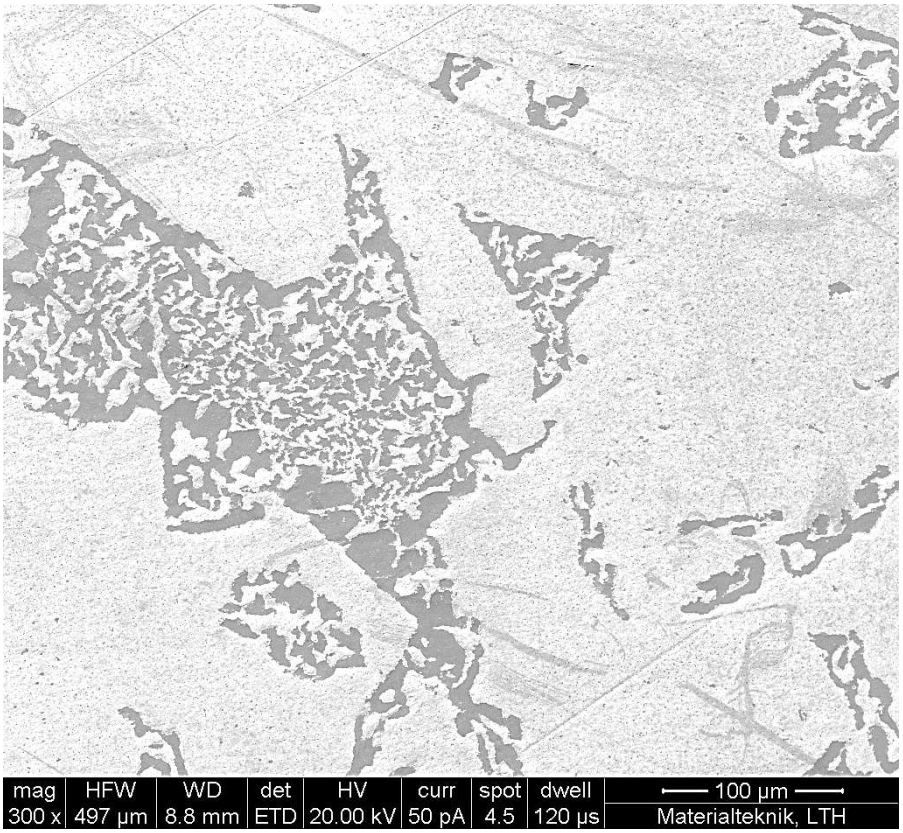
LABORATORY REPORT ON CHARACTERISATION OF TIN-BISMUTH ALLOY WITH SEM



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1. AIM AND OBJECTIVES

The aim of this report is to understand which kind of alloy and which are its characteristics using the scanning electron microscope and its three detectors: secondary electrons, back-scattered electrons and secondary electrons (X-Ray) spectroscopy. The information that is possible to obtain from SEM belong to topography, chemical composition and crystal orientation. The main objective is to understand which is the position in the phase diagram of the given alloy and, from this, give some indications on the composition. Furthermore, it could be possible to have an idea about the metallurgical process, for instance the cooling rate. In this specific report has been analysed Sn-Bi alloy that was assigned on the specimen.

2. BACKGROUND: SEM, EBS, EDS

2.1 HOW DOES SEM WORK?

The scanning electron microscope is a type of microscope that use electrons to produce the image, instead of using light, that means an extreme advantage in the resolution. The image on the right (2.1.1) shows the principal elements that compose the medium (Atteberry, 21 April 2009). First, the electron gun made by LaB6 filaments in this case[1], that are heated up until a beam of electrons is produced. This beam, of smallest size as possible, is accelerated by the positive electric potential applied to the anode plate below the electrons source: electrons are negatively charged and are attracted by the positive charge of the plate. Once they have passed the anode, they do not tend to go naturally where they should go, but they diverge and this is why condenser lenses are used. They create magnetic fields, also positively charged so that electrons keep moving in the same direction. When the beam cone passes the anode, it is converged and demagnifyed in a corresponding point in the image plane of the lenses; after it passes this plane, it

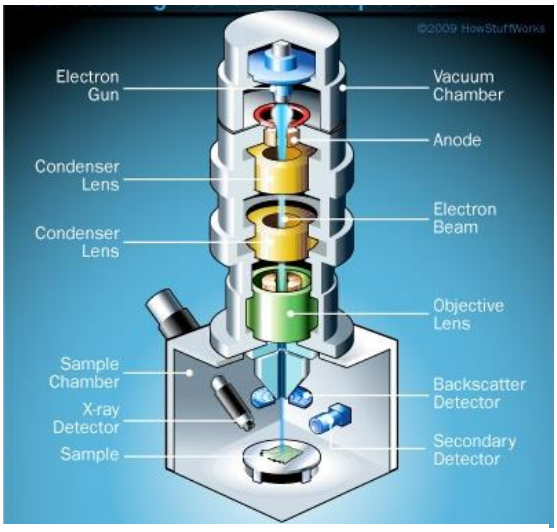


Figure 2.1.1: SEM cross section with components

[1] The most common type is thermionic gun

begins to diverge again into another cone with a higher angle than the upper one. It is then apply further conversion and demagnification to the image plane of the sample (figure 2.1.2 & 2.1.3) (Philips Electron optics, 1996).

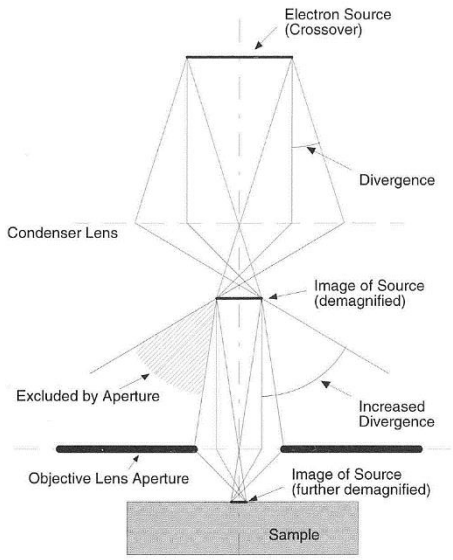


Figure 2.1.2: SEM Image formation

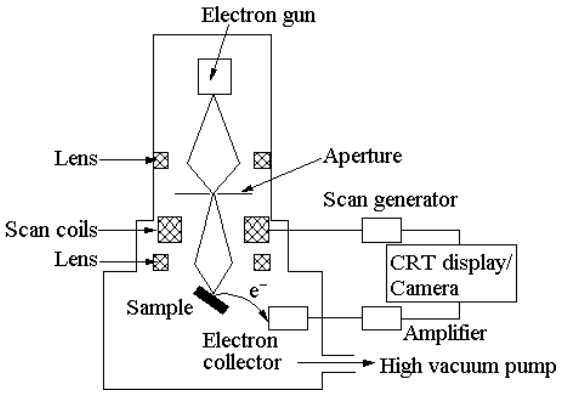


Figure 2.1.3: condenser lenses in SEM

Due to the fact that lenses exhibit mainly spherical and chromatic aberration, apertures are used to reduce the generated adverse effect. They are small holes that define the amount of electrons transmitted in the lens plane, discarding electrons that are farthest from the optical axes. This means a reduction of the current beam to obtain a smaller point size. Then, the electron beam hit the specimen collocated in a sample chamber to be insulated from external vibrations that can disturb the final image. The entire SEM works in a vacuum chamber for two main reasons: air particles of the atmosphere could be obstacles in the electrons path and electrons could not move freely towards the three detector; the second one is that they could distort the surface of the specimen (Atteberry, 21 April 2009).

2.2 THE THREE SIGNALS

The beam current hit the specimen and scan each pixel of each row from left to right. Properly not the entire current concur in the process, just imaging current is absorbed, but in SEM the difference between the two is negligible. The sample is scanned not only in the surface, but in a precise teardrop volume where electrons may interact anywhere several times (Philips Electron optics, 1996). This volume of interaction is composed of three different parts, shown in the picture below (2.2.1) that emit different signals. The primary electrons bombard the volume and two main reflected electrons can be detected: if the primary electron has an inelastic collision with one local electron, the primary one is scattered few nanometres away from the surface and the second one is ejected. The totality is so called secondary electrons, characterised by a low-energy meaning that, in the atomic structure, they very close to the nucleus and very stable. This imply that they necessary need to escape from a shallow part of the volume, more precisely the surface. In the other case, the primary electron collides elastically with the nucleus of a sample atom and it is scattered back. This explain why they are called back-scattered electrons and belong to a deeper part of the volume having a higher energy level. The SE offer the best imaging resolution and give information about the morphology of the specimen, while EBS provide knowledge on

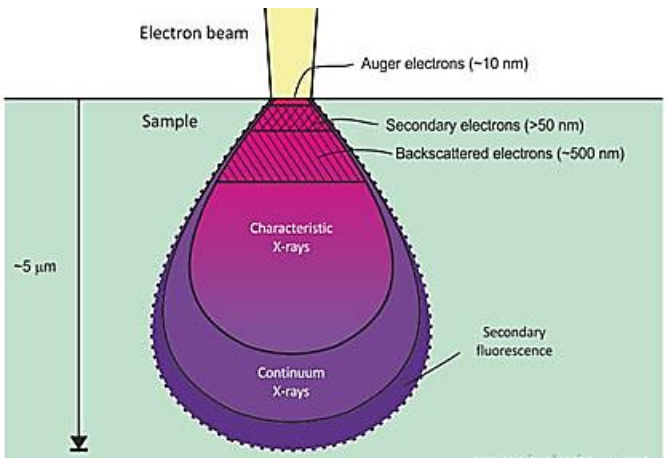


Figure 2.2.1: Volume of interaction and specification of the three different parts

the chemical composition using the x-ray detector (EDS). In fact, when the secondary electron is emitted, a gap is made in the shell and, due to the fact that the atom wants to achieve the most stable state, an electron from the upper shell (that means higher energy level) jump to the lower one. Then, ΔE between the two levels is emitted as electromagnetic radiations of X-ray (figure 2.2.2). So three different detectors are installed in the chamber to achieve these three different signals (E. Gavrilenko, 2014).

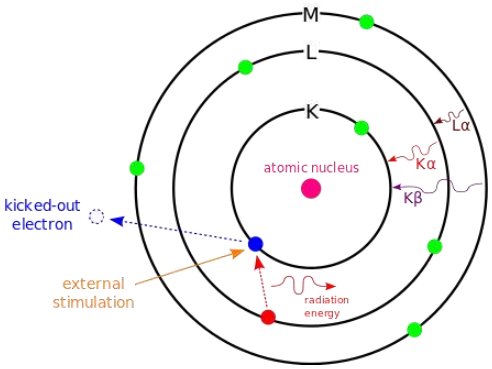


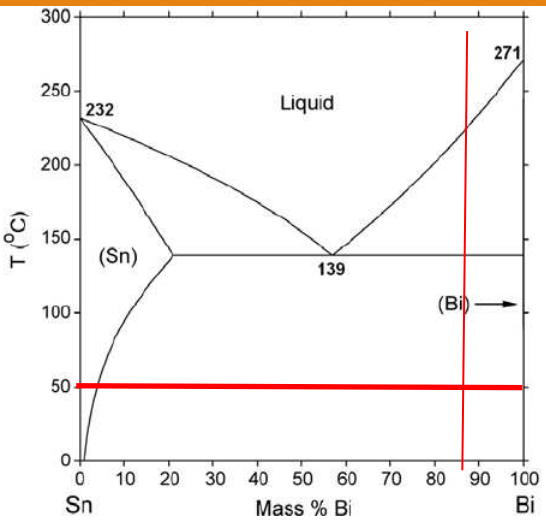
Figure 2.2.2: Basic principle of dispersive energy used in X-ray spectroscopy

3. EXPERIMENTAL

First of all, the given alloy has been cut and polished with silicon oxide in order to create a flat surface to analyse. This explain why in the composition has been found trace of silica. The sample is closed in the vacuum chamber and the plate is adjusted from the pc where also the images are produced. The type of microscope used is Philips XL30-ESEM with resolution: 3.5 nm and magnification: 400000 x. The more interesting advantages are a little specimen preparation and not necessity of conductive coating for a non-conductive material (in the wet mode). XT microscope control software has been used for processing images and EDAX software for reading the composition from EDS detector. An important step that need to be done at the very beginning is the focusing: it is zoomed on a particle reducing the scale up to 5 nanometres, then resolution is adjusted until that particle is clearly seen on the screen. Then the proper analysis can start and four quadrant are shown: the first in the left corner is related to SE signal, next to it there is EBS, in the low left corner is EDS results that are analysed in composition by the second software and the last quadrant is a camera looking inside the chamber.

4. RESULTS AND DISCUSSION

From the composition analysis, it is resulted that Sn-Bi was the given alloy, of which the binary phase diagram is on the right (graph 4.1). As shown, the solid solubility is possible for Bi in Sn and the limit is reached with the composition of 21% Bi mass and 79% of Sn, while there is no possibility for Sn to dissolve in Bi meaning that it is present just as pure metal. The diagram also shows the presence of an eutectic transformation at 139 degree integrate (Smallman, 2014, pp. 55-59). The question that need to be asked is if it possible to say which precise position (related to a precise T) in this diagram was occupied by the given alloy using the signals collected from SEM. To ask this question is necessary to analyse the images originated from the three different detectors and making possible hypothesis. Then, these hypothesis will be compared with the data from EDAX software (figure 4.5, 4.6, 4.7) about the alloy composition and finally confirmed



Graph 4.1: Phase diagram of Sn-Bi alloy with eutectic

or denied. The first picture (4.1) comes from the secondary electrons and it is a general overview of the alloy taken at 500 µm as scale. Due to the fact that concern the morphology, it is immediately evident that two distinguishable phases are present. The white lines on the left don't mean that is a bad conductor because they cross all phases, so they probably represent some dust or contamination during the preparation, but this has not been checked in the punctual chemical test.

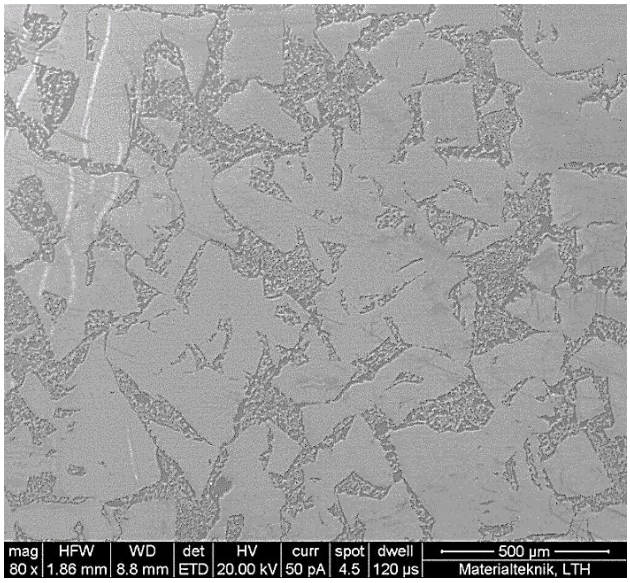


Figure 4.1: Secondary electron detector (ESEM microscope) 80x

The magnification is important to achieve details that are not visible from such a relatively large scale. Zooming down at 300x and remaining in the SE analysis (figure 4.2), also scratches and white particles are observed. Being the lines all over the sample, they are probable due to the preparation, while the white aggregates are silicon oxide as mentioned is the previous paragraph. This has been confirmed by the analysis of point four in figure 4.4 that has registered as 1.38 w% (graph 4.4, table 4.4).

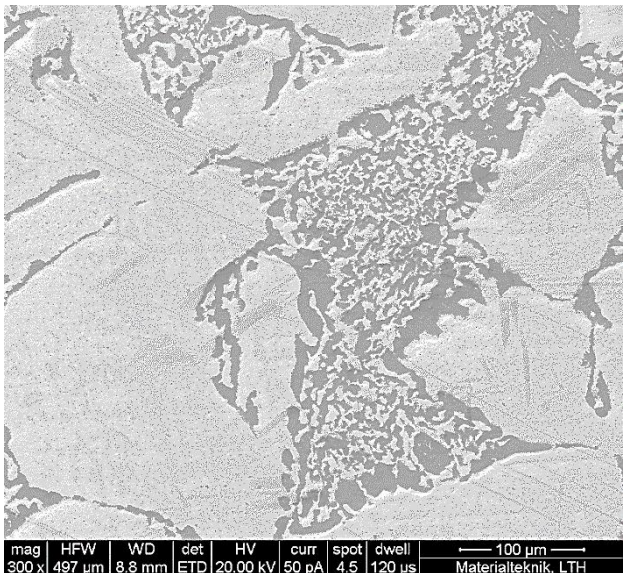


Figure 4.2: Secondary electron detector (ESEM microscope) 300x

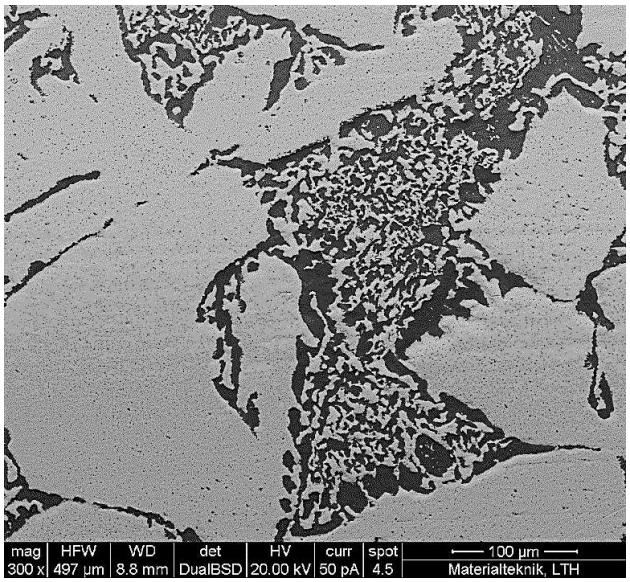


Figure 4.3: EBS detector (ESEM microscope) 300 x

It is important to remember when speaking about punctual analysis using EDS that in reality is never punctual, but an area near the point selected on the screen is analysed. From point 1 in EDS is not possible to see that, but later one when point 2 will be considered, it will show the presence of different weight % of different elements because it is not a "point" but a larger space analysed.

Moving to the back-scattered electrons (figure 4.3), some more information can be achieved about the composition. The adjusted contrast is extremely important in underlying that the two phases have different weight: one element is heavier than the other; more precisely the grey one is heavier than the black one, so the two metals have very different atomic number. The heaviness of crystalline solids depend mostly on the density that is influenced by the atomic weight and by the atomic arrangement. Materials, especially metallic materials, have different atomic mass that go in the density formula $= \frac{m}{v}$; for a constant volume value, an increasing mass determine an increase in density. The atomic arrangement is mostly governed by the coordination number and the lattice parameter, that means how many atoms are equidistant from the centre of the unite cell and the number (numbers) that describe the shape of this cell. HPC for example is a very close packed configuration because the distribution of atoms make them very close to each other determining low empty spaces. Another useful example is the comparison between BCC with atomic packaging factor=0,68 and FCC=0.74, and BCC cell is smaller so it has less empty space resulting more dense than the other one

and, as consequence, more heavy (Smallman, 2014, pp. 27-31). According to the chemical composition from the software, this analysis is true because the grey part is Bi with ρ = 9750 kg/m^3 and base centered monoclinic lattice, while the black part is Sn with ρ =7280 kg/m^3 and cube centered tetragonal lattice (Engineering ToolBox-Metals and Alloys, 2004).

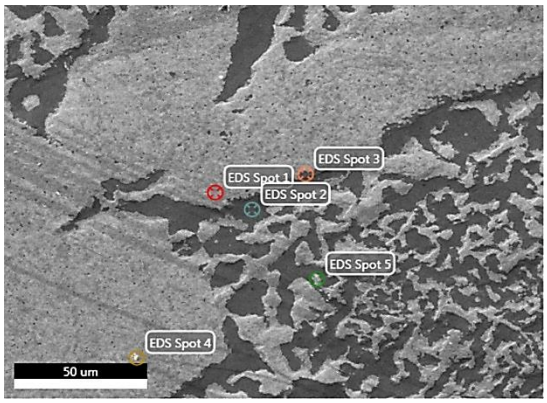
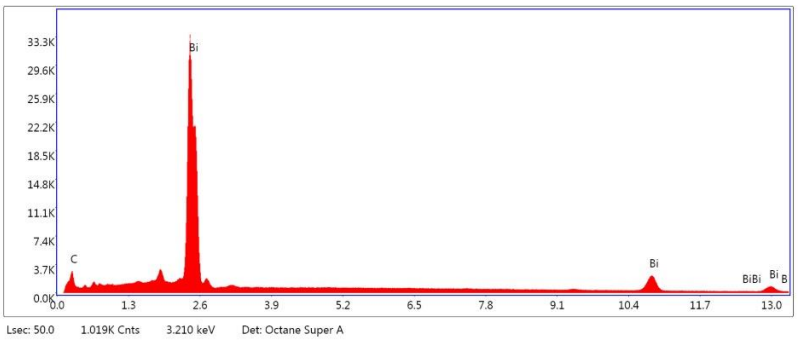


Figure 4.4: Spots of EDS analysis (ESEM microscope)

Then, how can be supposed from the microscope which are the two phases of the two solid components and where is the position in the phase diagram? The key element from figure 4.3 is the appearance of the grey and dark grey part. The first one is clearly α phase of the heavy element or bismuth because clear formed grains are distinguishable. As shown in the phase diagram (graph 4.1) Bi cannot dissolve Sn in it and in fact, looking at the EDS spot 1 in figure 4.4, Bi is the only element present without any traces of tin (graph 4.2). Therefore, the dark grey part with some light grey scratched points remind to the eutectic phase; actually the typical feature of α and β phase formed together below the eutectic temperature is lamellae shape, at least for iron-carbon system where this appearance is remarkable. Generally variations may occur according to the material. The EDS spot 2 in figure 4.4 reveals that primary β grains (Sn) and secondary α grains (Bi) are forming (graph 4.3). So the final structure is primary grains of α in a eutectic matrix of α and β. Using the lever rule, it is possible to know the fraction of α and β in the eutectic phase.

Looking at the composition, the first phase shows 87.5% of Bi (table 4.2) while the second phase 92.19% of Sn and 3.08% of Bi (table 4.3). Knowing the composition of the two phases on x axis is possible to find which is the position in the phase diagram using the lever rule: it is on the right side because of α phase, below the Te temperature because there is eutectic phase and using the compositions it is found the red horizontal line in the graph 4.1. Then, information on the T of phases is given looking at the y axis: the T is around 58/60 degree integrate.

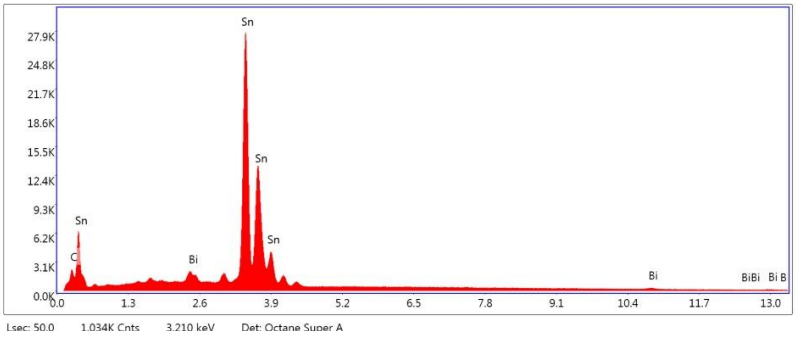
It has to be pointed out that the accuracy of EDS contains some limitations and this is why in the three table above the Error% need to be considered. In fact, in EDS some elements can show overlapping of X-ray emission peaks; just atoms that are enough excited emit radiations and these radiations can have any direction and it may happen that some are not able to escape from the specimen and be detected (Wikipedia-X-ray spectroscopy, 2018).



Graph 4.2: EDS spot 1-Det 1

Table 4.1: Composition spot 1

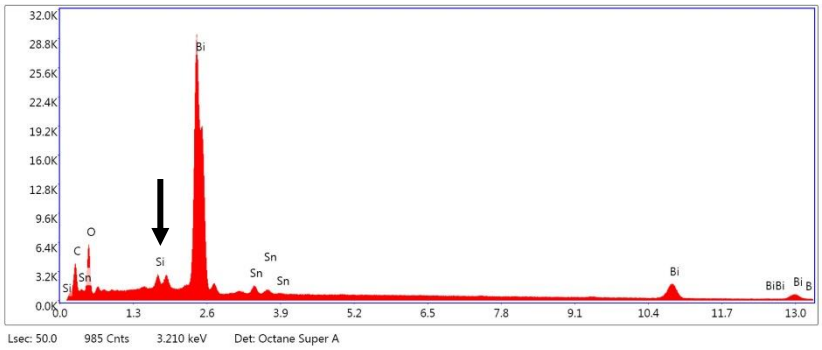
Element	Weight %	Atomic %	Error %
CK	12.5	71.31	7.11
BiM	87.5	28.69	1.84



Graph 4.3: EDS spot 2-Det 1

Table 4.2: Composition spot 2

Element	Weight %	Atomic %	Error %
CK	4.74	33.27	5.10
BiM	3.08	1.24	6.05
SnL	92.19	65.49	1.35



Graph 4.4: EDS spot 4-Det 1

Table 4.3: Composition spot 4

Element	Weight %	Atomic %	Error %
CK	11.97	42.13	7.13
OK	15.45	40.83	9.74
Sik	1.38	2.08	7.72

Another element that can be analysed is how the alloy has been cooled down. A larger cool down, that means a low rate of cooling, allow the alloy to develop the eutectic phase, while a lower cool down that means a higher cooling rate, bring the formation of something different. In this case the formation of two phases and in particular the eutectic phase, let think that the process of cooling has been slow. Another marker is given from the shape of eutectic phase that are elongated points that are formed when cooling is slow and atoms have time to distribute easily. In contrast, in rapid cooling they tend to be condensed and close to other forming lines (lamellae) with low space between them. Generally more information can be achieved from T-T-T diagram, but Sn-Bi system is a quiet simple alloy and this further analysis in not necessary.

A very good characteristic of the alloy is its low melting point that lead to present and possible future applications. For this reason and adding that bismuth tend to expand slightly when solidified, it is used a lot for solders especially in food processing equipment and cupper waters pipe. For the same characteristic, the alloy is used for fire detection (Indium Corporation). The final application that deserve to be mentioned is when Sn-Bi electrode is used to electrochemically deteriorate Cd^{2+} that has been found toxic for human body even in low concentration. The system was tried in the past for rice and it was successful, so future further development are hopeful (Dawei, 2012, pp. 472-474).

5. CONCLUSION

In conclusion, tin-bismuth alloy was the one assigned and analysed with SE, EBS and EDS detectors in ESEM microscope. It has been possible to see two phases and find out that the final structure is primary grains of α in a eutectic matrix of α and β. Using the EDS chemical analysis that gives compositions, has been found the precise position in the phase diagram of Sn-Bi and the relative temperature. The process has been supposed at low cooling rate or, in other words, the alloy has been cooled down slowly.

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