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Intermetallic phase particles in cast AlSi5Cu1Mg and AlCu4Ni2Mg2 aluminium alloys

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ABSTRACT

Purpose: In the technical Al alloys even small quantity of impurities - Fe and Mn - causes the formation of new phase components. Intermetallic particles form either on solidification or whilst the alloy is at a relatively high temperature in the solid state, e.g. during homogenization, solution treatment or recrystallization. The exact composition of the alloy and casting condition will directly influence the selection and volume fraction of intermetallic phases. The main objective of this study was to analyze the morphology and composition of complex microstructure of intermetallic phases in cast AlSi5Cu1Mg and AlCu4Ni2Mg2 aluminium alloys.

Design/methodology/approach: In this study, several methods were used such as: optical light microscopy (LM), scanning (SEM) electron microscopy in combination with X-ray analysis (EDS) using polished sample, and X-ray diffraction (XRD) to identify intermetallics in cast AlSi5Cu1Mg and AlCu4Ni2Mg2 aluminum alloys.

Findings: The results show that the microstructure of cast AlSi5Cu1Mg and AlCu4Ni2Mg2 aluminum alloys in T6 condition consisted a wide range of intermetallic phases. By using various instruments (LM, SEM, XRD) and techniques (imagine, EDS) following intermetallic phases were identified: β-Al_5FeSi, α-$Al_{15}(FeMn)_3Si$ - in AlSi5Cu1Mg alloy and Al_7Cu_4Ni, $Al_{12}Cu_{23}Ni$, Al_2CuMg, AlCuFeNi - in AlCu4Ni2Mg2 alloy.

Research limitations/implications: In order to complete and confirm obtained results it is recommended to perform further analysis of the investigated aluminium alloys. Therefore it is planned to include in a next studies, microstructure analysis of the alloys by using transmission electron microscopy technique (TEM).

Practical implications: Since the morphology, crystallography and chemical composition affect the intermetallic properties, what involves changes of alloy properties, from a practical point of view it is important to understand their formation conditions in order to control final constituents of the alloy microstructure.

Originality/value: This paper proposes the best experimental techniques for analysis of the intermetallic phases occurring in the cast AlSi5Cu1Mg and AlCu4Ni2Mg2 aluminium alloys. This study has showed that the chemical phenol extraction method for the cast aluminium alloy is applicable.

Keywords: Metallic alloys; Microstructure; Electron Microscopy; Intermetallic phases

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MATERIALS

1. Introduction

Commercial aluminium alloys contains a number of second-phase particles, some of which are present because of deliberate alloying additions and others of which arise from common impurity elements and their interactions. Coarse intermetallic particles are formed during solidification - in the interdendric regions, or whilst the alloy is at a relatively high temperature in the solid state, for example, during homogenization, solution treatment or recrystallization [1-20]. They usually contain Fe and other alloying elements and/or impurities. In aluminium alloys besides the intentional additions, transition metals such as Fe, Mn and Cr are always present. Even not large amount of these impurities causes the formation of a new phase component. The exact composition of an alloy and the casting condition will directly influence a selection and volume fraction of intermetallic phases [14-19]. Depending on a composition a material may contain $CuAl_2$, Mg_2Si, $CuMgAl_2$, and Si as well as Al(Fe,M)Si particles, where M denotes elements such as Mn, V, Cr, Mo, W, or Cu. During homogenization or annealing treatments, most of as-cast soluble particles from the major alloying additions such as Mg, Si, and Cu are dissolved, and intermediate-sized 0.1 to lμm dispersoids, of the AlCuMgSi type, can form. Dispersoids can also result from the precipitation of Mn-, Cr-, or Zr-containing phases. A size and distribution of these various dispersoids depend on the time and temperature of the homogenization and/or annealing processes. Fine intermetallic particles (<lμm) are formed during artificial aging of heat-treatable alloys and are more uniformly distributed than constituent particles or dispersoids. Dimensions, shape and distribution of these particles may have important effects on the ductility of alloys and more needs to be known regarding their formation, structure and composition [1-3,14-22].

For example, the coarse particles can influence the recrystallization, fracture, surface, and corrosion behavior, while the dispersoids control grain size and provide stability to the metallurgical structure. The dispersoids can also affect the fracture performance and may limit strain localization during deformation. The formation of particles drains solute from the matrix and, consequently, changes the strength properties of the material. This is specially relevant in the heat-treatable alloys, where depletion in Cu, Mg, and Si can significantly change the metastable precipitation processes and age hardenability of a material [2,21-28]. Therefore, particle characterization is essential not only for choosing the best processing routes, but also for designing optimized alloy composition [15-18].

Thus, particle characterization is important not only to decide what sort of processing courses should be applied, but also for designing optimized chemical composition of a material. A variety of microscopic techniques are well appropriate to characterize intermetallics but only from a small section of an analyzed sample. From commercial point of view it is extremely advantageous to provide use quick, reliable and economical examination technique capable of providing data of particles from different locations of a full scale-sized ingot. One of these methods is dissolving the matrix of an aluminium alloy chemically or electrochemically [1-3]. Since in these alloys intermetallic particles extraction is to a certain extent complex - most of the particles dissolve more effectively than matrix, a variety of processes designed to dissolve aluminium alloys have been developed recently. Currently, there is no single method that can isolate all type of particles from different aluminium alloys. The aim of this paper is to check if chemical phenol extraction method is applicable to isolation of intermetallic particles from the casting alloys of AlSi5Cu1Mg and AlCu4Ni2Mg2. Therefore, a few of dissolution techniques are reviewed and the results of identification of isolated intermetallics are reported.

2. Material and methodology

The investigation has been carried out on the AlSi5Cu1Mg and AlCu4Ni2Mg2 casting aluminum alloys. Table 1 shows the chemical composition of the type of aluminium alloy used throughout this study. Investigated AlSi5Cu1Mg and AlCu4Ni2Mg2 alloys were delivered in the T6 condition - solution heat treated at 520°C for 5h followed by water cooling and artificially aging at 250°C for 5h followed by air cooling – AlCu4Ni2Mg2 alloy and solution heat treated at 515°C for 5h followed by water cooling and artificially aging at 225°C for 5h followed by air cooling - AlSi5Cu1Mg.

Table 1.
Chemical composition of AlSi5Cu1Mg and AlCu4Ni2Mg2 alloys (% mas.) Al bal

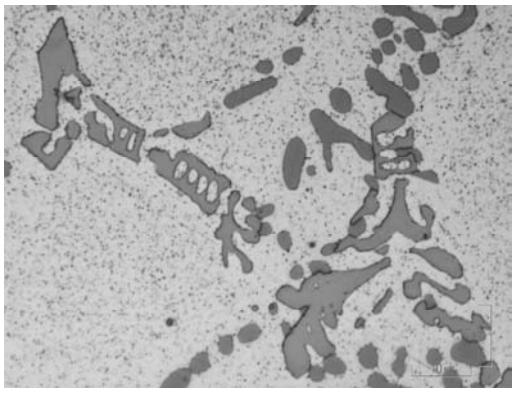
Alloy	Si	Cu	Mn	Mg	Ni	Zn	Fe
AlSi5Cu1Mg	5.0	2.1	0.8	0.4	-	<0.3	0.2
AlCu4Ni2Mg2	0.1	4.3	<0.1	1.5	2.1	0.3	0.1

The microstructure of examined alloys was observed using an optical microscope - Nikon 300 on polished sections etched in Keller solution (0.5 % HF in 50ml H_2O). Morphology of specimens was made in the scanning electron microscope HITACHI S-3400 (SEM), operating at 6-10 kV in a conventional back-scattered electron mode. Chemical composition of the intermetallics was made by EDS attached to the SEM using the software of Thermo Noran. The intermetallic particles from investigated AlSi5Cu1Mg and AlCu4Ni2Mg2 alloys were extracted chemically in phenol. The samples in form of disc were cut out from the rods of ∅12 mm diameter. Then ~0.8 mm thick discs were prepared by two-sided grinding to a final thickness of approximately 0.35 mm. The isolation of phases was performed according to following procedure: 1.625g of the sample to be dissolved was placed in a 300ml flask containing 120mm of boiling phenol (182°C). The process continued until complete dissolution of the sample occurred ~10 min. The phenolic solution containing the residue was treated with 100ml benzyl alcohol and cooled to room temperature. The residue was separated by centrifuging a couple of times in benzyle alcohol and then twice more in methanol. Dried residue was refined in the mortar. After sieving of residue ~0.2 g isolate was obtained. The intermetallic particles from the powder extract were identified by using X-ray diffraction analysis. The X-ray diffraction analysis of the powder was performed using ARL-XTR'a diffractometer- Cu Kα radiation at 40 kV.

3. Results and discussion

The microstructure of investigated AlSi5Cu1Mg alloy in T6 condition is shown in Figures 1 and 2a. It consists of different precipitates showed variations in brightness and color. From Figures 1 and 2, we can see that the precipitates present are: fine dispersed (I), spherical (II), rod-like (III) and "Chinese script"(IV). The characteristics of these phases are presented in the Table 2.

a)



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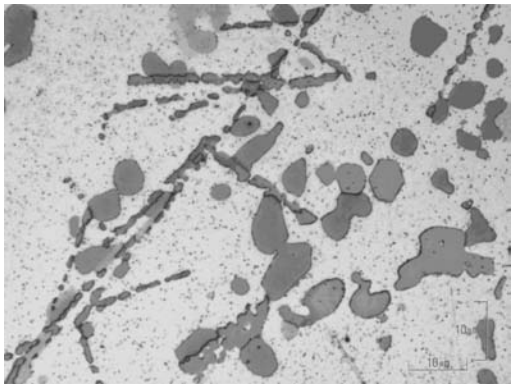
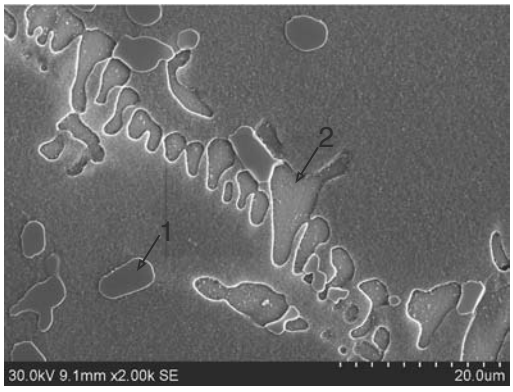


Fig. 1. The microstructure of the AlSi5Cu2Mg alloy in the T6 condition

a)



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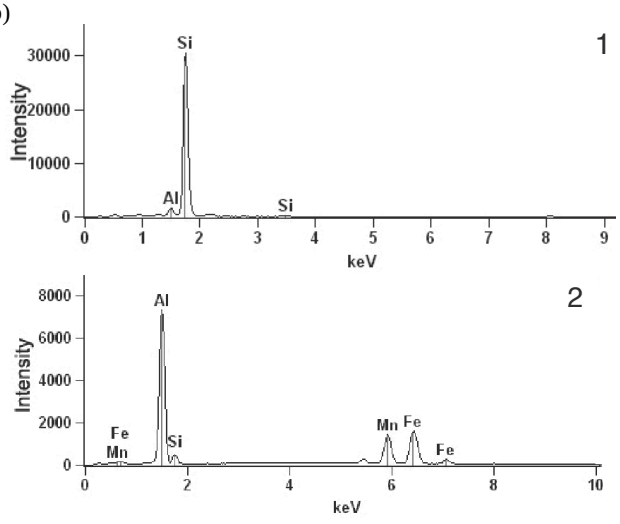


Fig. 2. a) Image from scanning electron microscope (SEM) of the AlSi5Cu2Mg alloy in the T6 condition; b) EDS spectra

Figure 2 shows scanning electron micrographs and EDS analysis of particles in investigated AlSi5Cu2Mg alloy.
The EDS analysis performed on the phases presented in microstructure of the alloy revealed, that spherical in shape inclusions (II) are the eutectic silicon ones, whereas the rod-like (III) and "Chinese script" shaped (IV), are inclusions of the phase consisting of *Al*, *Si*, *Mn* and *Fe* (Fig. 2 and Tab. 3)

Table 2.
The characteristics of the phases in the AlSi5Cu2Mg alloy

The characteristics		The phase number			
		I	II	III	IV
Color	Unetched	-	Dark gray	Fair gray	Fair gray
	Etched	-	No changes observed	Well shaped edges, the color changes into dark gray	Well shaped edges, the color changes into dark gray
Shape			Spherical in shape	Rod-like	„Chinese script"
Distribution			In the interdendritic areas of the α-Al alloy	In the interdendritic areas of the α-Al alloy and forming clusters	In the interdendritic areas of the α-Al alloy

Table 3.
The chemical composition of the intermetallic inclusions in the AlSi5Cu2Mg alloy

	Chemical composition (%wt)		
	II	III	IV
Phase	Si: 85-95.0	Si: 7.3-9.8 Mn: 13.5-21.5 Fe: 4.2-6.0	Si: 7.3-9.8 Mn: 13.5-21.5 Fe: 4.2-0.0
	Si	α-AlFeMnSi	α-AlFeMnSi

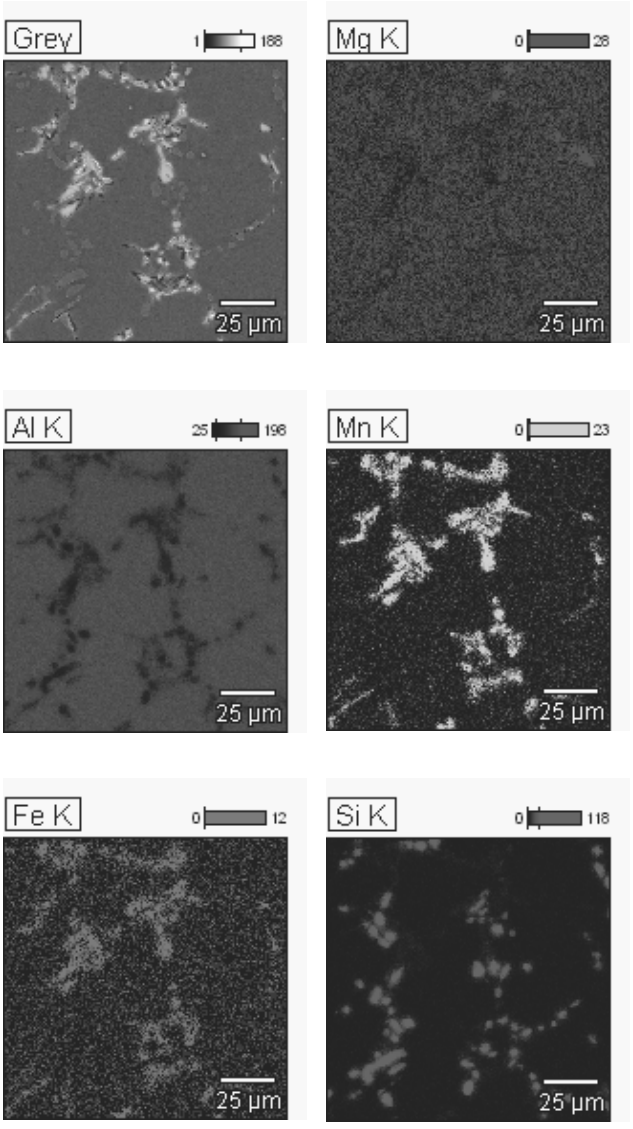


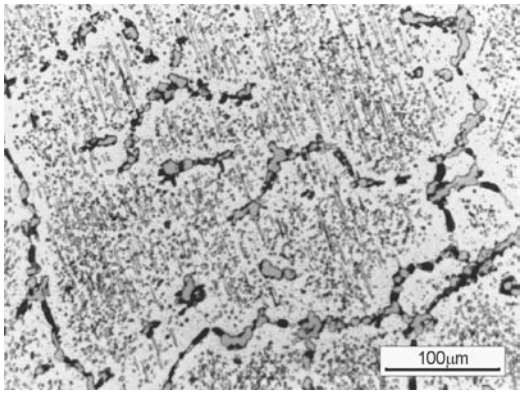
Fig. 3. The surface distribution of the alloying elements in the area of Si and “Chinese script” shaped inclusions occurrence

The results in Fig. 3 are displayed in colors to enhance the higher intensity values of given elements. Black represents the lowest concentration, while glaring colors represents the maximum concentration. The darker is the area on the map, the lower is content of the element in that area. The presence of Al and Mg is evidently highest in the matrix, while Si, Mn and Fe are at their maximum levels on the large "chinese script" shaped light precipitates.

Figures 4 and 5a shows the microstructure of investigated AlCu4Ni2Mg2 alloy in T6 condition.

The analyzed microstructure consists different precipitates varied in shape, i.e.: fine spherulite and strip-like (I), complex rod-like (II) and ellipse-like (III). The characteristics of these phases are presented in Table 4.

a)



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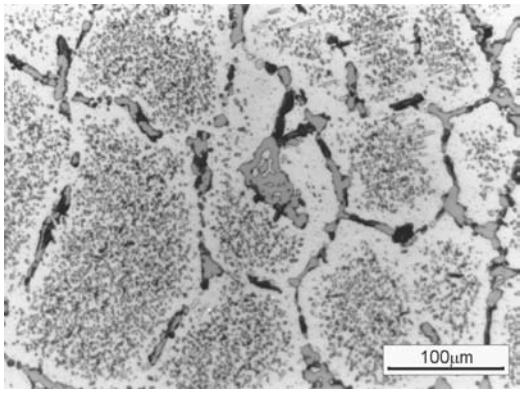


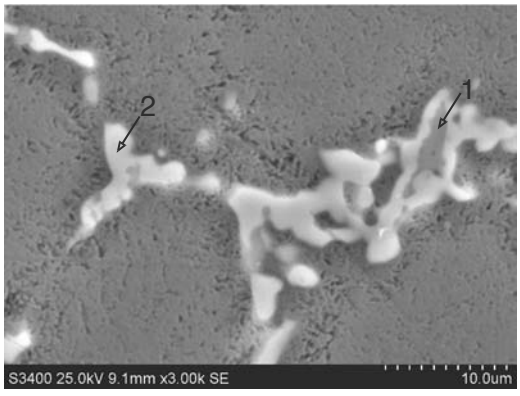
Fig. 4. Optical metallography pictures of the AlCu4Ni2Mg2 alloy in the T6 condition

In order to identify the intermetallic phases in the examined alloy, series of intensity maps were performed for the element line Mg-K, Al-K, Fe-K, Ni-K, Cu-L at 4,837 keV (Fig. 5). The maximum pixel spectrum clearly shows the presence of Ni and Cu in the scanned microstructure. To verify the presence of the elements in the identified phase, two region of the mapped phase with high nickel and copper concentration was marked and their spectrums were evaluated. The EDS analysis revealed that the complex rod-like (II) consisting of *Al*, *Cu* and *Ni* and ellipse-like (III) besides *Al*, *Cu* and *Ni* contain Fe.

Table 4.
The characteristics of the phases in the AlCu4Ni2Mg2 alloy

The characteristics		The phase number		
		I	II	III
Color	Unetched	-	Fair gray	Fair gray
	Etched	-	Well shaped edges, the color changes into dark gray	The color changes into dark
Shape		Spherulite and strip-like	Complex rod-like	Ellipse-like
Distribution		Homogeneous in the matrix the α-Al alloy + poor in the boundary zone	In the interdendritic areas of the α-Al alloy	In the interdendritic areas of the α-Al alloy

a)



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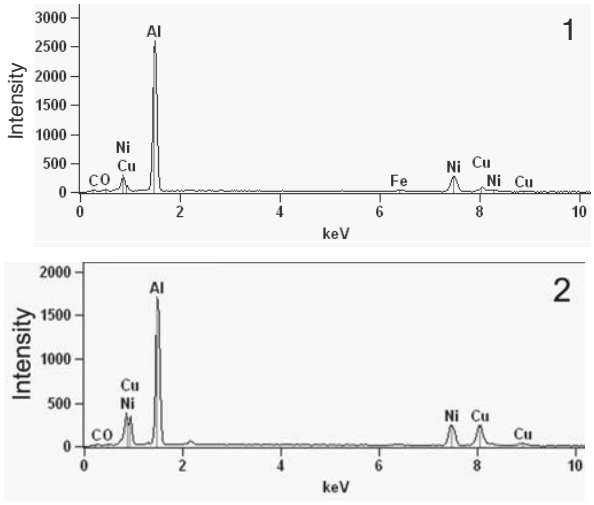

Fig. 5. a) Images from scanning electron microscope (SEM) of the AlCu4Ni2Mg2 alloy in the T6 condition; b) The corresponding EDS-spectra were acquired in positions indicated by the number 1 and 2

In addition, the quantification result (Table 5) shows that these and other detected elements are present in the identified phase. This phase is Al_7Cu_4Ni, $Al_{12}Cu_{23}Ni$ which is an important intermetallic phase for this type of alloy.

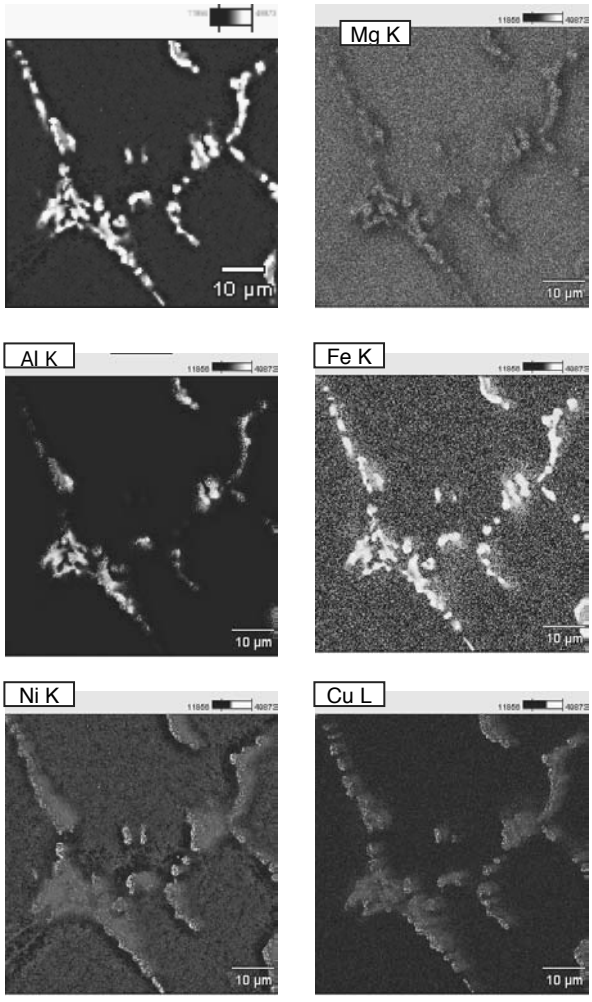

Fig. 6. The surface distribution of the alloying elements in the area

Table 5.
Chemical composition in 1-2 aera, % mass

Alloy	Al-K	Fe-K	Ni-K	Cu-L
AlCu4Ni2Mg2 – point 1	64.18	2.26	21.63	11.94
AlCu4Ni2Mg2 – point 2	43.91	-	20.29	35.80

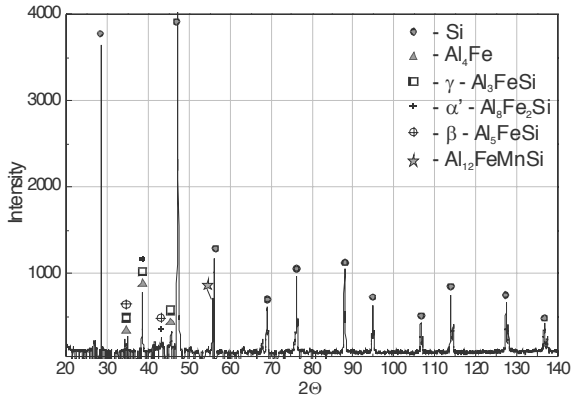

Fig. 7. The X-ray diffraction from the particles extracted from: AlSi5Cu2Mg investigated alloy

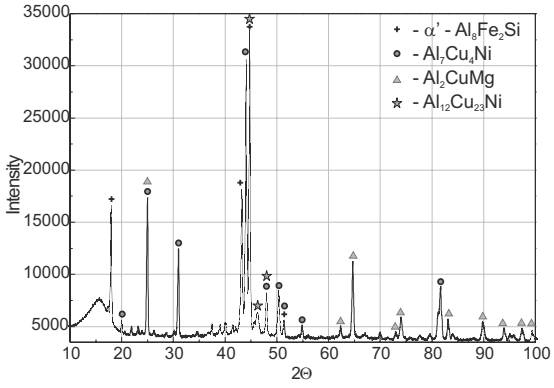

Fig. 8. The X-ray diffraction from the particles extracted from AlCu4Ni2Mg2 investigated alloy

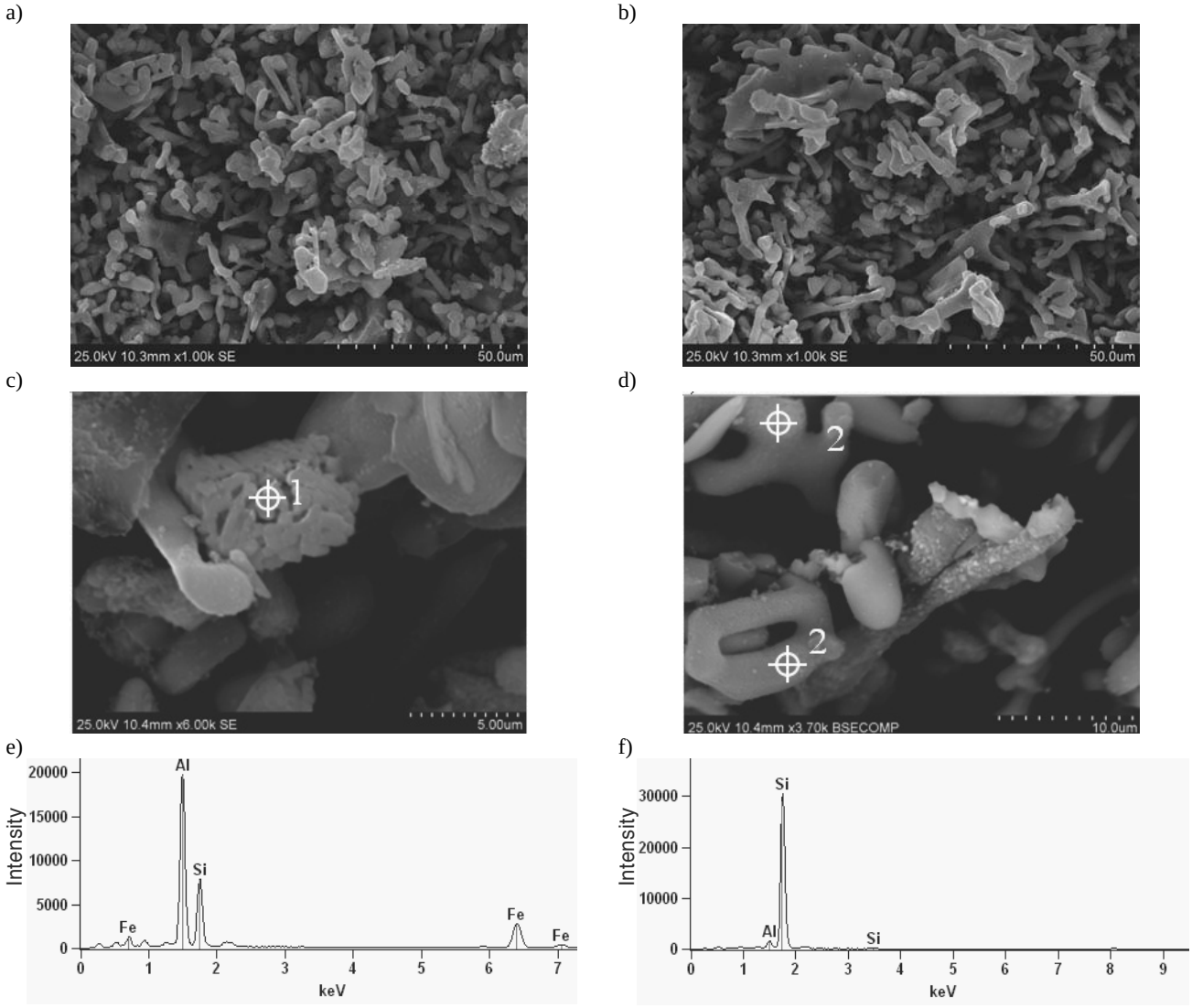

Fig. 9. a-d) SEM micrographs and EDS X-ray spectrum, e) - analysis from point 1, f) - analysis from point 2) of the particles extracted from the AlSi5Cu1Mg alloy

Microstructure of the examined alloys - AlSi5Cu2Mg and AlCu4Ni2Mg2 in T6 state consists primary precipitates of intermetallic phases combined with highly dispersed particles of hardening phases. Based on SEM chemical composition results made on the microstructure of the examined alloys one can assumed that observed phases in AlSi5Cu2Mg alloy were precipitates of strengthening phases of either β-Mg_2Si and Θ-A_2Cu. However, precipitates of only hardening Θ-Al_2Cu phase were determined in the microstructure of AlCu4Ni2Mg2 alloy.

The phenol extraction method was successfully applied to the examined alloys. The results of the analysis of the particles extracted from AlSi5Cu1Mg and AlCu4Ni2Mg2 alloy by SEM are consistent with the particles expected from these alloys, and this was further confirmed from X-ray diffraction pattern. Since it is rather difficult to produce detailed identification of intermetallics using only one method therefore XRD technique was utilized to provide confidence in the results of phase classification based on metallographic study. X-ray diffraction pattern from the constituents extracted with boiling phenol form the solution Al alloy is shown in Figure 7 and 8. The observed peaks confirmed SEM results. The majority of the peaks were from Si, AlFeSi and AlFeSiMn particles in AlSi5Cu2Mg alloy (Fig. 7) and AlCuNi, AlCuMg, AlFeSi in AlCu4Ni2Mg2 alloy (Fig. 8).

On the other hand, it is nearly impossible to make unambiguous identification of the all intermetallics present in an aluminium alloy which are rather complex, even applying all well-known measuring techniques. Diffraction analysis is one of the most powerful and appropriate technique giving the possibility to determine most of verified intermetallics based on their crystallographic parameters.

Our analysis shows that the difficulties of having reliable results on the all possible existing phases in a microstructure of an alloy, is related to preparation of phase isolation. The residue is separated by centrifuging and since some of the particles are very fine and available sieves are having too big outlet holes there is no chance prevents them from being flowing out from a solution. Therefore it is planning to perform an observation of samples of the examined alloys using transmission electron microscopy technique TEM in order to compare and confirm present results.

Figures 9 and 10 shows scanning electron - SEM micrographs of the particles from the AlSi5Cu1Mg and AlCu4Ni2Mg2 alloys extracted by using the phenolic dissolution technique. The particles in AlSi5Cu1Mg and AlCu4Ni2Mg2 alloys have irregular shape.

Intermetallic particles with complex morphology from the AlSi5C1Mg alloy are shown in Fig. 9. White crosses indicate positions of the electron probe for EDS acquisition, see x-ray map and spectra below. EDS-spectrum from the residue a chemical composition of Al, Si, and Fe (Fig. 9e,f).

Other particles with complex morphology from the AlCu4Ni2Mg2 alloy are shown in Fig. 10. The EDS spectra revealed the presence of Al, Cu, Fe and Ni - bearing particles in the extracted powder (Fig. 10b,d). The EDS results proof that analyzed particles are AlCuNi.

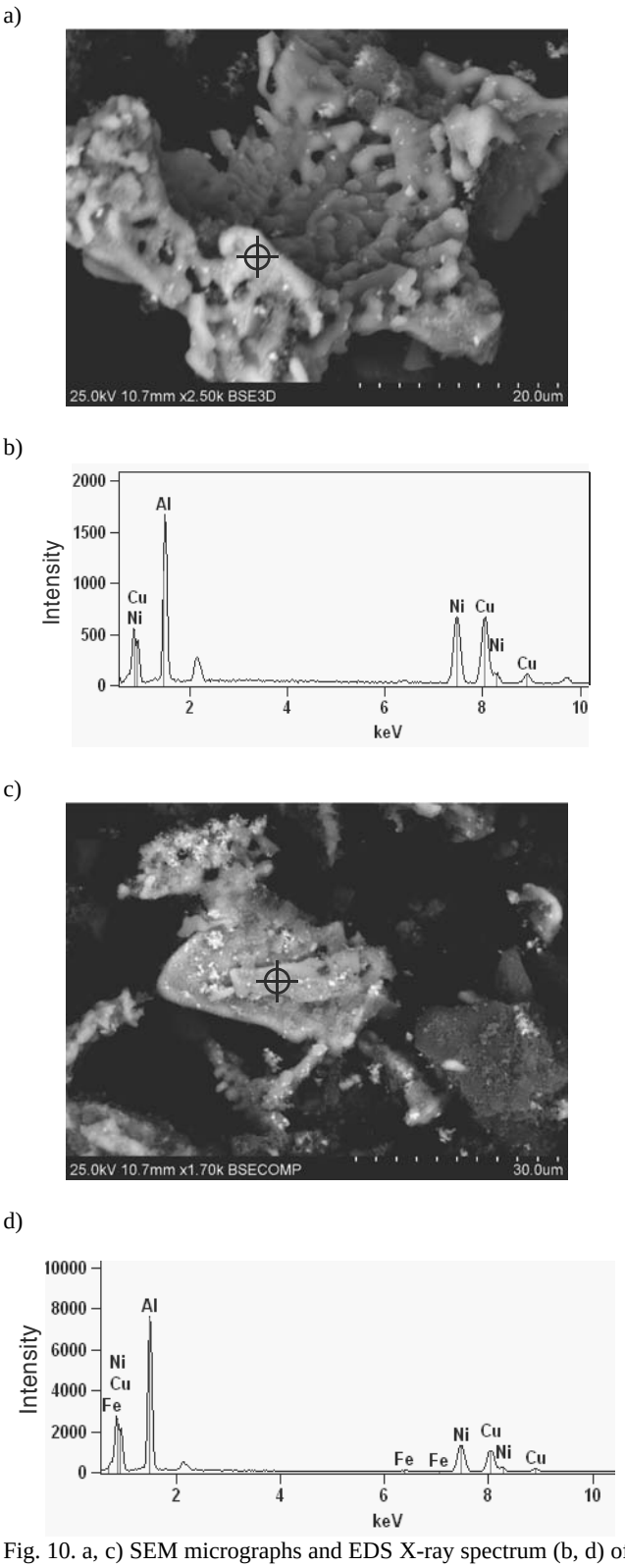

Fig. 10. a, c) SEM micrographs and EDS X-ray spectrum (b, d) of the particles extracted from the AlCu4Ni2Mg2 alloy

4. Conclusions

The electron energy-dispersive X -ray spectrometry (EDS) analysis technique evidenced that *AlSi5Cu2Mg* alloy microstructure is composed of only one type of the intermetallic phase, the *α–AlFeMnSi* phase. However, the as-cast alloy AlCu4Ni2Mg2 is mainly composed of intermetallics of AlCuNi type and as well as precipitates of Al_2CuMg, AlCuFeNi phase. In both cases determination of all intermetallics occurred was based on two, it would appear incomparable technique, one yield chemical information while the XRD data yield crystallographic data. Basing on literature data the only technique allowing to verify the type of phases precipitates in the alloy is XRD. Only crystallographic data can strictly defined type of phases in the examined alloys. So far, there is no other technique existing for examination of isolate phases. All interested in phase's isolation are supporting the chemical results with XRD analysis as a technique to characterization of crystalline phases of the residue. Thus, in present research this technique was used to confirm the results from microstructure observation.

Since the EDS method is considered as a basic one, the thorough investigation by the use of the TEM method is carried on to confirm the results of XRD analysis. The results will be published soon. Nonetheless, even the preliminary analysis showed in both cases, that the chemical composition, morphology, shape (rod-like or "Chinese script") and distribution of the intermetallic phase depend on the condition of solidification process and applied heat treatment.

Acknowledgements

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