kW and P_b = 25 kW for the first and the second melting process, respectively.

It has been found that during the single and double-melting the overall removal efficiency η is 22 % regardless of the increase in the electron beam power; the Mo/W proportion in the cast and after the melting remains unchanged. Hence, the electron beam melting and compacting of this scrap material is not economically viable.

Conclusions

A more appropriate technological regime (conditions) for EMBR of waste materials, containing molybdenum or its compounds, is the double-melting process at short e-beam treatment (up to 10-min heating time) regardless of the electron beam power.

The obtained results show that when the initial material contains molybdenum compounds or molybdenum that is mechanically mixed with another refractory metal (e.g. W), the electron beam melting and refining process is applicable only in the cases where no strict requirements for the chemical composition and structure of the recycled/refined material are demanded. In such cases metal impurities, which are chemically bonded with Mo or that have similar thermo-physical properties to those of Mo (e.g. W), cannot be removed.

After double electron beam melting of Mo strips the molybdenum purity increases 10 times. This is mainly due to the high removal efficiency of impurities that have high concentration in the source material (Fe, Nb). The obtained pure molybdenum could be reused in various areas such as metallurgy, energy industry, electronics, medicine, etc.

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