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Improving the synthesis process of tribological materials based on tin sulphides by adding graphite as additive

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Abstract: The aim of this research was to study the effect of graphite addition in the process of synthesis of tribological materials based on tin sulphides. The tin sulphides powders were synthesized from selected precursors by pyrometallurgical method in rotary tilting tube furnace. The thermodynamic parameters of the synthesis were determined using HSC Chemistry software modelling package. In addition, the synthesis process was also characterized by thermal analysis method: Simultaneous Differential Scanning Calorimetry and Thermogravimetry (DCS-TGA). The characterization of the synthesized tin sulphides powders included analysis of chemical composition by optical emission spectroscopy, phase composition identification by X-ray diffraction (XRD) and examination of morphology, as well as elemental composition by Scanning Electron Microscopy (SEM) with Energy-Dispersive Spectroscopy (EDS). The hexagonal SnS_2 and orthorhombic Sn_2S_3 phases were formed after thermal treatment of starting powders in nitrogen atmosphere. The obtained results indicate the positive effects of the graphite addition which enables synthesis of tin sulphide powders with appropriate content of sulphide phases with minimal loss of sulphur.

Keywords: tribology; tin sulphide; graphite; pyrometallurgical method

INTRODUCTION

In recent decades, there has been an increasing interest to produce the new materials for tribological applications, due to constant development of modern equipment.[1-3]

Concerns in the use of compounds containing lead, cadmium, antimony etc. as tribological materials have been raised, since these metals are harmful for human

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health and the environment.[4-6] According to U.S. Environmental Protection Agency and the International Agency for Research on Cancer these metals have high degree of toxicity and so they are classified as human carcinogens.[7]

Many studies have been focused on finding acceptable substitutes for conventional tribological materials and results [8,9] of all these investigations have shown that tin sulphides powder is good alternative for compounds containing heavy metals as a safe and inexpensive material. Moreover, tin sulphides powder is safer for the environment and technically superior with respect to other alternatives.[10,11] Tin sulphides are generally prepared by a variety of methods including hydrometallurgical and pyrometallurgical routes.[12-17]

The formation of tin sulphides from solutions involves precipitation of desired product, but this method implies too high costs because solutions must be regenerated, and exhausted materials disposed.

Pyrometallurgical method for synthesis of tin sulphides involves direct reaction of the elements at high temperatures and vapor transport.[18-20] Since this method is economically feasible process it can be also used for synthesis of tribological materials based on tin sulphides. Nevertheless, there are still disadvantages of this method. The one of the major disadvantages is evaporation of significant amounts of sulphur. During the thermal treatment intensive exothermic reaction occurs due to the sulphur auto ignition temperature (230–235 ºC), causing a rapid temperature increase.[18] Significant amount of sulphur evaporates, thus does not diffuse into tin powder. These losses are directly reducing diffusion of sulphur into tin powder and the possibility of the corresponding tin sulphides formation. Also, the process is not ecologically safe, because of the abundant emission of gasses, include in elemental S and/or SO_2.

Besides, the current ecological demands necessitate that future preparation of metal sulphides should not produce high volume of waste product, such as sulphur containing gases.[6]

In previous work of authors,[18] tin sulphides powder was synthesized without addition of graphite. Powder mixture containing 60 % Sn and 40 % S was homogenized and placed in a furnace, heated from temperature of 25 to 170 °C and maintained at this temperature for 2 h in nitrogen atmosphere. Then the reaction mixture was gradually (5ºC/min) heated until the exothermic reaction was occurred (t = 263°C). Finally, nitrogen gas flow was stopped, and the furnace was allowed to cool down to room temperature. The obtained product of the reaction was the mixture of SnS and Sn_2S_3 phases with sulphur content of 28.58 %. It was found that the loss of sulphur was significant.

Based on formerly obtained results,[18] the present research included development and optimization of synthesis process of tin sulphides powder by pyrometallurgical route. The effects of the graphite addition on the synthesis of tribological materials based on tin sulphides were analysed. By application of an appropriate

temperature-time regime and additive (graphite) as a catalyst for the synthesis, the minimal loss of sulphur provides reduced adverse impact on the environment.

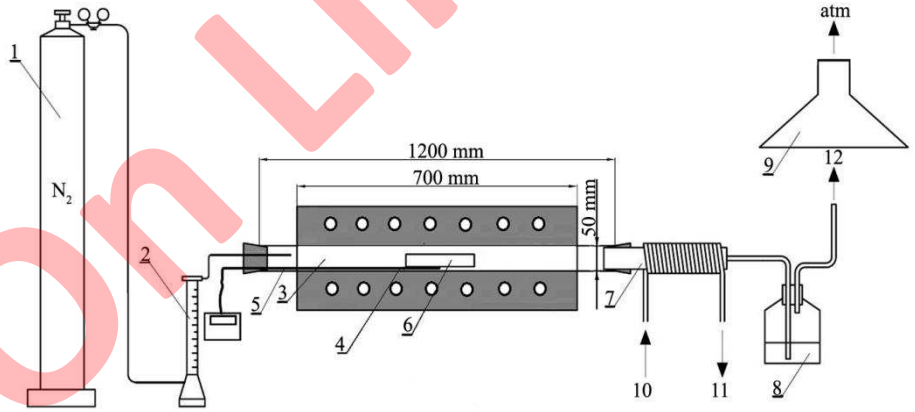
EXPERIMENTAL

Graphite is added in order to remove existing oxides in tin powder which are present unavoidably, as well as for preventing possible oxidation of powders during synthesis process. Moreover, graphite has also been added to improve the lubricating characteristics of the product.[21] For efficient synthesis of the tin sulphides powder, removing oxides and preventing possible oxidation phenomena, should be done by using minimal amount of graphite according to the available scientific[10] and patent literature.[22]

HSC Chemistry software package 6.12 are used for the analysis of chemistry and thermodynamic parameters of the processes for synthesis of tin sulphides powders.[23]

Raw materials used for the experimental test performed in this work were: tin obtained by air atomization ("Sinterfuse" Užice, Serbia), powder with characteristic size 90 % <63 μm), commercial sulphur (Solvay & CPC Barium Strontium GmbH & Co, powder with characteristic size <45μm, purity 99.95 %) and commercial graphite (powder with characteristic size <64μm, purity 95 %). Commercial available tin sulphides powder was used for comparative analysis.

Experiments were carried out in a rotary tilting tube furnace (ST-1200RGV). The furnace is equipped with a system for cooling and outlet gas washing system. Figure 1 shows schematic view of the apparatus used for synthesis of tin sulphides powder by pyrometallurgical method. Graphite powder (5 wt.%) was added to the tin and sulphur powder mixture with a weight ratio of 60:40. After homogenization of the powders in double cone mixer for 15 minutes and sieving through 1mm sieve, the sample was placed in a small ceramic boat in the middle of quartz tube and heated to 550ºC for 1h in N_2 gas flow (200ml/h at a heating rate 10 ºC / min).



1 - nitrogen bottle, 2 - rotameter, 3 - quartz tube, 4 - tube furnace, 5 - control thermometer, 6 - metal boat with sample, 7 - cooler, 8 - washing apparatus, 9 - hood, 10 & 11 -inlet and outlet of cooling water, 12 -off-gas

Fig. 1. Schematic view of the apparatus used for synthesis of tin sulphide powder

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis performed on an iCAP 6000 spectrometer (ThermoScientific) was used for quantitative and

qualitative chemical analysis on synthesized tin sulphides powders. The phase composition of the products was characterized by XRD diffractometer, Rigaku Corporation Ultima +. The morphology of the obtained powders was studied by Scanning Electron Microscopy (SEM) JEOL JSM-5800 at 20 kV. The chemical composition of the samples was analysed using an Energy Dispersive Spectrometer (EDS) Isis 3.2, with a SiLi X-ray detector (Oxford Instruments, UK) connected to the SEM and a computer multi-channel analyser. The DSC and TGA analysis of the system, (60 % Tin + 40 % Sulphur) and 5 % Graphite, were performed from ambient temperature to 600 °C using a DSC-TGA analyser (Model SDT Q600) with a heating rate of 10 °C / min. During the measurements pure nitrogen (N_2) was used as a purging gas at a speed of 5 cm^3 / min.

RESULTS AND DISCUSSION

Results of the thermodynamic analysis of synthesis process of tin sulphides powders with and without the addition of graphite are discussed. Crucial for this analysis was the application of appropriate condition for synthesis.

Thermodynamic data calculated by the Reaction Equation option of HSC Chemistry software package 6.12 shows that tin oxide could be carbothermally reduced to metallic tin when the temperature reaches 550 °C. At this temperature reaction has a negative Gibbs energy which enables the spontaneous occurring of reaction.

The entropy and enthalpy for formation of tin sulphides increases with increasing temperature, in the following way: SnS <SnS_2 <Sn_2S_3. On the other hand, the Gibbs energy decreases as follows: Sn_2S_3 <SnS_2 <SnS (Table 1).

Table 1. The entropy, enthalpy and Gibbs energy of formation of tin sulphides

	$2Sn+S_2(g)=2SnS$			$Sn+S_2(g)=SnS_2$			$4Sn+3S_2(g)=2Sn_2S_3$		
T / °C	ΔH / kJ mol^{-1}	ΔS / J $mol^{-1}\cdot K^{-1}$	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS / J $mol^{-1}\cdot K^{-1}$	ΔG / kJ mol^{-1}	ΔH / kJ mol^{-1}	ΔS / J $mol^{-1}\cdot K^{-1}$	ΔG / kJ mol^{-1}
25	-348.24	-177.62	-299.72	-270.71	-192.91	-218.02	-456.93	-281.73	-379.98
50	-347.63	-175.59	-290.89	-270.18	-191.11	-208.42	-456.06	-278.79	-365.97
100	-347.10	-174.04	-282.15	-269.70	-189.74	-198.90	-455.24	-276.44	-352.09
150	-346.59	-172.76	-273.48	-269.26	-188.64	-189.44	-454.46	-274.46	-338.32
200	-346.08	-171.62	-264.87	-268.85	-187.72	-180.03	-453.69	-272.75	-324.64
250	-359.89	-198.95	-255.81	-275.63	-201.12	-170.41	-467.27	-299.62	-310.53
300	-359.09	-197.51	-245.89	-275.13	-200.20	-160.38	-466.28	-297.80	-295.59
350	-358.15	-195.92	-236.06	-274.57	-199.28	-150.39	-465.16	-295.93	-280.75
400	-357.05	-194.23	-226.30	-273.97	-198.35	-140.45	-463.93	-294.03	-266.00
450	-355.81	-192.45	-216.64	-273.32	-197.42	-130.56	-462.59	-292.11	-251.35
500	-354.42	-190.59	-207.06	-272.63	-196.50	-120.71	-461.14	-290.18	-236.79
550	-352.89	-188.68	-197.58	-271.89	-195.57	-110.91	-459.59	-288.23	-222.33
600	-351.22	-186.71	-188.19	-271.11	-194.65	-101.15	-457.94	-286.29	-207.97
650	-348.99	-184.19	-178.96	-270.28	-193.73	-91.44	-456.18	-284.33	-193.70
700	-348.07	-183.22	-169.77	-269.41	-192.81	-81.78	-454.33	-282.38	-179.53

The combined Tpp phase stability - Ellingham diagram for Sn-N-S system is shown in Fig. 2. Considering the logarithmic sulphur vapor pressure of 5.07 kPa[24]

and experimental temperature of 550 °C it was found that the most stable phases of tin sulphides are SnS_2 and Sn_2S_3 (marked as red dot on the diagram). At these temperatures the vapor pressure of sulphur is such that it shows a saturation of the atmosphere with the sulphur vapor in the furnace. This means that the amount of sulphur gas phase necessary to react with the melted tin is sufficient to establish a contact between mentioned phases. Further, the diffusion of sulphur into tin is enabled to form appropriate tin sulphides powder.

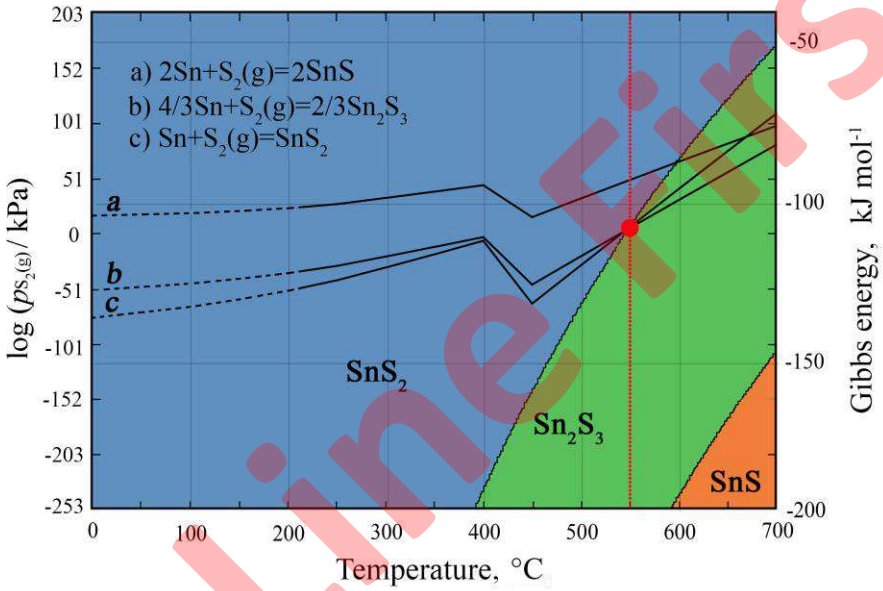


Fig 2. Combined Tpp phase stability - Ellingham diagram for Sn-N-S system

According to the reactions a-c given in the Fig. 2, it can be clearly seen that with increasing temperature up to 400 °C, the possibility of the formation of SnS, SnS_2 and Sn_2S_3 slightly decreases. The sudden increase of sulphide phase extraction occurred when temperature had reached 400 °C. This trend is followed up to 450 °C. Tin sulphides powder obtained at this temperature contains adequate ratio of sulphide phases. The thermodynamic stability of the SnS_2 and Sn_2S_3 phases is greater than that of SnS phase (the Gibbs free energy is more negative) at temperature of 550 °C. SnS_2 and Sn_2S_3 phases should be obtained at 550 °C as shown in Fig. 2 (marked as red dot) which agrees with the stability fields of sulphides.

It can be seen from Fig. 3. that DSC curve (blue line) has three well marked endothermic effects. Also, from Fig. 3. weight loss (27.33 wt.%) on TGA curve (green line) was evident. The first endothermic effect with a peak at 117.4 °C on DSC curve without a recorded changing in the mass on the TGA curve

corresponded to solid phase transition (melting of Sulphur). This evidence is well confirmed by literature experimental data (119.20 ºC).

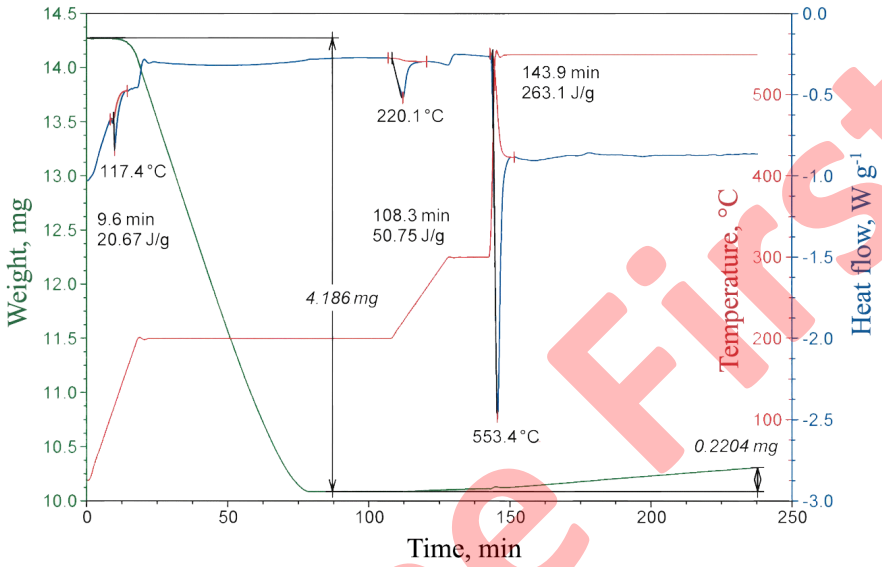


Fig 3. DSC/TGA thermal characterization of system (60 % Sn + 40 % S) + 5 % C

During further heating it was observed a weight loss that starting at about 200ºC in the TGA curve and this corresponds to evaporization of volatile component (elemental Sulphur). The second endothermic effect with a peak at 220.1 °C corresponds to the melting of the tin (together with its oxides). The third endothermic effect with a peak at 553.4 °C is due to a formation of sulphides which can be demonstrated by an increase in the mass of the sample on the TGA curve.[10]

ICP-OES analysis was used to quantify the elements present in each sample of a tin sulphides powder (Table 2).

Table 2. Chemical analysis of the studies tin sulphides powders obtained by ICP-OES test

Sample of tin sulphides powder	Content of the element, %						
	Sn	S	Pb	Cu	Fe	Ni	Zn
Without graphite addition[18]	64.62	28.58	0.17	0.22	0.10	-	0.0057
With graphite addition	60.79	30.21	0.0108	0.54	0.049	0.0007	0.0179
Commercial	59.48	31.83	0.0209	0.0033	0.0148	0.0019	0.0072

The results of ICP-OES analysis showed that sample of tin sulphides powder synthesized without graphite addition, system 60 % Sn + 40 % S, contain 28.58 % of sulphur. This result indicates a great loss of sulphur, because

diffusion of the sulphur into tin was prevented. Finally, SnS and Sn_2S_3 crystal phases were formed, which was further confirmed by XRD analysis (Fig. 4(a)).

The addition of graphite resulted in greater content of sulphur in sample of tin sulphides powder synthesized in the present experiment, (60 % Sn + 40 % S) + 5 % C system, which enabled formation of SnS_2 and Sn_2S_3 phases.

Graphite, as an additive initiate the reaction between the sulphur and tin and provides better diffusion of the sulphur, thus reducing its loss (10.33 %) and favouring the formation of SnS_2 phase.

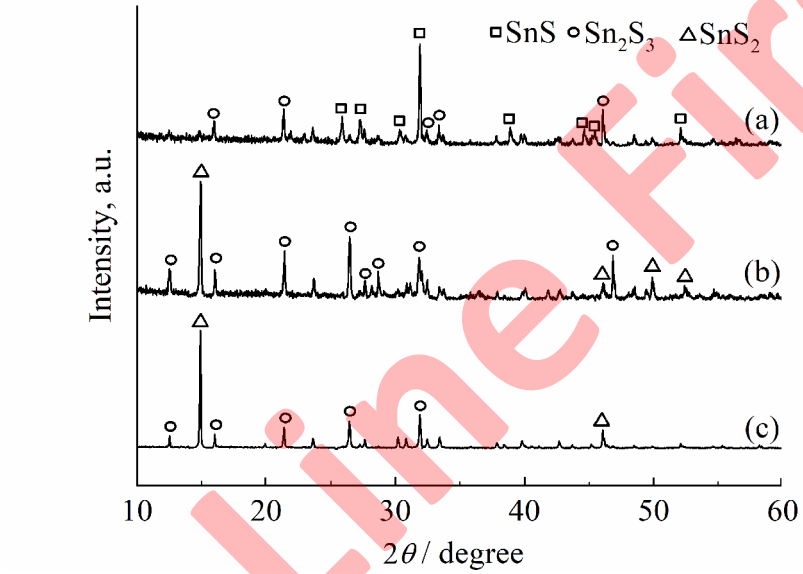


Fig 4. XRD patterns of tin sulphides powder: (a) without graphite addition, system 60 % Sn + 40 % S, (b) with graphite addition, system (60 % Sn + 40 % S) + 5 % C, (c) commercial tin sulphides powder

Fig. 4(b) shows the XRD patterns for the obtained tin sulphides powder in the present work. The intensity of diffraction peaks is assigned to the SnS_2 and Sn_2S_3 phase which is in accordance with the HSC analysis. Other phases were not detected denoting the high purity of the product. The strong and sharp diffraction peaks in the both pattern indicate that the product is very high crystallized.

The X-ray diffraction analysis of the commercial tin sulphides powder indicates two phases, SnS_2 and Sn_2S_3 with high level of crystallinity (Fig. 4(c)). Also, from the XRD patterns it can be seen that no impurities are detected in the sample.

The X-ray diffractograms of the synthesized tin sulphides powder with graphite addition are almost identical to the diffractograms of the commercial tin

sulphide powder. The patterns show that both powders are composed of crystal SnS_2 and Sn_2S_3 phases, without presence of SnS phase.

The synthesized tin sulphides powder without addition of graphite had a layered crystal structure with prismatic and octahedral crystals as confirmed with SEM image (Fig. 5(a)).

The EDS analysis showed that the product is only composed of Sn and S and based on Sn to S atomic ratio it was determined the presence of SnS phase (Fig. 5(b)) and Sn_2S_3 phase (Fig. 5(c)), both orthorhombic phases.

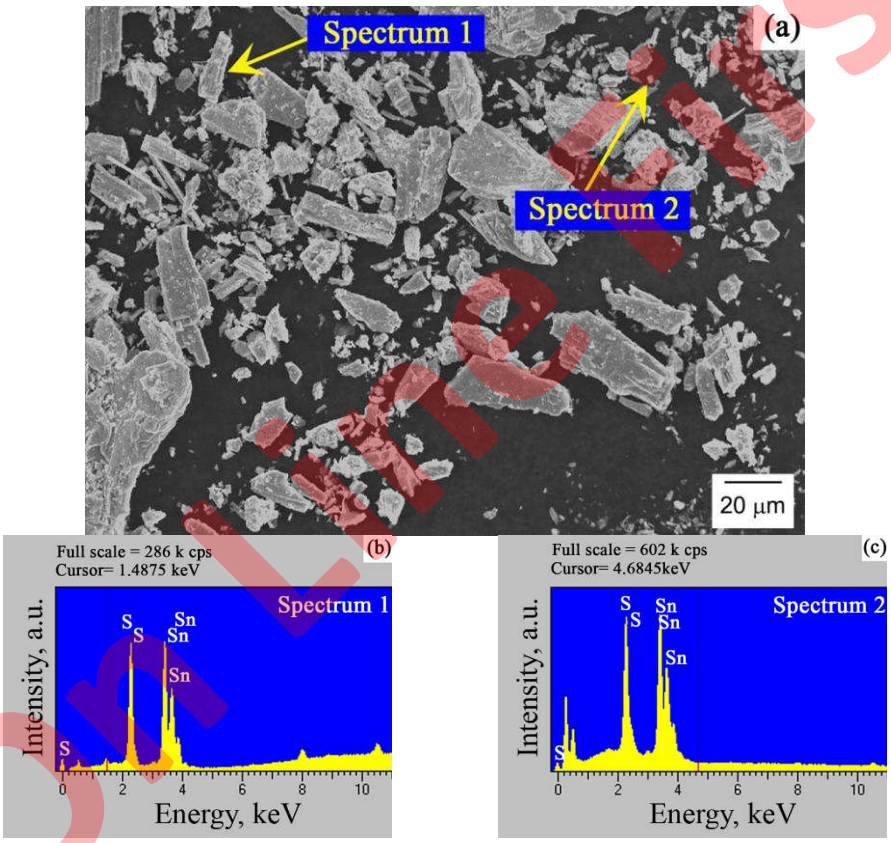


Fig. 5. The synthesized tin sulphides powder without graphite addition, (60 % Sn + 40 % S) system: (a) SEM image and EDS spectrums for (b) SnS phase and (c) Sn_2S_3 phase

The SEM images showed that hexagonal layered and ribbon-like octahedral crystals basically compose the synthesized tin sulphides powder with graphite addition (Fig. 6(a)). It is very common characteristic of SnS_2 and Sn_2S_3 systems. The SEM images have revealed the particle size of 1-50 microns and also confirm the high crystallinity of the sample, as pointed out by the XRD

diffractograms. The results of XRD and SEM analysis were in accordance with thermodynamic analysis.

The data generated by EDS analysis consist of spectra showing peaks corresponding to the tin and sulphur. The atomic ratio of tin/sulphur corresponded to SnS_2 phase (Fig. 6(b)) and Sn_2S_3 phase (Fig. 6(c,d)).

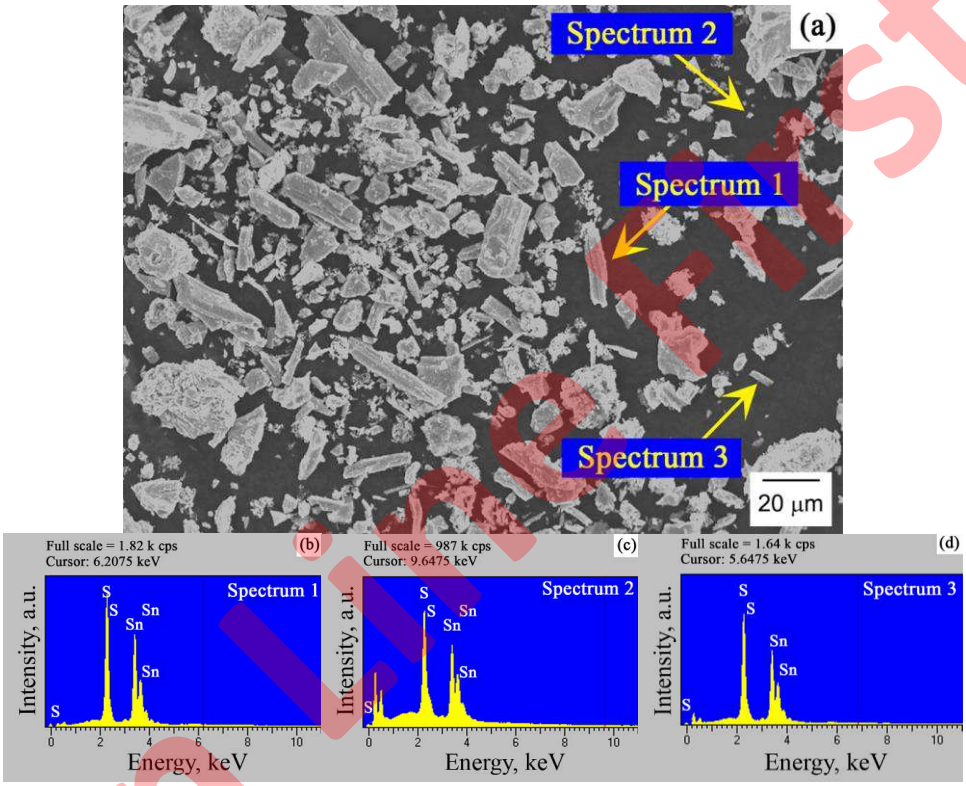


Fig. 6. The synthesized tin sulphides powder with graphite addition, (60 % Sn + 40 % S) + + 5 % C system: (a) SEM image and EDS spectrums for (b) SnS_2 phase and (c,d) Sn_2S_3 phase

The SEM image shows crystal structure of hexagonal lamellas, octahedral and orthorhombic crystals of commercial tin sulphides powder (Fig. 7(a)). The particle size of commercial tin sulphides powder was in the range of 1-50µm, same as particles size from synthesized tin sulphides powder with graphite addition.

The results of EDS analysis confirmed that the obtained tin sulphides powder consists of a SnS_2 phase (Fig. 7(b)) and Sn_2S_3 phase (Fig. 7(c)).

Evident is the significant presence of hexagonal crystals of SnS2 phase in sample of tin sulphides powder that obtained with the addition of the graphite as well as in the commercial powder.

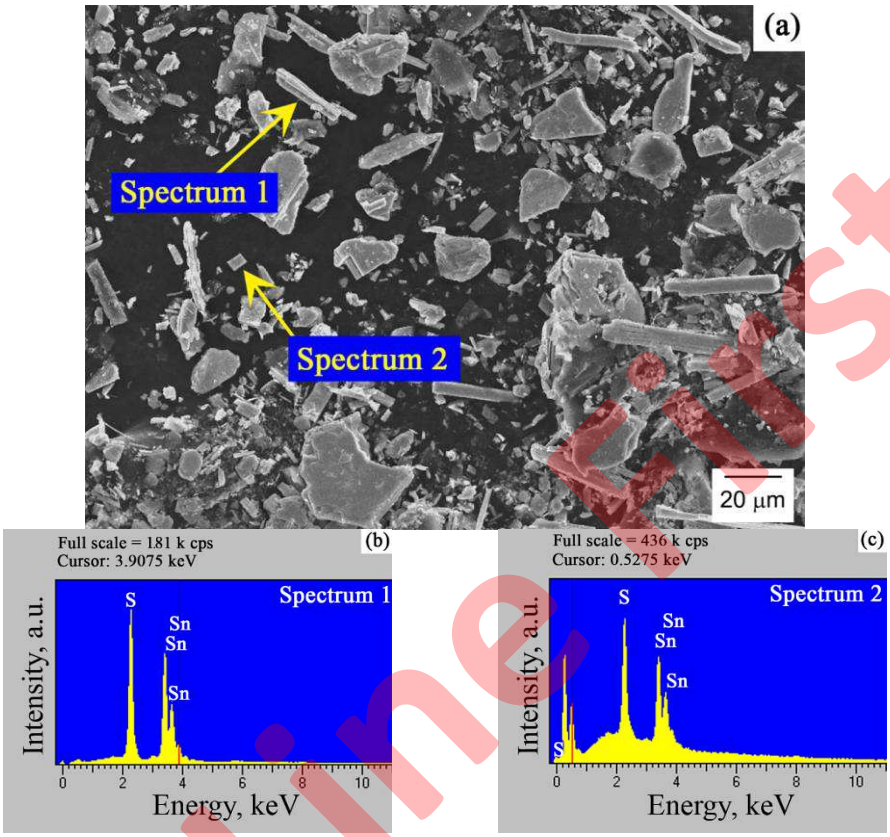


Fig 7. The commercial tin sulphides powder: (a) SEM image and EDS spectrums for (b) SnS_2 phase, (c) Sn_2S_3 phase

SEM-EDS analysis confirmed that the tin sulphide powder synthesized with the addition of graphite is nearly identical with the commercial tin sulphide powder.

CONCLUSION

The experimental results clearly indicated that the addition of graphite plays important roles in the synthesis of tin sulphides powder. There are three main functions of the addition of graphite in the production of tin sulphides powder:

1. It removes oxides in tin powder and prevents possible formation of oxides
2. Favours the formation of hexagonal SnS_2 and orthorhombic Sn_2S_3 phases;
3. It reduces the amount of unreacted S powder and its loss which evaporates in the form of elemental S and/or SO_2 into the atmosphere during reaction.

Comparative analysis of commercial tin sulphides powder and tin sulphides powder obtained with graphite addition showed no significant difference in structure, chemistry and phase composition between powders.

The tribological material based on tin sulphides was synthesized through a simple, inexpensive and environment-friendly method. In addition, the process is inexpensive and can be used for industrial production of high grade tribological materials based on tin sulphide with required properties.

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И З В О Д

УНАПРЕЂЕЊЕ ПРОЦЕСА СИНТЕЗЕ ТРИБОЛОШКИХ МАТЕРИЈАЛА НА БАЗИ СУЛФИДА КАЛАЈА УЗ ДОДАТАК ГРАФИТА КАО АДИТИВА

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Циљ овог истраживања је било проучавање утицаја додатка графита на процес синтезе триболошких материјала на бази сулфида калаја. Прахови калај сулфида су синтетисани од изабраних прекурсора пирометалуршким поступком у ротационој нагибној пећи. Термодинамички параметри процеса синтезе сулфида калаја одређени су применом "HSC Chemistry" програма. Поред тога, процес синтезе је окарактерисан методом термичке анализе: симултаном диференцијалном скенирајућом калориметријом и термогравиметријском анализом (DCS-TGA). Карактеризација синтетисаних прахова сулфида калаја је обухватила анализу хемијског састава оптичком емисионом спектроскопијом, одређивање фазног састава рендгенском дифракционом анализом (XRD) и испитивање морфологије као и елементарног састава скенирајућом електронском микроскопијом са енерго дисперзијоном анализом (SEM-EDS). Након термичког третмана полазних прахова у атмосфери азота формирана је хексагонална SnS_2 и орторомбична Sn_2S_3 фаза. Добијени резултати указали су на позитивне ефекте додатка графита чиме је омогућена синтеза праха сулфида калаја са одговарајућим садржајем сулфидних фаза уз минималан губитак сумпора.

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