Identification of Phases Formed by Cu and Ni in Al–Si Piston Alloys

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This paper presents the results of identifying and analyzing the phases present in the microstructure of 4 aluminum piston alloys with different chemical composition. Optical microscopy and scanning electron microscopy were used to study the microstructure of the samples and EDS analysis was used to identify the composition of the phases. The phase stoichiometry was identified by comparing the results of EDS analysis with the results reported in the studied literature. The results show that different intermetallic phases can appear depending on the chemical composition of the microstructure of aluminum piston alloys

Keywords: Piston - Aluminum piston alloys - Aluminum multicomponent alloys - Intermetallic phases

INTRODUCTION

Pistons are mostly made of aluminum multicomponent alloys (Al–Si–Cu–Ni–Mg), which represent a special group of industrial alloys that are used in the automotive industry due to a combination of good casting and mechanical properties [1–5], high strength at elevated temperatures (e.g., up to 350 °C) [1,5] and also resistance to sudden temperature changes [1–5]. Different types of piston alloys contain various amounts of major and minor alloying elements. The usual content of alloying elements is: 11–23 wt.% Si, 0.5–3 wt.% Ni, 0.5–5.5 wt.% Cu, 0.6–1.3 wt.% Mg, up to 1.0 wt.% Fe and up to 1 wt.% Mn [3–5]. The mechanical properties of aluminum piston alloys are defined by their micro and macro structures.

Major alloying elements: Si, Cu, Ni, Mg and Fe are primarily responsible for defining the microstructure and mechanical properties of aluminum alloys [1,5]. Silicon is added to improve castability and fluidity, as well as to reduce shrinkage and to give superior mechanical and physical properties (the more Si an Al–Si alloy contains, the lower is the thermal expansion coefficient). Cu is the second major alloying element in these alloys. It has great impact on the strength and hardness of Al–Si alloys in as-cast and heat-treated conditions. Copper forms $CuAl_2$ intermetallic phase with aluminum. In addition, Cu reduces the corrosion resistance of aluminum alloys and increases stress corrosion susceptibility in certain alloys.

However, copper and nickel can create Cu_4NiAl_7 phase, which reduces the intensity of hardening alloys with aging and the overall speed of recrystallization. Nickel can appear in the form of compact particles Al_3Ni phase, which is distributed in sequence, or in the form of T-Al_9FeNi phase that occurs with Al_3Ni phase [5]. Besides, nickel can be dissolved in phases Cu_2Al_7 and $Al_6(CuFe)$, and iron together with copper in Al_3Ni phase. The presence of manganese leads to the formation of FeMnNi compounds. In the Al–Si alloys, iron forms Cu_2FeAl_7 phase in the presence of copper, while in the presence of magnesium $Al_8FeMg_3Si_6$ is formed [2,5].

The Mg role is also to improve the strength and hardness of Al–Si alloys in both as-cast and heat-treated conditions (magnesium reacts with silicon and produces Mg_2Si intermetallic). The presence of other alloying elements in pistons alloys such as copper and magnesium leads to the formation of two additional intermetallic phases: Al_2CuMg, the so-called S-phase, and more complex $Al_xMg_5Cu_4Si_4$, W-phase. Iron has limited solubility in solid aluminum (at 655 °C maximal solubility is 0.05 %), reacts with aluminum and silicon to form a thermodynamically stable Al_5FeSi phase [2,5]. Morphology of this phase is in platelet form, but seen as needle-like in a two-dimensional metallographic cross section. As a consequence, one of the major difficulties with Al-Si alloys is that iron. The iron present in large enough quantities, can lead to this particular intermetallic having harmful effects on physical and mechanical properties of cast parts. In addition, these compounds are very hard, with the result that machining

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Alloys	Chemical composition (wt.%)										
	Si	Cu	Ni	Mg	Fe	Mn	Cr	Ti	Zr	V	Al
A	13.12	1.11	0.89	0.85	0.59	0.18	0.09	0.07	≈ 0.03	≈ 0.01	residual
B	13.05	3.58	1.01	0.90	0.52	0.19	0.09	0.07			
C	12.95	3.91	1.91	1.02	0.42	0.18	0.09	0.07			
D	11.20	5.41	2.09	0.53	0.37	0.25	0.09	0.07			

Tab. 1 - Nominal chemical composition of the experimental alloys.

Tab. 1 - Composizione chimica nominale delle leghe sperimentali.

cast parts with relatively high iron content can be difficult, resulting in high casting finishing costs.

Heat treatment process does not change the size and distribution of this phase [4,5]. In order to ensure that cast components have good mechanical properties their as-cast microstructures must be closely monitored.

Al–Si piston alloys have different structure depending on the content of silicon and other alloying elements. The results of previous tests show dependence between the combination of alloying elements, casting conditions and heat treatment given to different microstructures [1–5]. The structural composition of material has a direct impact on the physical and mechanical properties of the casting. Taking into account that the Si crystals are a primary phase in eutectic and hypereutectic piston alloys, therefore the sequence of solidification is: L→(Si), L→(Al)+(Si), L→(Al)+(Si)+Y and L+Y→(Al)+(Si)+Y, where Y is: (Al_3Ni, Al_2Cu, Mg_2Si, Al_3CuNi(Al_3Ni_2), Al_7Cu_4Ni, Al_9FeSi, Al_5FeSi, $Al_8FeMg_3Si_6$ and $Al_5Cu_2Mg_8Si_6$) [1–11], while primary aluminum phase also appears in the microstructure in hypoeutectic alloys. Based on the previous studies of all authors, it has been shown that only these phases may be present in the casting in the Al–Si piston alloys.

Taking into account that the mechanical properties of these alloys are significantly influenced by the share, shape and distribution of the above phases, this paper aims to analyze the presence of these phases in different aluminum piston alloys.

MATERIAL AND EXPERIMENTAL PROCEDURE

Four different piston alloys (Table 1) of approximately eutectic composition were used to analyze the microstructure. The content of the alloying elements varied between: 11.20–13.12 wt.% Si, 1.11–5.41 wt.% Cu, 0.89–1.91 wt.% Ni, 0.53–1.02 wt.% Mg and 0.37–0.59 wt.% Fe, to ensure separation of the dominant phase in each of the test structures. In the real case, there is a change in the mean concentrations of alloying elements due to redistribution of the rich or depleted melt, which can lead to a change in the mean concentrations significantly above or below the nominal value and to the creation of conditions for the formation of new phases. Any change during the entire curing process (primary, secondary and tertiary) of piston alloys has a significant impact on the concentration profiles of the alloying elements in the remaining liquid phase. Therefore, several alloys with different ratios of the main alloy elements were investigated.

The melting of alloy for piston cast was performed in tub-like electro-resistant inclined furnace, type RIO 750, with power of 80 kW and capacity of 120 kg/h.

The preparation of Al-alloy was performed in electro-resistant muffler-like furnace with black lead muffler, type RIO 250, with power of 85 kW. For improving its mechanical properties, during preparation, the piston casting was exposed to melt treatment processes (refining, modification and degasification). All three operations were performed at 725±5 °C. The temperature of the melt was measured using a Ni–Cr–Ni digital pyrometer.

The casting of investigated pistons was performed on semi-automatic machines in the manufacturing conditions in the PDM-Serbia Concern. The casting was performed into a metallic mold according to a predefined internal procedure from the manufacturer of the pistons.

An optical microscope (Olympus GX51) with magnification up to 1000x was used for visualization and collecting data for determining the microstructure of the material. Sample micrographs were acquired by an Olympus DP70 color digital camera (12.5 megapixel resolution). The samples were observed under a scanning electron microscope (SEM-Tescan Vega3 SB) using magnifications between 200x and 5000x. Qualitative and quantitative assessments of the chemical compositions of phases were done using an energy dispersive spectrometer (EDS-Bruker).

RESULTS AND DISCUSSION

The following can be observed in the microstructure of all investigated aluminum piston alloys by using the light optical micrographs: an Al-matrix (white), primary Si (blue) and different gray tones: multicomponent phases containing Al, Mg, Cu, Ni, Si, Fe and Mn (Fig. 1a 200x and Fig. 1b 500x). Primary silicon crystals are clearly visible under an optical microscope in all 4 investigated alloys.

The investigated alloys are of approximately eutectic composition. The identification of possible intermetallic phases as well as the solidification process has been defined by Belov [3], Manasijevic [1] and other authors [11] in their published papers. After the separation of primary crystals and eutectic reaction depending on the chemical composition of alloys, complex intermetallic phases are separated. Identification of other complex intermetallic phases present is not possible using optical microscopy, so a SEM was used in this case, which is capable of identifying other phases in combination with EDX. EDX mapping was done in order to better identify the phases. Each phase has its own key elements, as given in Table 2, which can be used to filter the possible crystallographic phases. Additionally, EDX mapping also provides useful information to predict the possible phases where the key elements show higher contrast.

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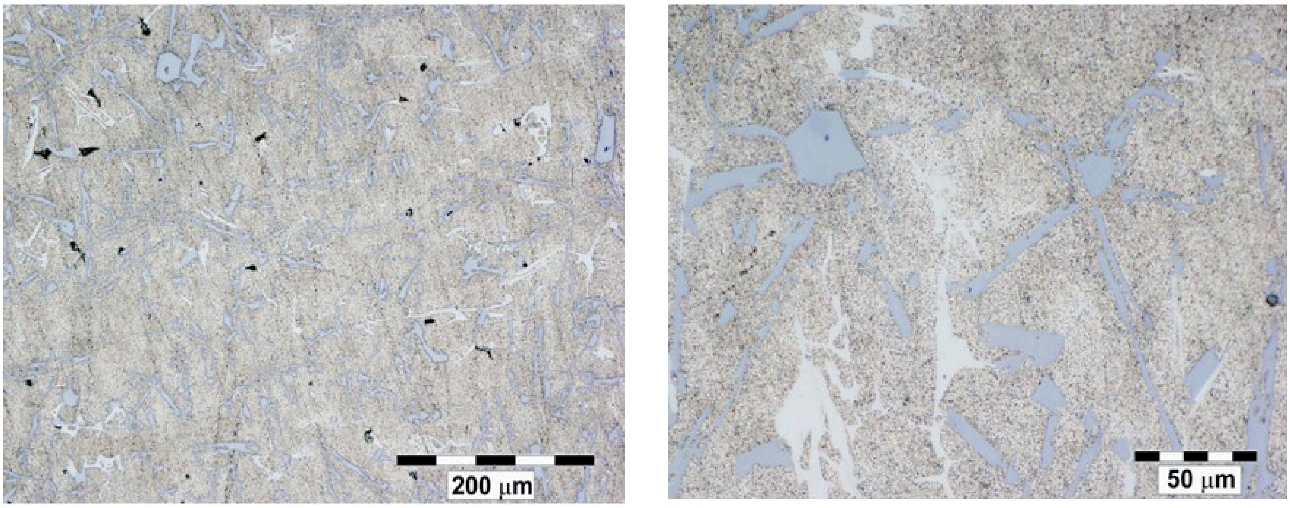
a)



b)

Fig. 1 - Microstructure of alloy B.

Fig. 1 - Microstruttura della lega B

Phases	Al_3Ni	Al_2Cu	Mg_2Si	Al_7Cu_4Ni	Al_9FeNi	Al_5FeSi	$Al_5Cu_2Mg_8Si_6$
Chemical composition, wt.% [3,4]	42 Ni	52.5 Cu	63.2 Mg 36.8 Si	38.5–50.7 Cu 11.8–22.2 Ni	4.5–14.0 Fe 18–28 Ni	25–30 Fe 12–15 Si	20.3 Cu, 31.1 Mg 32.9 Si
Key elements [4,10]	Ni	Cu	Mg	Ni, Cu	Fe		Mg, Cu

Tab.2 - Key elements in various intermetallic phases.

Tab.2 - Gli elementi chiave in varie fasi intermetalliche.

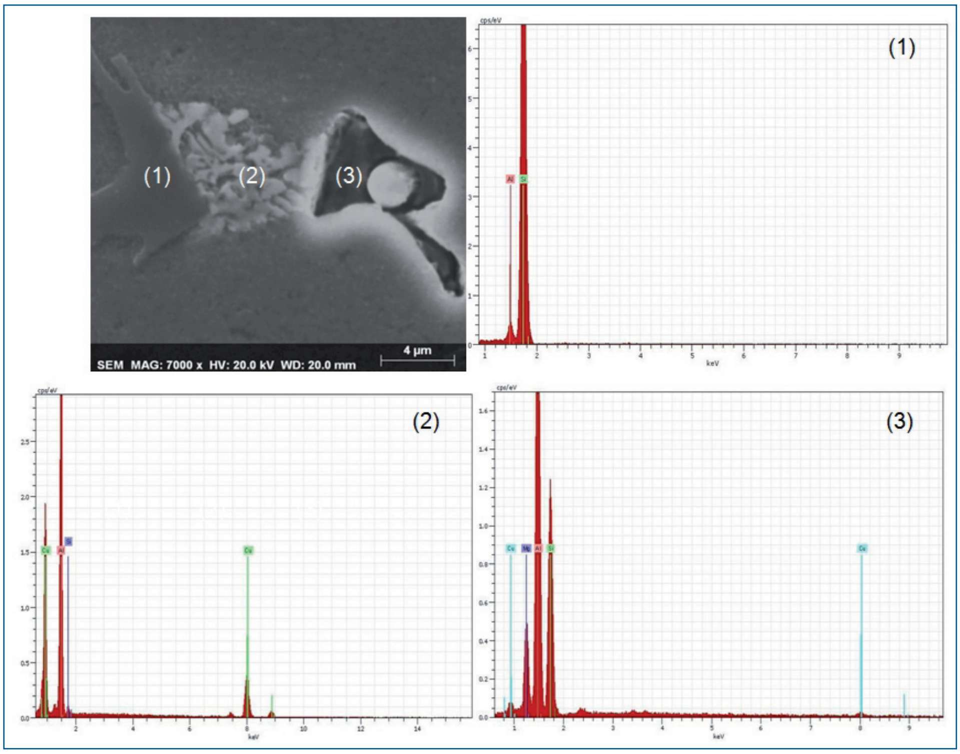


Fig. 2 - SEM micrographs of alloy A.

Fig. 2 - Micrografie SEM della lega A.

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In the previous published papers [1,3], authors have shown that, at approximately 554–530 °C, the Mg_2Si and

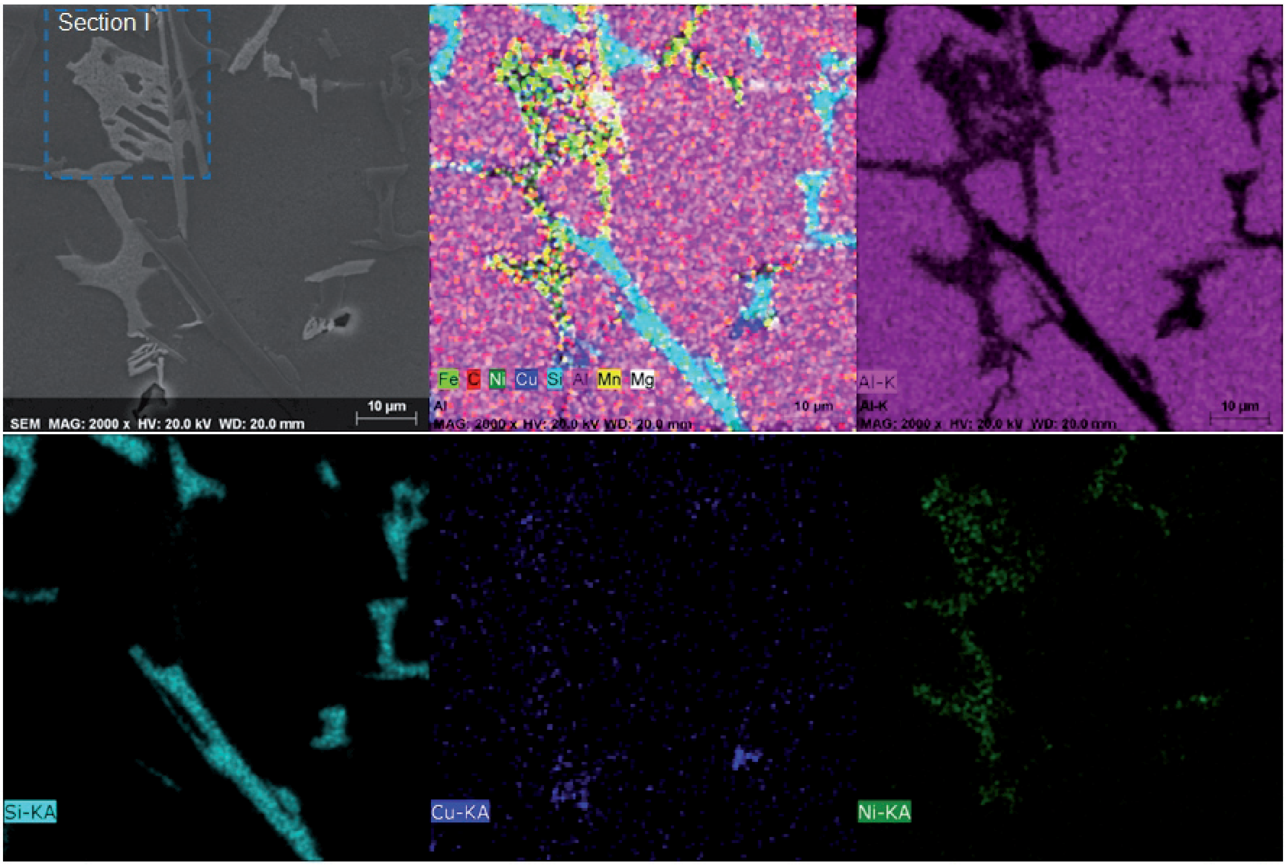

Fig.3 - SEM micrographs with characteristic morphology of the alloy C.

Fig.3 - Micrografie SEM con morfologia caratteristica della lega C.

$Al_8Mg_3FeSi_6$ phases begin to precipitate in Al–Si alloys. At approximately 530–503 °C, a "massive" or "blocky" Al_2Cu phase (containing approximately 52.5 wt.% Cu) forms together with Al_5FeSi platelets, while at approximately 515–503 °C, a fine Al-Al_2Cu eutectic phase forms (containing approximately 24 wt.% Cu). If the melt contains more than 0.5 wt.% Mg, an ultra-fine $Al_5Mg_8Cu_2Si_6$ eutectic phase also forms at this temperature. This phase grows from the two previously mentioned Al_2Cu phases. These phases have been identified in the microstructure of all of the investigated piston alloys. Fig. 2 shows a SEM analysis of alloy A microstructure, where 3 phases are visible: primary crystals of Si (1), Al_2Cu (2) and Mg_2Si (3). The Figure also shows EDS spectra for the identified phase. The EDX results were used to identify the stoichiometry for the particular phases based on the data reported in the literature.
In addition to the presented phases in the microstructure of Al–Si piston alloys, phases formed by Cu and Ni have been identified. Fig. 3 shows the microstructure of alloy C, where EDS mapping was done in addition to characterization by SEM microscopy in order to better identify the phases. Fig. 3 shows the SEM analysis of the microstructure of alloy C from Table 1, EDS mapping of all elements and EDS mapping of other key elements.
Fig. 4 shows a qualitative analysis of the phases conducted by EDX scanning electron microscopy of the marked zone (Section I) in Fig. 3. Based on the conducted analysis (the results are given in Figure 4 and in Table 3) and using key elements (Table 2), the phases present in the microstructure were identified as follows: Al_3Ni (1), Al_9FeNi (2), Al_9FeNi (3) and Al_5FeSi (4).
An additional SEM observation combined with X-ray spot microanalysis for the investigated alloy was performed to identify the morphology and stoichiometry of the observed Cu enriched phases. This analysis confirmed the earlier assertion that Cu enriched phases appear in three main morphologies: blocky, eutectic type and fine eutectic type. Quantitative X-ray microanalysis for revealed stoichiometries of the copper phases (Table 2) is presented in Fig. 5.
Fig. 5 shows a SEM microstructure analysis of piston alloy B, EDS mapping of key and all other. The following are SEM micrographs with characteristic morphology of Cu enriched phases found in the investigated alloys: eutectic type ((Section II) phase Al_7Cu_4Ni.) and fine eutectic type ((Section III) phase Al_2Cu.).
In the second step, a linear EDS analysis was conducted of element distribution of selected phase (Section II) in Fig. 5. The results of the EDS element distribution analysis are shown in Fig. 6b (the spot of linear analysis is indicated in Fig. 6a). Based on the obtained results, a change is visible in the element concentration along the analyzed line in phase Al_7Cu_4Ni.
Fig. 6c shows fine eutectic type Al_2Cu phase, whose EDS

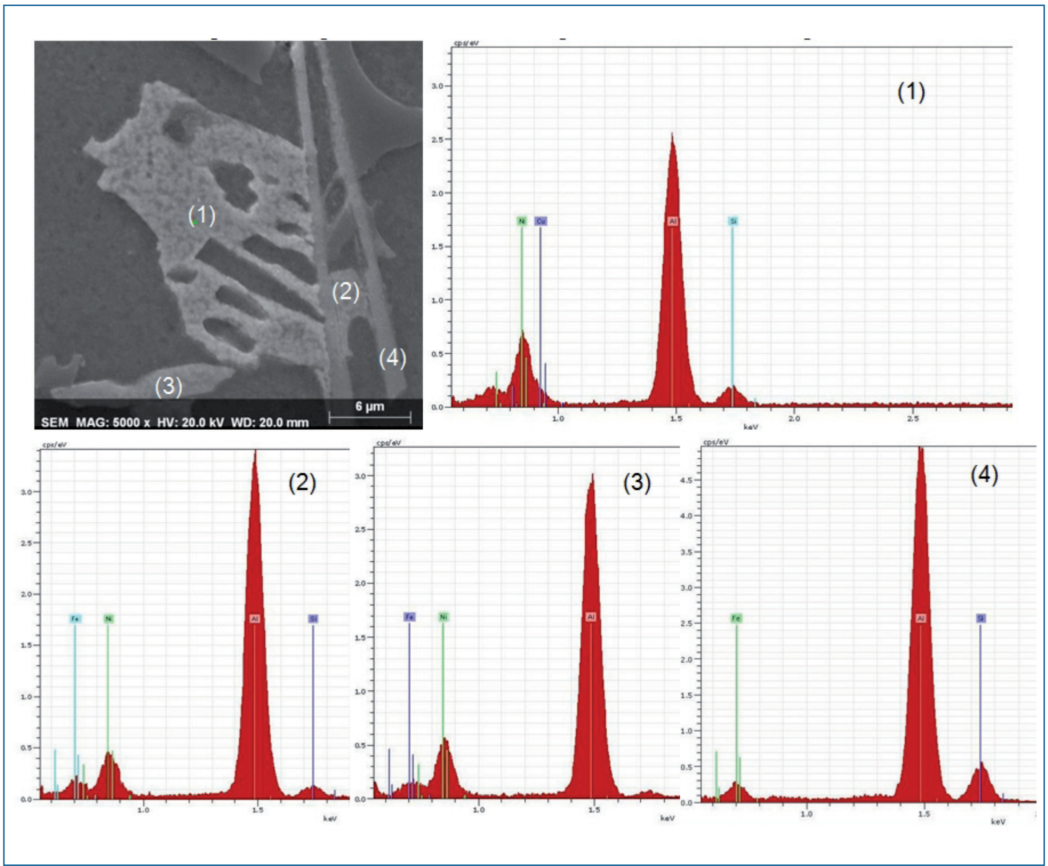

Fig. 4 - SEM micrographs with characteristic morphology.

Fig. 4 Micrografie SEM con caratteristica morfologia.

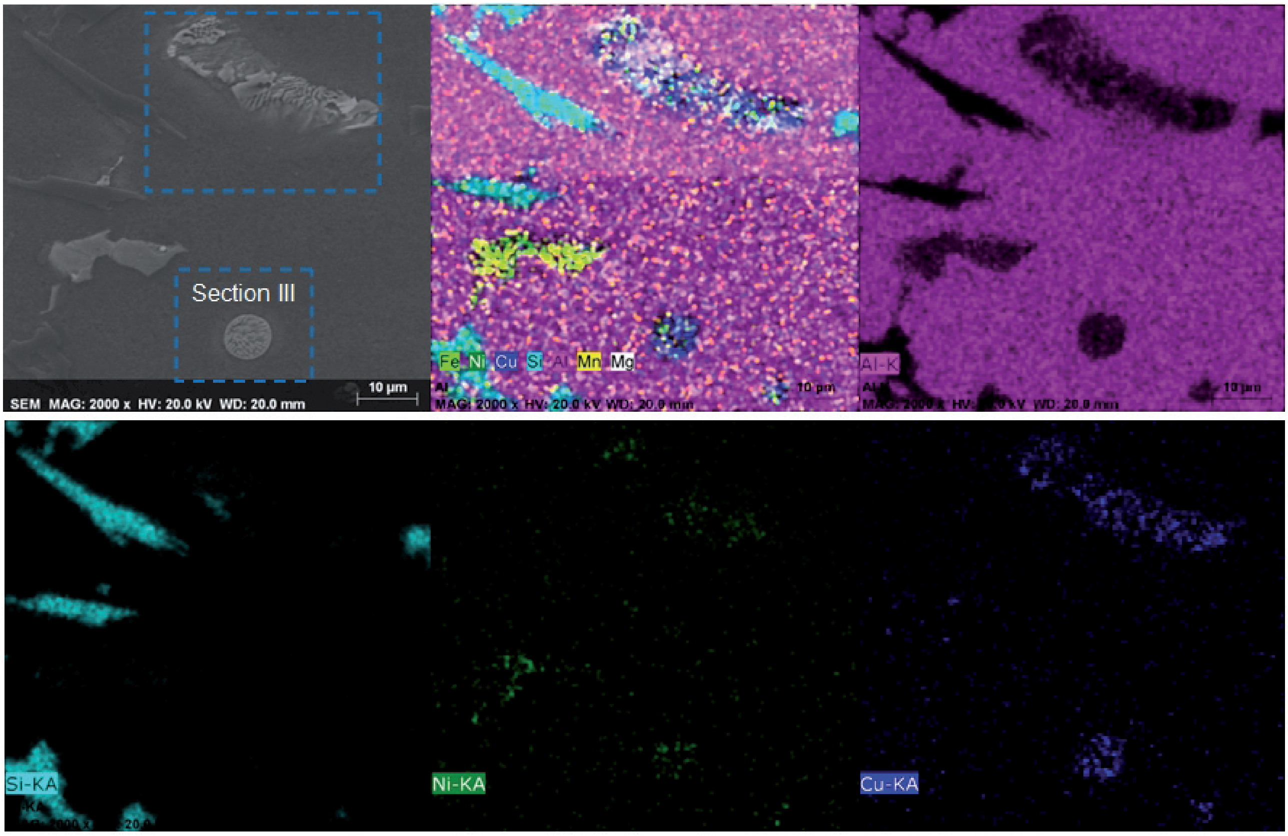

Fig. 5 - SEM micrographs with characteristic morphology of Cu enriched phases and their EDX elemental maps.

Fig. 5 - Micrografie SEM con morfologia caratteristica di fasi arricchite al Cu e loro mappe EDX.

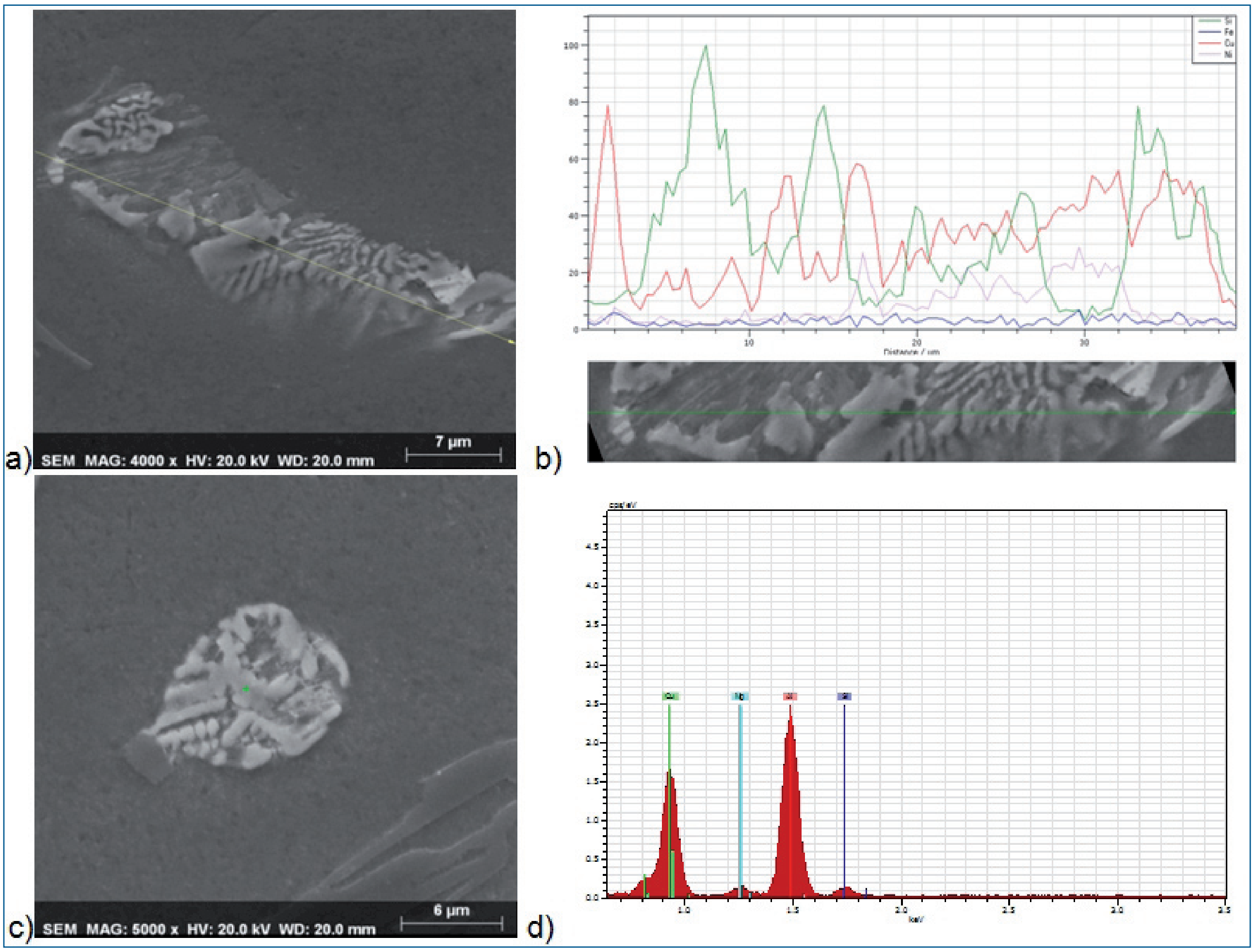

Fig. 6 - SEM micrographs with characteristic morphology of Cu enriched phases, a) linear analysis, results of linear analysis, c) Al2Cu phase and d) results of EDS analysis.

Fig. 6 - Micrografie SEM con morfologia caratteristica di fasi arricchite al Cu, a) analisi lineare, risultati di analisi lineare, c) fase Al_2Cu e d) i risultati dell'analisi EDS.

analysis is given in Fig. 6d. The results of the EDS analysis of the Al_2Cu phase are given in Table 3. The Al_7Cu_4Ni phase forms in equilibrium with aluminum, and some copper can replace nickel in Al_3Ni_2 [2,5–8]. The ternary phase has a range of existence, with a structure that varies with composition and the dissolved copper controls the lattice parameter; nickel has little or no effect [2,5].

The typical composition of the Al_2Cu phase given in Table 3 contains higher Cu and extremely low Ni contents. This phase is largely different in crystal structure and chemical composition compared with the Al_3Ni_2 and Al_7Cu_4Ni phases, making the identification easier.

The next phase that appears is Al_9FeNi. It is characterized by high chemical content of Ni and key element Fe (Table 2), as can be seen in Table 3. Based on the presented analysis of investigated aluminum piston alloys from Table 1, the phases present in the investigated alloys were defined (Table 4).

CONCLUSION

Based on the analysis of the experimental test results presented in this paper and the available data from the literature, it could be concluded that it depends on the Ni/Cu ratio which of the following phases (Al_3Ni_2, Al_7Cu_4Ni and Al_2Cu) will be formed. By increasing the Ni content at the expense of Cu, the phase formation goes in the direction of $Al_3Ni_2 \rightarrow Al_7Cu_4Ni \rightarrow Al_2Cu$ (or in reverse), which may also be seen in Table 4 based on the changes in composition.

The results presented in this paper are only an introduction to further ongoing research. In addition to the identification of all possible phases occurring in the cast microstructure, further research will be aimed at the attainment of their optimal combination in some sections of the piston as well as the development of a satisfactory mathematical model to be used for envisaging different scenarios of the solidification of piston alloys.

Phase	Composition, wt.%						Figs.	E.g.
	Al	Si	Cu	Ni	Mg	Fe		
Si	4.01	95.99					Fig.2	(1)
Al_2Cu	49.53 46.55		42.42 48.32				Fig.2 Fig. 6	(2)
Mg_2Si		37.87			62.24		Fig.2	(3)
Al_3Ni	52.49			36.56			Fig.4	(1)
Al_9FeNi	75.02			25.78		12.16	Fig.4.	(2)
	58.70			33.89		7.41		(3)
Al_5FeSi	9.73	9.73				23.24	Fig.4.	(4)
Al_3Ni_2	40.96		32.96	23.16				
Al_7Cu_4Ni	44.37		41.13	17.50			Fig.6	
$Al_5Cu_2Mg_8Si_6$		31.82	20.00		31.32			

Tab. 3 - Typical composition of various intermetallic phases observed in the alloy.

Tab. 3 - Composizione tipica delle varie fasi intermetalliche osservata nella lega.

Alloys			
A	B	C	D
(Si), (Si)+(Al), Al_7Cu_4Ni, Mg_2Si, Al_2Cu, Al_5FeSi	(Si), (Si)+(Al), Al_3Ni_2, Mg_2Si, Al_7Cu_4Ni, $Al_5Cu_2Mg_8Si_6$, Al_5FeSi, Al_2Cu	(Si), (Si)+(Al), Al_3Ni, Al_3Ni_2, Mg_2Si, Al_7Cu_4Ni, $Al_5Cu_2Mg_8Si_6$, Al_5FeSi, Al_2Cu	(Si), (Si)+(Al), Al_3Ni, Al_3Ni_2, Al_7Cu_4Ni, $Al_5Cu_2Mg_8Si_6$, Al_2Cu

Tab. 4 - The phases present in investigated alloys.

Tab. 4 - Le fasi presenti nelle leghe indagate.

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Identificazione delle fasi formate da Cu e Ni in leghe Al-Si per pistoni

Parole chiave: Alluminio e leghe

Questo articolo presenta i risultati dell' identificazione e analisi delle fasi presenti nella microstruttura di quattro leghe di alluminio per pistoni con diversa composizione chimica. Per studiare la microstruttura dei campioni sono state utilizzate microscopia ottica e microscopia elettronica a scansione ed è stata effettuata l'analisi EDS per identificare la composizione delle fasi. La fase stechiometrica è stata identificata confrontando i risultati delle analisi EDS con i risultati riportati in letteratura. I risultati mostrano che possono apparire diverse fasi intermetalliche a seconda della composizione chimica della microstruttura delle leghe di alluminio per pistone utilizzate.