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Research Article

The production of open cell Ni-foam using KBr as spacer and oxidation shield via powder metallurgy technique

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ABSTRACT

Metallic materials having a porosity of 70% or more are generally referred as highly porous metals. In this study, highly porous pure nickel materials were produced by powder metallurgy route. In the production process, potassium bromide was used both as a space-holder phase and as an oxidation shield. In the method, firstly, nickel and potassium bromide powders were mixed according to the desired void ratio. The obtained nickel-potassium bromide powders were pressed in a hydraulic press and turned into pellets (diameter: 13mm). Then, these pellets were pressed again in a wider mold (diameter: 21mm) so that all surfaces were covered with potassium bromide, and the encapsulation process was carried out. These capsules were embedded in potassium bromide in an alumina crucible for sintering. The sintering process was carried out in an open atmosphere at 1050 °C for 60 minutes. After the sintering process, the crucibles were kept in water to dissolve the crystallized potassium bromide around and inside the sample. Density, macrostructure, microstructure and EDS analyzes were performed on the samples. It was observed that open cell pores (58.3 - 78.1% vol) with diameters varying between 5 and 500 µm, which are homogeneously distributed in nickel, have been successfully obtained. In addition, it was proved that nickel foam materials can be produced in different sizes and designs.

1. Introduction

With the development of technology, the need for lighter and stronger metals is increasing. Also, in some applications, such as high temperature filters or fuel cells, it is desirable for the metal to have a high surface area. Therefore, metallic foams gain importance. Terms such as metal foam and porous metal have the same meaning. Metal foams are cellular structures in the form of solid metal that contain many voids or pores within their volume. In this way, very light (low density) and strong metallic construction materials, filter materials, heat exchangers, solid oxide fuel cells and materials having vibration and/or impact absorbing properties can be produced [1-6]. There are two types of metal foams, open-cell (containing interconnected voids) and closed-cell [1, 7, 8]. The open-celled one of these appeals to many areas such as filters, heat exchangers, fuel cells, etc.

On the other hand, porous Nickel (Ni) foam materials are used in many high-tech applications due to their functional properties (good electrical and thermal conductivity, high specific surface area, sound absorption and gas-liquid permeability). Examples of these applications are heterogeneous catalysis systems, high temperature filters, heat exchangers and solid oxide fuel cells [5, 9, 10]. Different methods such as powder metallurgy (PM), casting, infiltration casting and electrodeposition can be used in the production of porous Ni. Among these, the PM method is advantageous compared to others in terms of being suitable for open-cell foam production, allowing precise dimensional tolerances and high purity production [11-14]. In addition, it is possible to good control the volume fraction, geometry and size of the pores by the PM method. However, as in other high-temperature manufacturing methods, one of the biggest problem in PM is the oxidation of the metallic material to be produced due to the high temperature of the sintering process [15-18]. In order to prevent this, "vacuum", "inert gas (argon etc)" or "reducing gas" atmospheres, which are called protective atmospheres, must be created in the sintering furnace during production, and this increases the production cost.

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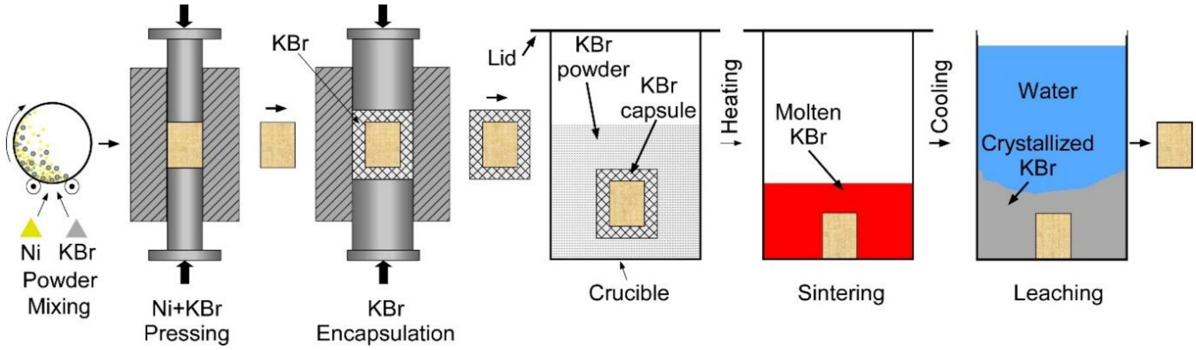

Figure 1. Schematic summary of the production process.

According to a method discovered recently (2019) to solve this problem in the PM method, it has been proven that the oxidation of Titanium metal sintered in potassium bromide (KBr) salt is not more than materials sintered in inert atmosphere [19]. Thus, a significant reduction in production costs is possible. The article by Dash et al. [19], published in the "Nature", was reported on scientific news websites such as The American Ceramic Society with the headline of "No more inert atmospheres—Molten salt synthesis prevents oxidation of materials in air" [20]. Briefly, the researchers carried out the encapsulation process by pressing the pelleted Titanium (Ti) powder into the KBr salt. It is reported that thanks to this encapsulation, KBr becomes gas-tight at room temperature and prevents contact of metal pellets with the atmosphere and oxidation during sintering up to its melting temperature of 734 °C. Then, the encapsulated pellets were placed in an alumina crucible containing KBr powder (salt bed), and filled the remaining part of the crucible with KBr powder. After the sintering process, water was used to dissolve the salt which passed from the liquid phase to the solid phase with cooling, and this water was evaporated to obtain KBr again (recycling) [19]. It was reported that 1.02 kg of KBr can be dissolved in 1 liter of water at 100°C [21]. Therefore, KBr can be used repeatedly. In another study by Roy et al. [22], Ti_2AlN and V_2AlC (MAX phase) ceramics were sintered between 900 – 1100 °C using PM method in KBCl-NaCl salt environment. As a result, they proved that when molten salt is used instead of inert gas atmosphere or vacuum, oxidation does not occur in the sintered samples and the productions take place in an economical way. Therefore, in both studies [19, 22], it is stated that sintering in KBr environment is ecologically positive, sustainable, energy and cost efficient and can be used in industrial applications.

The use of salts such as sodium chloride (NCl), carbamide (CH_4N_2O) and ammonium bicarbonate (NH_4HCO_3) as space holders in the production of porous metals is seen in the studies in the literature [1, 5, 10, 23]. In addition, Noor et al. used KBr as a space holder in the production of porous Ti foams and obtained porosity values ranging from 16 to 31% [24]. However, there is no study in the literature regarding the use of KBr as both space holder and oxidation shield in porous Ni production.

The aim of this study can be defined as the production of highly porous Ni foams by PM method using KBr salt powder as both a space holder and an oxidation protective shield to reduce production costs. As a result of the studies, Ni foams having open porosity up to 78.1% were produced by creating voids in the Ni owing to the water-soluble feature of KBr. Moreover, thanks to KBr molten salt shielded synthesis, Ni metal was sintered without using a protective atmosphere.

2. Materials and Methods

2.1 Mixing, Pressing, Sintering and Leaching

The methods followed in the production process were made as described below and summarized schematically in Figure 1.

- First of all, Nickel (powder size 2 µm, purity 99.5%, manufacturer: Molchem) and Potassium Bromide (KBr, purity: 99.5%, manufacturer: EduKim) powders were weighed on precision balance (RADWAG AS220.R2) to contain more than 70% KBr by volume. The stereo microscope image showing the morphology and size of the KBr powder were given in Figure 2.
- The weighed powders were poured into the mixing bowl without binder and mixed dry in a horizontal mechanical mixer using zirconia balls (ball to powder ratio, 1:2) at 250 rpm for 2 hours.
- The prepared powder mixtures were placed in a metal mold (Ø = 12 mm) and cold pressed in a hydraulic press with a pressure of 200 MPa. Thus, Ni+KBr pellets were obtained (see Figure 3 (a)) without any binder.

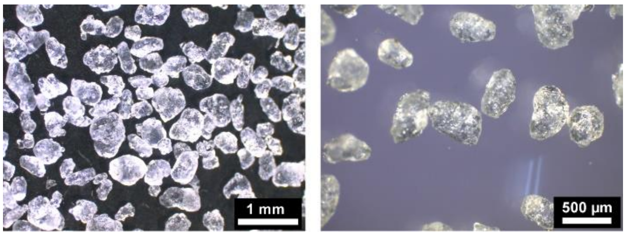

Figure 2. Stereo microscope images of KBr salt powder at different magnifications (average grain size 500 µm).

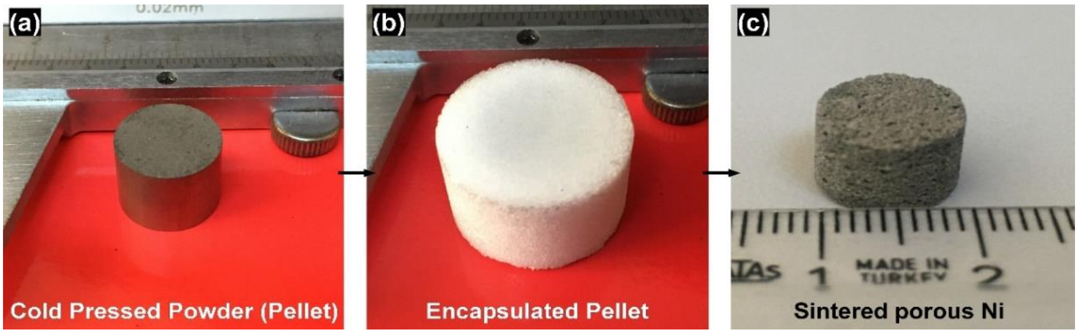

Figure 3. Image of cold pressed Ni+KBr pellet (a), KBr encapsulated pellet (b) and sintered porous Ni foam (c).

- The cold pressed powder pellets were placed in a larger diameter (Ø = 21 mm) metal mold containing KBr powder and pressed again under 200 MPa pressure after adding KBr powder to remaining part of the mold. Thus, the Ni+KBr pellets were completely encapsulated with the KBr and made ready for sintering (see Figure 3 (b)).
- Alumina crucibles were used for the sintering process. First of all, a salt bed was formed by adding KBr powder to the floor of the crucibles, and encapsulated pellets were placed on these beds. Then the inside of the crucibles was completely filled with KBr powder (exceeding the size of the pellets). Another alumina was left on the alumina crucibles as a lid (without any compression, gasketing, etc.).
- These crucibles were placed in the sintering furnace (Protherm-muffle furnace) and sintered for 60 minutes at a sintering temperature of 1050 °C (heating rate 5 °C/min) in normal atmosphere (without using any additional protective gas, vacuum etc.).
- The cooling process was carried out in the furnace. After cooling, the crucibles were soaked in hot water to dissolve KBr, which both crystallized in the crucible and dispersed in Nickel. Thus, sintered Nickel samples in porous (foam) structure were obtained (see Figure 3 (c)).

2.2 Characterizations

Density, macrostructure and microstructure (with optical microscope and scanning electron microscope) analyzes of the produced samples were performed. The density of the porous nickel foams was calculated by measuring the mass and the volume from their physical dimensions. A stereo microscope (Leica) was used for optical microstructure examinations. In addition, TESCAN VEGA3 Thermionic Emission Scanning Electron Microscope (SEM) and Energy Dispersion Spectrometer (EDS - Oxford/Inca) were used for detailed microstructure studies and elemental distribution analysis, respectively.

3. Results and Discussions

3.1 Macrostructure and Density Analysis

In Figure 4, a macrostructural photograph of Ni foams having different porosity and designs was given. It was determined that the samples could be produced in different porosity ratios.

In addition, the manufacturability of Ni foams with different designs was also tested and produced successfully. As seen in Figure 4, it was possible to produce designs such as inner part hollow outer part porous (ring shaped) which is the preferred geometry in many filter applications, inner part dense outer part porous used in some cathode applications where both strength and excess surface area are desired and outer part dense inner part porous for some insulation and heat exchanger applications.

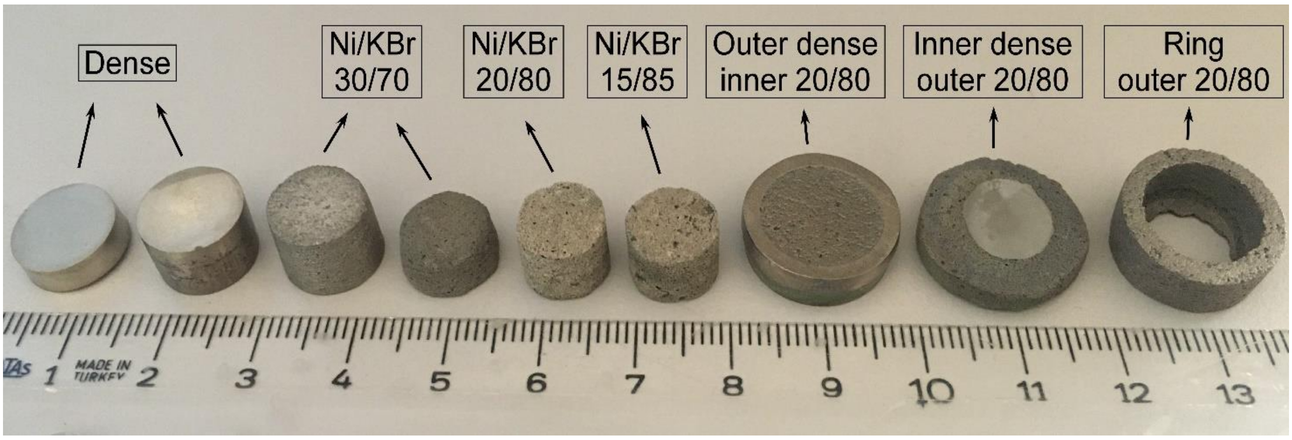

Figure 4. Macro view of Ni foams with different porosity and designs

On the other hand, it was determined that there is an upper limit in terms of porosity value in the production of Ni foam by powder metallurgy method using KBr. The production of foams with a KBr ratio greater than 85% was not possible with this method. As seen in Figure 5, a concave bending occurred from the center of the cylinder bases of the samples that were tried to be produced with the KBr ratios between 85% and 90%. Above 90% KBr, sintering did not occur and the samples were fragmented into particles. Because the excess KBr in the composition prevented Ni powder particles from coming into contact with each other and neck formation during sintering. Therefore, diffusion did not occur.

As seen in Table 1, the production of Ni foams having open porosity up to 78.09% by volume was achieved. Amount of closed porosity increased with decreasing KBr ratio. This was an expected result. Because as the amount of KBr decreased, the nickel particles covered the KBr particles like a cell wall. This caused the KBr space holders to be trapped inside the Ni cell. The relative density value of the dense Nickel sample without KBr was measured as approximately 95%. Therefore, it was possible to achieve a density reduction of approximately 82% by means of porous nickel foams.

3.2 Analysis by Optical Microscopy

Images of porous Ni foams produced by powder metallurgy method in KBr medium, obtained from stereo optical microscope, were given in Figure 6 (a-f). When Figure 6 (a and b) was examined, it was observed that the porosities were homogeneously distributed in the samples with a Ni/KBr ratio of 20/80. In Figure 6 (c and d), the microstructures of the samples at higher magnification were given. The porosities had an interconnected (open-cell) morphology. It was concluded that Ni and KBr powders were successfully mixed during the powder preparation process, since the porosities were homogeneously dispersed

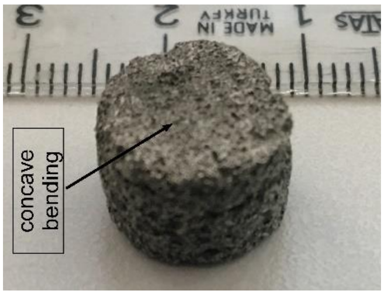

Figure 5. Macro view of the concave bending from the center of the surface that occurs in samples containing more than 85% KBr.

Table 1. Density and porosity values of Ni foam.

Ni/KBr (vol %)	Density (g/cm^3)	Closed porosity (vol %)	Open porosity (vol %)
30/70	2.99	11.66	58,34
20/80	2.03	9.09	70.91
15/85	1.52	6.91	78.09

Figure 6 (e) shows the image of the sintered sample without KBr encapsulation, while Figure 6 (f) demonstrates the sintered sample with KBr encapsulation. Accordingly, as a result of not performing the KBr encapsulation process, an oxidation layer of approximately 330 μm thickness formed on the outer surfaces of the sample. This oxidation (NiO) layer was seen in green (Figure 6 (e)).

On the other hand, as seen in Figure 6 (f), no oxidation layer was found on the surface of porous Ni foam sintered after KBr encapsulation. This indicated that encapsulation with KBr prevented oxidation of the metal sample as in an inert or vacuum atmosphere. Dash et al. [19] reported that a capsule wall thickness of 4 mm and pressure of 200 MPa would be sufficient for KBr to act as a gas-tight capsule. In this study, since the thickness of the KBr capsule for Ni foams was at least 4 mm, the Ni foam samples were protected from oxidation by encapsulation during sintering up to 734 °C, the melting temperature of KBr. When the KBr melted at about 734 °C and went into the liquid phase, the Ni foam samples sank to the bottom of the KBr liquid in the crucible. Thus, the Ni foam samples were protected from oxidation by encapsulation until the transition of KBr to the liquid phase, and after the liquid phase, they sank into the the KBr liquid and did not come into contact with the atmosphere (oxygen).

3.3 Microstructural Analysis by SEM

Scanning electron microscope (SEM) images of Ni foams with 70.9% open porosity at different magnifications were presented in Figure 7 (a-d).

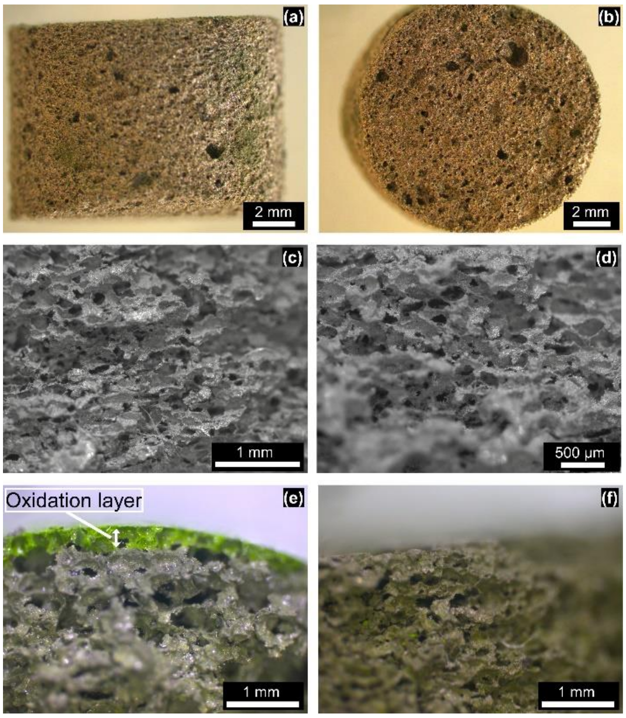

Figure 6. Images of Ni foam samples taken from stereo optical microscope, (a and b) general view, (c and d) morphology of porosities, (e and f) the effect of encapsulation with KBr on oxidation.

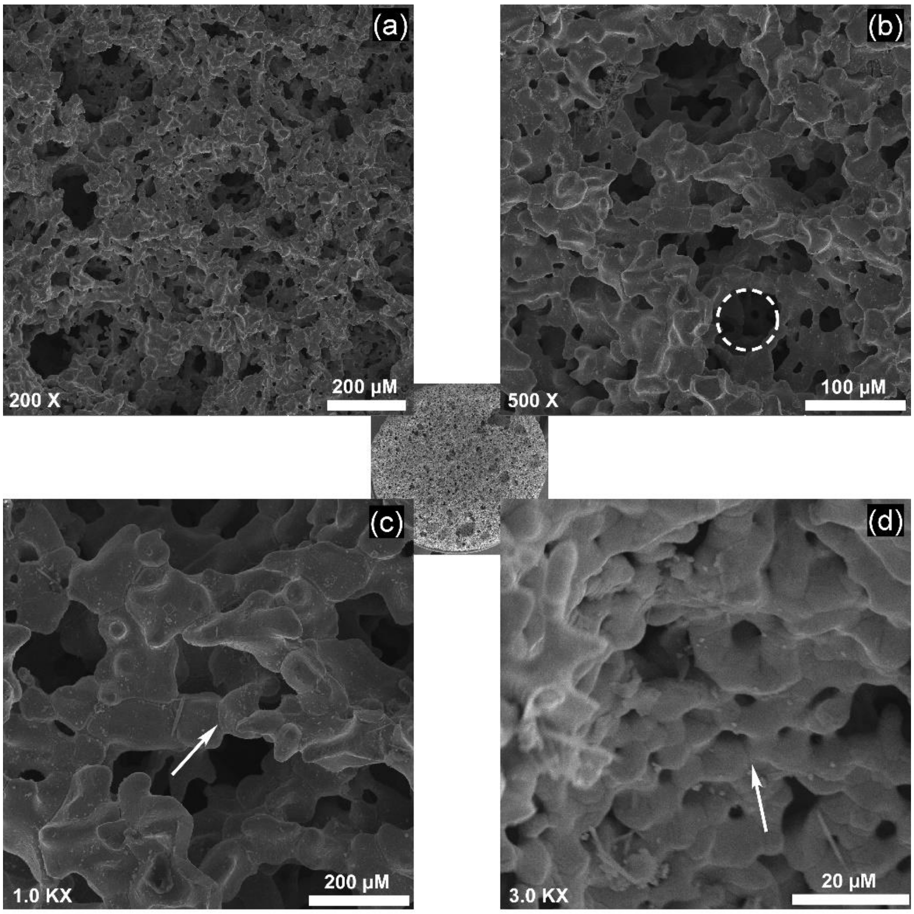

Figure 7. Microstructural images of porous Ni foam sample taken at different magnifications by SEM. (a) 200X, (b) 500X, (c) 1000X and (d) 3000X.

As can be seen from the images, the samples contained interconnected (open) porosities and the porosities were homogeneously distributed in the microstructure. The diameters of the porosities ranged from about 5 µm to 500 µm. Accordingly, it was understood that powder preparation and sintering parameters were appropriate. When the interfaces between Ni powder particles were examined (shown by arrows in Figure 7 (c and d)), it could be said that the neck characteristic of sintering formed between the particles, and both bonding and growth occurred through diffusion from these neck regions. Therefore, the sintering process with powder metallurgy route was successful and the powder particles formed a strong bond with each other. On the other hand, some small pores having diameter less than 5 µm were present in the microstructure, as clearly seen in Figure 8 (d). It was thought that this situation took place due to the crunch of the KBr space holders during pressing. The same situation was reported by Wang at al [25], who used NaCl as space holder for Cu foam production.

Figure 8 showed the results of the energy dispersive x-ray spectroscopy (EDS) analysis made from three different points of the Ni foam sample surface and the points where the point analysis was made. In the spectra obtained from the EDS analysis, the presence of any element other than Nickel was not found. According to these results, it has been understood that Nickel foams can be produced successfully in KBr environment without oxidation.

4. Conclusions

In this study, highly porous Ni foams having open porosities were produced by using KBr as both space-holder and oxidation shield. Also, the manufacturability of Ni foams with different designs was tried. With this method, it was possible to produce Ni foam materials in different designs (with inner dense outer porous, inner porous outer dense, ring shaped, etc.). There was an upper limit for the porosity ratio in Ni foam production with this method. In the experiments, it was observed that a concave bending occurred on the surfaces of the samples with a KBr ratio above 85%. The sintering process was not successful in the samples containing 90% or more KBr by volume. It was observed that the porosities were in interconnected (open) morphology and homogeneously distributed in the structure. In addition, porosity diameters ranged from 5 to 500 µm. While an oxidation layer was formed on the surface of the samples sintered without KBr encapsulation, it did not form on the encapsulated samples. In this way, the samples were protected from oxidation during sintering thanks to KBr molten salt.

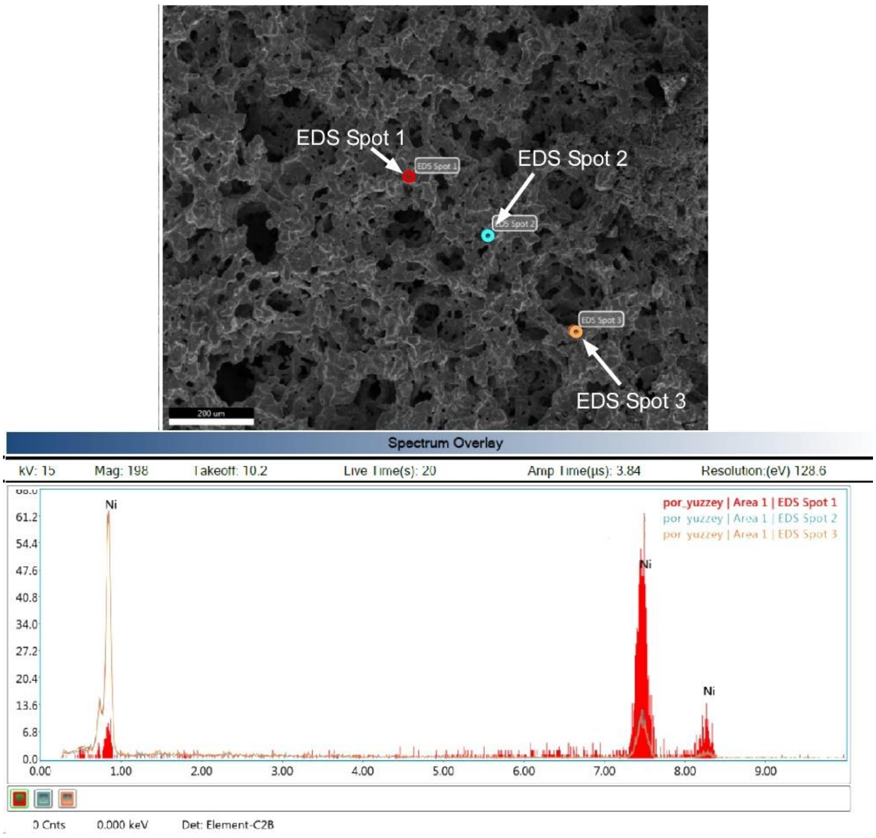

Figure 8. EDS analysis points and EDS spectra.

Declaration

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

Author Contributions

Mustafa Guven Gok is responsible for all section of the study.

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