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CHEMICAL COMPOSITION AND PHASE CONSTITUTION OF RECYCLED METALS FROM COMPUTER SCRAP

Studies done on recycled products gained from computer boards have been presented. Alloys fabricated by melting of computer boards were investigated in detail. It was found that the alloy is segregated into two regions – copper and iron rich, in which other alloying elements, forming either solid solutions or intermetallic phases, are dissolved. Scale from melting and sediment from etching metals in hydrochloric acid were also studied. In the scale fluxing agents and residual of metals were gathered, whereas in the sediment some amount of noble metals was detected. Microscopic investigations and chemical composition measurements were performed on alloys from melted boards as well as on the scale and the sediment.

1. INTRODUCTION

Waste management is a huge global challenge and is also an international task. It consist of many issues, like waste monitoring and collecting, materials recovery and recycling, and also hazardous substances utilization, and law regulations [1–4]. In several countries there are special government programs which control and regulate the waste management. For example, in Japan, the waste system covers four specified house appliances and roughly 2/3 of these discarded appliances are collected and recycled formally by the manufactures [5]. The remaining 1/3 is exported as used items or scrap. Consequently, the government of Japan has issued guidelines for the reuse and recycling as countermeasures against illegal dumping and to regulate the export of e-scrap. Especially, electronic waste (e-waste, e-scrap) management is an interesting issue. Waste electric and electronic equipment (WEEE) is no longer a problem of ecologists and national parks wardens who trace illegal dumps but becomes also a source of precious

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materials. In the light of dynamic technological development, rapidly increases request for rare and precious metals [6, 7]. Electric and electronic industry is among the main users of these types of metals: cell phones, computer boards and other minor electronic devices. Life of such equipment is short. One can assume that, only cell phones are exchanged every 1.5 years. The market is permanently supplied with new solutions and current electronic equipment is quickly replaced by new devices [8]. Vast amount of metals, accumulated in WEEE, will before long become an important source of their supply. In Poland, in 2010, only less than 3 kg of electronic scrap, per inhabitant, was collected. It is less than 4 kg recommended by the EU directive, although, in our region, it has been fulfilled in Czech, Slovak Republic and Hungary [9]. In Poland, there is a growing number of enterprises which collect WEEE. However, most of them sell it abroad or simply, after partial disassembly, direct it to scrap-yards. It is a great loss. In electronic equipment, beside noble metals such as gold, silver, platinum or palladium, are also accumulated tones of, equally precious, copper, tin and lead. An extensive report on this issues was prepared and published in February 2009 by M. Schluep from Swiss Federal Laboratories of Materials Science and Technology (EMPA) by order of United Nations Environmental Programme (UNEP) [1]. This report, among various environmental information, comprises also data on materials content in electronic equipment. For example 1 t of cell phones (about 6 thousand pieces) contain 340 g of gold, 140 g palladium, 3.5 kg silver and 130 kg copper. Thus, WEEE is currently considered as an important source of metals. Examples of Scandinavia or Switzerland prove that on WEEE one can earn money.

Recycling of precious metals, especially for countries, which are not rich in natural resources, may make them less sensitive to price fluctuations in the global market and political actions. Computer hard disc drives (HDDs) contain also neodymium magnets. Currently 97% of rare earth metals is possessed in China. Limitations of ores extraction, observed in this country in recent years, inclines European countries, Japan and the USA to activity towards resuming exploitation in own, previously closed mines and obtaining rare earth metals in the process of recycling. Nevertheless, metals which are contained in WEEE are not available directly but they require complex processing and refining technologies. This is mostly due to a great variety of materials comprised in a single device. It makes electronic scrap difficult to recycle. For example, as it was reported by Umicore, computer boards contain 60 elements [10]. Thus, alloys obtained from e-waste consist of components being a mixture of solid solutions and intermetallic phases, usually containing tens of elements.

Most frequently used refining methods comprise hydrometallurgy, pyrometallurgy and precipitation from solutions [1, 10]. However, variety extraction methods are investigated. For instance, extraction of copper, zinc, cadmium and nickel from solutions received by the leaching of e-scrap has been reported in [11]. On the other hand, ball milling and powder metallurgy might be used to gather metals from e-waste [7]. What is worth of emphasizing, biohydrometallurgy can become a promising technology of

recovering metals from industrial waste [12]. For example, noble metals like gold can be extracted from electronic scrap by bacteria [13]. To make these processes more effective, it is important to recognize chemical composition and phase constitution of typical alloys obtained from electronic scrap.

In this study, products produced by melting of computer electronic scrap, were examined. Their phase constitution, morphology and chemical composition were evaluated in order to gain data necessary for further recovery of constituting elements. Alloy, ingot and melt are the phrases used exchangeable. Similarly, phrases section and region have the same meaning.

2. EXPERIMENTAL

Alloys, scale and sediment have been delivered by the P.P.H.U. POLBLUME Zbigniew Miazga Enterprise. These materials are products obtained by chemical or thermal processing done on computer boards (grade III). The alloys were gained as a result of melting boards in around 1200 °C. The scale is a residue from melting and casting alloys and is usually a mixture of metal oxides, impurities and fluxing agents. Some amount of the scale was milled due to further XRD examination. The sediment came from etching boards with hydrochloric acid in order to remove solder and release resistors which contain traces of noble metals. Before the study of chemical composition, the sediment was milled and fraction with particles smaller than 300 µm was used for investigations.

The alloys were initially subject to macroscopic observations. Subsequently, optical and scanning electron microscopy (SEM) were used for investigations. Moreover, SEM images obtained using the BSE mode, allow one to distinguish differences in chemical composition. Density was evaluated by means of the helium pycnometer. Chemical composition was carried out with the use of fluorescent X-ray spectroscopy with dispersion of wavelength (XRF Bruker S4 Explorer) and energy dispersive spectroscopy (EDS). The error reached 0.5%. Chemical composition of tiny objects obtained by the EDS technique might be however slightly incorrect due to their small dimensions. In such a case, it is a possibility to collect signal from surrounding section. Phase constitution was obtained by the X-ray diffraction method using the Rigaku Miniflex II diffractometer (CuK α radiation).

3. RESULTS AND DISCUSSION

3.1. STUDIES OF THE ALLOYS

Chemical composition of ingots originating from various melts differed slightly, depending on the type of boards. Good reproducibility of results was found. All the

alloys showed a presence of grey and yellow sections. In this paper, the results for a single melt, typical of computer boards, are given. Macroscopic images of the ingot are shown in Fig. 1. One can clearly see a presence of the two regions, having respectively grey and yellow colour. Additionally, spherical, yellow inclusions are present in the grey region.



Fig. 1. Macroscopic images of a sliced ingot

Results of the spectroscopic investigations confirm predictions based on macroscopic observations. The grey region contains, on average, 71%³ of iron, 15% of copper and around 1% of nickel and silicon. Chemical composition studies of the yellow part reveal substantial (78.3%) amount of copper as well as meaningful concentration of tin – 6.4%. In this part of the alloy such elements as Fe, Pb, Ag, Zn, Mn, Sb and Ni are also present.

Measurements of density give mean values of 7.8 ± 0.2 and 8.0 ± 0.2 g/cm³ for the grey and yellow parts, respectively. Taking into consideration colours of these parts of the alloy and densities of iron and copper, which are 7.9 and 8.9 g/cm³, respectively, one can conclude that the grey part is rich in iron and contains dissolved elements, whereas the yellow part is copper rich and contains dissolved lighter elements.

SEM microstructures of the alloy, in a back-scattered electrons mode, are shown in Fig. 2. The melt is inhomogeneous. Separation into two different parts is visible (Fig. 2a). On the grey section (at the top of Fig. 2a), one can notice spherical, yellow inclusions. On the other hand, in the yellow fragment (at the bottom of Fig. 2a), dendritic, grey grains, as well as white precipitations in the grain boundaries are present.

The grey, iron rich section is shown in Fig. 2b in greater magnification. One can distinguish three basic regions: dark matrix (1), large, brighter dendrites in the matrix (2) and spherical, yellow inclusions (3). These elements were subject to EDS microanalysis ($\pm 0.5\%$). Chemical composition of dark matrix (1) reveals mostly Fe (94.6%) with Si, Ni, Cr and Mo dissolved in small proportions. Large, brighter dendrites (2) are also rich in iron but its concentration is lower (83.2%) and the alloy contains more Ni (5.7%) and Si (2.7%). Spherical, yellow inclusions (3) are copper rich (84%) and contain 7.3% of tin, as well.

³The results are given in terms of weight percent.

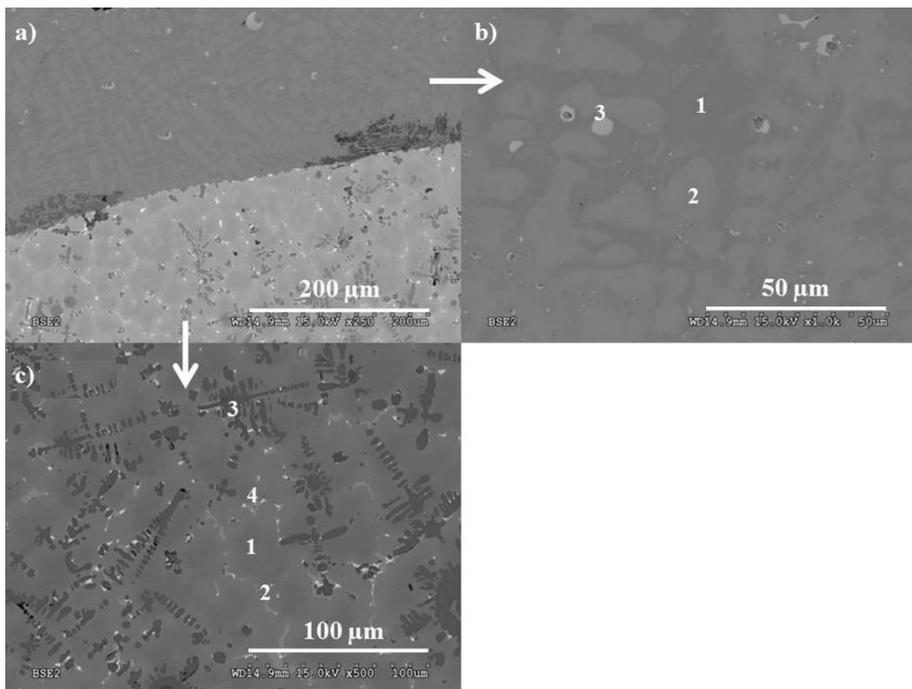


Fig. 2. SEM microstructures of the ingot: a) interface between two sections (magnification 250 \times), b) the grey section (magnification 1000 \times), c) the yellow section (magnification 500 \times)

The yellow section is presented, in greater magnification, in Fig. 2c. One can distinguish there various microstructural elements such as: dark (1), and brighter (2) matrix grains, dark dendrites (3), and bright grain boundaries (4). EDS technique was used to determine chemical composition of these objects. Dark matrix grains (1) are Cu rich (90.2%). They contain also 3.3% of Sn. Microanalysis of brighter grains (2) reveals smaller Cu concentration (86.5%) but higher Sn content (10.2%). This effect results from dendritic segregation in the alloy. Brighter grains contain also 0.4% of Ag. Dark dendrites (3) consist principally of Fe (85%), but they contain, in smaller proportion, Ni and Si, as well. The bright network in the grain boundaries (4) contains concentrated Pb (59.7%) and smaller amount of Sn (3.8%) and Ag (5.3%).

X-ray phase analysis was used to determine the types of constituting phases. These studies play an additional role to the spectroscopic and EDS analyses. Due to volumetric character of this study, the results refer both to the matrix and the inclusions. Results of these analyses are shown in Fig. 3a (for the grey part) and Fig. 3b (for the yellow part). The results are characterized by a very good reproducibility for various melts from computer boards. In the grey section one can distinguish the presence of iron phases, such as $Mn_{0.04}Fe_{0.96}$ and $Fe_{0.9}Ni_{0.1}$ accompanied by W_6Fe_7 and $Cu_{0.91}Sn_{0.09}$ and Cu. The yellow part is dominated by the copper-tin phase $Cu_{0.91}Sn_{0.09}$ and, in smaller proportion, iron

rich phases: with manganese $Fe_{0.3}Mn_{0.7}$ and with nickel $Fe_{0.08}Ni_{0.32}$. Silver and lead were also detected. Reflections marked as unknown were difficult to recognize.

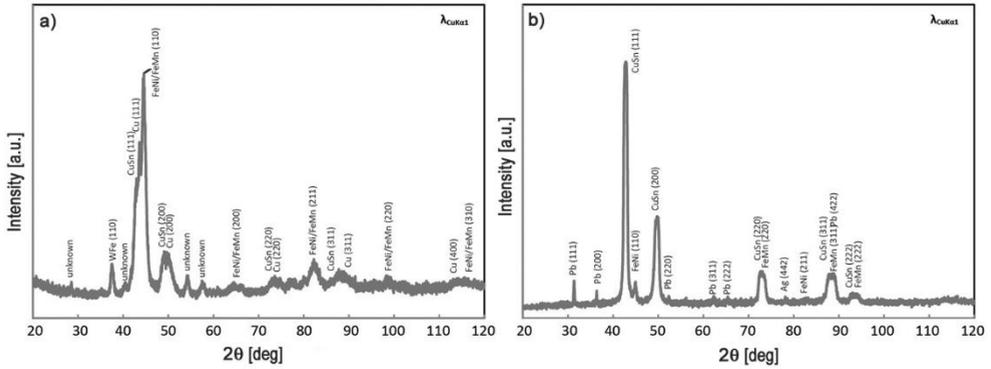


Fig. 3. Diffraction patterns of the ingot: a) the grey section, b) the yellow section

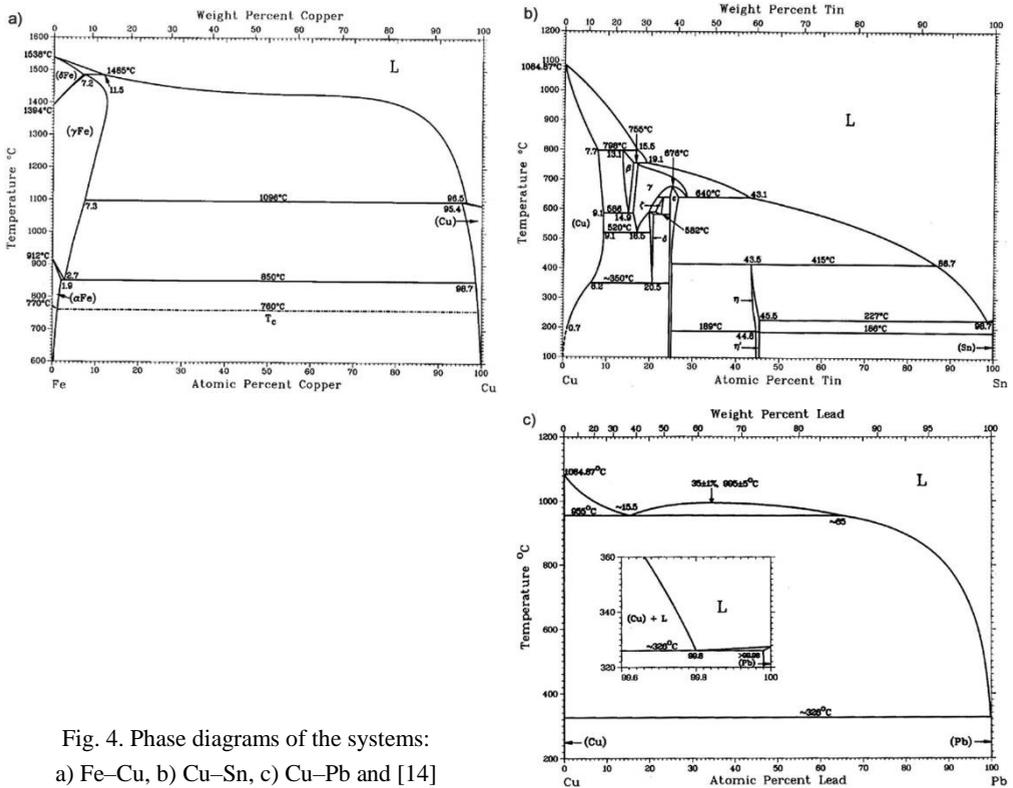


Fig. 4. Phase diagrams of the systems: a) Fe–Cu, b) Cu–Sn, c) Cu–Pb and [14]

The existence of the two different sections observed in the alloy, and of the phases detected by the XRD one can explain based on binary phase equilibrium diagrams [14].

The Cu–Fe system is shown in Fig. 4a. Above liquidus, around 1800 K, exists homogeneous liquid phase. Below this temperature, dendritic crystals of iron start to crystallize from the liquid. Then, around 1300–1100 K, an equilibrium exists between the mixture of Fe and Cu crystals, both having face centered cubic structure (fcc).

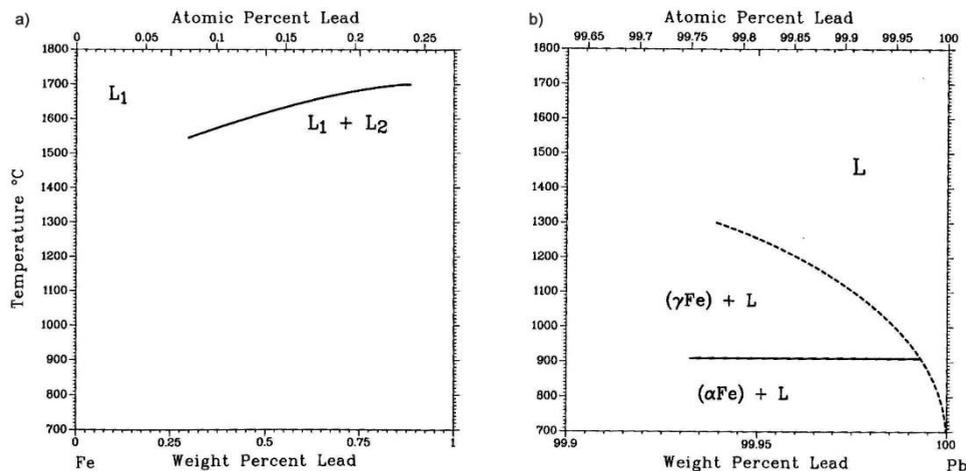


Fig. 5. Phase diagram of the system Fe–Pb in the range of low (a) and high (b) concentrations of Pb [14]

At room temperature, the mixture of face centered cubic structure of Cu is in equilibrium with body centered cubic structure (bcc) of Fe crystals. In the liquid solution, there are also dissolved other elements which diffuse to the solid solutions either with copper or with iron or, in case of lack of solubility, they exist individually, e.g. Pb. Therefore, the lack of mutual solubility of iron and copper explains the existence of the two different phases in the alloy. It seems that iron forms intermetallic phases and probably solid solutions with such elements as Mn and Ni.

According to Cu–Sn phase diagram (Fig. 4b), copper can form solid solution with tin. Lead does not form solutions neither with Cu (Fig. 4c) nor with Fe (Fig. 5a, b). Lead stays in the liquid solution and finally solidifies in the grain boundaries of Cu-rich parts of the alloy. This was also confirmed by SEM observations, where, in BSE mode, the brightest objects correspond to Pb rich places. Lead has the greatest atomic number Z , among elements present in the alloy, thus it scatters electrons stronger than other elements.

3.2. STUDIES OF THE SCALE

In the bulk scale, grinded surface, reveals an existence of metallic elements (Fig. 6). Density measurements show the mean value of $2.6 \pm 0.1 \text{ g/cm}^3$.

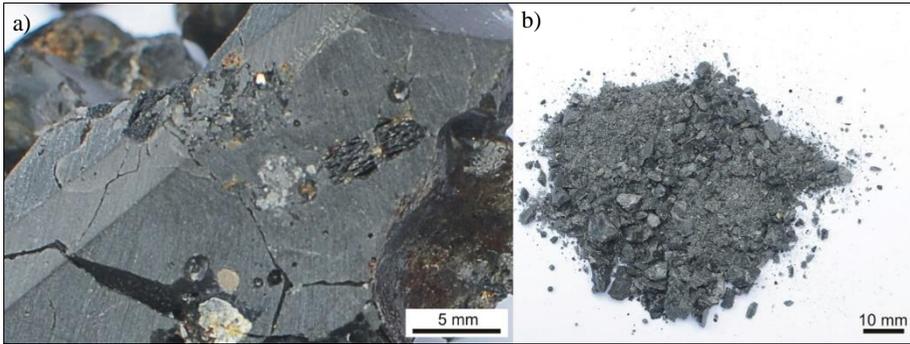


Fig. 6. Macroscopic image of the scale in a form of a monolithic rock (a) and of a crushed powder (b)

As a result of spectroscopic studies, as much as 21 elements were detected with quantum error of $\pm 0.5\%$. Larger amounts of Si (22.9%) and Ca (16.6%) are observed. A number of metallic elements can be distinguished as well, mostly Al (9.2%) and Fe (2.3%). The most characteristic elements of microstructure of the scale are shown in Fig. 7. Bright sections (1) contain mainly Pb (91.6%). Darker regions (2) consist of Cu (70%) and Sn (25.5%). The darkest sections (3), besides tin content around 10%, are the richest in Cu (85.8%). Dendritic crystals (4) consist mostly of Pb (40%) and Zn (47.1%).

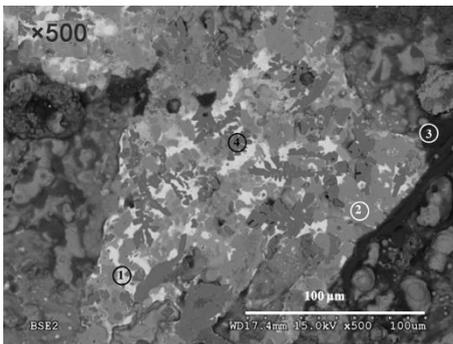


Fig. 7. SEM image of the scale

The scale was milled in order to refine the structure and to enable magnetic separation. One section of the milled scale is shown in Fig. 8a. Dark sections (1) contain glaze being a component of the scale, and comprise mainly Ca (24.4%), Si (35.5%), and Al (34.6%). Brighter parts (2) are of metallic type and contain mostly Cu (85.6%) with dissolved alloying elements. The brightest, elongated sections (3) consist of copper-tin alloy: Cu (68.3%) and Sn (22.3%). Some amount of lead is present there, as well. Thus the scale contains remains of metals from the melt.

Another particle obtained from the milled scale is shown in Fig. 8b. In this figure, at the first sight, huge, bright fragments are visible, probably of metallic type. It is however possible to distinguish more regions. Brighter (1) and darker (2) sections have similar chemical composition, based on copper and tin, however, they differ in Cu/Sn proportion. Brighter region (1) contains 86.5% of Cu and 11.2% of Sn, while the darker one (2) consists of 90.7% of Cu and 5.8% of Sn. Small amount of Ag was found in those regions, as well. In the figure, very bright areas (3) are also visible. Their composition does not differ from that of brighter and darker sections (1, 2). It is possible that this signal comes from surroundings. This can be due to measurement conditions (excitation space can be larger than dimensions of examining objects). Furthermore, on the border of image, one can also see dark section (4), which consist of Fe (73.7%) with dissolved Ni (14.3%). Several measurements display also some amounts of Pt, as well. Taking into account noble metals, detected in the scale, it was observed that Ag is associated with Cu, whereas Pt is associated with Fe.

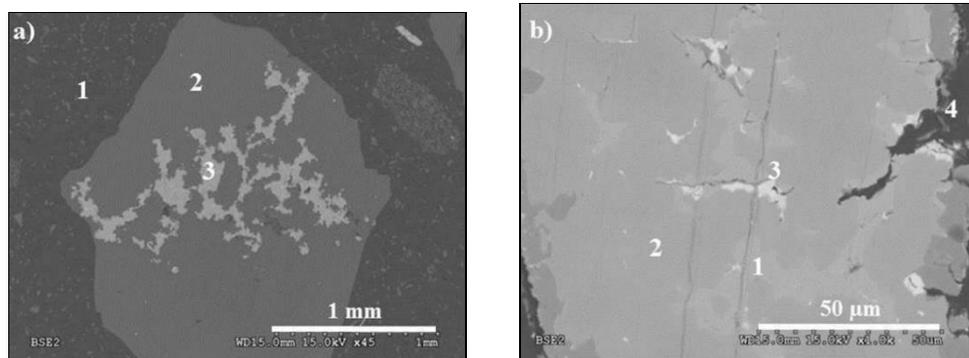


Fig. 8. Various regions of the specimen of the milled scale; magnifications: a) 45 \times , b) 1000 \times

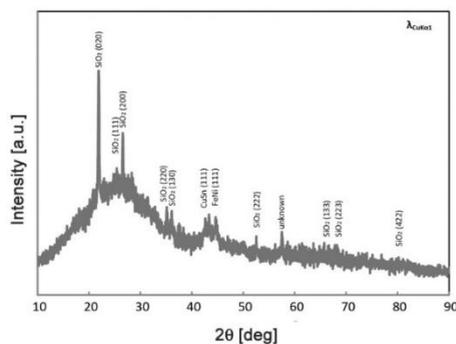


Fig. 9. Diffraction pattern of the milled scale

Diffraction pattern of the milled scale is shown in Fig. 9. One can clearly notice a large, blurred peak, which comes from amorphous part of the scale. It is also possible to distinguish several small peaks, which are associated with SiO_2 phase, and peaks

which refer to $\text{Cu}_{0.9}\text{Sn}_{0.1}$ and $\text{Fe}_{0.75}\text{Ni}_{0.25}$ phases. The peaks referred to $\text{Fe}_{0.75}\text{Ni}_{0.25}$ phase had higher intensity for the scale subjected to magnetic separation. This fact can be used as a hint for separation techniques.

3.3. STUDIES OF THE SEDIMENT

The sediment is a residue from etching the computer boards in hydrochloric acid. The sediment contains remains of electronics, cables, polymeric O-rings, washers etc. (Fig. 10). In order to get an average sample, the sediment was milled. Only fraction with particles smaller than $300\ \mu\text{m}$ was examined. Its mean density was $2.1 \pm 0.1\ \text{g/cm}^3$.



Fig. 10. Elements after milling the sediment

In the sediment, as many as 24 elements were detected using the XRF spectroscopy. Large differences in chemical composition were noticed, in dependence to the place of collecting samples. The chemical composition is generally dominated by Cl (23.5%), what is undoubtedly due to previous etching in hydrochloric acid. According to ionic compounds solubility, one can conclude that all chlorides are pretty soluble in water, except for lead and silver chlorides. These ones create insoluble compounds and it must be pointed that Pb and Ag were detected in further measurements. Apart from that, the presence of chlorine, can be just residue after evaporated liquid. Besides chlorine, minor amounts of all elements existing in the alloy were detected in the sediment.

The sediment was subjected to SEM observations, as well. Fragments (particles), which differ in colour and morphology, are shown in Fig. 11a–d.

The sediment was examined by the EDS technique in terms of its chemical composition ($\pm 0.5\%$). Particles rich in Ba (71.5%) and Pb (23.7%) are shown in Fig. 11a, in Fig. 11b, particles rich in silver are presented. One can distinguish there bright section, being a pure silver, and grey matrix which contains huge amounts of Ag (86.1%) and 13.2% of Sn. In Figure 11c, particles consisting of Sn and Pb (1), are shown. Their chemical composition nearly corresponds to that of the eutectic in Sn–Pb system. Probably, as a result of segregation in multi-element systems, there are also visible dark

segments (2), which contain 12.2% of Al, and very bright inclusions (3) consisting mostly of Au (76%) and Ag (8.8%). Lead usually do not create solutions with other elements that is why particle, presented in Fig. 11d, mostly consist of pure Pb (98.9%).

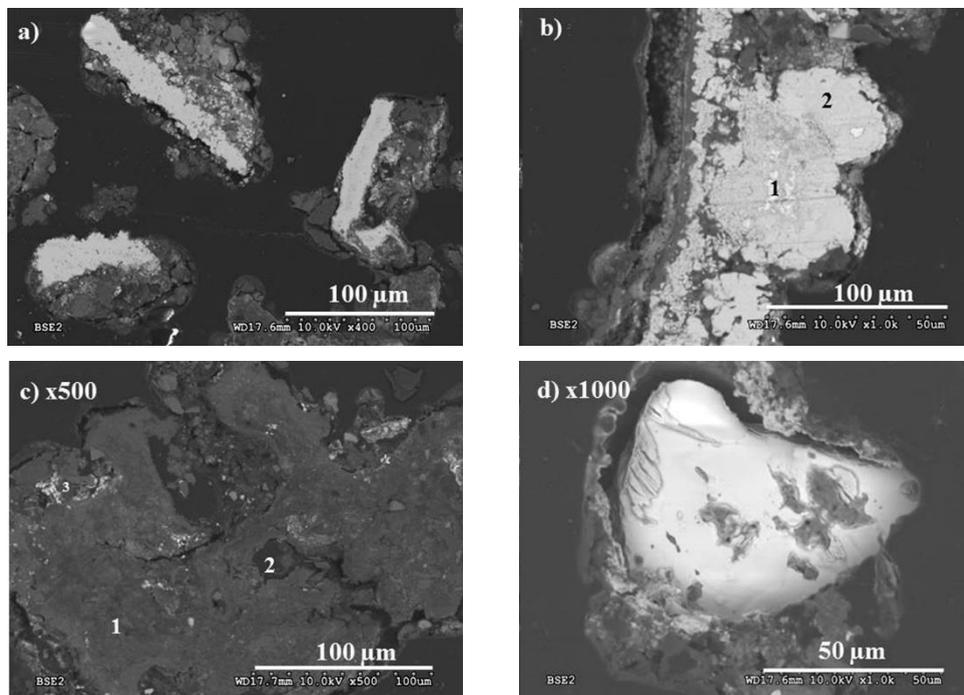


Fig. 11. SEM images of the sediment: a) particles rich in Ba and Pb, magnification 400×, b) particles rich in Ag, magnification 1000×, c) particles rich in Sn and Pb, magnification 500×, d) particles rich in Pb, magnification 1000×

To conclude, chlorine remains in the sediment after etching in hydrochloric acid. Chlorine can exist either in insoluble compounds (AgCl , PbCl_2) or as residue after evaporation of the liquid. Thus, occurrence of significant amount of lead is evident. Presence of barium can be explained due to the fact that this element is frequently used in electronic equipment (barium ferrites or liquid crystals displays). Tin probably comes from solder, which is dissolved in acid. Noble metals like Au and Ag are expected due to the acid etching idea. Rare earth elements were also detected.

4. SUMMARY

Due to the lack of mutual solubility of Fe and Cu in a solid state, the alloy consists of two insoluble parts, iron and copper rich. The alloy in the iron rich section forms solutions or intermetallic phases, mostly with elements such as Mn or Ni. The alloy in

the copper rich regions contains mostly Sn and Ag. Lead is insoluble neither in Fe nor in Cu, and remains in the grain boundaries where it solidifies as pure Pb.

In the scale, 21 elements were found. Despite silicon and calcium occurring in large amounts, many metals, mostly aluminum and iron, were detected.

The sediment consists mostly of chlorine originating from hydrochloric acid. Significant amounts of lead and tin were detected, and also minor residues of etched metals (Au or Ag), and even rare earth elements.

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