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EFFECT OF CERIUM ADDITIONS ON THE AlSi17 CASTING ALLOY

DODATEK CERIJA LIVNI ZLITINI AlSi17

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The influence of the primary silicon phase and of eutectic silicon on the solidification process of hypereutectic Al-Si alloys with the addition of cerium is presented. The solidification was analyzed by a simple thermal analysis and a simultaneous thermal analysis, and the microstructures were examined with conventional light microscopy and scanning electron microscopy. The simultaneous refinement of both the primary and the eutectic silicon particles was achieved with cerium additions. The results showed that the addition of cerium had a very positive influence on the alloy's tensile strength.

Keywords: hypereutectic Al-Si alloys, cerium, silicon refinement, modification

Članek opisuje vpliv dodatka cerija na primarno fazo silicija in na evtektski silicij pri strjevanju nadevtektskih Al-Si-zlitinah. Proces strjevanja je bil analiziran z enostavno in s simultano termično analizo. S konvencionalnim svetlobnim mikroskopom ter z elektronskim mikroskopom je bila opravljena mikrostrukturna analiza. Z dodatkom cerija je bilo doseženo udrobnjevanje tako primarno izločene faze silicija kot tudi evtektskega silicija. Preiskave so pokazale, da ima dodatek cerija pozitiven učinek na natezno trdnost zlitin.

Ključne besede: nadevtektske Al-Si zlitine, cerij, udrobnjevanje silicija, modifikacija

1 INTRODUCTION

The application of aluminium alloys for automotive parts, such as pistons, cylinder liners, engine blocks and other parts is important because of the alloys' wear resistance, heat resistance and low thermal expansion.[1,2] The dominant group of Al-Si foundry alloys contains the mass fraction of Si between 5 and 25 %, and additions of Mg, Ni and Cu. Silicon, as the major alloying addition, represents one of the most effective ways to obtain high-quality aluminium casting alloys, mainly because of their high fluidity due to the relatively large volume of the Al-Si eutectic.[3, 4] Al-Si alloys with more than 12 % Si have a hypereutectic microstructure, usually consisting of a primary silicon phase in a eutectic matrix. These alloys are used for engine blocks or cylinder liners, and are the ideal solution for the substitution of cast-iron cylinder liners in the manufacturing of a monolithic engine block.[5, 3]

The primary silicon phase has a harmful effect on the extrudability, machinability, strength, and ductility of the alloy, since coarse silicon phases lead to premature crack initiation and fracture when in tension.[4] With the aim to avoid these problems, the structural modifications are achieved with the addition of elements that refine the silicon phases to a better shape.[1]

The use of silicon modifiers and high cooling rates refines the primary silicon particles.[6] Sodium and strontium are both effective modifiers of the Al-Si eutectic, but it is difficult to control and maintain the modification effect of sodium because of the volatilization and oxidation losses, especially when longer holding times and higher temperatures are required. Strontium does not cause such problems; however, it is reported that it may cause micro- and macroporosity in Al-Si alloy castings.[7] The refinement of primary silicon grains is usually achieved with the addition of phosphorus to the melt. The diagram in **Figure 1** shows the influence of phosphorus additions on the size of the primary silicon grains[8]. It is reported[4,7–12] that rare-earth elements are capable of modifying the Al-Si eutectic too, and it has also been proved that rare-earth elements

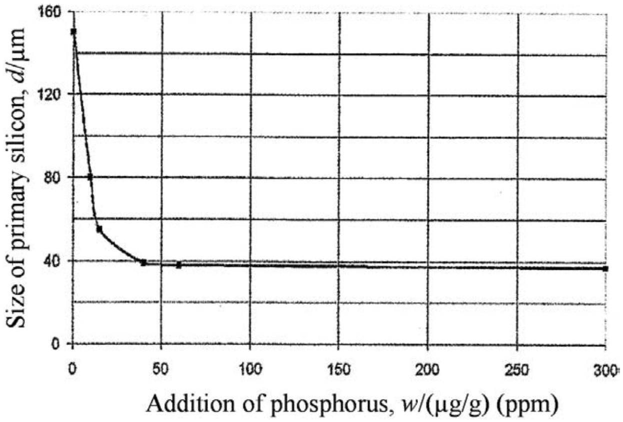

Figure 1: Influence of phosphorus additions on the refinement of primary silicon particles[7]
Slika 1: Vpliv dodatka fosforja na udrobnitev primarnega silicija[7]

represent one way to achieve longer effects for refining agents.[7] It is, for example, mentioned in reference[13] that cerium did not refine the primary silicon grains, but it had a moderate effect on modifying the silicon eutectic. A small cerium addition could provide ternary high-temperature stable τ_1 and τ_2 phases in equilibrium with the Al-Si-rich melt. These phases might act as nucleation sites for (aluminium) or (silicon) particles in both hypo- and hypereutectic Al-Si alloys.[14] Kowata et al.[15] reported that the primary Si in hypereutectic Al-20 % Si alloys was refined with rare-earth metals.

The goal of the present investigation was to check the possibility of whether cerium acted as a refining agent for the primary silicon phase and the silicon eutectic in the pure AlSi17 alloy and in the commercial AlSi17CuMg alloy. The influence of various cerium additions on the tensile strength was also examined.

2 EXPERIMENTAL

Pure Al-Si alloys with the mass fraction of Si 17 % and the commercial AlSi17CuMg alloy and various additions of cerium were used for the experiments. The alloys were melted in an electric resistance furnace in a 3-kg crucible and cerium was added as a 99.9 % pure metal. The melt with a temperature of 750 °C was poured into the measuring cast-iron cell for the thermal analysis. The cooling curve was recorded with a K-type thermocouple at a cooling rate of approximately 20 K/s. With the Thermo-Calc program we recorded all the thermodynamically possible equilibrium phases existing under the defined conditions. The equilibrium binary phase diagram was determined and the composition of the microstructure could be predicted. The samples for light microscopy were prepared with a standard metallographic procedure and examined with an Olympus BX61 light microscope equipped with a DP 70 video camera. The simultaneous thermal analysis (STA) of specimens of the starting materials was performed with the STA 449 Netzsch apparatus. Two equal corundum cups were placed on the platinum sensor. One contained the examined material, the other one, which was empty, represented the reference material. The measurements were carried out in a protective atmosphere of 99.999 % pure argon. The specimens were heated up to 720 °C at a heating rate of 10 K/min and cooled with the same cooling rate to room temperature.

3 RESULTS AND DISCUSSION

To act as a nucleus, the compound must precipitate prior to the primary silicon phase. A thermodynamic simulation of the AlSi17 alloy with 80 µg/g (ppm) phosphorus was made with the Thermo-Calc program, and **Figure 2 a** shows that the AlP compound precipitates before the primary silicon phase.

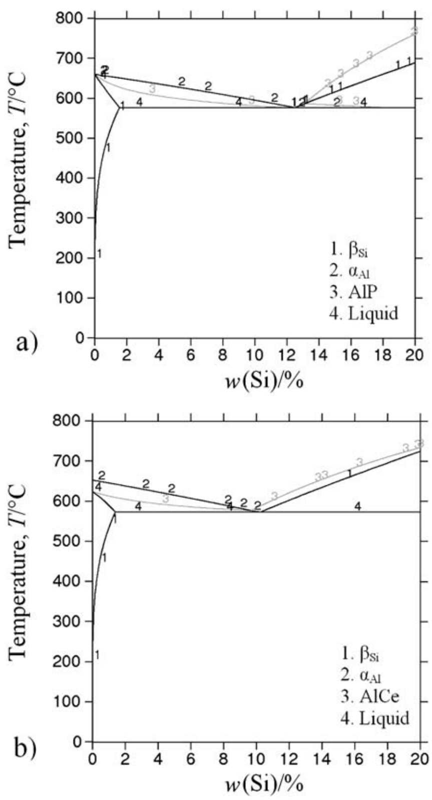

Figure 2: Isopleth diagram of AlSi17 alloy with 80 µg/g (ppm) P (a), and the mass fraction of Ce w(Ce) = 4.5 % (b)

Slika 2: Izopletni fazni diagram zlitine AlSi17 z 80 µg/g (ppm) P (a) in masni delež Ce w(Ce) = 4,5 % (b)

The evidence that cerium also forms nuclei, a simulation with the Thermo-Calc program, was carried out for various additions of cerium. **Figure 2 b** presents the isopleths of the phase diagram for the AlSi17 alloy with 4.5 % Ce. It is evident that the AlCe compound precipitated before the primary silicon. The several proposed mechanisms of refinement for primary silicon grains by the addition of phosphorus can be summarized as follows. The widely accepted and popular theory is based on the nucleation of silicon grains on the AlP compound when phosphorus is added to the alloy. It has been proposed that the AlP compound with the melting point above 982 °C and a cubic structure similar to that of silicon, acted as a nucleation agent and with heterogeneous nucleation produced the refinement of the primary grains [4].

The modification effect of the cerium addition on the solidification of the AlSi17 alloy is shown on the cooling curve in **Figure 3**. The addition of 0.5 % Ce affected the primary silicon size distribution, and this could be seen on the cooling curve without undercooling. The solidification time was shorter than with the pure AlSi17 alloy. The diagram demonstrates that the alloy with 4.5 % Ce had a lower liquidus temperature, below 600 °C. At the same time, the solidification time was longer than for the pure alloy. The idea that added cerium formed nuclei for the primary silicon precipitation was refuted,

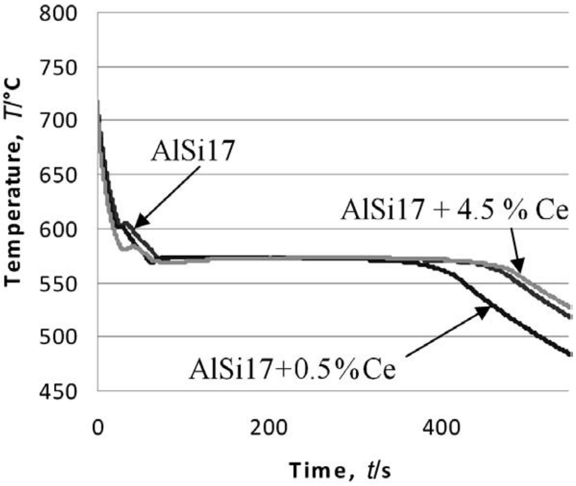

Figure 3: Effect of cerium addition on the AlSi17 alloy
Slika 3: Učinek dodatka cerija na zlitino AlSi17

since the liquidus temperature was lower than with the pure alloy.

Figure 4 shows the microstructures of the unmodified (**a**) and modified AlSi17 alloy with 1 % Ce (**b**) in the light microscope. It demonstrates that this addition modified the size of the primary silicon grains, from coarse shapes to fine polyhedral shapes. Also, the microstructure of the eutectic was finer.

The microstructure of the AlSi17 alloy with 4.5 % Ce is presented in **Figure 5**. It demonstrates that the higher

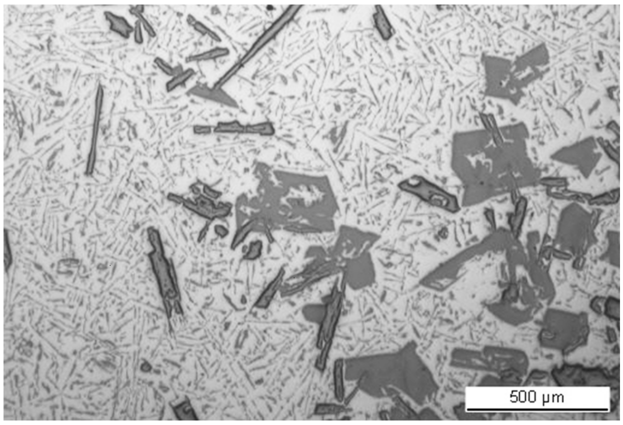

Figure 5: AlSi17 alloy with *w* = 4.5 % Ce
Slika 5: Zlitina AlSi17 z *w* = 4,5 % Ce

cerium content does not cause the refinement of the primary silicon grains. A phase with a highly polyhedral shape that contained cerium was found in the microstructure.

STA was performed with specimens from the thermal analysis. **Figure 6** indicated that the liquidus temperature of the alloy decreased with an increasing cerium content. The greatest reduction of the liquidus temperature was with the alloy containing 1 % Ce, and the drop was from 686.6 °C (pure AlSi17 alloy) to 591.9 °C.

With the aim to prove that pure cerium possibly forms nuclei, the sample containing 1 % cerium was

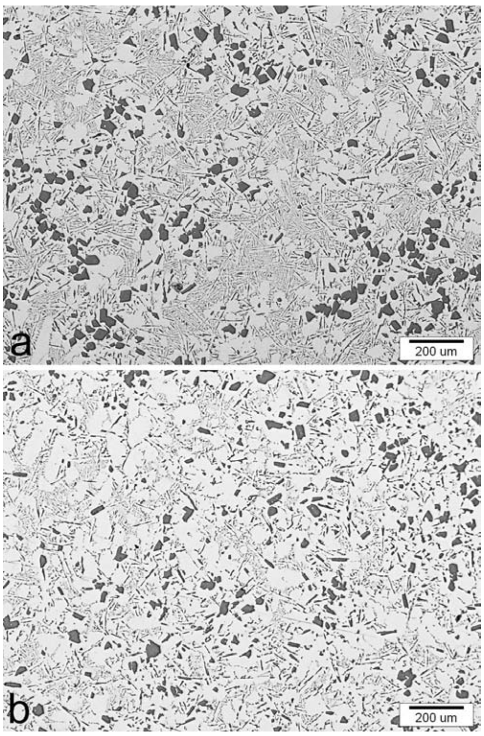

Figure 4: Microstructures of the AlSi17 alloy (a) and the alloy with *w* = 1 % addition of cerium
Slika 4: Mikrostruktura zlitine AlSi17 (a) in zlitine z dodatkom *w* = 1 % cerija

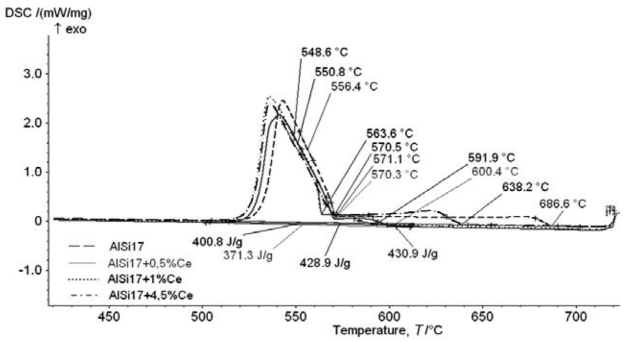

Figure 6: DSC-curves for the AlSi17 alloy with various additions of cerium
Slika 6: DSC-krivulje zlitine AlSi17 z različnimi dodatki cerija

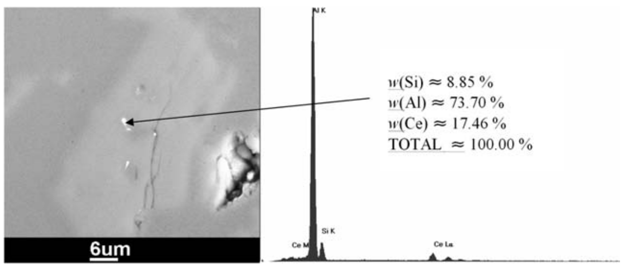

Figure 7: Scanning electron micrograph of the AlSi17 with *w* = 1 % Ce
Slika 7: Posnetek z vrstičnim elektronskim mikroskopom zlitine AlSi17 z *w* = 1 % Ce

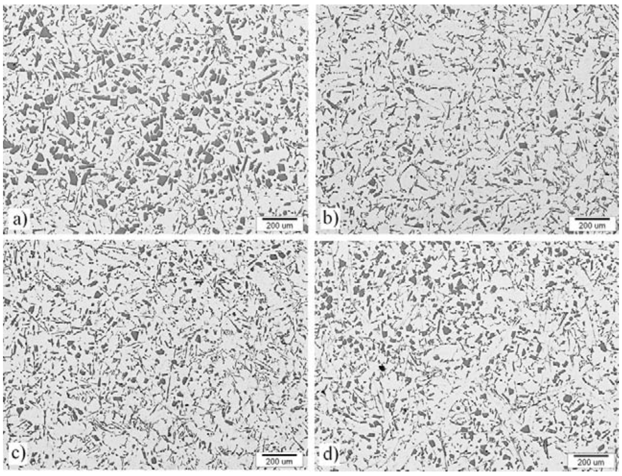

Figure 8: Influence of cerium additions on the microstructure of the AlSi17CuMg alloy; a) pure alloy, b) with mass fractions $w = 0.5$ % Ce, c) with $w = 1$ % Ce, d) with $w = 1.5$ % Ce

Slika 8: Vpliv dodatka cerija na mikrostrukturo zlitine AlSi17CuMg, a) brez dodatka, b) z masnimi deleži $w = 0,5$ % Ce, c) z $w = 1$ % Ce, d) z $w = 1,5$ % Ce

examined with a scanning electron microscope. **Figure 7** shows a micrograph of the examined alloy. Cerium did not form any nuclei for the precipitation of the primary silicon phase and precipitated on the surface of the primary silicon phase itself.

The examination of various cerium additions to the commercial AlSi17CuMg alloy with the mass fractions 1.6 % Cu, and 0.3 % Mg was performed too. **Figures 8 a to 8 d** show the microstructures of the base AlSi17CuMg alloy (a), of alloys with 0.5 mass % Ce (b), with 1 mass % Ce (c) and with 1.5 % Ce. The addition of 1 % Ce had the greatest effect with regards to refining the primary silicon phase and also of the Al-Si eutectic.

The influence of cerium additions on the mechanical properties of the AlSi17CuMg alloy was determined with tensile tests. The results of the tensile strength tests are presented in **Table 1**. It was found that the cerium additions had a positive influence on the tensile strength.

Table 1: Tensile strengths of the examined test samples
Tabela 1: Natezne trdnosti preiskovanih vzorcev

Alloy	Pure alloy	with w = 0.5 % Ce	with w = 1 % Ce	with w = 1.5 % Ce
AlSi17CuMg	170 MPa	192 MPa	195 MPa	186 MPa

4 CONCLUSIONS

The refinement of the primary silicon and of the eutectic silicon morphology was achieved with additions of cerium (up to 1 % Ce) to hypereutectic Al-Si alloys. The best results for the microstructural and strength properties were obtained with the addition of 1 % Ce. With an increase in the cerium additions, the precipitation temperature of the primary silicon phase decreased. The addition of 1 % Ce produced the greatest reduction in the liquidus temperature, from 686.6 °C to 591.9 °C.

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