STUDIES AND RESEARCH ON WASTE $MoSi_2$ HEATING ELEMENTS

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The capitalization of the used heating elements based on $MoSi_2$ from the melting furnaces and heat treatments furnaces is economically justified. The paper analyzes the molybdenum market, morphologically and structurally characterizes the $MoSi_2$ and SiO_2 compounds found in the heating elements and proposes the recovery of molybdenum in the form of MoO_3. The powder obtained from used heating elements ground in a jaw crusher was analyzed by Scanning Electron Microscopy SEM and Energy Dispersive X-ray Spectrometry - EDX. To identify the constitution phase of the powders, we used a Panalytical X'PERT MPD X-ray diffractometer with a CuKα radiation source.

Keywords: molybdenum disilicide; used heating elements; recovery; microstructural characterization; phase analysis

1. Introduction

Molybdenum is a rare metal in nature (it is the 54th most abundant element in the Earth's crust with an average of 1.5 parts per million [1]). Although known and used since antiquity (as Molybdaeum) when its ores were confused with lead, it was not until 1768 that Carl Wilhelm Scheele established that molybdenite (MoS_2) is a sulfur compound of an unknown metal and converted molybdenite in oxide (powder); in 1782, at the suggestion of Carl Wilhelm Scheele, Peter Jacob Hjelm obtained molybdenum powder (chemically reduced carbon monoxide) [2].

Molybdenum found practical use in the late 19th century, under the auspices of World War I when the supply of tungsten fell; it began to replace tungsten in impact-resistant steels - shields - with twice the atomic weight than tungsten [3]. After the World War II, molybdenum found its many applications: it increases the hardness, thermal and corrosion resistance of steels, becoming indispensable in the aeronautical and cosmonautical industry (missiles); when

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making protective layers; nuclear medicine and roentgen lamps; MoS_2 + Graphite is a good lubricant even at high temperatures; superalloys, nickel based alloys, chemicals, electronics and many other applications (Fig.1). Molybdenum disilicide ($MoSi_2$), a refractory metal silicide, is mainly used as a heating element [4, 5].

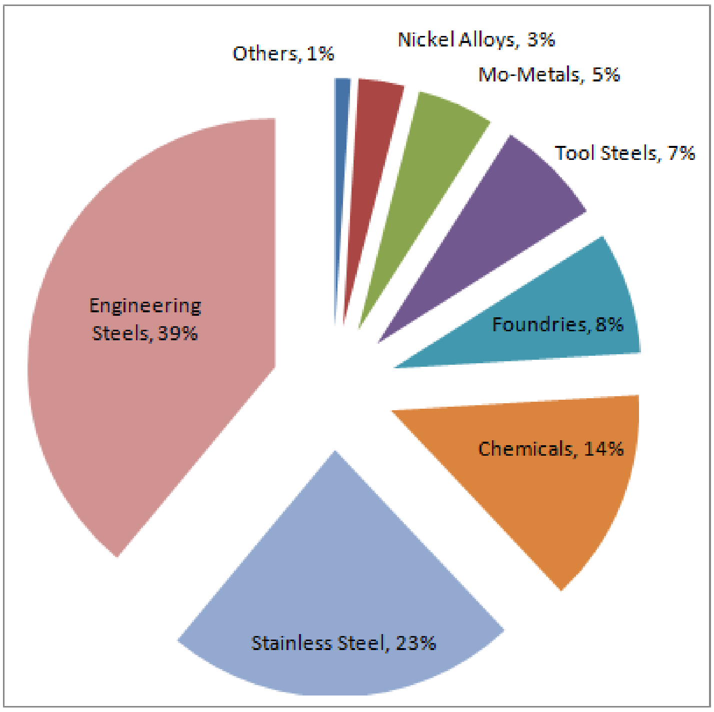


Fig. 1. Technical uses of Molybden, 2019 (Total volume year: 2019 – 259,100 tonnes Mo [1]

About 99% of molybdenum are obtained from molybdenite ores (MoS_2) including copper-molybdenum ones. In the ore composition, the molybdenite concentration varies between 0.01 to 0.25%, associated with other sulfides minerals of other metals (cooper). Important mineral reserves have: China, USA, Peru and Chile. Molybdenum major producers are US, China and Chile [6, 7 and 8]. After extraction from the mine, the preparation of ores follows the standard stages (crushing, grinding, floatation, leaching). Oxidizing roasting involves the conversion of insoluble molybdenum sulfide into easily soluble molybdenum trioxide using ammoniacal or alkaline solutions. The resulting ammonium molybdate solution is then converted to any one of a number of molybdate products by crystallization or acid precipitation. These can be further processed by calcination to pure molybdenum trioxide [9]. Molybdenum metal is produced by hydrogen reduction of pure molybdic oxide or ammonium molybdate.

Molybdenum is expected to trade at 18.43 USD/Kg by the end of this quarter, according to Trading Economics global macro models and analysts' expectations. Tradingeconomics.com estimates it to trade at 15.84 in 12 month's time [10].

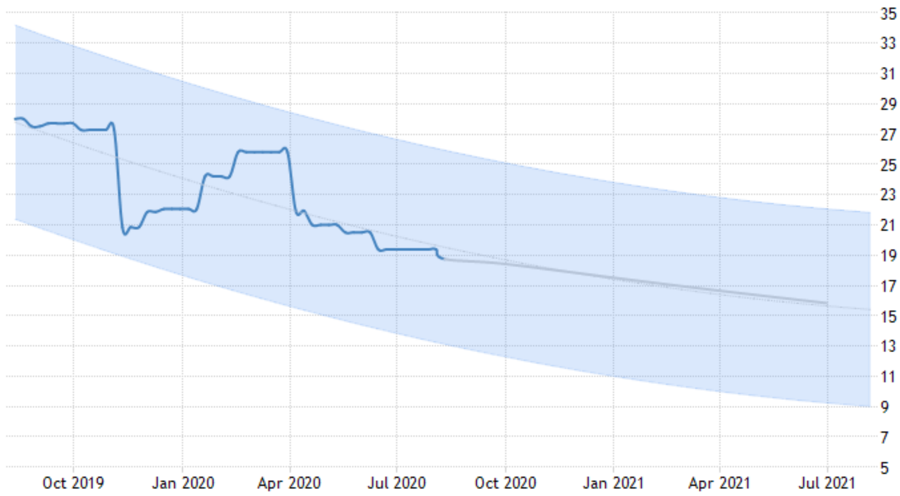


Fig. 2. Forecast for Molybdenum prices [10]

About 73% of the molybdenum supply comes as a by-product of the copper industry and only 27% of the molybdenum mines (China is the largest producer of molybdenum mining). Over 80% of primary molybdenum consumption is used in the steel and alloys industry (eg ilium). The crisis caused by the COVID-19 pandemic that led to a global economic crisis caused the price of molybdenum oxide to fall by 18% in the first quarter of 2020 but forecasts [10] anticipate that the steel industry will recover from next year 2021.

Molybdenum disilicide is commercially used as a heating element (Fig. 3); this is an intermetallic compound, a silicide of molybdenum, a refractory ceramic. It has moderate density (6.3 g/cm^3), melting point 2030°C, excellent high-temperature oxidation resistance, and high electrical and thermal conductivity; at high temperatures it forms a passivation layer of silicon dioxide, protecting it from further oxidation [9].

Fig. 3. $MoSi_2$ heating elements U-type [11]

2. Materials and methods

In the laboratories of the Polytechnic University of Bucharest (Romania) there are such heating elements obsolete (broken) - lifetime of the heating elements it is several years of use, depending on the number of cycles of use of the furnaces, and currently, we are trying to find a use of these materials (to process them under powder form and to be used for air plasma spraying, or in the production of multiphase composites based on Mo-Si-Al-C system).

$MoSi_2$ heating element is a High-Density Material consisting of molybdenum disilicide and self-forming glaze of silicide dioxide. It can be used up to Furnace Temperature of 1800^0C and it can withstand many years of service because of its strength [12]. The main properties are shown in Table 1.

Table 1

Properties of molybdenum disilicide

Property	Value	Measure unit
Density	5.6	g/cm^3
Porosity	< 1	%
Hardness	8.58 – 9.60	GPa
Compression strength	1400 - 1500	MPa
Resistivity: - at room temp - at 1700°C	3.5×10^{-7} 4.0×10^{-6}	Ω·cm

Worn heating elements from $MoSi_2$ were recovered from various furnaces (melting furnaces, heat treatment furnaces), and transformed into powder and small cracks (Fig. 4) using a jaw crusher.

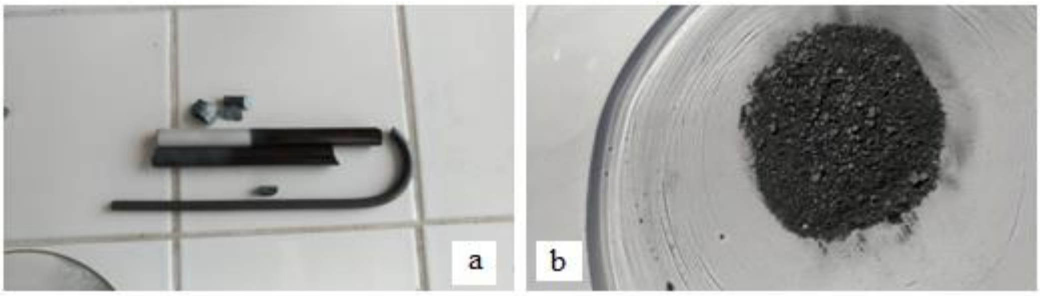


Fig. 4. Processing of worn heating elements made of $MoSi_2$: a) broken $MoSi_2$ heating elements; b) powder and small cracks of $MoSi_2$

The morphology and microstructure of the powders were analyzed by SEM (Quanta Inspect F50, with a field emission gun - FEG with 1.2 nm resolutions and an Energy Dispersive X-ray Spectrometer - EDX having 133 eV resolutions at MnKα).

To identify the phase constitution of the powders, we used a Panalytical X'PERT MPD X-ray diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) in the range 2θ = 10–90º.

3. Results and discussion

$MoSi_2$ is known to have a C11 b-type body-centered tetragonal structure at temperatures <1900°C and a C40-type hexagonal structure at temperatures >1900°C [13]. The crystallographic parameters are presented in Table 2.

Table 2

Crystallographic parameters of $MoSi_2$ compared to SiO_2

Crystallographic parameters	**$MoSi_2$**	**SiO_2**
Crystal system	Tetragonal	
Space group	I4/mmm	P41212
Space group number	139	92
a (Å)	3.2000	4.5200
b (Å)	3.2000	4.5200
c (Å)	7.8500	7.4960
Alpha (^{0})	90.0000	
Beta (^{0})	90.0000	
Gamma (^{0})	90.0000	
Calculated density (g/cm^3)	6.28	-
Volume of cell (10^6pm^3)	80.38	153.15
Z	2	4
RIR	-	3.53

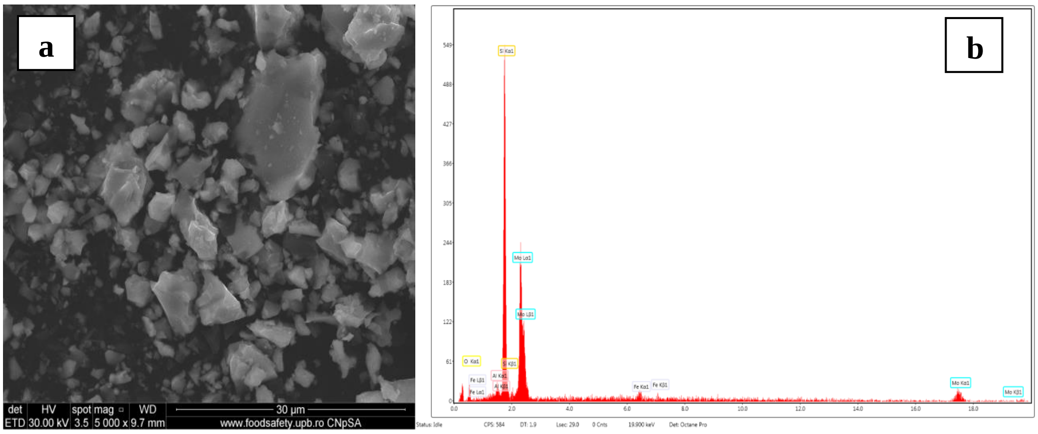


Fig. 5. SEM-EDX characterization of $MoSi_2$ powdery material: a) SEM micrograph; b) EDX spectrum

The morphology and microstructure of the $MoSi_2$ powder material were characterized using SEM-EDX analysis (Figures 5 to 8). The phase constitution of the powder was determined by X-ray diffraction (XRD) using Cu Kα radiation (Fig. 9).

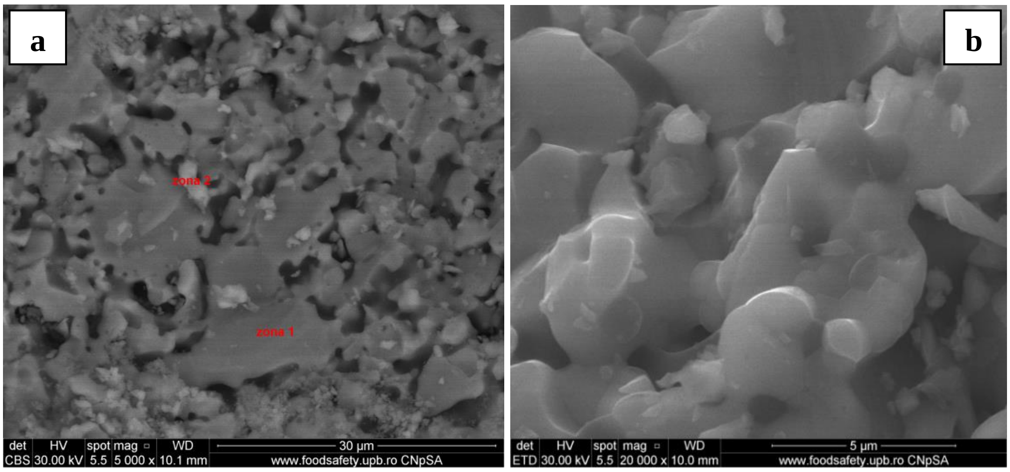
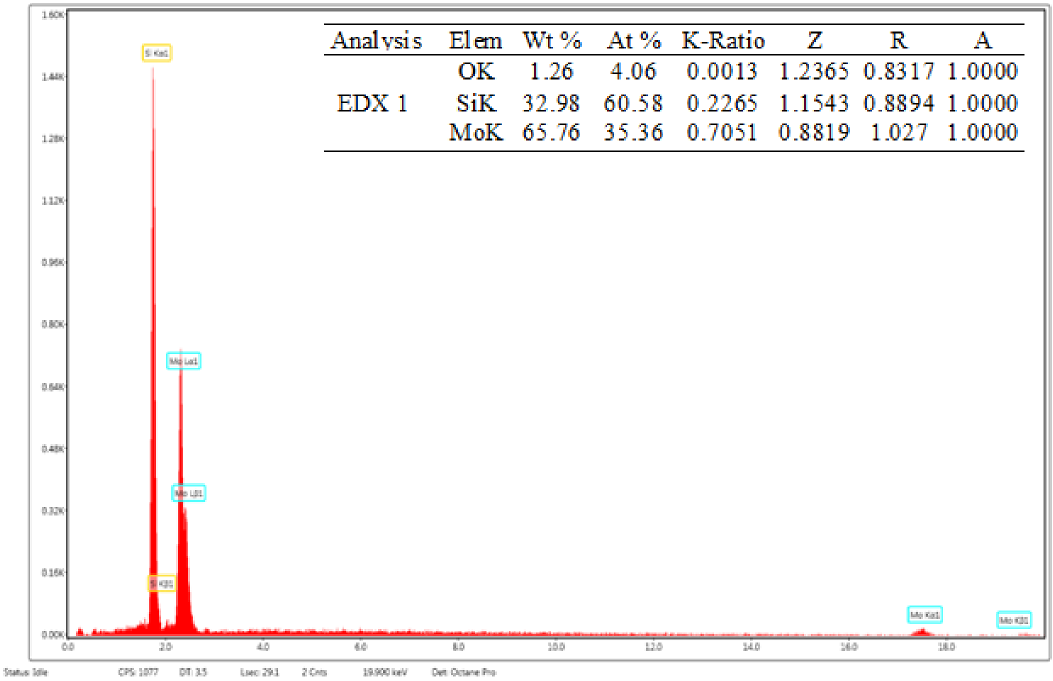
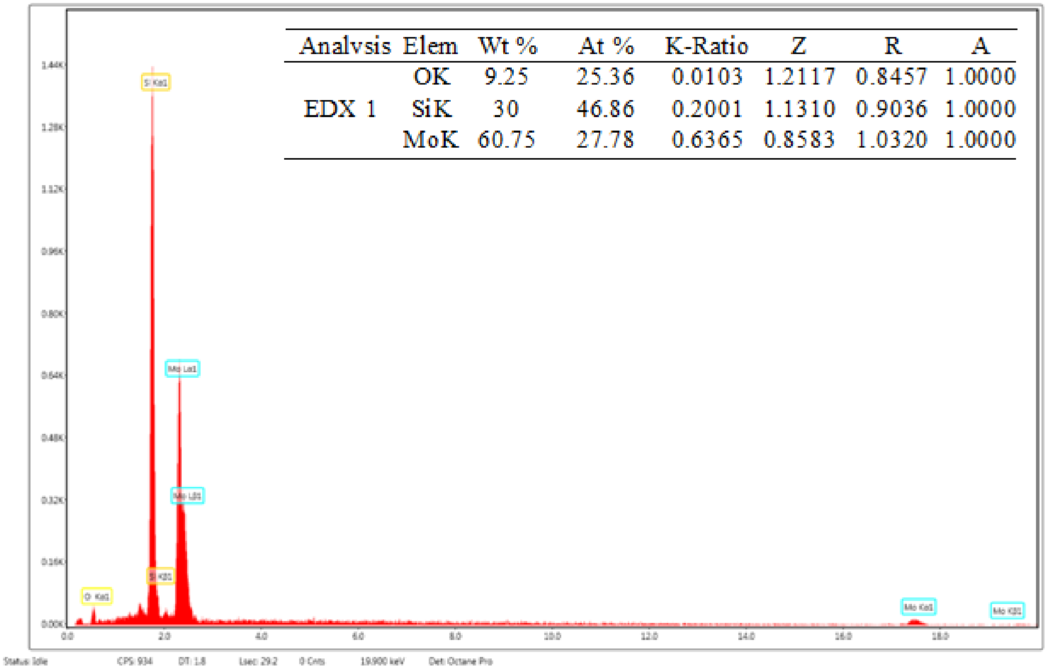


Fig. 6. SEM micrographs of $MoSi_2$ powders showing: a) two characteristic micro-areas for EDX analyses; b) high magnification morphology of particle surface



Analysis	Elem	Wt %	At %	K-Ratio	Z	R	A
	OK	1.26	4.06	0.0013	1.2365	0.8317	1.0000
EDX 1	SiK	32.98	60.58	0.2265	1.1543	0.8894	1.0000
	MoK	65.76	35.36	0.7051	0.8819	1.027	1.0000

Fig. 7. EDX spectrum for micro-area 1



Analysis	Elem	Wt %	At %	K-Ratio	Z	R	A
	OK	9.25	25.36	0.0103	1.2117	0.8457	1.0000
EDX 1	SiK	30	46.86	0.2001	1.1310	0.9036	1.0000
	MoK	60.75	27.78	0.6365	0.8583	1.0320	1.0000

Fig.8. EDX spectrum for micro-area 2

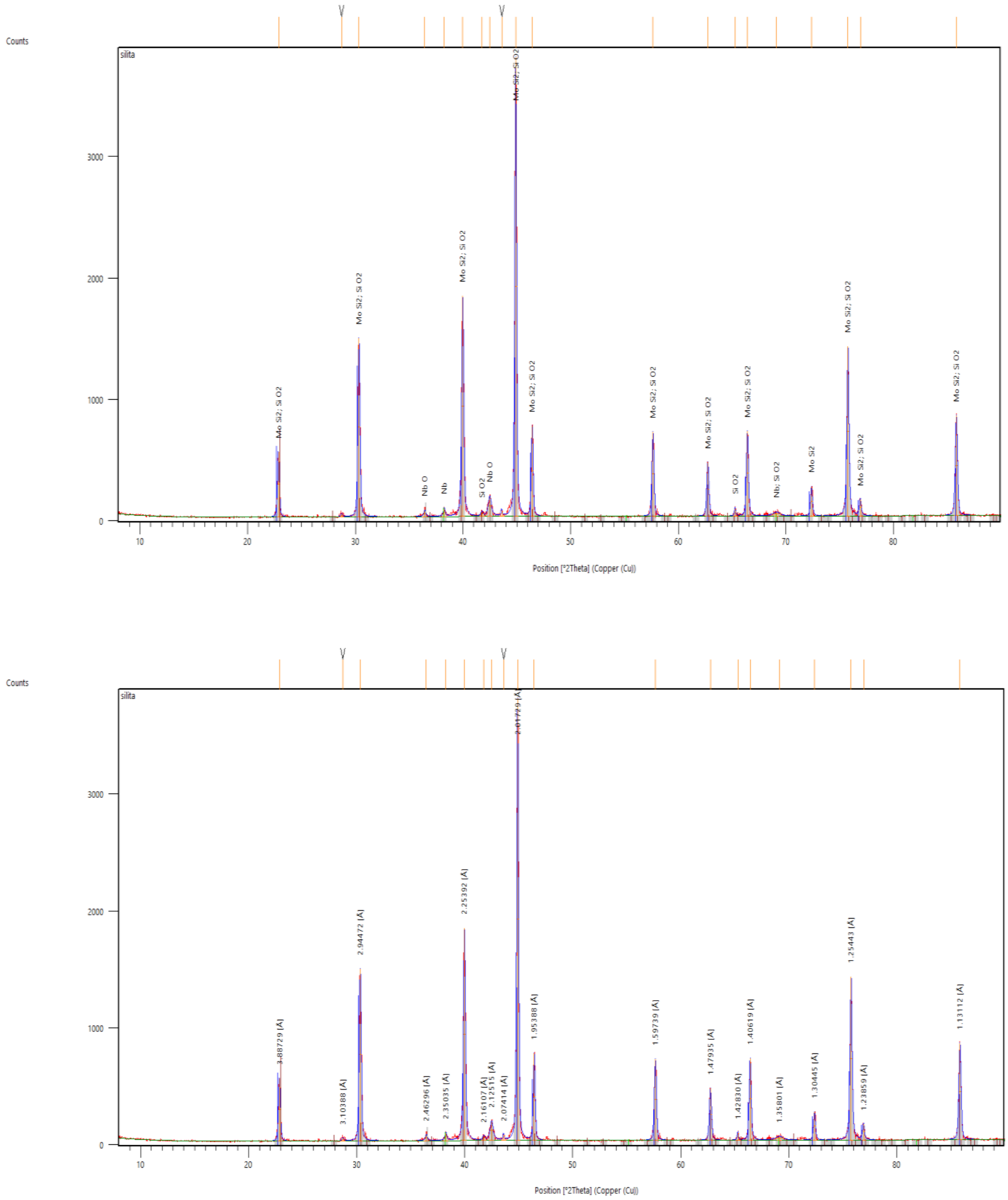


Fig. 9. XRD patterns for molybdenum disilicide

Table 3

The X-ray diffraction indexation sheet in Figure 9

Peak list

No.	h	k	l	d [A]	2Theta (deg)	I (%)
1	0	0	2	3.92000	22.665	45.0
2	1	0	1	3.87080	22.957	100.0

3	1	0	1	2.96000	30.168	95.0
4	1	1	1	2.94000	30.378	21.9
5	1	1	0	2.26000	39.856	70.0
6	2	0	0	2.26000	39.856	12.9
7	2	1	0	2.02140	44.800	0.3
8	1	0	3	2.02000	44.833	100.0
9	1	1	2	1.96000	46.284	40.0
10	2	1	1	1.95170	46.492	8.9
11	2	0	0	1.60000	57.559	30.0
12	2	2	0	1.59810	57.634	2.4
13	2	0	2	1.48000	62.728	20.0
14	3	0	1	1.47710	62.865	2.5
15	1	0	5	1.42300	65.547	5.1
16	1	0	5	1.41000	66.229	25.0
17	3	1	1	1.40400	66.548	2.8
18	0	0	6	1.30800	72.160	16.0
19	2	1	3	1.25700	75.586	45.0
20	2	0	4	1.24100	76.736	10.0
21	2	2	0	1.13200	85.762	30.0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	MO1	Mo	0.00000	0.00000	0.00000	0.2000	1.0000	2a
2	SI1	Si	0.00000	0.00000	0.33543	0.3700	1.0000	1d

In the diffraction analyzes (Fig. 9) it is observed that the $MoSi_2$ peaks are accompanied by those of SiO_2. This is because $MoSi_2$ is capable of forming a protective SiO_2 scale (thin, layer on the surface of $MoSi_2$) at elevated temperatures; unfortunately, it degrades its high temperature mechanical properties. The powder obtained can be further processed, in order to obtain a marketable product. For example, the powder must be finely ground in a ball mill (brought to 1.2 - 1.5 microns). Calcinations in air at about 500^0C follows, which results in MoO_3 and SiO_2 according to the reaction:

$$2MoSi_2 + 7O_2 = 2MoO_3 + 4\,SiO_2$$

The separation of the two components can be done as follows: after calcinations, the mixture of MoO_3 and SiO_2 will be placed in a circular oven and heated to over 1155^0C (MoO_3 boiling point). MoO_3 can be discharged into the Ar stream [14].

4. Conclusions

Molybdenum is a rare and expensive metal so its recovery from waste by any technique is necessary and justified. In the research and production units there are significant quantities of waste from the heating elements made of $MoSi_2$ that can be recovered.

By analyzing the samples in powder form resulting from the processing of the heating elements made of $MoSi_2$, their structure and morphology were highlighted. X-ray diffraction analyzes confirmed the presence of $MoSi_2$ and SiO_2. Following the studies carried out in this paper, a cheap and efficient method of recovering molybdenum in the form of MoO_3, a salable product, will be proposed.

R E F E R E N C E S

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