www.czasopisma.pan.pl www.journals.pan.pl

Arch. Metall. Mater. **64** (2019), 4, 1315-1319

DOI: 10.24425/amm.2019.130096

K. PACHUT*[#], J. ŻELECHOWSKI*, S. BOCZKAL*

APPLICATION OF X-RAY DIFFRACTION TO ANALYSE PHASE COMPOSITION OF ALUMINIUM ALLOYS FOR PLASTIC WORKING

An attempt was made to determine phase composition of commercial aluminium alloys using X-ray diffraction. Samples for phase composition analysis were selected from the group of aluminium alloys covered by the EN 573-3:2013 standard [1]. Representative samples were taken from eight groups of alloys with different chemical composition (at least one sample from each group). The diffraction intensity was measured with a standard X-ray diffractometer in Bragg-Brentano geometry in a way that allowed identification of the weakest diffraction peaks.

As a results of the performed research it has been shown that X-ray phase analysis can be used to identify the matrix of aluminium alloys, Si and crystalline intermetallic phases such as Mg_2Si, $Al_{93.38}Cu_{6.02}Fe_{24}Si_{16.27}$, $Al_{4.01}MnSi_{0.74}$, $MgZn_2$, $Al_{17}(Fe_{3.2}Mn_{0.8})Si_2$, $Al_{65}Cu_{20}Fe_{15}$, and Cu_3Mn_2Al. The detectability limit of the above-mentioned phases is better than 0.5%. The research has also shown that X-ray phase analysis is applicable in the investigation of phase transformations taking place in aluminium alloys.

Keywords: Aluminium alloys, X-ray diffraction, qualitative phase analysis

1. Introduction

Aluminium alloys are widely used in the global economy, mainly due to the favourable relationship between functional properties and production costs. The main alloying constituents used in the production of aluminium alloys are copper, manganese, magnesium, silicon, zinc and iron. All aluminium alloys for plastic processing are suitable for deformation strengthening. Additionally, alloys from the 3000 and 5000 series can be solution hardened (by Mn and Mg respectively dissolved in solid aluminium). In turn, alloys from the 2000, 6000 and 7000 series are dispersion hardened. Various diffraction methods are now considered the best tool for phase identification. Studies of the phase composition of aluminium alloys are based, among others, on the method of X-ray phase analysis, which consists in identification of the features of a crystal structure related to the distribution of diffraction patterns intensity. The X-ray phase analysis uses the phenomenon of X-ray diffraction and a comparison of the empiric diffractogram with a database of powder diffraction patterns.

2. Test materials and methods

To analyse the phase composition, samples of commercial aluminium alloys classified in the PN-EN 573-3 standard [1] were taken. Alloys from the 1000 series described in the standard are sometimes called metallurgical or pure aluminium with an aluminium content exceeding 99%. The 2000 series alloys, also known under the trade name Duralumin, contain several percent of copper, while the 3000 series alloys contain a few percent of manganese. The 4000 series symbols are used in the standard to designate aluminium-silicon alloys with the chemical composition similar to silumins used in foundries. The 5000 series includes aluminium and magnesium alloys, while the 6000 series is composed of aluminium alloys with magnesium and silicon. The 7000 series aluminium alloys are alloys containing several percent of zinc, magnesium and copper. The 8000 series aluminium alloys contain iron and silicon. Phase analysis was carried out on the following aluminium alloys: EN AW1050A, EN AW2017A, EN AW3104, EN AW4045, EN AW5754, EN AW6082, EN AW7075 and EN AW7003, and also EN AW8011. All alloys were in the near-phase equilibrium state. The chemical composition of selected alloys is summarized in Table 1.

The X-ray phase analysis was performed using a standard X-ray diffractometer with an energy-dispersive detector in Bragg-Brentano geometry [2,3]. A sufficiently long measurement time and an optimized aperture set were provided to obtain diffractograms with a satisfactory signal-to-noise ratio. Based on previous own studies, it was assumed that X-ray diffraction would occur in the crystalline fraction of the sample with crystallites larger than a fraction of a micrometre.

As a result of the X-ray diffraction measurements, sets of numbers were obtained, which were next processed into a graphi-

* ŁUKASIEWICZ RESEARCH NETWORK – INSTITUTE OF NON-FERROUS METALS, LIGHT METALS DIVISION, 19 PIŁSUDSKIEGO STR., SKAWINA, 32-050, POLAND

[#] Corresponding author: kpachut@imn.skawina.pl

TABLE 1

The chemical composition of aluminium and aluminium alloys in percentage by mass

Numerical	Si	Fe	Cu	Mn	Mg	Zn
EN AW-1050A	0.25	0.40	0.05	0.05	0.05	0.07
EN AW-2017A	0.2-0.8	0.7	3.5-4.5	0.4-1.0	0.4-1.0	0.25
EN AW-3104	0.6	0.8	0.05-0.25	0.8-1.4	0.8-1.3	0.25
EN AW-4045	9.0-11.0	0.8	0.3	0.05	0.05	0.1
EN AW-5754	0.4	0.4	0.1	0.5	2.6-3.6	0.2
EN AW-6082	0.7-1.3	0.5	0.1	0.1-0.45	0.6-1.0	0.2
EN AW-7003	0.3	0.35	0.2	0.3	0.5-1.0	5.0-6.5
EN AW-7075	0.4	0.5	1.2-2.0	0.3	2.1-2.9	5.1-6.1
EN AW-8011	0.3-1.1	0.4-1	0.1	0.1	0.05	0.1

cal form. The range of diffractions intensities was selected in such a way that it was possible to identify the reflections of the lowest intensity. The Xray phase analysis was based on the compatibility of empirical diffractograms with the diffractograms of crystalline substances described in the identification catalogue [4]. To confirm the occurrence of phases identified by X-Ray diffraction conducted chemical composition analysis in micro-areas using the SEM Inspect F50 microscope with an EDS X-ray microanalysis device. For each of the samples, images of microstructure were made in 4000× magnification, in a working voltage of 20 kV. EDS spectra recorded in graphic form and the average percentage of each element were generated using a dedicated Team program.

3. Results and discussion

TABLE 2

Percent be weight of elements included in the phases of analyzed alloys

Number of spot \ Element		Results of chemical composition						
		Al	Si	Fe	Cu	Mn	Mg	Zn
3104	Spot 1	70.0	6.2	9.1	-	14.2	0.8	-
5754	Spot 1	71.1	4.7	15.9	-	6.1	2.1	-
5754	Spot 2	52.5	20.1	-	-	-	10.0	-
6082	Spot 1	68.7	7.8	14.7	1.3	6.5	1.0	-
6082	Spot 2	47.0	16.7	0.8	-	0.8	29.0	-
7075	Spot 1	73.6	3.7	10.9	3.7	3.3	2.2	2.7
7075	Spot 2	59.0	16.4	-	1.2	-	5.1	4.0
8011A	Spot 3	63.5	9.4	27.1	-	-	-	-

The X-ray diffraction produced strong reflections from the alloy matrix and weak reflections from other alloying constituents.

As a result of the analysis of the diffractogram of the EN AW1050A aluminium, diffraction reflections that might originate from silicon and an intermetallic phase with the $Al_{93.38}Cu_{6.02}Fe_{24}Si_{16.27}$ stoichiometry were identified. The EN AW1050A aluminium does not contain deliberately introduced

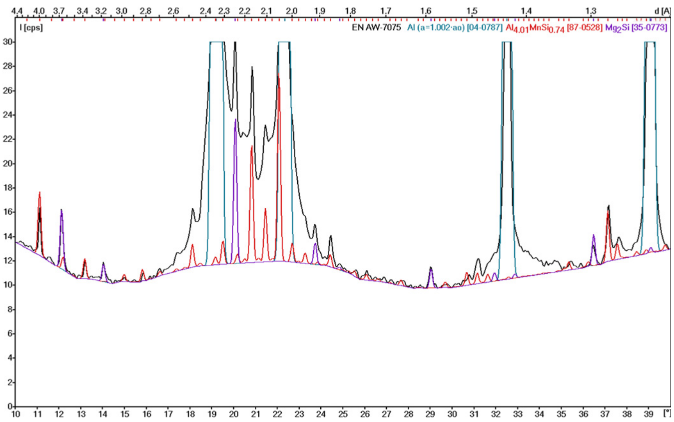

Fig. 1. Diffraction pattern of EN AW-7075 alloy. Intensity scale factor = 40:1

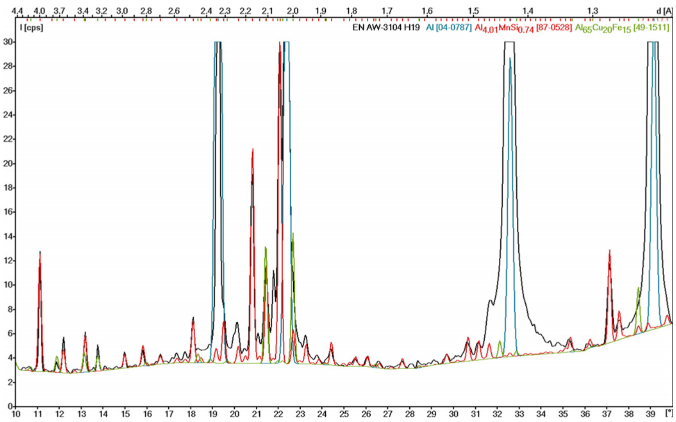

Fig. 2. Diffraction pattern of EN AW-3104 alloy. Intensity scale factor = 20:1

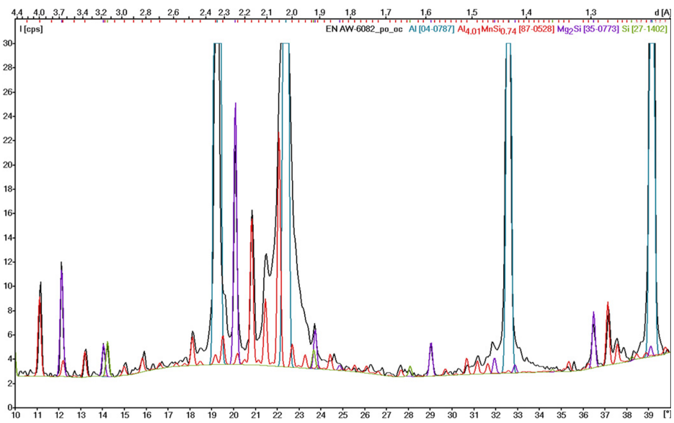

Fig. 3. Diffraction pattern of EN AW-6082 alloy. Intensity scale factor = 100:1

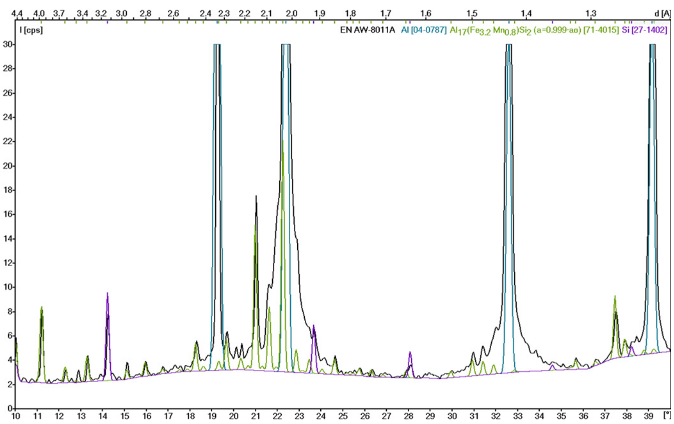

Fig. 4. Diffraction pattern of EN AW-8011 alloy. Intensity scale factor = 80:1

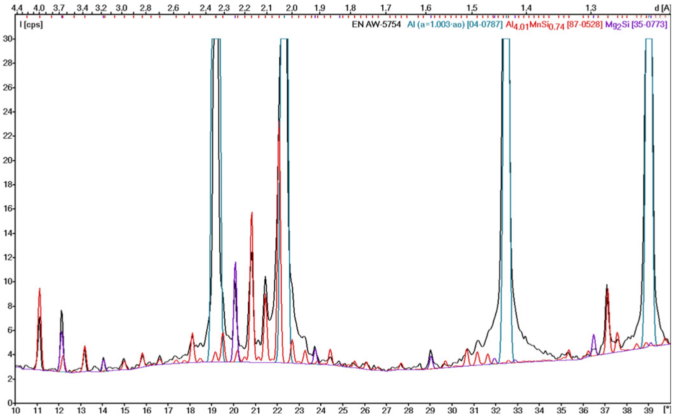

Fig. 5. Diffraction pattern of EN AW-5754 alloy. Intensity scale factor = 30:1

alloying additions. Elements such as silicon, iron, copper, manganese, magnesium, zinc and titanium are present in 1050A aluminium as impurities originating from electrolysis or recycling [5]. This means that the impurities present in the EN AW1050A aluminium formed the $Al_{93.38}Cu_{6.02}Fe_{24}Si_{16.27}$ intermetallic compound and free silicon in the crystalline form. The proportions of concentration of elements in $Al_{93.38}Cu_{6.02}Fe_{24}Si_{16.27}$ are roughly in line with the proportions of these constituents in the standard chemical composition of 1050A aluminium.

As a result of the analysis of the diffractogram of the EN AW-2017A aluminium alloy, the crystal structure of the examined alloy was found to be consistent with the crystal structure of the two phases with the Cu_3Mn_2Al and Mg_2Si stoichiometry. From the EN 573-3 standard [1] it follows that the EN AW-

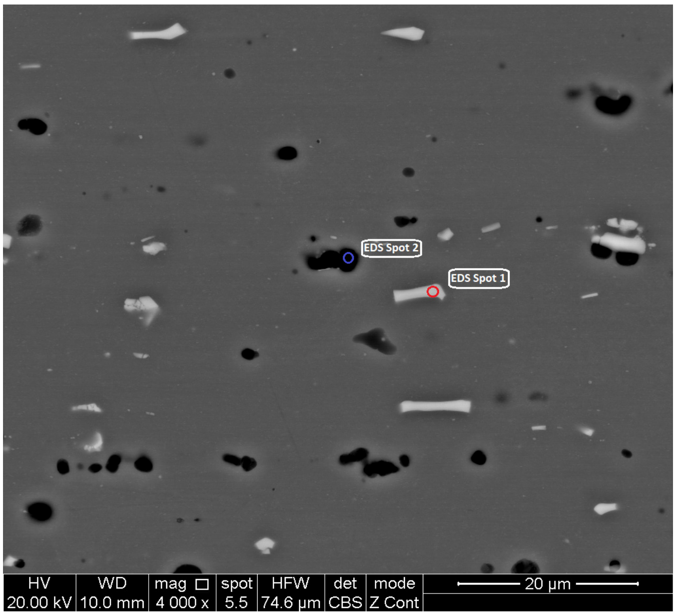

Fig. 6. Scanning electron microscope image of EN AW-7075 alloy

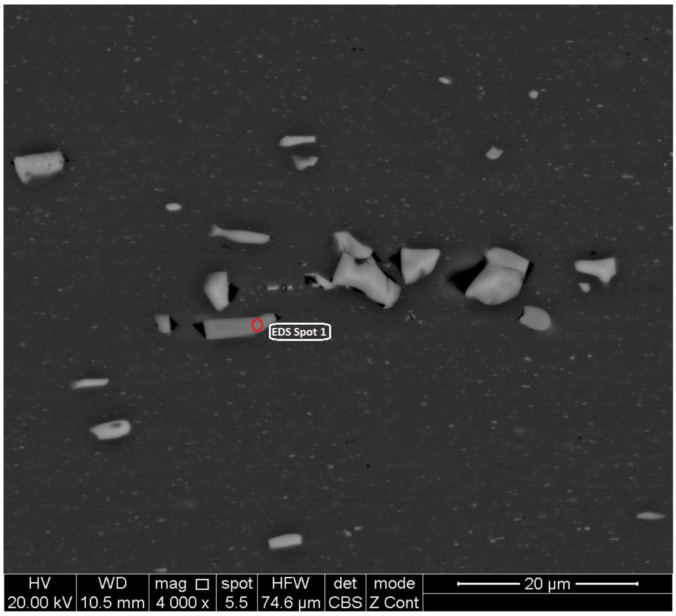

Fig. 7. Scanning electron microscope image of EN AW-3104 alloy

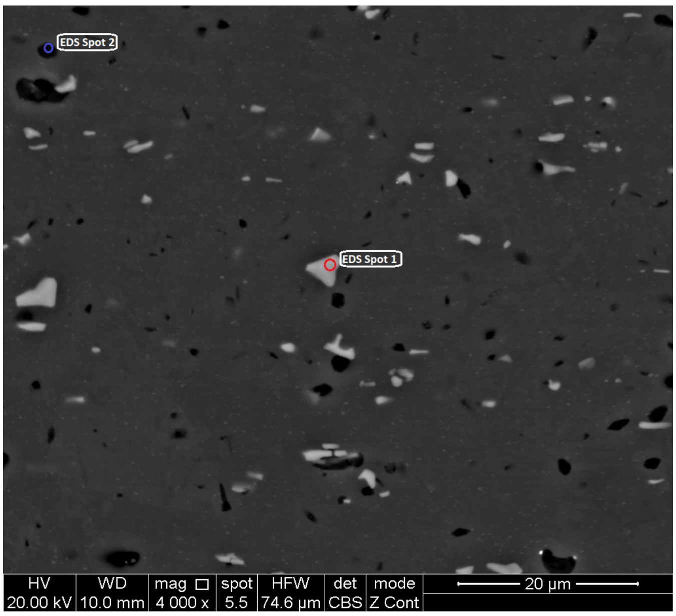

Fig. 8. Scanning electron microscope image of EN AW-6082 alloy

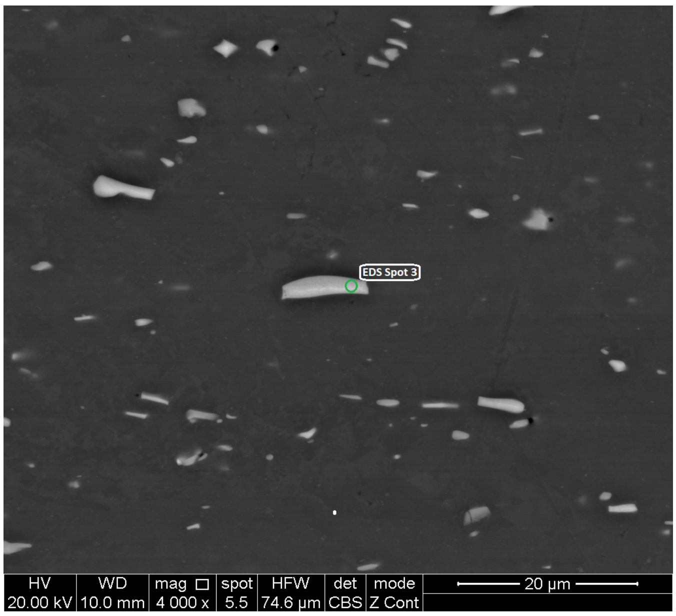

Fig. 9. Scanning electron microscope image of EN AW-8011 alloy

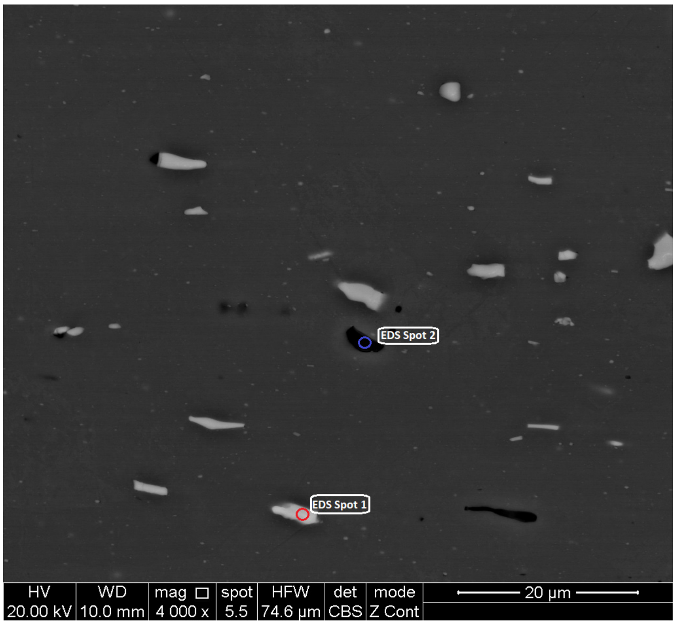

Fig. 10. Scanning electron microscope image of EN AW-5754 alloy

2017A alloy can contain from 0.2% to 0.8% silicon and from 0.4% to 1.0% magnesium. This means that the Mg_2Si phase could form in this alloy in a weight concentration ranging from about 0.6 wt% to about 1.5 wt%. The detectability threshold of the Mg_2Si phase in this alloy was estimated at about 0.35%. The possibility of identification of the Mg_2Si phase in the 2000 series alloys is known from the literature [6]. According to the Al-Cu phase equilibrium diagram [7], one could expect the occurrence of the $CuAl_2$ phase in the EN AW-2017A alloy, but it turns out that in the presence of other chemical elements, copper included in the alloy composition does not form this phase.

Careful analysis of the diffractogram of the EN AW-3104 aluminium alloy has revealed a consistency between the crystal structure of the precipitates of intermetallic phases and the crystal structure of the phase with the $Al_{4.01}MnSi_{0.74}$ stoichiometry. The theory claims that in Al-Mn alloys with the addition of several atomic percent silicon, two stable phases may occur. These are the α-Al_9Mn_2Si and β-Al_9Mn_3Si phases [8]. The stoichiometry of the $Al_{4.01}MnSi_{0.74}$ phase is similar to the stoichiometry of the α-Al_9Mn_2Si phase. The atomic ratio in the α-Al_9Mn_2Si phase is 9:2:1 respectively, while in the $Al_{4.01}MnSi_{0.74}$ phase it is 5.4:1.4:1 respectively, thus indicating a similar proportion of chemical elements and similar stoichiometry.

The diffractogram of the EN AW-4045 aluminium alloy has confirmed the consistency between the crystal structure of the precipitates and silicon. The maximum solubility of Si in Al ranges from 0.1 at% to 1.5 at% at a eutectic temperature of 577°C and drops to 0.005 at% at 300°C. The binary Al-Si phase equilibrium diagram [9,10] shows that silicon practically does not dissolve in aluminium at room temperature and does not form intermetallic compounds with this element. So, in the case under discussion, the diffraction was only from silicon and aluminium. The literature also confirms that in pure Al-Si alloys, no intermetallic compounds are formed [11].

From the 5000 series, alloys designated with the symbol EN AW-5754 was selected for studies of the phase composition. In this alloy, the presence of the Mg_2Si and $Al_{4.01}MnSi_{0.74}$ intermetallic phases was identified. The Mg_2Si phase could form in the EN AW-5754 alloy [1] and reach a weight concentration of about 1.1 wt%. The detectability threshold of the Mg_2Si phase in this alloy was estimated at about 0.1%. The main alloying constituent in the 5000 series alloys is magnesium. According to Mondolfo [10], each 1% of magnesium dissolved in a solid solution increases the lattice parameter by 0.005Å, which in the diffractograms of Al-Mg alloys shifts the diffraction reflections towards smaller θ angles. The change in the position of diffraction reflections results from the change in the lattice parameter of the alloy matrix, which is a solid solution of magnesium in aluminium. The literature confirms that the Mg_2Si phase can be identified in the 5000 series alloys [12].

Careful analysis of the diffractogram of the EN AW-6082 alloy has revealed a consistency between the crystal structure of the examined alloy and the crystal structure of the intermetallic phases with the $Al_{4.01}MnSi_{0.74}$ and Mg_2Si stoichiometry. The same alloy was examined by X-ray diffraction in two different states, i.e. before and after heat treatment. In the state before heat treatment, the diffractogram of the EN AW-6082 alloy was found to be inconsistent with the diffractogram of the Mg_2Si phase. This means that either the Mg_2Si phase does not form crystals or the size of the crystals is smaller than 1 μm, thus preventing the occurrence of diffraction. A heat treatment was carried out to bring the alloy to the state of phase equilibrium and allow in this way for the crystallization of intermetallic compounds with stable stoichiometry. The diffractogram of the EN AW-6082 alloy after heat treatment has revealed the crystal structure of the alloy consistent with the $Al_{4.01}MnSi_{0.74}$ and Mg_2Si intermetallic phases. As a result of the heat treatment, the diffraction intensity of the Mg_2Si phase has increased several times, which means that a larger volume of the crystals of this phase was released from the alloy. The calculations show that the EN AW-6082 alloy in the state of phase equilibrium may contain from 0.95 wt% to 1.89 wt% of Mg_2Si. The detectability threshold of the Mg_2Si phase in this alloy was estimated at about 0.3%. From literature it follow that Mg_2Si phase can be identified in the 6000 series alloys [12].

From the 7000 series, alloys designated with the symbols EN AW-7003 and EN AW-7075 were selected for studies of the phase composition. In the EN AW-7003 alloy, the intermetallic phases with the $Al_{4.01}MnSi_{0.74}$ and $MgZn_2$ stoichiometry were identified. It was calculated that in EN AW-7003 alloy, the $MgZn_2$ phase could form and reach a concentration ranging from about 3.2 wt% to 6.4 wt%. The detectability threshold of the $MgZn_2$ phase in this alloy was estimated at about 0.5%. The Mg-Zn phase equilibrium diagram [13] shows that at a content of about 21.8% Zn and 78.2% Mg, a eutectic with a melting point of 340°C is formed. A metastable phase is formed during the eutectoid decomposition of the Mg_7Zn_3 phase and also during precipitation from the solid solution [14]. The presence of the $MgZn_2$ phase in the structure of alloys from the 7000 series was also detected during microstructure examinations of the

Al-Zn-Mg-Cu alloy obtained by Rapid Solidification. Using X-ray diffraction methods, the presence of a solid solution of aluminium and $MgZn_2$ was detected [15]. In the alloy designated as EN AW-7075, intermetallic phases with the $Al_{4.01}MnSi_{0.74}$ and Mg_2Si stoichiometry were identified. It was calculated that in the EN AW-7075 alloy in the state of phase equilibrium may contain about 1.1 wt% of Mg_2Si. The detectability threshold of the Mg_2Si phase in this alloy was estimated at about 0.2%. The possibility of identification of the Mg_2Si phase in the 7000 series alloys is known from the literature [18].

From the 8000 series, the EN AW-8011A alloy was selected for studies of the phase composition in two different states, i.e. before and after heat treatment. The heat treatment of the EN AW-8011A alloy was carried out at 600°C for 100 hours and its purpose was to bring the alloy closer to the state of phase equilibrium. On the diffractogram made before heat treatment, reflections from the $Al_{17}(Fe_{3.2}Mn_{0.8})Si_2$ intermetallic phase and free silicon were identified. This means that in the EN AW-8011A alloy, silicon crystallized in free form (chemically unbound). After heat treatment, the diffraction reflections from the free silicon were present no longer, but the presence of a phase with the $Al_{17}(Fe_{3.2}Mn_{0.8})Si_2$ stoichiometry was identified. This means that either the silicon dissolved in the intermetallic compound during heat treatment or together with aluminium formed a eutectic which, being a very fine mixture of constituents, has resulted in a significant widening of reflections and disappearance of diffraction. Atoms of iron and manganese have ions of similar dimensions, a similar number of electrons and similar basic physicochemical properties. In intermetallic compounds it is possible to substitute iron atoms with manganese atoms. This phenomenon no major changes in the crystal structure of these phases [19].

4. Summary and conclusions

1. In the examined aluminium alloys, Al, Si and the following intermetallic phases were identified: $Al_{93.38}Cu_{6.02}Fe_{24}Si_{16.27}$, $Al_{4.01}MnSi_{0.74}$, Si, Mg_2Si, $MgZn_2$ and $Al_{17}(Fe_{3.2}Mn_{0.8})Si_2$ as well as Cu_3Mn_2Al.

2. The aluminium alloys described in the EN 573-3 standard may contain numerous alloying elements and impurities, which means that in these alloys the state of phase equilibrium is not always compatible with the well-known binary phase equilibrium diagrams.

3. X-ray phase analysis is applicable as a tool to control phase transformations in commercial aluminium alloys.

4. As a result of the conducted studies it was shown that the detectability threshold of X-ray phase analysis depends on the type of substance examined and assumes the value of a fraction of percent. For example, in the EN AW-6082 alloy it is possible to identify the Mg_2Si phase at a concentration of about 0.3%.

5. The EDS result is consistent with the chemical composition of the phases identified by X-ray diffraction.

REFERENCES

[1] EN 573-3 Aluminium and aluminium alloys. Chemical composition and form of wrought products. Chemical composition and form of products.

[2] B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, Prentice Hall, Third Edition, 2001.

[3] Z. Bojarski, E. Łągiewka, Rentgenowska analiza strukturalna, Wyd. Uniwersytetu Śląskiego, Katowice 1995.

[4] Powder Diffraction File. Release 2018, PDF-4+, International Centre for Diffraction Data, Pensylvania, USA 2018.

[5] Z. Bonderek, S. Rzadkosz, Mechanizacja procesów rafinacji ciekłych stopów, VIII Konferencja Odlewnicza, Technical 2005.

[6] F. Zhang, L.E. Levine, A.J. Allen, C.E. Campbell, A.A. Creuzinger, N. Kazantseva, J. Ilavsky, In situ structural characterization of ageing kinetics in aluminium alloy 2014 across angstrom-to-micrometer length scales **111**, 385-398 (2016).

[7] N. Saunders, Cost 507 – Thermochemical database for light metal alloys **2**, 28-33 (1991).

[8] G. Trambly de Laissardière, D. Nguyen-Manh, D. Mayou, Indirect Mn-Mn pair interaction induces pseudogap in density of states of Al(Si)-Mn approximants, J. Non-Chris. Solids **334-335**, 347-351 (2004), DOI: 10.1016/j.jnoncrysol.2003.11.068

[9] S. Shankar, Y. Riddle, Makhlouf M. Makhlouf, Eutectic Solidification of Aluminium-Silicon Alloys, Metallurgical and Materiaals Transformactions A **35A**, 3038 (2004).

[10] L.F. Mondolfo, Aluminium Alloys: Structure and Properties, Butterworths, London 1976.

[11] E. Kovács-Csetényi, C.R. Vassel, I. Kovács, Determination of the Solubility of Si in Dilute Al-Si Alloys by Low-Temperature Resistivity Measurements, Phys. Stat. Sol. **17**, K123 (1966).

[12] S.W. Banovic, T. Foecke, Metall. Mater. Trans. **34A6**, 657 (2003).

[14] G. Mrówka-Nawrotnik, J. Sieniawski, M. Wierzbicka, Intermetallic phase particles in 6082 aluminium alloy, Archives of Materials Science and Engineering **28**, 2, 69-76 (2007).

[15] M. Mezbahul-Islam, A. Omar Mostafa, M. Medraj, Essential Magnesium Alloys Binary Phase Diagrams and their Termochemical Data, Journal of Materials **1** (2014).

[16] J.J. Park, L.L. Wyman, WADC Tech. Rep. 57-504, Astia Document No. AD142110, 1-27 (1957), Published in Phase Diagrams of Binary Magnesium Alloys, 1988.

[17] L. Lityńska-Dobrzyńska, J. Dutkiewicz, W. Maziarz, A. Góral, Microstructure of Rapidly Solidified Al2Zn3Mg1.5Cu Alloy with Zr and Sc Addition, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta Street, Kraków.

[18] Xiaomei Li, M.J. Starink, Analysis of Precipitation and Dissolution in Overaged 7xxx Aluminium Alloys Using DSC, Sci Forum **331-337**, 1071-1076 (2000).

[19] M. Warmuzek, A. Gazda, J. Sieniawski, G. Mrówka, Processes of the Formation of the Fe(Mn)-Bearing Intermetallic Phases in the Al-Fe(Mn)-Si Alloys. Foundry Research Institute, Kraków.