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Key words: Al-Si-Cu cast alloys, age-hardening, Fe-rich intermetallic phases, Cu-rich intermetallic phases, mechanical properties

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IDENTIFICATION AND ANALYSIS OF INTERMETALLIC PHASES IN AGE-HARDENED RECYCLED AlSi9Cu3 CAST ALLOY

Purpose: The influence of age-hardening solution treatment at temperature 515°C with holding time 4 hours, water quenching at 40°C and artificial aging by different temperature 130°C, 150°C, 170°C and 210°C with different holding time 2, 4, 8, 16 and 32 hours on changes in morphology of Fe-rich $Al_{15}(FeMn)_3Si_2$ and Cu-rich (Al_2Cu, Al-Al_2Cu-Si) intermetallic phases in recycled AlSi9Cu3 cast alloy.

Material/Methods: Recycled (secondary) AlSi9Cu3 cast alloy is used especially in automotive industry (dynamic exposed cast, engine parts, cylinder heads, pistons and so on). Microstructure was observed using a combination of different analytical techniques (scanning electron microscopy upon standard and deep etching and energy dispersive X-ray analysis – EDX) which have been used for the identification of the various phases. Quantitative study of changes in morphology of phases was carried out using Image Analyzer software NIS-Elements. The mechanical properties (Brinell hardness and tensile strength) were measured in line with STN EN ISO.

Results/Conclusion: Age-hardening led to changes in microstructure include the spheroidization of eutectic silicon, gradual disintegration, shortening and thinning of Fe-rich intermetallic phases and Al-Al_2Cu-Si phases were fragmented, dissolved and redistributed within α-matrix. These changes led to increase in the hardness and tensile strength in the alloy.

1. Introduction

Aluminium alloys are preferred for the automotive industry because of theirs lightweight. Usage aluminium alloys for the automotive components saves about 55% weight in comparison with steel [1]. In the automotive industry, AlSi9CuX series casting alloys have become increasingly important in recent years too, mainly thanks to good casting characteristics and appropriate mechanical properties [2, 3].

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Recycled aluminium alloys are made out of aluminium scrap and workable aluminium garbage by recycling [4]. Production of primary aluminium alloys belongs to heavy source fouling of life environs. Approximately 45 kWh is need to produce one kg of primary aluminium, while by remelting only about 2.8 kWh to produce one kg of secondary aluminium [5]. Care of environment in industry of aluminium is associated with the decreasing consumptions resource as energy, materials, waters and soil, with increase recycling and extension life of products [4].

Because of the increasing use of recycled AlSi9CuX cast alloys, a strict control of their microstructures is necessary. The mechanical properties and microstructure of aluminium cast alloys are dependent on the composition, melt treatment conditions, solidification rate, casting process and the applied thermal treatment. The mechanical properties of Al-Si alloys depend, besides the Si, Cu, Mg and Fe-content, in the grain size, dendrite arm spacing, porosity distribution or profile [6].

AlSi9CuX alloys usually have some coexisting elements, such as Cu (2-4%), a certain amount of Fe, Mn, Mg and Zn that are present either undeliberately, or they are added deliberately to provide special material properties. These elements partly go into solid solution in the matrix and partly form intermetallic particles during solidification. The influence of intermetallic phases on mechanical and fatigue properties depends on size, volume and morphology of these phases [7]. The formation of these phases should correspond to successive reactions during solidification with an increasing number of phases involved at decreasing temperature. In practice, Bäckerud et al. [8] identified five reactions in Al-Si-Cu alloy:

609°C: α-dendritic network;
590°C: Liq. $\rightarrow$ α-phase + $Al_{15}Mn_3Si_2$ + Al_5FeSi;
575°C: Liq. $\rightarrow$ α-phase + Si + Al_5FeSi;
525°C: Liq. $\rightarrow$ α-phase + Al_2Cu + Al_5FeSi + Si;
507°C: Liq. $\rightarrow$ α-phase + Al_2Cu + Si + $Al_5Mg_8Si_6Cu_2$.

The alloy and its heat treatment presented in this work is a part of a larger project and the same microstructural and mechanical property details of the alloys have already been published [9-10]. The present work is focused on the study of the changes of Fe-rich and Cu-rich intermetallic phases during age-hardening.

2. Experimental work

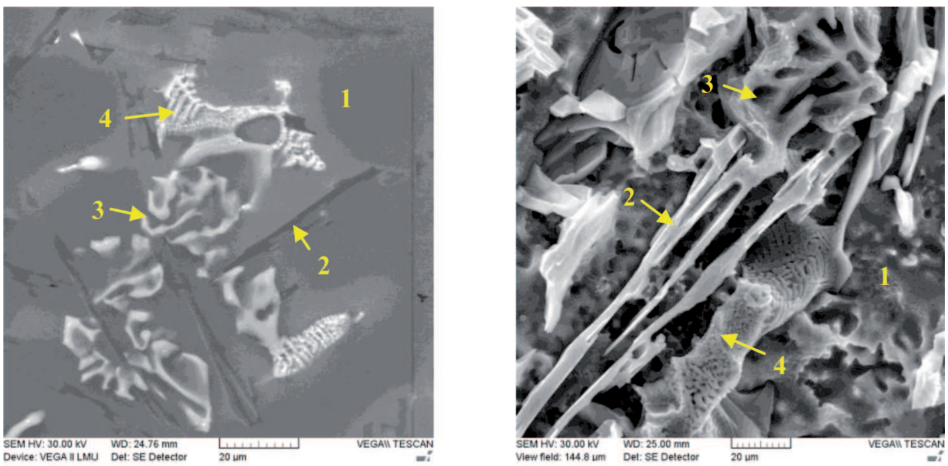
Recycled (secondary) AlSi9Cu3 alloy was as the experimental material used. The melt was not modified or grain refined, and its chemical composition was: 9.4% Si, 2.4% Cu, 0.9% Fe, 0.28% Mg, 0.24% Mn, 1.0% Zn, 0.03% Sn, 0.09% Pb, 0.04% Ti, 0.05% Ni, 0.04% Cr.

AlSi9Cu3 cast alloy has lower corrosion resistance and is suitable for high temperature applications (dynamic exposed casts, where the requirements on mechanical properties are not so high) – it means to max. 250°C.

Stucture of experimental material

The microstructures of experimental material was studied by SEM observation with EDX analysis using scanning electron microscope VEGA LMU II linked to the energy dispersive X-ray spectroscopy (EDX analyser Brucker Quantax). Samples were etched by standard reagent (0.5% HF). Some samples were also deep-etched for 15 s in HCl solution in order to reveal the three-dimensional morphology of the Si-phase and intermetallic phases [9-10].

The structure of hypoeutectic AlSi9Cu3 cast alloy consists (Fig. 1) of α-phase (1), eutectic (Si in α-phase – 2) and intermetallic Fe- (3) and Cu-rich (4) phases [9-10]. The α-phase precipitates from the liquid as the primary phase in the form of dendrites and is nominally comprised of Al and Si. Experimental alloy was not modified so that eutectic Si particles (2) are in the form of platelets, which on scratch pattern are in the form of needles (Fig. 1b).



a) etch. 0.5 % HF b) etch. HCl

Fig. 1. As-cast structure of AlSi9Cu3 cast alloy, SEM

Heat treatment

Al-Si-Cu alloy is seldom use in its untreated state due its relatively poor mechanical properties. In recent years, mechanical properties of these materials are improved by chemical treatment, reducing the porosity, solid solution hardening and precipitation hardening [11].

Precipitation hardening is the most commonly heat treatment process used in improving the mechanical properties of aluminium alloys [12]. Experimental cast samples were therefore age-hardened. The first step of age-hardening is the solution treatment at 515°C with holding time 4 hours, which involves dissolution of soluble phases. The second step is water quenching at 40°C for the formation of a super-saturation solid solution and the third step is artificial aging at different temperature 130°C, 150°C, 170°C and 210°C with different holding time 2, 4, 8, 16 and 32 hours, which is the precipitation of solute atoms.

After age-hardening the samples were subjected to mechanical tests (Brinell hardness and strength tensile). For every cast state and each aging time, a minimum of five specimens were tested.

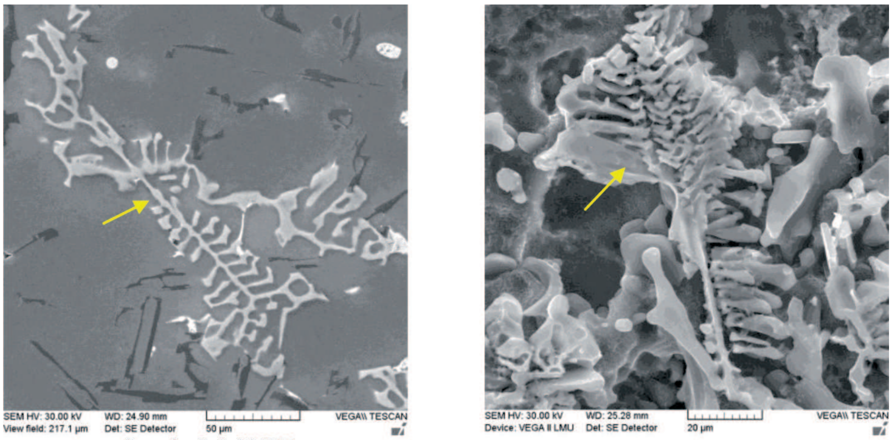
Evolution of Fe-rich phases during age-hardening

Iron is one of the most critical alloying elements, because Fe is the most common and usually detrimental impurity in cast Al-Si alloys. The Fe impurity in recycled cast alloys results mainly from the use of steel tools and scrap materials. The solubility of Fe is very low in aluminium alloys so most iron forms intermetallic phases [6, 7, 13].

According to [14], the two main types of Fe-rich intermetallic phases occurring in this Al-Si-Cu alloy are Al_5FeSi and $Al_{15}(FeMn)_3Si_2$. Al_5FeSi phases precipitate in the interdendritic and intergranular regions as platelets. This phase is more unwanted; because it can cause high stress concentrations, thereby increasing crack imitation and decreasing the ductility [6]. The deleterious effect of Al_5FeSi can be reduced by increasing the cooling rate or superheating the molten metal. Another way that might by used to suppress the formation this monoclinic phase is converting the morphology by the addition of a suitable "neutralizer" like Mn, Co, Cr, Ni, V, Mo and Be.

The most common addition has been Mn. The excess in Mn content may reduce Al_5FeSi phase and promote formation Fe-rich phases $Al_{15}(FeMn)_3Si_2$ in the form of „skeleton like“ or in the form of „Chinese script“ [6, 14]. The phase $Al_{15}(FeMn)_3Si_2$ is considered less harmful to the mechanical properties than the needle-like phase. For formation of Fe-rich intermetallic phases in the form of Chinese script, not in the form of platelets, it is required that the proportion Fe : Mn was 2 : 1. Alternatively, if % Fe in aluminium alloy exceeds the value of 0.45%, the addition of Mn should not be less than half % of Fe [15].

In the experimental recycled AlSi9Cu3 cast alloy that contains less than 0.9% Fe and 0.24% Mn, there were only Fe-rich $Al_{15}(FeMn)_3Si_2$ phases (Fig. 2) observed.



a) etch. 0.5 % HF b) etch. HCl

Fig. 2. Morphology of $Al_{15}(FeMn)_3Si_2$ phases in AlSi9Cu3 cast alloy, SEM

The type, morphology and quantity of iron in the melt influence mechanical properties of aluminium alloys. Nevertheless, the shape of iron compounds is more influential than the quantity of those iron compounds. The evolution of the Fe-rich phases during age-hardening is described in Fig. 3. In the untreated state, the phase $Al_{15}(FeMn)_3Si_2$ has a compact skeleton-like form (Fig. 3a). Solution treatment of this skeleton like phase by 515°C leads to fragmentation, spheroidization and segmentation (Fig. 3b). Fig. 3c, Fig. 3d, Fig. 3e and Fig. 3f shows that the process of artificial aging furthermore markedly affected the Fe-rich phase's morphology. The $Al_{15}(FeMn)_3Si_2$ phase was dissolved and fragmented to smaller skeleton particles.

The influence of heat treatment on Fe- phase morphology was described by quantitative metallography [16] using the Image Analyzer NIS Elements 3.0 to quantify average area of $Al_{15}(FeMn)_3Si_2$ phases (Fig. 4).

Maximum average area of Fe-rich phases was observed by untreated state (322 μm^2). It is probably connected with casting of the experimental material. Minimum average area of Fe-rich phases (less than 50 μm^2) was observed after age-hardening by holding time greater or equal to 4 hours independently of temperature of artificial aging (130, 150 or 170°C).

Evolution of Cu-rich phases during age-hardening

Cu intermetallic phases in unmodified aluminium alloys, with tetragonal crystal structure solidified in two morphologies after Al-Si eutectic reaction.

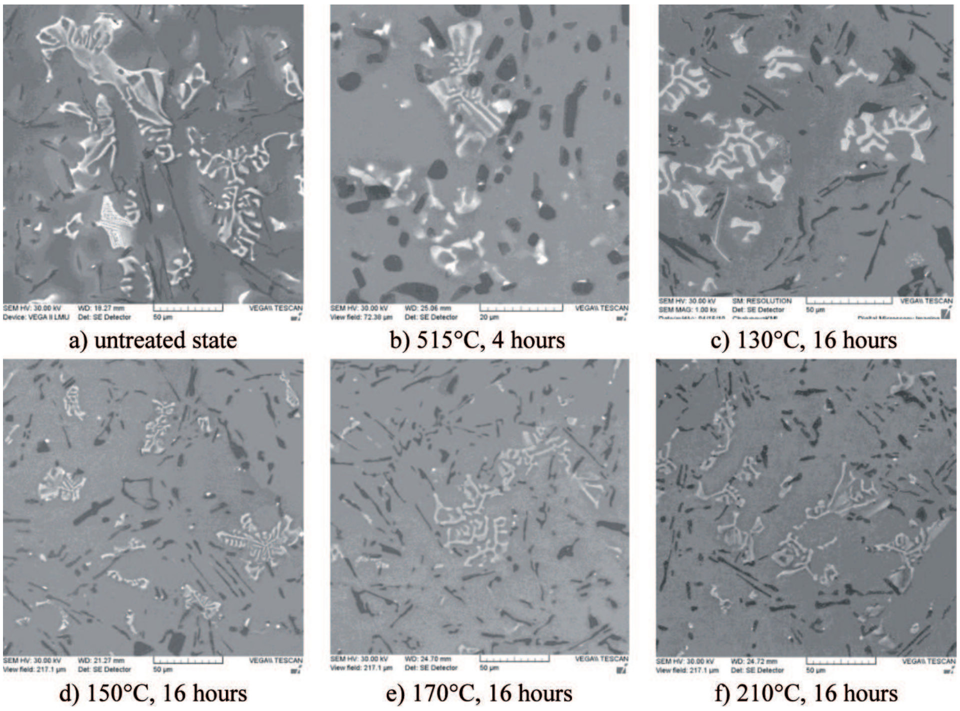


Fig. 3. Changes in morphology of $Al_{15}(FeMn)_3Si_2$ phases during age-hardening, etch. 0.5% HF, SEM

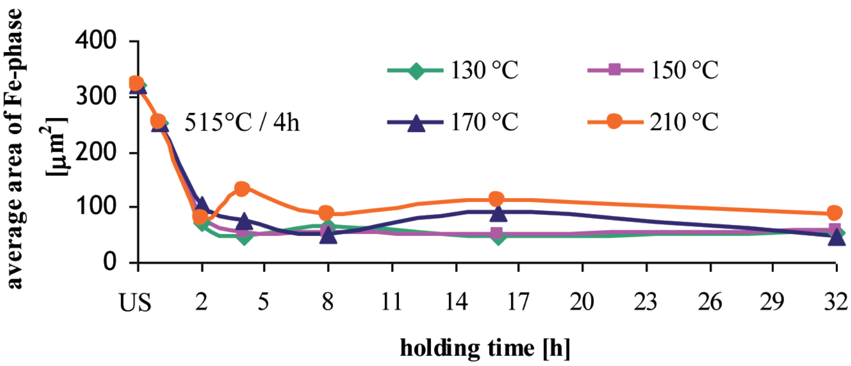
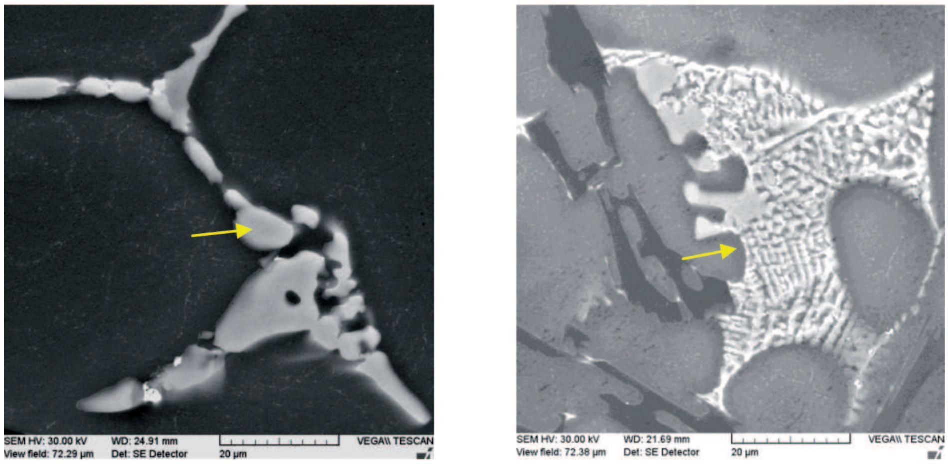


Fig. 4. Changes in average area of Fe-rich phases, (US – untreated state)

The first ones are of massive or blocky form (Al_2Cu – Fig. 5a) with high copper concentration ~38 – 40% Cu and the second ones have fine ternary eutectic form (Al-Al_2Cu-Si – Fig. 5b) [10, 17].

The effect of copper appears primarily as an increased amount of dispersed microporosity. Half or more of the copper can be found as a component of intermetallic compounds [17].



a) Al_2Cu b) Al-Al_2Cu-Si

Fig. 5. Morphology of Cu-rich phases, etch. 0.5% HF

The Al_2Cu phase was observed in the experimental material in very small amount, so we measured changes of Al-Al_2Cu-Si phase after age-hardening. Al-Al_2Cu-Si phase without heat treatment (untreated state) occurs in the form of compact oval troops (Fig. 6a). After solution treatment 515°C with holding time 4 hours, these phase disintegrated into coarsened globular particles and these occurs along the Fe-rich phase (Fig. 6b) [9]. After age-hardening, the compact Al-Al_2Cu-Si phase disintegrates into separate Al_2Cu particles or fibres. The amount of these phases was not precisely visible on optical microscope. On SEM microscope, we observed these phases in the form of very small particles for every temperatures and holding times of artificial aging (Fig. 6).

The average area of Al-Al_2Cu-Si phases obtained by quantitative metallography in age-hardened samples is shown in Fig. 7. Maximum value of the average area of Cu-rich phases was measured in untreated as-cast state (156 μm^2) and the minimum average area was estimated by age-hardening at temperature 170°C with holding time 16 hours (1.531 μm^2). In order to observe the Cu-phases, we had to use a great magnification, because otherwise we could not clearly see these very fine elements.

Small precipitates of Al_2Cu (hardening constituent), incipient by age-hardening, were invisible in the electron microscope, so observation using TEM microscopy was necessary.

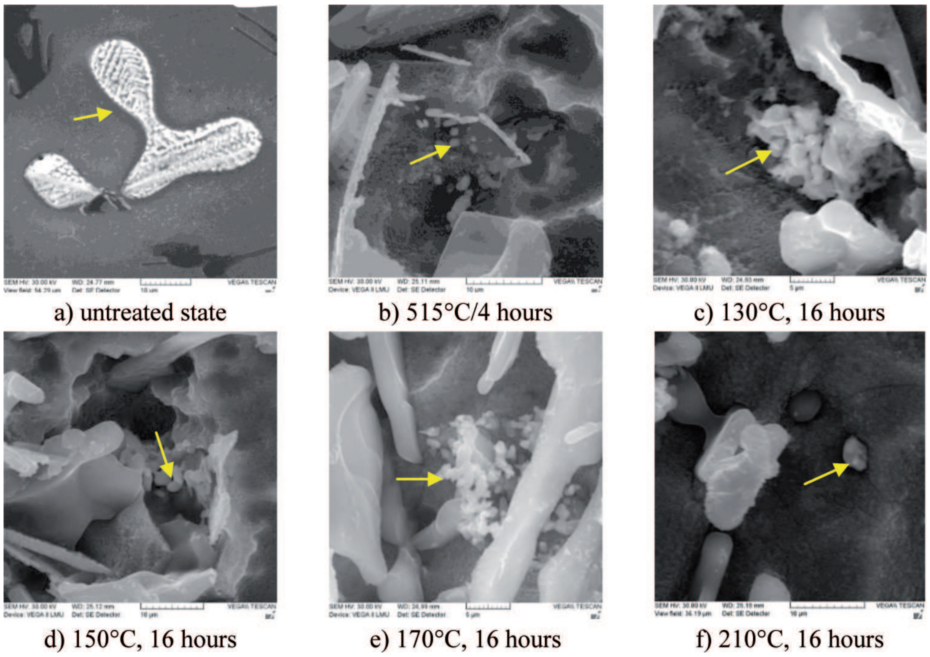


Fig. 6. Changes in morphology of Al-Al_2Cu-Si phases, etch. HCl, SEM

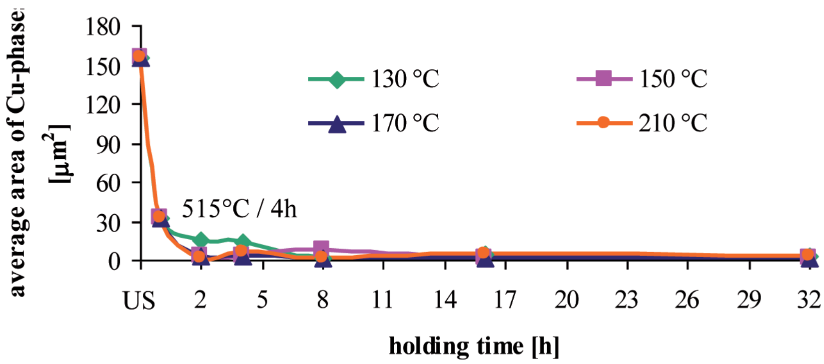


Fig. 7. Changes in average area of Cu-rich phases, (US – untreated state)

Effect of hardening on mechanical properties

The changes in morphology of Fe-rich and Cu-rich intermetallic phases during age-hardening make changes in mechanical properties, too. Hardness measurement was performed by a Brinell hardness tester with a load of 62.5 Kp, 2.5 mm diameter ball and a dwell time of 15 s. The Brinell hardness value at each state was obtained as an average of at least six measurements. Fig. 8 shows the influence of age-hardening on the Brinell hardness. It can be seen that there is an obvious age-hardening phenomenon for each curve. At the early stage of aging for temperature 130 and 150°C, the hardness increases with aging time until it reaches the first peak (after 4 h). At intermediate stage of aging, after a little decrease, the hardness increases again and reaches the potential second peak for temperature 130 and 150°C after 32 h. The final stage of aging, when the hardness decreases as a result of over-aging, was not observed. For samples aged at temperature 170°C, a single aging peak after 8 hours and next a hardness high plateau from 8 to 32 hours was measured.

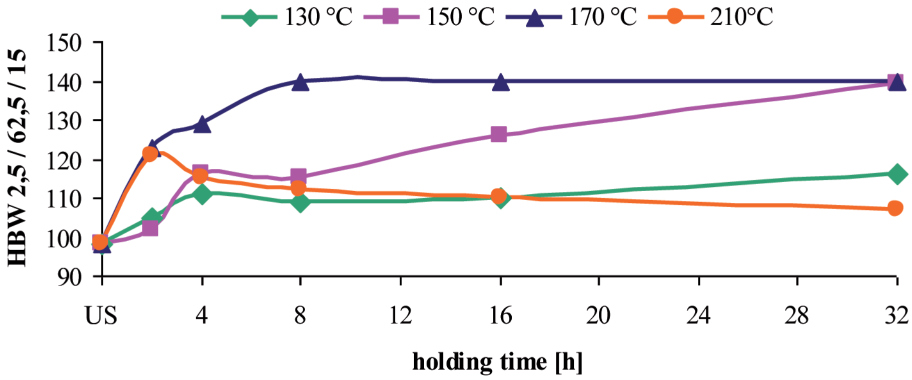


Fig. 8. Influence of heat treatment on hardness, (US – untreated state)

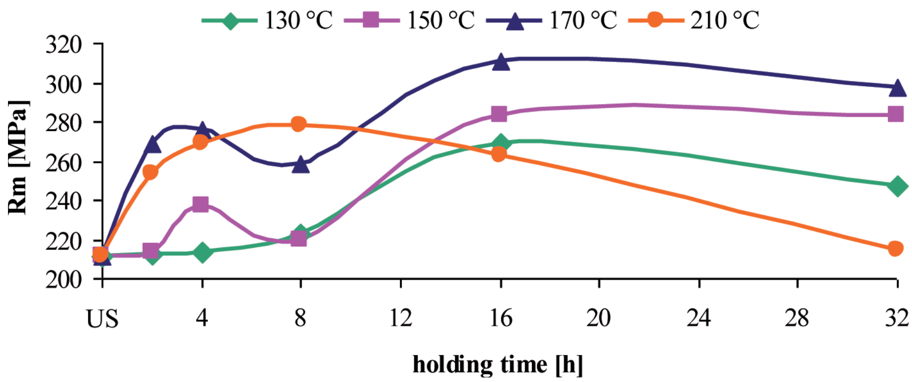


Fig. 9. Influence of heat treatment on strength tensile, (US – untreated state)

The early stage of aging for temperature 210°C by 2 hours was measured. The second aging peak was not observed. After aging time longer than 2 hours, the hardness decreases as a result of over-aging. The age-hardening peaks are correlated with their precipitation sequence. The first hardness peak of age-hardening curve is attained depending on the high density GP zones (especially GP II zones), while the second one is acquired in terms of metastable particles. The aging plateau corresponds to the continuous transition from GP zones to metastable phases. The highest Brinell hardness was 140 HBS for artificial aging 170°C from 8 to 32 hours and the lowest one was 98 HBS (by untreated state).

In order to investigate the double-peak phenomenon of the AlSi9Cu3 alloy, we have measured its tensile properties. The results are shown in Fig. 9. It can be seen that the double aging peaks appear for temperature values of 130, 150 and 170°C. The first aging peak was observed after holding time 4 hours and the second aging peak after 16 hours. For temperature 210°C, there was only one aging peak after 8 hours measured. The highest strength tensile was obtained for artificial aging 170°C from 16 hours (311 MPa) and the lowest one was 211 MPa (by untreated state).

3. Conclusion

In the present study, microstructural characteristic – the evolution of the Fe-rich and Cu-rich intermetallic phases in recycled AlSi9Cu3 cast alloy during age hardening were investigated. From the analysis of the results the following conclusions can be drawn:

- In $AlSi_9Cu_3$ cast alloy we observed Fe-rich phases $Al_{15}(FeMn)_3Si_2$. Skeleton-like $Al_{15}(FeMn)_3Si_2$ phase was dominant thanks to the presence of Mn. The morphology and size of iron phases were dependent on the heat treatment. The age-hardening caused great changes in Fe-rich phases. Skeleton-like $Al_{15}(FeMn)_3Si_2$ phases were dissolved and fragmented into small particles (average area reduces from 322 to 47 μm^2).
- Cu-rich phases' solidified in two distinct morphologies: in the form of blocky phase Al_2Cu and as fine spherical Al-Al_2Cu-Si ternary eutectic. The age-hardening caused changes of Cu-rich intermetallic phases, too. Compact Al-Al_2Cu-Si eutectic was fragmented, dissolved and next redistributed within α-matrix. The dissolution of Cu-rich phases during hardening holding increases the concentration of Cu and other alloying elements (Mg, Si) in the aluminium matrix. Cu also creates dispersed intermetallic precipitates and increases the overall matrix strength by the mechanism called the precipitation strengthening effect. Unfortunately, because these Al_2Cu precipitates are very fine, their area fractions cannot be quantified using image analysis.
- The mechanical properties (Brinell hardness and tensile strength) increase after age-hardening for all artificial temperatures. The „optimum" schedule for mechanical properties is as follows: solution treatment: 4 h at 515°C; water quenching at 40°C; artificial aging: 16 h at 170°C. In this schedule, the following properties are obtained: HB >98 (cca 140 HB); R_m >211 MPa (cca 311 MPa);

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Identyfikacja i analiza faz międzymetalicznych w utwardzanych przez starzenie stopach odlewniczych $AlSi_9Cu_3$ z recyklingu

S t r e s z c z e n i e

Cel: Badanie wpływu utwardzania przez starzenie przesycanie w temperaturze 515°C z czasem przetrzymywania 4 godz., hartowanie wodne w 40°C, starzenie przyspieszone w różnych temperaturach: 130°C, 150°C, 170°C i 210°C, przy czasach przetrzymywania: 2, 4, 8, 16 i 32 godziny na zmiany w morfologii stopów odlewniczych AlSi9Cu3 z recyklingu wzbogaconych żelazem ($Al_{15}(FeMn)_3Si_2$) lub miedzią (Al_2Cu, Al-Al_2Cu-Si).

Materiał i metody: Pochodzący z recyklingu (wtórny) stop odlewniczy aluminium AlSi9Cu3 jest powszechnie używany, zwłaszcza w przemyśle motoryzacyjnym (dynamiczne, odkryte odlewy, części silnika, głowice cylindrów, tłoki itp.). Mikrostrukturę odlewów badano stosując kombinację różnych technik analitycznych (elektronowa mikroskopia skaningowa w połączeniu z analizą rentgenowską z dyspersją energii (EDX), standardową i z głębokim wytrawianiem), co pozwoliło identyfikować różne fazy międzymetaliczne. Ocena ilościowa zmian w morfologii tych faz została przeprowadzona przy wykorzystaniu oprogramowania analizatora obrazów (Image Analyzer NIS-Elemets). Właściwości mechaniczne (twardość w skali Brinella i wytrzymałość na rozciąganie) były mierzone zgodnie z normą STN EN ISO.

Wyniki i wnioski: Utwardzanie przez starzenie prowadzi do zmian w mikrostrukturze, które polegają na sferoidyzacji krzemu eutektycznego, stopniowej dezintegracji, skracaniu i ścienianiu faz międzymetalicznych wzbogaconych żelazem. Fazy Al-Al_2Cu-Si podlegały fragmentacji, zostały rozpuszczone i redystrybuowanie w osnowie α stopu. Zmiany te prowadzą do wzrostu twardości stopu i jego wytrzymałości na rozciąganie.