Electron Beam Melting and Recycling of Nickel

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Experimental and theoretical investigations of the process parameters at electron beam melting and refining (EBMR) of nickel samples with the purpose of improving the composition of the performed ingots are presented and discussed. Dependencies of the purification for different inclusions on the important technological parameters (e-beam power, refining time, etc) are obtained and the achieved purification degree is 99.5%.

Introduction

Nickel is a metal suitable for producing special alloys with good mechanical, anticorrosion, magnetic and thermoelectrically properties that are preserved at very low temperatures. Nickel alloys have also useful electronic and special magnetic properties. Those unique characteristics allow nickel and its alloys to have different applications. For example they are used in production of gas turbines, nuclear reactors, special chemistry apparatuses, vacuum devices and alkaline batteries. Nickel is appropriate for anticorrosion coverage and catalyzers.

Bulgaria is not a traditional producer of nickel due to lack of raw material. Years ago some non-ferrous metals enterprises in Bulgaria produced nickel in limited quantities as a concomitant procedure in production of other non-ferrous metals. In the recent years, due to a discontinued operation of large metallurgical plants and closing of entire sectors of the Bulgarian economy such as electro-vacuum and electronics and manufacturing, there are accumulated significant amounts of metal and metal-containing wastes, which are expensive and strategically important. These are pure metals with valuable and unique properties the recycling and reuse of which became more imperative. There is a significant amount of nickel scrap with low concentrations of impurities - waste from the electro-lamp manufacture, which can be recycled and reused.

Among the modern metallurgical methods the electron beam method (EB) for melting and refining in vacuum [1-4] has proven its advantages as effective, ecological and energy saving opportunity for recycling and processing of waste metals with unique properties and their reuse. One advantage of the method is that it effectively enough can be applied for refining of metals with a low content of impurities. Conditions for further refining of pure metals are much more specific and differ significantly from the conditions for the refining of metals with high content of impurities due to the specificity and diversity of concurrent refining processes.

This work presents the results of studies and analysis of the thermodynamic and kinetic conditions for the recycling of waste nickel (strips and screens from automobile lamps) with low content of impurities by electron beam melting and refining (EBMR) in vacuum.

Experiments: experimental conditions of EBMR of nickel

Two series of experiments on electron beam melting and refining were carried out using installation ELITE-60 in the laboratory "Physical problems of electron beam technologies" at the Institute of Electronics, Bulgarian academy of
Sciences (IE-BAS). Maximum power of the electron gun is 60 kW, and an accelerating voltage is 25 kV. The working vacuum pressure was 5.8x10\(^{-3}\) Pa (Fig.1).

![Fig. 1. Principal scheme of the electron beam melting and refining: (a) drip process: 1 - horizontal feeder of the started metal rod; 2 - generated droplets; 3 - molten pool (in the water-cooled crucible); (b) picture of a top surface of the formed ingot in the crucible during EBMR process.](image)

In each of the experimental series values of technological parameters were measured and controlled – e-beam power \( (P_b, \text{ kW})\), or energy density of the electron beam \( (\Phi_b, \text{ kW/cm}^2)\); melting rate \( (q_G, \text{ g/min})\); dimensions and composition of the metal before and after refining. In the first series of experiments the goal is to determine the optimal values for which to achieve a high degree of refining with the least energy consumed in a single electron beam refining. In these EB recycling of nickel, the starting (raw) material is made from welded strips (diameter of 45 mm) of nickel with a low content of impurities. The strips are fed horizontally into the melting zone, and the refined metal is crystallized in a crucible with a diameter of 50 mm. The experiments were carried out with a focused electron beam \( (\Phi_b = 20 \text{ mm}) \) with \( P_b = 12, 15 \text{ and } 17 \text{ kW} \), respectively, \( p_b = 4, 5 \text{ and } 6 \text{ kW/cm}^2 \). The rate of melting \( q_G \) is: 63.8, 106.3 and 148.8 g / min. The influence of the process parameters electron beam power \( P_b \), respectively beam power density \( \Phi_b \) and melting rate \( q_G \), respectively duration of electron beam impact \( \tau \) (in min) per gram liquid metal, on the changes in the concentration of impurities in the nickel is investigated.

In the second series of experiments nickel strips made from screens of scrapped automobile lamps are refined twice in the crucible (diameter of 60 mm). The beam power in the first refinement is 3.75 kW and in the second EBMR – 16.25 kW. The aim is to determine whether the multiple refining contributes for improving the quality of the new material - chemical composition and structure of the refined metal at EBMR with starting material with a low content of impurities. Results for the chemical analysis of the samples before and after each electron beam melting are obtained by emission spectral analysis. The starting (initial, before EBMR) and the final (after EBMR) concentrations of Si, Fe, Mg, Co, Cu and Mn are measured.

The temperature of the molten metal is measured in the center of the molten pool surface (Fig.1b) twice: in the initial moment \( (\tau = 0 \text{ min}) \) and after 5 min heating of the metal surface \( (\tau = 5 \text{ min}) \). The beam diameter was 30 mm, the range of \( P_b \) is 8.75 – 18.75 kW. The measurements were made with optical pyrometer QP-31 using special correction filters during the experiments. Results concerning the formed structure of the metal samples are obtained via metallographic analysis.

**Results and discussion**

The time for the refining of molten metal with thickness \( l_v = 1 \text{ cm} \) from the molten pool is calculated by the formula:

\[
(1) \quad \tau_v = B \cdot l_v \cdot q_G^{-1},
\]

where \( B \) is a constant determined by:

\[
(2) \quad B = \frac{\pi D^2 \rho}{4A}.
\]

\( \rho = 8.91 \text{ g/cm}^3 \) is the density of nickel; \( D \) is the diameter of the crucible; \( A = 1 \) is a coefficient related to the shape of the liquid pool [5].

The value of \( B \) in the case of nickel, casted into a copper crucible with a diameter of 5 cm is 174.86 g / cm. The refining time in the crucible \( \tau_v \) is 2.7 min, 1.6 min and 1.2 min for melting rates \( (q_G) \) 63.8 g / min; 106.3 g / min and 148.8 g / min, respectively. More precise values for \( \tau_v \) can be obtained using experimental or simulation data for the profile of the liquid zone in the upper portion of the formed ingot.

Chemical analysis data for the impurities’ concentration of the starting materials (before EBMR) and of the ingots after EBMR of Ni is obtained and analyzed. The removal of the impurities depends on the temperature up to which the molten metal is superheated and on the refining time.

The temperature of the metal in the center of the liquid pool is measured in the crucible while increasing the energy beam density (defined as the mean density of the beam spot on the molten metal) with \( \Delta P = 0.2 \text{ kW/cm}^2 \) for \( p_b \) in the range 1.2 kW / cm\(^2\) – 2.8 kW/cm\(^2\) and 5 min- heating at each value of \( p \).

Figure 2 presents dependencies between the measured temperatures in the liquid pool and the heating time of the e-beam for three beam powers.
The results show that in the investigated technological range of the e-beam powers the temperature of the molten metal varies between 2000 and 2500 K with amplitude less than 50K for a fixed beam power.

![Graph showing temperature variation in the molten pool in terms of \( p_b \) and \( \tau \).]

As metal used in the production with special requirements for chemical composition, nickel scrap used as starting material in both series experiments does not contain some of the most harmful to its properties metallic impurities such as Pb, Se and Bi, forming fast melting eutectic with nickel.

The results for the chemical analysis of the starting material show presence of impurities Co, Fe, Si, Cu, Mn, Mg and Al. It is studied if the concentrations of these impurities are changed for different EB regimes.

Refining in EB melting occurs in the volume of the liquid metal pool or on the reaction surfaces of liquid metal/vacuum in several reaction zones. In the case of drip melting method (Fig.1a) the reactive zones are three: the front of the molten raw material, the molten metal drops and liquid pool in the water-cooled crucible [5,6]. The efficiency of the refining processes does not depend on the working pressure in the vacuum chamber. It depends on the partial pressure of the components involved in the chemical interactions.

Depending on the thermodynamic conditions of the melting and on the type of removed impurities, the electron beam refining may be carried out by distillation or degassing. Regardless of the manner of removal, the efficiency of refining depends on the ratio of the partial pressures of the impurities \( (p_i) \) or of their compounds \( (p_{MeO}) \), relative to the partial pressure of the refined metal \( (p_R) \). It is possible to have an effective removal of impurities, which meet the ratios \( (p_i) > (p_R) \) and \( (p_{MeO}) > (p_R) \) [6].

Partial pressures of the elements and their compounds depend on the temperature in varying degrees. The vapor pressure of metals and their oxides play a decisive role in the EBMR process. If the vapor pressure of an impurity is significantly greater than that of the base metal, the impurity may be distilled off, leaving the pure metal. Table 1 shows the values of the vapor pressures for Co, Si, Cu, Al, Fe, Mn, Mg and Ni during EBMR. For Al, Mn, Fe, and Mg, which can turn out to be impurities of Ni, vapor pressures at the measured temperature range (2000-2500 K) are significantly greater (2-4 orders) than the pressure of the base metal (Ni). At conditions of EBMR the refining occurs in evaporation of these impurities from the surface of the liquid metal. In this case the refining process is efficient and the losses of the base refining metal (Ni) are minimal.

**Table 1.**

Vapor pressures \( p_i \) Pa of metals for the temperature range of 2000 - 2500K. [7].

<table>
<thead>
<tr>
<th>Element</th>
<th>2000 K</th>
<th>2500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1</td>
<td>5.10^2</td>
</tr>
<tr>
<td>Co</td>
<td>10</td>
<td>1.10^3</td>
</tr>
<tr>
<td>Cu</td>
<td>7.10^2</td>
<td>1.10^4</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>2.10^3</td>
</tr>
<tr>
<td>Fe</td>
<td>1.10^2</td>
<td>4.5.10^3</td>
</tr>
<tr>
<td>Al</td>
<td>8.10^2</td>
<td>2.10^4</td>
</tr>
<tr>
<td>Mn</td>
<td>2.10^2</td>
<td>8.10^3</td>
</tr>
<tr>
<td>Mg</td>
<td>8.10^4</td>
<td>5.5.10^6</td>
</tr>
</tbody>
</table>

Removal of impurities depends on the temperature to which the molten metal is superheated, which depends on the e-beam power, and on the refining time. Obtained and analyzed data from chemical analysis of the started material (before EBMR) and ingots after EBMR for nickel is presented in Figure 3. It is found that the concentrations of the controlled impurities decrease during the first minute of the refining process. When increasing the beam power the refining time may be reduced to 0.4 s/g.
Table 2.

<table>
<thead>
<tr>
<th>Degree of refining for metallic impurities at EBMR of Ni.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of Ni after EBMR</td>
</tr>
<tr>
<td>$\eta=100.\left(\frac{C_0-C}{C_0}\right)$, %</td>
</tr>
<tr>
<td>$p_b$, kW/cm$^2$</td>
</tr>
<tr>
<td>4kW/cm$^2$</td>
</tr>
<tr>
<td>5kW/cm$^2$</td>
</tr>
<tr>
<td>6kW/cm$^2$</td>
</tr>
<tr>
<td>C of Ni %</td>
</tr>
<tr>
<td>$p_b$, kW/cm$^2$</td>
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<tr>
<td>4kW/cm$^2$</td>
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<tr>
<td>5kW/cm$^2$</td>
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<tr>
<td>6kW/cm$^2$</td>
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</table>

Fig. 3. Inclusions' concentrations at EBMR of Ni. Dependence of impurity concentration $C$ on process parameters $P$ and $\tau$ for Si, Fe, Mg, Co, Cu, Mn.

Table 2 shows the calculated values for the achieved degree of refinement for each of the studied technological regimes. The total concentration of the impurities in the initial material is 0.632% (the concentration of Ni in the initial material is 99.37%). The maximum degree of refining $\eta=99.5\%$ was achieved during treatment for 0.94 s on every gram of metal with an electron beam power $P_b = 15$ kW (beam power density $P_b = 5$ kW/cm$^2$). The final concentrations of nickel in the obtained ingots after EBMR are also presented in table 2. Equally good refining can be achieved by continuous refining at low e-beam power density (4 kW/cm$^2$; 0.94 s / g) or at the short-term impact of the electron beam with a higher energy density (6 kW/cm$^2$; 0.4 s / g). Under optimum technological conditions of EBMR of nickel scrap 2N nickel with purity 4N is obtained.

Table 3 presents results from chemical analysis of double-refined nickel screens from automobile lamps by EBMR as well as the initial concentration of impurities and the level of refining. The initial concentration of nickel is 99.7%. Impurities with a partial pressure less than or close to the value of the partial pressure of nickel, such as silicon, cobalt, and copper, do not change their concentrations. For volatile metallic impurities such as manganese, iron, magnesium and aluminum a degree of refining higher than 80% is achieved. A total degree of refining of 64% has been achieved and nickel with purity of 99.9% has been obtained.

Metallographic analysis of different Ni samples, refined under various process conditions is made. The structure of the nickel samples is developed using a solution of (HNO$_3$ + 3 HCl). The metallographic pictures are obtained using Leica DM750M microscope and Leica EC3 colorfull digital camera. Figure 4b shows structures in nickel ingots obtained after EBMR at electron beam power density $p = 5$ kW/cm$^2$ and refining time $\tau = 0.4$ s / g; 0.6 s / g and 0.94 s / g.

The results of the metallographic study of nickel after EBMR show that by increasing the purity of the metal, the structure is significantly improved. Impurities concentrate in the grain boundary and their amount gradually decreases and disappears yielding clean grain boundaries. One can observe the formation of grain clusters which is characteristic of the structures of the pure metals. This presents further evidence for the effective refining in electron beam metal recycling.

In Table 3 are presented results from chemical analysis of double-refined nickel screens from automobile lamps by EBMR as well as the initial concentration of impurities and the level of refining. The initial concentration of nickel is 99.7%. Impurities with a partial pressure less than or close to the value of the partial pressure of nickel, such as silicon, cobalt, and copper, do not change their concentrations. For volatile metallic impurities such as manganese, iron, magnesium and aluminum a degree of refining higher than 80% is achieved. A total degree of refining of 64% has been achieved and nickel with purity of 99.9% has been obtained.
Conclusion
A possibility to obtain a high purity nickel through recycling of nickel scrap using EBMR in vacuum was shown. From the analysis of the results obtained it was found that in the case of a single EBMR of nickel the removal of impurities such as Si, Al, Mg, Fe, Co, Mn and Cu, depends on the e-beam power and on the refining time. Equally good results have been obtained at longer refining time with lower electron beam lower and at shorter heating with higher beam power. Which regime should be chosen becomes a matter of the specific case and specific calculations. From the regimes investigated, the best result is obtained at heating time of 1s for each gram of metal using an electron beam with density of 5 kW/cm² - maximum degree of refining 99.5% and final substance nickel consistency of 99.99% with structure lacking impurities along the border of well formed large grains. In EBMR of nickel with low impurity content it is appropriate to apply repeating refining process (double refining), wherein the stronger influence comes from the beam power and not from the length of the refining time.

Impurities with thermodynamic limitations, i.e. their partial pressures are lower than the partial pressures of nickel, can not be removed. Such impurities are silicon, copper and cobalt.

The obtained results give the opportunity for the suitable technological regimes to be chosen so that pure Ni with improved composition can be obtained by EBMR.

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REFERENCES


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