Effects of process parameters on electron beam melting technogenic materials for obtaining rare metals

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Abstract. In this paper, effects of electron beam melting process parameters (e-beam power, refining time, etc.) and the number of melting operations for fulfilling the requirements concerning the composition and the structure of metals obtained after e-beam processing are studied. Results obtained at electron beam melting of molybdenum and tungsten technogenic materials are presented and discussed. The refining efficiency is evaluated and effective technological regimes (process parameters) for production of metals which meet specific requirements for high-purity and good-quality structure after electron beam melting of Mo and W technogenic materials are proposed.

1. Introduction

A sustainably increasing demand for high-purity metals with wide range of applications such as production of special alloys, hi-tech devices in electronics, electrical engineering, transport, military, petroleum, chemical industries, instrument engineering, etc. has been observed in the recent decades. The majority of these metals have a high value of the stock utilization index. For ferroalloys metals such as tungsten and molybdenum the index values are 2.88 % and 1.51 % respectively. This means there is a high risk for depletion of the world's mineral resources. Recycling of electronics scrap and urban waste has a great potential for obtaining a large part of the metals needed [1, 2].

Due to the high melting temperature, the classic method for extracting the rare metals molybdenum and tungsten includes reduction of their oxides to metal powder, which afterwards is blended into compact metal by sintering. This method of processing does not provide good enough ductility and weldability (ability to be welded). The physicochemical properties of sintered tungsten and molybdenum are anisotropic and they depend on the powder’s initial conditions, purity, and structure before the sintering process [3]. The metal obtained after reduction has a high percentage of impurities and it needs to be further refined. Vacuum-arc melting and electron beam melting are the two well-established refining methods in the industrial manufacturing of pure tungsten and molybdenum and their alloys in countries such as the U.S. and Russia.

Processing of metal-containing technogenic materials (wastes) by melting with vacuum-arc and electron beam methods is environment-friendly and economically viable solution. With vacuum-arc
method, the metals are melted in furnaces with melting electrodes in copper water-cooled crucible. This method, however, does not provide high enough metal purity. Low casting velocity is not possible as well as no separate control of melting speed and heating is possible, which results in weak metal refining.

In modern electrometallurgy, the electron beam melting and refining is most perspective for making high purity refractory and reactive metals and alloys, superalloys and also for purification of silicon for photovoltaic applications and recycling technogenic materials containing expensive metals and alloys [4-8, 1, 2]. The refining process is efficient as it takes place in high-vacuum chambers with high energy electron beams that can be accurately controlled regardless of the metal being processed. The method allows for a selection of process parameters in order to meet the requirements for the composition and structure of the refined metal. The method also allows for casting metal ingots with improved structure, surface, properties and free of unwanted impurities [9-14]. For the regeneration of small quantities of expensive metal to be competitive, maximum compliance of the processed material to the particular requirements is needed or high purity materials (alloys) need to be obtained.

In the present work, electron beam melting (EBM) method in processing technogenic materials containing the rare metals molybdenum and tungsten was investigated. Different EBM technological schemes for studying the effect of e-beam treatment on removal of impurities were used. The relationship between the purity of the materials and the melting process parameters such as refining time, beam power and number of melting operations is investigated and discussed.

2. Results and discussion

2.1. Experimental procedure

The raw (source) materials used in the experiments are two types technogenic materials – cuttings of molybdenum strips with purity of 98.21% molybdenum and used (spent) tungsten electrodes with 97.69% tungsten and 0.34% thorium. For the experiments the raw materials have been pre-processed and prepared – oil removal treatment and they have undergone chemical and metallographic analysis. The experiments were performed using 60 kW electron beam equipment for melting and refining ELIT-60 in the Institute of electronics at the Bulgarian Academy of Sciences, laboratory “Physical problems of electron beam technologies”. The source material was placed in the water-cooled copper crucible with a diameter of 50 mm and a height of 60 mm and then the material surface was irradiated (heated) by the e-beam (figure 1). The working vacuum pressure was $3\cdot6 \times 10^{-3}$ Pa.

Figure 1. Schematic diagram of the electron beam melting process: 1) electron beam; 2) metal liquid pool; 3) solidifying metal ingot; 4) water-cooled side walls of the crucible; 5) water-cooled bottom.

Appropriate technological regimes (process parameters) for which the thermodynamic and kinetic limitations are taken into consideration, that depend on the chemical composition, were applied to each particular raw material. The chemical composition of the samples before and after EBM processing was defined by emission spectral analysis.
2.2. **EBM of molybdenum technogenic material**

The source material consists of Mo strips cuttings with purity of 98.21% and the main impurities are Fe 1.3%, Nb 0.2% and Zr 0.1%. The other controlled impurities are W, Mn, V, Ti, Al and Si and their concentration is under 650 ppm.

Experiments were performed in two refining cycles – (i) in single melting (EBM1) for heating time \( \tau \) of 5 min with beam power \( P_b \) of 19 kW and (ii) in double-melting (EBM2, in two operations) for the same refining time \( \tau = 5 \text{ min} \) with \( P_b = 17 \text{ kW} \) at the first melting process (EBM2\( _1 \)) and \( P_b = 22 \text{ kW} \) at the second melting operation (EBM2\( _2 \)), respectively.

Table 1 presents the data for the chemical composition of the metal samples before and after EBM processing and the concentrations of all controlled impurities are shown. The removal efficiency \( \eta \) of impurities for each technological regime (process conditions) was evaluated and this is the key indicator for selection of refinement process conditions. The results are given in table 2.

| Concentration | Fe  | Nb  | Zr  | W  | Mn | V  | Ti  | Al  | Si  |
|---------------|-----|-----|-----|----|----|----|-----|-----|-----|
| Before EBM    | 1.3 | 0.2 | 0.1 | 0.065 | 0.0055 | 0.0035 | 0.0025 | 0.003 | 0.0025 |
| After single EBM, C (%) | 0.5 | 0.1 | 0.1 | 0.055 | 0.0035 | 0.003 | 0.0015 | 0.002 | 0.0015 |
| After double EBM, C (%) | 0.15 | 0.0 | 0.1 | 0.045 | 0.0015 | 0.0015 | 0.001 | 0.0015 | 0.001 |

**Table 2.** Values of the removal efficiency \( \eta \) at EBM of molybdenum.

| \( \eta, \% \) | \( \eta_{Fe} \) | \( \eta_{Nb} \) | \( \eta_{Zr} \) | \( \eta_{W} \) | \( \eta_{Mn} \) | \( \eta_{V} \) | \( \eta_{Ti} \) | \( \eta_{Al} \) | \( \eta_{Si} \) | \( \eta_{total} \) |
|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|----------------|
| After single EBM | 61.54 | 50 | 0 | 15.38 | 36.36 | 14.28 | 40 | 33.33 | 40 | 54.75 |
| After double EBM | 88.46 | 100 | 0 | 30.77 | 72.73 | 57.14 | 60 | 50.00 | 60 | 82.12 |

The analysis has revealed that after e-beam melting processing only Zr has not changed its concentration \( \eta_{Zr} = 0\% \) for the applied regimes, while Nb after double-melting operation (EBM2) has been completely removed \( \eta_{Nb} = 100\% \). For each of the other controlled impurities, the removal efficiency (the degree of refining) increases approximately two times after double-melting processing of the molybdenum technogenic material (table 2).

It has been found that the overall removal efficiency \( \eta_{total} \) is 54.75% in the case of single refining, while for double-melting \( \eta_{total} = 82.12\% \) and the purity of the obtained Mo (99.68%) increases with one order of magnitude (tables 1, 2). This is mainly due to the high extent of removal of impurities that have high concentration in the source material (such as Fe and Nb) for which there are no thermodynamic limitations for their refinement.

To reveal the microstructure of Mo specimens, a chemical etching with the reactive prepared by mixing 68% HNO\(_3\) acid, 98% H\(_2\)SO\(_4\) and distilled water in a 1: 1: 1 ratio was used. The etching time was 20-30 s. In this study, optical microscopy Leica DM2500 with digital camera Leica EC3 was used to investigate the topography of microstructures of polished and etched surfaces at different magnification.

The basic parameters that influence the macro- and the microstructure of Mo are the temperature gradient \( G \) and the cooling rate \( R \) [15]. When the \( G/R \) ratio is big, i.e. the temperature gradient is high and the cooling rate is low, big planetary grains are formed out. The \( G/R \) ratio decreases with the increase of cooling rate and the microstructure of molybdenum transforms to equal-axed grains or a dendrite structure. If impurities are present in the smelt and the cooling is fast, at first a dendrite matrix is formed, next the eutectic smelts solidify, and finally the remaining liquid phase of the basic metal crystallizes. In the sample of the source material, a fine crystalline structure is observed, while in the sample obtained after double-melting at high temperature and total refining time of 10 min, well-formed cubic-shaped crystals are observed (figure 2). They correspond to the crystalline structure of pure Mo cooled down at a very low rate.
2.3. EBM of tungsten technogenic material

The source material for e-beam melting spent electrodes of tungsten consists of rods of W with diameter of 5 mm and purity of 97.69% and content of Th 0.34%. In accordance to the task’s requirements, the content of thorium should be reduced to 0.2% and the concentration of other impurities present in the initial material should also be reduced, so that the purity of tungsten after the refining is higher than 99%.

A series of experiments have been carried out with the source material being exposed to single e-beam melting (EBM1) at power of 12 kW (EBM11) and 17 kW (EBM12) for 40 min and processing (EBM13) at power of 22 kW for 30 min. The purity of tungsten increases after e-beam melting in each of the investigated single melting regimes EBM11, EBM12 and EBM13 (table 3). The effect is obvious after a double process of refining (EBM2) where the tungsten, obtained after single refining processing for 40 min at beam power of 17 kW (EBM21), is refined for a second time for 40 min at power of 12 kW (EBM22). As a result, the tungsten purity obtained is 99.9% which is higher in comparison to the tungsten purity achieved for each of the investigated single refining regimes (table 3).

Table 3. Purity of W and impurities’ concentration at EBM of tungsten.

| Concentration       | W   | Th | S   | Cu | Fe |
|---------------------|-----|----|-----|----|----|
| Before EBM          | 97.69 | 0.34 | 0.29 | 0.36 | 0.32 |
| After single EBM11, C (%) | 99.00 | 0.0  | 0.06 | 0.34 | 0.31 |
| After single EBM12, C (%) | 99.43 | 0.0  | 0.0  | 0.29 | 0.18 |
| After single EBM13, C (%) | 99.73 | 0.0  | 0.0  | 0.19 | 0.0  |
| After double EBM, C (%) | 99.9 | 0.0  | 0.0  | 0.05 | 0.0  |

Table 4. Values of the refining efficiency ($\eta$) at EBM of W.

| $\eta$ (%) | $\eta_{\text{Th}}$ | $\eta_{S}$ | $\eta_{\text{Cu}}$ | $\eta_{\text{Fe}}$ | $\eta_{\text{total}}$ |
|------------|-------------------|------------|-------------------|-------------------|------------------|
| After single EBM11 | 100   | 79.31   | 5.55  | 3.12  | 56.71  |
| After single EBM12 | 100   | 100     | 19.44  | 43.75  | 75.32  |
| After single EBM13 | 100   | 100     | 47.22  | 100   | 88.31  |
| After double EBM  | 100   | 100     | 86.11  | 100   | 95.67  |

The results of the chemical analysis of the samples obtained after e-beam thermal processing shows that in all investigated regimes, the thorium is removed and in the contents of the metal samples after melting there is no thorium present (table 3). The overall refining efficiency at tungsten processing, defined by the reduced concentrations of all other controlled impurities (Fe, Cu and S), after single refining depends on the power of the e-beam (i.e. on the heating temperature). Its values change between 56.71% at 12 kW (EBM11) to 88.31% at 22 kW (EBM13) regardless of the fact that at higher
EB power the refining duration is shorter (table 4). As a result of double refining processing, the overall removal efficiency obtained is 95.67% and the tungsten is with purity of 99.9% (tables 3, 4).

3. Conclusions

In this paper, the effects of EBM process parameters on removal of impurities in processing of molybdenum and tungsten technogenic materials for obtaining pure metals are investigated. The results obtained show that the multiple electron beam melting is most appropriate for refining technogenic materials with high concentration of Mo and W.

With double e-beam refining of molybdenum technogenic material, the overall removal efficiency and the removal efficiency of each of the controlled impurities increase 1.5 to 2 times after the second melting process and the concentration of molybdenum increases with more than one order of magnitude compared to the concentration in the source material.

With EBM of spent tungsten electrodes, the results obtained are even more explicit: higher refining efficiency is obtained by increasing the number of melting processes rather than by increasing the power of the electron beam. The highest purity of tungsten (99.9%) achieved is obtained after a single melting operation (88.31%).

Effective technological regimes (process parameters) for production of metals which meet specific requirements for high-purity and good-quality structure after EBM processing molybdenum and tungsten technogenic materials are proposed.

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