UDK 669.714

MICROSTRUCTURAL STUDIES OF Al-Mg-Si-Mn AND Al-Mg-Ge-Mn CASTING ALLOY

V.Boyko(1), T.Link(1), N.Korzhova(2), T.Legkaya(3) and K.Mykhalenkov(4)

(1)Technical university Berlin, Berlin, Germany
(2)Institute for Problems of Materials Science of NASU, Kiev, Ukraine
(3)Kurdjumov Institute for Metal Physics of NASU, Kiev, Ukraine
(4) National technical university of Ukraine "KPI", Kiev, Ukraine

Реферат (укр.)

Наведені результати є розширенням розуміння процесів формування структури ливарних сплавів системи Al-Mg-Si, а також того, яким чином присутність легуючих елементів Cu, Zn, Li, Sc, Zr впливає на їх механічні властивості. Було встановлено, що введення 0,5% літію подрібнює структуру евтектики і зменшує розміри первинних кристалів силіциду магнію. Введення скандію, або у сукупності із цирконієм проявляє потужний ефект зерноподрібнення. Так само впливають і додатки бору. На противагу промисловим силумінам, в яких введення стронцію сприяє формуванню тонковолокнистої евтектики, в сплавах Al-Mg-Si такий ефект не спостерігається. Встановлено, що спільне введення Sc+Zr істотно впливає на механічні властивості ливарних сплавів Al-Mg-Si-Mn. Особливо цей ефект проявляється при підвищених температурах. При температурі випробування 250°C тимчасовий опір сплаву сягає 230 МПа.

Реферат (рус.)

Представленные результаты являются расширением нашего понимания процессов формирования структуры литейных сплавов Al-Mg-Si и того, как присутствие Cu, Zn, Li, Sc, Zr влияет на окончательные механические свойства сплавов этой группы. Установлено, что введение 0,5% лития способствует измельчению эвтектики и уменьшению размеров первичных кристаллов силицида магния. Введение только скандия, или в сочетании с цирконием проявляет сильное зерноизмельчающее действие, также как влияет и добавка бора. В противовес промышленным силуминам, где введение стронция приводит к формированию тонковолокнистой структуры эвтектики, в сплавах Al-Mg-Si такой эффект не наблюдается. Было установлено, что совместное введение Sc+Zr оказывает значительное влияние на механические свойства сплавов Al-Mg-Si-Mn, особенно при высоких температурах. Добавка указанных элементов способствует повышению временного сопротивления разрыву до 230

МПа при темпераmуре 250°C.

Abstract (Engl.)

Represented results are the extension of our understanding of Al-Mg-Si casting alloys structure formation of and how presence of Cu, Zn, Li, Sc, Zr do effect on their mechanical properties. It has been found that addition of 0.5wt%Li refine the eutectic structure and reduces the size of primary Mg_2Si crystals, simultaneously. Sc separately and together with Zr promotes powerful grain refinement effect. Addition of boron also refines α-Al grains. In contrast commercial Al-Si casting alloys where Sr addition strongly affect on formation of fine fibers of eutectic Si in Al-Mg-Si alloys it does not affect on the formation of Mg_2Si eutectic lamellas. It has been found pronounced effect of Sc+Zr on the mechanical properties of Al-Mg-Si-Mn alloys especially at elevated temperatures. Addition of these elements increases strength of an alloy up to 230 MPa at 250°C.

1. Introduction

The Al alloys is a group of casting materials that are in tonnage terms the second most popular after ferrous castings. The Al alloys have been divided into several systems that were identified based on their alloying elements. Aluminum-Silicon and especially Al-Si-Mg alloys are the most abundant among cast alloys and have wide-spread applications, especially in the aerospace and automotive industries. It constitutes from 80 to 90% of the total Al castings produced world wide [1]. The dominant group of Al–Si foundry alloys contain between 5 and 25 wt.% Si, with Mg, Ni and Cu additions. Considerable advantages of this system are relatively high strength, good corrosion resistance together with good castability.

During last 15 years several new casting alloys were developed where composition and subsequently phase equilibra shifted from Al-Si-Mg side to Al-Mg-Si. Several alloys with nominal composition Al-3-5%Mg-1-2%Si-0.6%Mn[1] were successfully introduced into the foundry practice [2-6]. However, there were little part of researches on the structure formation and strengthening mechanisms of Al-Mg-Si-Mn casting alloys performed or published until now. For Al-Mg-Ge casting alloys what is considered as very promising candidates for application at elevated temperature scientists paid small attention has been paid and only information about structure of precipitates in this system can be found [7-9].

Both Al-Mg-Si and Al-Mg-Ge systems displays common feature is the existence of quasibinary section were congruently melting binary compound

---

[1] all compositions are given in wt%, otherwise specified.

(intermetallics Mg_2Si or Mg_2Ge) on one face and one on a different face (Al) might form a quasi-binary section. By other words, ternary alloys with composition inside of quasibinary section might be considered as binary.

During solidification of Al-Mg-Si or Al-Mg-Ge alloys undergoes eutectic reactions $L \rightarrow (\alpha\text{-Al}) + Mg_2Si$ at 594°C and $L \rightarrow (\alpha\text{-Al}) + Mg_2Ge$ at 623°C, subsequently. These temperatures are one of the highest eutectic temperatures among commercial Al-alloys. Together with this other strengths of alloys based on these systems have to be considered. They have good castability, corrosion resistance, small solidification range and ability to be age hardened. The last one plays important role for increasing mechanical properties of castings.

One of the most interesting features of Al-Mg-Si alloys is low Si concentration in Al-based solid solution. This provides an opportunity for Al-Mg-Si alloys to be additionally alloyed with elements supplied formation of nano-size precipitates during aging thus increasing precipitation strengthening effect.

2. Purpose of the research

However the information on structure formation and precipitation strengthening effect of the new generation of casting alloys is scanty. Therefore, the purpose of this work is to generate consistent and comprehensive description of structure formation of Al-Mg-Si and Al-Mg-Ge casting alloys based on recent experimental data.

3. Experimental procedure

The nominal composition of base alloy (BA1) was Al-7%Mg-3%Si-0.6%Mn and it was kept constant throughout all melts. For alloys with Ge the composition Al-4.34%Mg-6.49%Ge-0.6%Mn (BA2) has been chosen as base material. Resistant furnace with graphite crucible was used in all experiments. Average batch weight also was kept at the same level about 300 g. To each melt after addition of master alloys argon blowing system was applied for homogenization of temperature and metal cleaning from non-metallic particles and hydrogen. Addition of alloying elements to al were made by use of Al-26% Si, Al-25%Mn, Al-2%Sc, Al-10%Zr, Al-50%Mg, Al-5%Li and Al-20%Ge master alloys. Al, Cu and Zn of chemical purity were added as pure elements. After 10 minutes of argon blowing melt surface was skimmed from dross's and metal poured into steel mold with temperature 20°C. This condition provides cooling rate of about 10-15 K/s prior to solidification. After cooling ingots were sectioned for metallographic investigations and differential scanning calorimetry. All metallographic investigations were performed using light microscope Zeiss Axioscope, scanning electron and transmission microscopes

(Zeiss Evo and Philips CM30T operated at 300 kV, subsequently). Mechanical tests were performed using Instron 3360 Series dual column universal testing system.

4. Results and discussion

According to the established Al-Mg-Si phase diagram structure of hypoeutectic alloy consists of aluminum solid solution (α-Al) and Mg_2Si intermetallic phase [10]. X-ray diffraction obtained from BA1 and light microscopy investigations confirmed this phase composition (Fig. 1). There was no other phases has been detected in the base material.

Quantification of EDX spectra confirmed relatively high Mg concentration in solid solution (in the range between 2.8 – 3.1 at.%) and low Si content – about 0.29 at.% in the alloy matrix. From Fig. 3 regular eutectic (α-Al)+Mg_2Si structure can be seen with average interlamella distance of 1 μm. Composition of intermetallic compound was found is 44.3 at.%Mg and 25.4 at.%Si (Mg/Si ratio = 1.77) which is very close to stoichiometric composition of Mg_2Si. Nearly same elements content has been found in the crystals with regular polyhedral morphology (42.02 at.%Mg and 27.3 at.%Si) represents Mg_2Si primary phase.

For Al-Mg-Ge preferential eutectic morphology is the rod-like and the structure also contains areas with plate-like eutectic needles growing outwards from large (size range from 50 to 100 μm) crystals. EDX analysis performed on thin foil make clear that the composition of large crystals is 55.2 at.%Mg 26.2 at.%Ge. From this elements content and morphology it can be deduced that these phase is the Mg_2Ge primary crystals. It is worth noting that primary crystals exhibits not only polyhedral morphology. Some of the crystals with dendritic morphology been observed in the alloys structure.

In contrast to Al-Mg-Si system Al-based solid solution in Al-Mg-Ge-Mn does not contain Mg which is replaced by Ge. Quantification of EDX spectra shows that sold solution consist of 99.2 at%Al, 0.52 at%Ge and 0.29 at%Mn. TEM investigations of both Al-Mg-Si and Al-Mg-Ge systems reveal needle shaped precipitates situated on grain boundaries (Fig. 3) and inside of Al matrix (Fig. 4) which is often named as discontinuous. For Al-Mg-Ge such type of precipitates consists of 94.2%Al and 5.1%Ge. In addition 0.7 %Mn is dissolved in this precipitates. Considering alloys after addition of Sc+Zr the composition of discontinuous precipitates is believed to be $Al_3(Sc_{1-x}Zr_x)$. Similar precipitates also were observed in Al-Mg-Si alloys after alloying with Cu+Zn which is growth outwards from Mg_2Si lamellas. This precipitates mechanism, which is sometimes referred to as cellular precipitation, is commonly described as a decomposition of supersaturated solid solution into α-Al and $Al_3(Sc_{1-x}Zr_x)$ at a moving grain boundary.

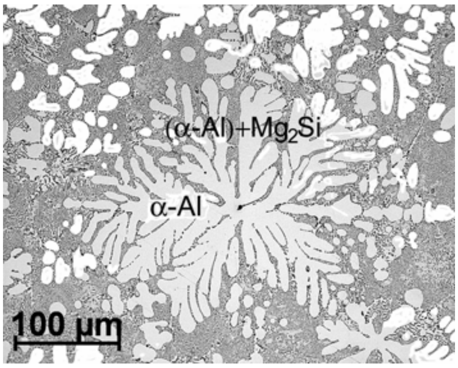


Fig. 1. Structure of base Al-7%Mg-3%Si-0.6%Mn alloy in as cast condition

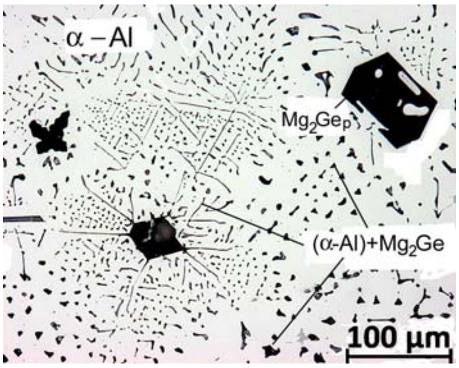


Fig. 2. Structure of Al-4.34%Mg-6.49%Ge-0.6%Mn in as cast condition

The driving force for the grain boundary migration is the volume free energy that is released during the precipitation. As the grain boundary moves, it leaves behind a characteristic fan shaped array of precipitates. As a result of their rather coarse nature and inhomogeneous dispersion, discontinuously precipitated $Al_3(Sc_{1-x}Zr_x)$ or Al_xGe contributes but little to the strength of the alloy, and also leads to a smaller amount of Sc, and subsequently Ge, in supersaturated solid solution being available for subsequent continuous precipitation. Thus discontinuous precipitation is in general regarded as an undesired precipitation mode. From the other hand it was found that discontinuous precipitate dissolves during homogenization treatment.

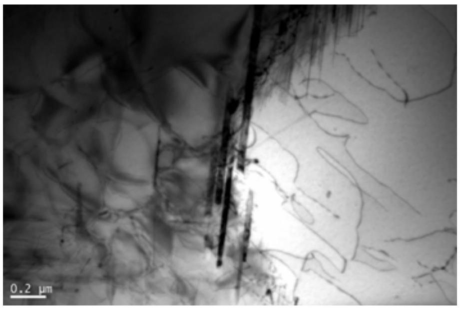


Fig. 3. Discontinuous precipitates on the grain boundary in Al-4.34%Mg-6.49%Ge-0.6%Mn in as cast condition

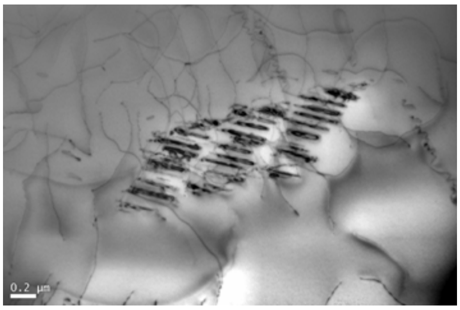


Fig. 4. Discontinuous precipitates in the matrix of Al-7%Mg-3%Si-0.6%Mn-0.22%Sc-0.14%Zr in as cast condition

From Fig. 5 and Fig.6 white particles in the centers of primary Mg_2Si crystal in base alloy and also in the middle of $Al_3(Sc_{1-x}Zr_x)$ primary particle has been observed. EDX analysis of these particles reveals that they consist mainly of Al and O thus can be identified as alumina. Previously authors [11] observed oxide particles in the centers of Al_3Ti and Al_8Mn_5 intermetallics suggesting multi-step heterogeneous nucleation mechanisms.

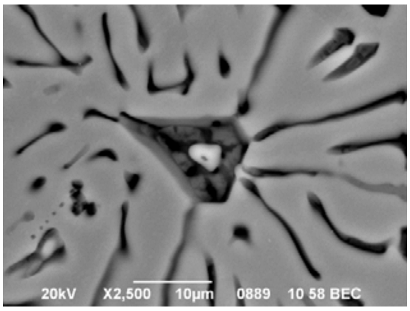


Fig. 5. Oxide inclusion as the nucleation particle inside of Mg_2Si *primary crystal*

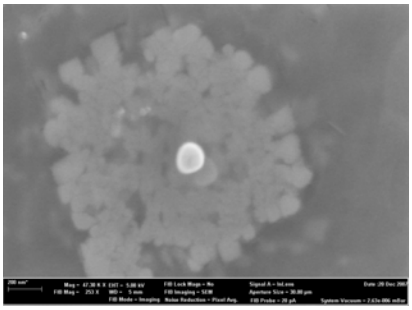
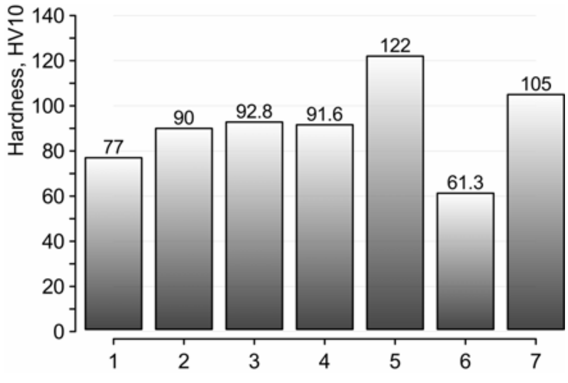


Fig. 6. Oxide inclusion in the center of $Al_3(Sc_{1-x}Zr_x)$ *primary phase*

In the heart of their hypothesis is the assumption that oxides are always present in aluminum alloy melts and can act as potent substrates for formation not matrix but intermetallics. Previously neither in literature nor in the authors own experiments oxide particles been observed in the grain centers of pure Al or its alloys. From the other hand alumina particles has been found in the centers of Mg_2Si primary crystals and $Al_3(Sc_{1-x}Zr_x)$ primary particles. From these results the sequence on nucleation events might be described as follows: primary intremetallic phases are nucleated on the surface of oxide particles dispersed in a melt. This action represented first step with following nucleation of other solid phases such as α-Al in the alloy after addition of Sc+Zr and primary Mg_2Si crystals. There is the second nucleation step.

Mechanical tests performed on specimens cut from ingots. For hardness measurements specimens in as cast condition were used. For tensile tests specimens after homogenization treatment were subjected. It is known that the highest temperature of homogenization might be the maximum saturation of solid solution can be achieved. Keeping this in mind maximum homogenization temperature and time were determined from the results of differential scanning calorimetry (DSC) measurements of melting and solidification process. It has been found that for base alloy maximum homogenization temperature for BA1 might exceed 580°C, but for the alloy after addition of Cu+Zn this temperature cant be over 490°C. This is because of the reactions (i) $L \leftrightarrow Q+(Si)+\Theta+(Al)$, where Q is quaternary phase in the Al–Cu–Mg–Si and reaction takes place at 503°C or (ii) $L \leftrightarrow Mg_2Si+S+\Theta+(Al)$ where S is ternary compound Al_2CuMg and Θ is binary phase Al_2Cu and reaction takes place at 500°C Using DSC analysis in a such a alloying system is difficult to distinguish what reaction is in the reality took place and due to this after recording last thermal effect of the cooling curve for the alloy with addition of Cu+Zn the highest possible homogenization temperature was determined (last heat effect minus 10°C). The same measurements performed with A356 casting alloy for keeping heat treatment condition on the as close as possible level for both materials.

From Fig. 7 changes in hardness HV10 for different alloys composition in as cast state can be seen. The highest value of HV10 recorded from BA1 alloy after addition of Cu+Zn where together with Mg_2Si intermetallic phase large number of ternary or quaternary phases was formed. These phases are hard and brittle. Due to this alloy displayed highest hardness. Lowest hardness was displayed by BA2 alloy (Al-Mg-Ge system) where eutectic structure consists of fine rods and thus exhibits lower volume fraction eutectic. And what is more, authors [12] that mechanically alloyed aluminum with Mg and Ge exhibits superplastic properties, what can be the subject for further investigation. This results in low hardness in comparison to saturated with intermetallics BA1+Cu+Zn alloy.



1-Al-7Mg-3Si; 2 - BA1; 3 - BA+0.2Sc+0.2Zr; 4-BA1 + 0.5Li; 5 – BA1 +1.5Cu+2.0Zn; 6 – BA2; 7 – BA1 + 1.5Cu

Fig. 7. Hardness of Al-7Mg-3Si-Mn alloys as a function of alloying elements content

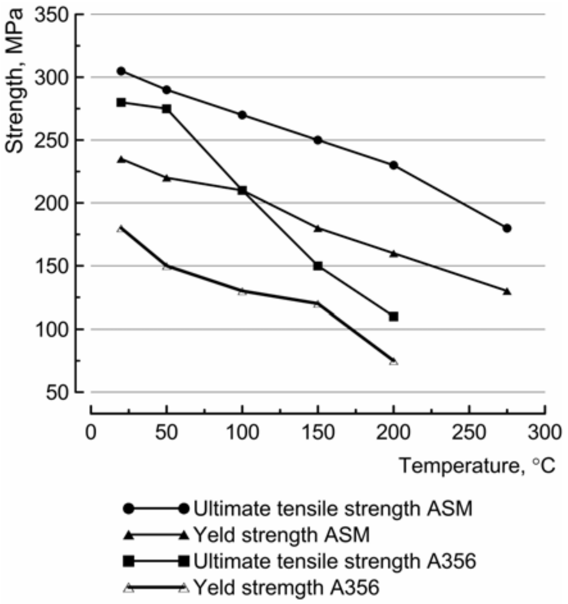


Fig. 8. Tensile strength of Al-7Mg-3Si-0.6Mn alloys additionally alloyed with 0.22 %Sc+0.14%Zr

Tensile tests were performed on BA1 alloy after addition of Sc+Zr and heat treatment of annealing at 300°C during 10 hours. In parallel specimens of A356 alloy cast under same conditions and T5 heat treated also were subjected to tests. Results of tests are displayed on Fig. 8 from which nearly equal values of ultimate tensile strength for ASM and A356 alloys might be seen. Increasing tests temperature results in simultaneous decreasing of ultimate and yield strength for both alloys. At 250°C BA1 alloyed with Sc+Zr displayed 200 MPa ultimate tensile strength and 140 MPa yield strength.

CONCLUSION

This work has demonstrated the recent results on the structure formation of Al-Mg-Si and Al-Mg-Ge casting alloys and their mechanical properties at elevated temperature. It was confirmed the existence of multi-step nucleation in Al-based alloy. Formation of α-Al matrix on the surface of $Al_3(Sc_{1-}xZr_x)$ phase previously nucleated on oxide particle and nucleation Mg_2Si eutectic lamellas on the surface of Mg_2Si primary crystals formed on the oxides both supports multi-step nucleation hypothesis.

It was established that the hardness of Al-Mg-Si-Mn and Al-Mg-Ge-Mn alloys is strongly influenced by presence of alloying elements. The highest hardness in as cast state has been found in the Al-Mg-Si-Mn alloy after addition of Cu+Zn what can be attributed to formation of hard complex intermetallic phases. Lowest hardness was found in Al-Mg-Ge-Mn alloy and this effect can only be explained by very fine eutectic structure and high plasticity of Al-solid solution. Comparative mechanical tests of BA1 alloy with addition of Sc+Zr displayed higher mechanical properties that tested under the same condition A356 commercial casting alloy.

ACKNOWLEDGMENTS

Authors wish to thank Dipl.-Eng. Michael Hill for his help in metallographic specimen’s preparation and invaluable help in thinning of foils for TEM investigations, Professor Walter Reimers for the discussions during investigation. Ms. V.Boyko wish to acknowledge German Academic Exchange Service (DAAD) for the financial support of this study.

REFERENCE

1. J. Campbell, Castings (third ed.), Butterworth-Heinemann, London (2003).
2. Pirs J., Zalar A. Investigations of the distribution of elements in phases present in G-$AlMg_5Si$ cast alloy with EDX/WDX spectrometers and AES // Microchimica Acta, Vol.101, N 1-6, 1990. - p. 295 – 304
3. Wuth M. C., Koch H., Franke A. J. Production of steering wheel frames with an AlMg5Si2Mn alloy // Casting Plant and Technology International. – 2000, Vol.16, N 1. – p.12 - 24
4. K.Mykhalenkov, V.Boyko, T.Link, N.Korzhova, T.Legkaya Microstructure characterisation of new Al-Mg-Si casting alloy containing Sc+Zr // Proceedings of the 3rd Conference "Special metallurgy: tomorrow, today and in future", Edit. by K.Mykhalenkov, Polytechnica, Kiev, 2008. – p.166-173

5. H.Koch, B.Lenczowski Al-Mg-Si cast aluminium alloy containing scandium // C22C 21/02 (2006.01), C22C 21/08 (2006.01) PCT/DE2004/002425, WO/2005/047554
6. K.Mykhalenkov, N.Korzhova, V.Boyko., T.Link, T.Legkaya Microstructure features of Al-Mg-Si casting alloys after additional alloying // Proceedings of the 3rd Conference „Casting of non-ferrous metals and alloys: science and technology", Zwierzyniec 10-12 June 2010, Poland. edit. by Z. Bonderek. – p.77-82
7. J. Zhang, Z. Fan, Y. Q. Wang, B. L. Zhou Microstructural evolution of the in situ Al-15wt.%Mg_2Si composite with extra Si contents // Scripta Materialia, Volume 42, Issue 11, 31 May 2000, Pages 1101-1106
8. R. Bjorge, C. D. Marioara, S. J. Andersen and R. Holmestad Precipitation in an Al-Mg-Ge Alloy // EMC 2008 14th European Microscopy Congress 1–5 September 2008, Aachen, Germany Volume 2: Materials Science. – p. 395-396
9. K. Matsuda, S. Ikeno, T. Munekata HRTEM study of precipitates in Al-Mg-Si and Al-Mg-Ge alloys // Materials science forum, 2006. - vol. 519-21 (1). – pp. 221-226
10. Barabash O.M., Sulgenko O.V., Legkaya T.N., and Korzhova N.P. Experimental Analysis and Thermodynamic Calculation of the Structural Regularities in the Fusion Diagram of the System of Alloys Al-Mg-Si // Journal of Phase Equilibria. – 2001, Vol. 22, No. 1. – p.5-11
11. Z. Fan, Y. Wang, Z. F. Zhang, M. Xia, H. T. Li , J. Xu, L. Granasy and G. M. Scamans Shear enhanced heterogeneous nucleation in some Mg- and Al-alloys // International Journal of Cast Metals Research. – 2009, Vol 22, N 1-4. – p. 1-5
12. F. Islam, A.K. Thykadavil, M. Medraj A computational thermodynamic model of the Mg–Al–Ge system // Journal of Alloys and Compounds. - 425 (2006). – p. 129–139