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Vpliv dodatka Zr na lastnosti Al zlitin

Influence of Zr addition on Al alloys properties

Povzetek

V moderni industrijski praksi se zgodi, da standardne aluminijeve livarske zlitine, tudi visoko kakovostne, ne izpolnjujejo strogih zahtev za aplikacije na različnih tehnoloških področjih. Eden od najbolj zanimivih sistemov aluminijevih zlitin je Al-Zn-Mg-Cu, ki je osnovni sistem za razvoj najboljših zlitin za kovanje tipa AA 7075 z visokimi mehanskimi lastnostmi. Zlitine z dodatkom cirkonija imajo velik potencial za razvoj aplikacij pri povišanih temperaturah. V procesu optimizacije mehanskih lastnosti aluminijevih zlitin se dodaja cirkonij v koncentracijah 0,1 - 0,25 mas. % in povzroči nastanek majhnih izločkov Al3Zr. V prispevku bomo govorili o preiskavah zlitin iz sistemov Al-X-Zr, z uporabo termodinamskih izračunov ravnotežij (Thermo-Calc), različnih termičnih analiz in opredelitvijo nastale mikrostrukture in ustreznih lastnosti z optično in vrstično elektronsko mikroskopijo.

Ključne besede: Al zlitine, dodatek Zr, termodinamika, termična analiza

Abstract

In modern industrial practice standard casting alloys, including high-quality materials, do not satisfy the rigorous requirements for applications in different areas of technology. One of the most attractive systems for new casting alloy developers is the Al–Zn–Mg–Cu, which is the basic system for development of the strongest wrought alloys of the AA7075 type. Alloys with the zirconium addition have significant potential for the development of applications at elevated temperatures. In the process of optimizing the mechanical properties of aluminium alloys, the addition of the 0.1 – 0.25 % (mass fraction in this article) of Zr was suggested in order to enhance the formation of small precipitates of Al3Zr. In this article, about the alloys from Al-X-Zr systems, will be discussed using thermodynamic equilibrium calculations (Thermo-Calc), various thermal analysis, optical and scanning electron microscopy in order to identify the generated microstructures and corresponding properties.

Key words: Al alloys, Zr addition, thermodynamics, thermal analysis

1 Uvod

Eden od najbolj zanimivih sistemov za aluminijeve zlitine je Al-Zn-Mg-Cu, ki je osnovni sistem za razvoj najboljših zlitin za kovanje tipa AA7075. Povprečna natezna

1 introduction

One of the attractive systems for new casting alloy developers is the Al–Zn–Mg–Cu system, which is the basic system for development of the strongest wrought alloys

trdnost za to zlitino v T6 stanju je do 570 MPa. Zlitine iz sistema Al-Fe-Ti imajo velik potencial za razvoj za aplikacije pri povišanih temperaturah. Dodatni legirni elementi, kot so krom, mangan in cirkonij se dodajajo za nadzor kristalnih zrn in podzrn in tako vplivajo na izboljšanje lastnosti. V procesu optimizacije mehanskih lastnosti aluminijevih zlitin je mogoče dodajati cirkonij v koncentracijah 0,1 - 0,25 mas. % in povzroči nastanek majhnih izločkov Al3Zr [2]. Dodatek Si in Fe zmanjša topnost Mn ter pospeši hitrost izločanje sekundarnih Mn-faz, kot je Al6(Fe,Mn), kakor tudi poveča tvorbo Al3Zr izločkov [1]. V skladu z literaturo [3], sta v sistemu Al-Fe-Mn-Si v ravnotežju dve glavni fazi: αAl in βSi ter: Al6(Fe,Mn) in α-AlMnFeSi. V Al-kotu sistema Al-Mn-Zr literatura ne poroča o ternarnih spojinah [4].

Med homogenizacijo se pojavijo spremembe v razvoju mikrostrukture zaradi večje hitrosti difuzije. Znano je, da ima Mn nizko difuzivnost v Al [5]. Eksperimentalne spremembe opažene pri Du [5] kažejo, da ima potek odvisnosti temperatura/čas, poleg začetne temperature ter lite strukture, prav tako velik vpliv na naravo izločkov in sestavo delcev.

Preiskovane so bile zlitine iz sistemov Al-X-Zr, z uporabo termodinamskih izračunov ravnotežij (Thermo-Calc), različnih termičnih analiz in opredelitvijo nastale mikrostrukture ter ustreznih lastnosti z optično in vrstično elektronsko mikroskopijo.

2 Eksperimentalno delo

Termodinamični izračun je bil narejen s Thermo-Calc programsko opremo z bazami podatkov TCAl1 in SSOL5. Z uporabo termodinamičnih izračunov so bili na podlagi kemične sestave narejeni izopletni fazni diagrami zlitin A1 in A2 (Tabela 1).

of the AA7075 type. The average value of ultimate tensile strength for this alloy in the T6 state is 570 MPa. Al-Fe-Ti-based alloys are considered to have a considerable potential for the development of materials for high-temperature applications. Other alloying elements such as chromium, manganese, and zirconium are added for the control of grain and subgrain structures, which also contribute to the strengthening. In the process of optimizing the mechanical properties of Al alloys, the addition of element Zr (0.1 – 0.15 %) was suggested in order to enhance the formation of small dispersions Al3Zr [2]. The addition of Si and Fe decrease the solubility of Mn, accelerate the precipitation rate of secondary Mn-bearing phases, such as Al6(Fe,Mn), as well as increase the formation of Al3Zr particles [1]. According to literature [3], two main phases beside (Al) and (Si) are in equilibrium regarding the Al-rich corner of the Al-Fe-Mn-Si system: Al6(Fe,Mn) and α-AlMnFeSi. No ternary compounds have been reported in Al-rich corner of the Al-Mn-Zr system [4].

During the homogenization changes in the evolution of microstructure due to higher rates of diffusion occur. Mn has been known to have a low diffusivity in Al [5]. Experimental changes observed by Du [5] suggest that, besides the starting temperature and the as-cast structure, the temperature/time history of the alloy also has an effect on the nature of the dispersoids and constituent of the particles.

Alloys from Al-X-Zr system were investigated using thermodynamic equilibrium calculations (Thermo-Calc), various thermal analysis, and optical and scanning electron microscopy, in order to identify the generated microstructures and corresponding properties.

Vzorci so bili staljeni v indukcijski peči v grafitnem loncu, čemur je sledila enostavna termična analiza. Iz podatkov, pridobljenih z meritvijo, so bile izrisane ohlajevalne krivulje in njihovi odvodi ter določene značilne točke strjevanja. Metalografske preiskave vzorcev so bile izvedene z vrstičnim elektronskim mikroskopom JEOL JSM-5610. Mehanske lastnosti so bile določene na napravi Instron 1255.

Tabela 1: Kemijska sestava litih vzorcev preiskovanih zlitin v mas. %

Table 1: Chemical composition of the as-cast samples % (mass fraction)

El.	Al	Mn	Zr	Fe	Si	Zn	Ti
A1	99,18	0,003	0,160	0,517	0,082	0,009	0,02
A2	99,62	0,002	0,001	0,238	0,096	0,002	0,02

3 Rezultati in diskusija

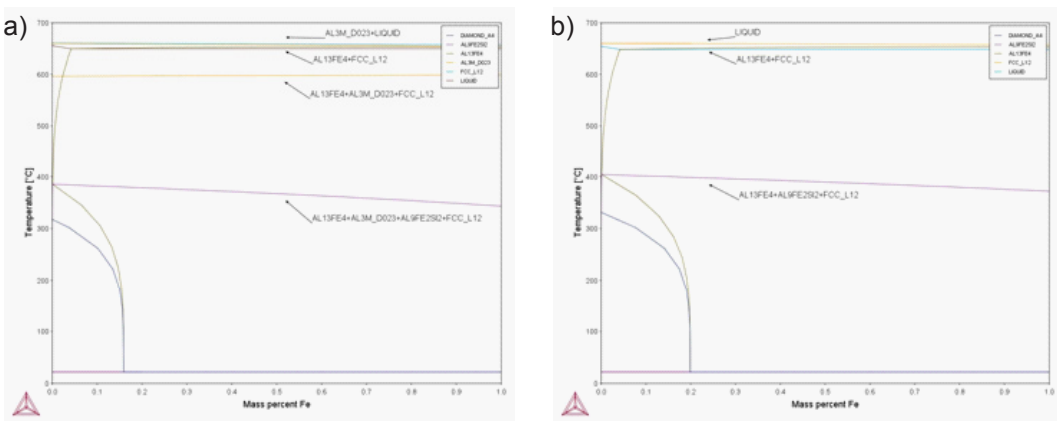
Na podlagi podatkov kemijske analize (Tabela 1) sta bila izrisana ravnotežna izopletna fazna diagrama vzorcev A1 in A2 (slika 1). Iz rezultatov kemičnih analiz

2. Experimental

Thermodynamic calculations were done with Thermo-Calc software (TCW5) using TCAl1 and SSOL5 database. Using the thermodynamic calculations the isopleth phase diagrams of alloys A1 and A2 (Fig. 1) on the basis of chemical composition (Table 1), were made. The samples were melted in the induction furnace in graphite crucible, furthermore simple thermal analysis was performed. From the data obtained in the programme Origin cooling curves and their derivatives were sketched, whereas the characteristic points were determined. Metallographic examinations of samples were performed by scanning electron microscope JEOL JSM-5610. Mechanical properties were analized using the Instron 1255.

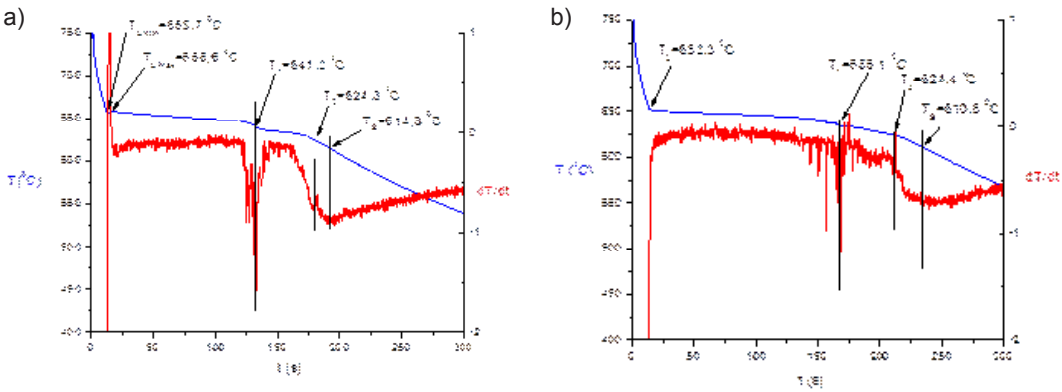
3 Results and Discussion

Based on the data of chemical analysis (Table 1) equilibrium isopleth phase diagrams of the sample A1 and A2 were sketched. From chemical analysis and Thermo-Calc results,



Slika 1: Izopletni fazni diagram za vzorca A1 (a) in A2 (b), Thermo-Calc, TCAl1

Figure 1: Isopleth phase diagram for sample A1 (a) and A2 (b), Thermo-Calc, TCAl1



Slika 2: Ohlajevalni krivulji vzorcev A1 (a) in A2 (b), (TLmin - minimalna likvidus temperatura, TLmax - maksimalna likvidus temperatura, TL – likvidus temperatura, T1 strjevanje faze 1, T2 – Strjevanje faze 2, Ts – solidus temperatura)

Figure 2: Cooling curves of the samples A1 (a) and A2 (b), (TLmin - minimum liquidus temperature, TLmax - maximum liquidus temperature, TL – liquidus temperature, T1 solidification of the phase 1, T2 – solidification of the phase 2, Ts – solidus temperature)

in ravnotežnih termodinamičnih izračunov lahko opišemo teoretični potek strjevanja obeh zlitin (Tabela 2).

Ohlajevalni krivulji vzorcev A1 in A2 sta prikazani na sliki 2.

Tabela 2: Potek strjevanja

Table 2: Course of the solidification

A1		A2	
651,1 °C	L + αAl + Al3Zr	651,8 °C	L + αAl
642,8 °C	L + αAl + Al3Zr + Al13Fe4	638,6 °C	L + αAl + Al13Fe4
638,6 °C	L + αAl + Al13Fe4	626,7 °C	αAl + Al13Fe4
633,3 °C	L + αAl + Al3Zr + Al13Fe4		
627,2 °C	αAl + Al3Zr + Al13Fe4		

T_L in T_S predstavljata likvidus in solidus temperaturo. Pri obeh vzorcih je opaziti sorazmerno dobro ujemanje med eksperimentalno dobljenimi in termodinamično izračunanimi podatki.

theoretical course of solidification of both alloys could be described (Table 2).

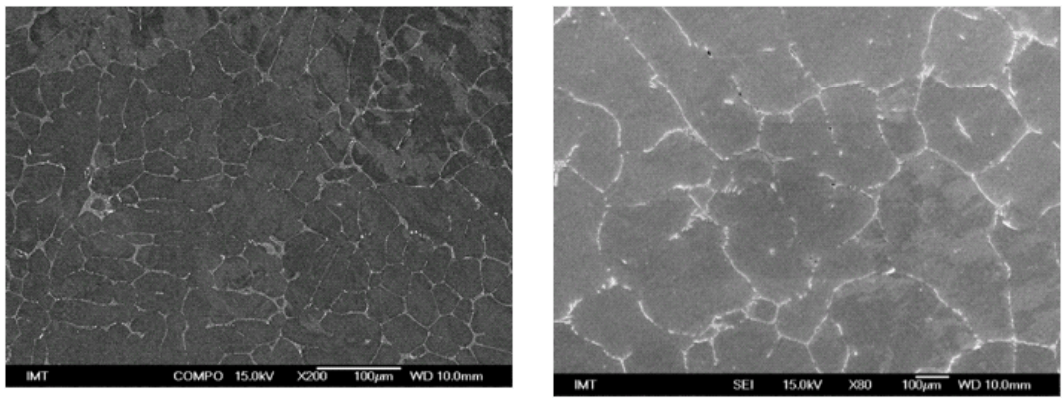
Cooling curves for samples A1 and A2 are shown on Fig. 2.

Tabela 3: Karakteristične temperature strjevanja dobljene s termično analizo.

Table 3: Characteristic temperatures determined with thermal analysis

A1		A2	
T_{Lmin}	655.7	T_L	652.3
T_{Lmax}	658.6		
T_1	641.2	T_1	635.1
T_2	624.3	T_2	624.4
TS	614.8	T_S	610.6

T_L and T_S represent liquidus and solidus temperatures, respectively. In the case of both samples, a relatively good comparison between the experimental and the thermodynamically calculated data was achieved.



a) b)

Slika 3: Mikrostrukturi zlitin A1(a) in A2 (b), SEM

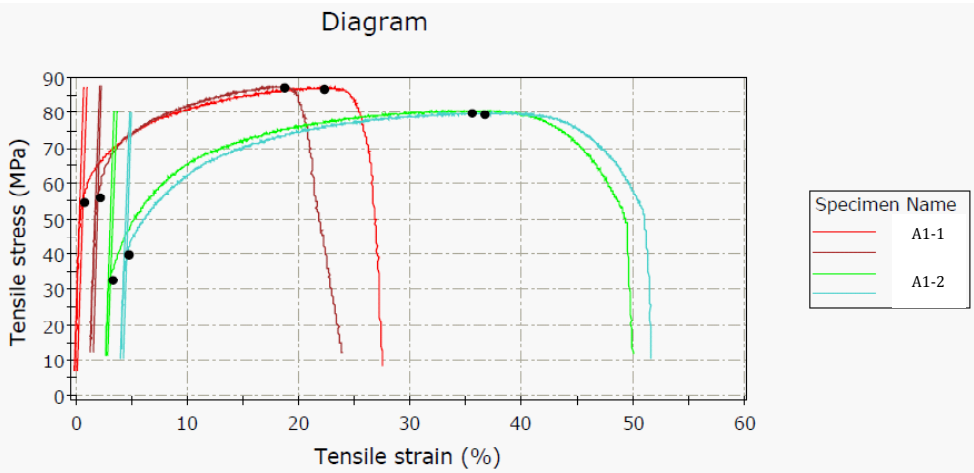
Figure 3: SEM snapshot of A1 (a) and A2 (b) sample

Mikroposnetki obeh zlitin (SEM) so prikazani na sliki 3.

V vzorcih A1 in A2 smo z EDS analizo določili vse faze, ki smo jih pričakovali na osnovi termodinamičnih izračunov. V zlitini A1 so prisotne naslednje faze: α_{Al}, $Al_{13}Fe_4$ in Al_3Zr (tabela 2). Poleg teh je EDS analiza pokazala še fazo titanovega

Results of SEM microscopy are presented on Fig. 3.

The samples A1 and A2 all the phases that were expected on the basis of thermodynamic calculations were found. In the alloy A1 following phases are present: α_{Al}, $Al_{13}Fe_4$ and Al_3Zr (Table 2). In addition, the EDS analysis showed



Slika 4: Mehanske lastnosti zlitin A1 in A2

Figure 4: Mechanical properties of A1 and A2

borida, kot posledica premodificiranja zlitine. V zlitini A2 pa je pri sobni temperaturi pričakovana mikrostruktura sestavljena iz faz: α_{Al} in $Al_{13}Fe4$ (tabela 2). Z EDS smo zaznali tudi fazo, ki vsebuje baker in je z termodinamičnim izračunom nismo določili.

Slika 4 in tabela 4 prikazuje rezultate nateznih preizkusov.

Tabela 4: Mehanske lastnosti A1 in A2

Table 4: Mechanical properties of A1 and A2

Vzorec / Sample	Rm (MPa)	A (%)	RP0,2 (MPa)
A1-1	87	20,4	55
A1-2	88	17,1	56
A2-1	81	41,2	33
A2-2	80	43,1	40

Opaziti je, da ima vzorec A1, ki vsebuje Zr, večjo mejo plastičnosti in natezno trdnost ter ustrezno manjši raztezek.

Na slikah 5 in 6 sta prikazana izopletna fazna diagrama za aluminijevi livarski zlitini AlSi9Cu3 in AlSi10Mg. Ravnotežni termodinamični izračun faznih diagramov je bil izveden s programom Thermo Calc in bazo podatkov TCAl1.

Podobno kot v gnetnih aluminijevih zlitina se pri dodatku cirkonija tvori faza Al_3Zr, ki se strjuje v zadnjem strjevalnem območju. Na osnovi termodinamičnega izračuna lahko sklepamo, da bi dodatek corkonija (0,1 – 0,25 mas.%) povečal mehanske lastnosti in povečal temperaturno stabilnost. Za potrditev sklepanega je potrebno opraviti laboratorijsko in industrijsko preizkušanje.

4 Zaključki

Okarakterizirani in analizirani sta bili dve zlitine: A1 (s Zr) in A2. S pomočjo kemijske sestave in termodinamskih izračunov je bila

the phase on base of titanium boride, as a result of overmodification of the alloy. At the alloy A2 at room temperature, the expected microstructure is composed of: α_{Al} and $Al_{13}Fe_4$ (Table 2). Using EDS analysis, the phase containing the copper was also detected, whereas at the thermodynamic calculations was not found.

Figure 4 and Table 4 show the result of mechanical tests.

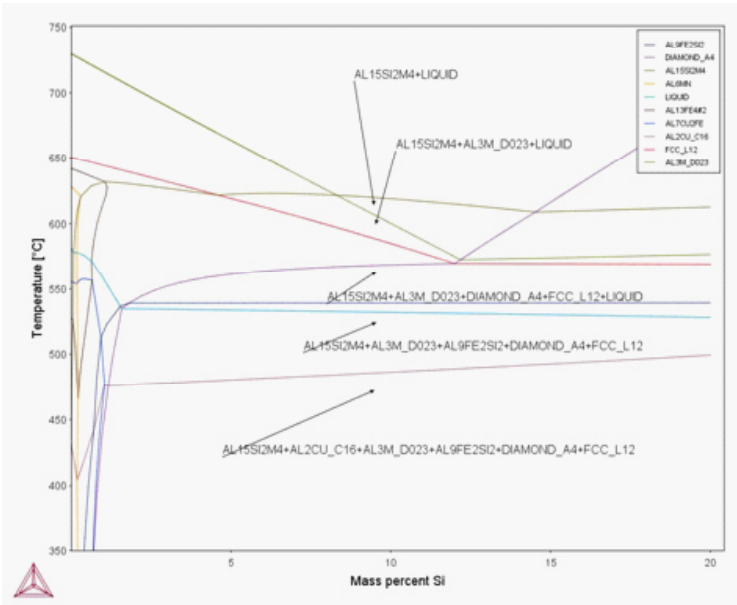
It could be seen that the sample A1 with Zr has higher yield and tensile strength and corresponding smaller elongation.

Figures 5 and 6 show isopleth phase diagrams for aluminium foundry alloys, AlSi9Cu3 and AlSi10Mg. Equilibrium thermodynamic calculation of phase diagrams was carried out with Thermo-Calc programme and database TCAl1.

Similar as in the forming aluminium alloys, the addition of zirconium causes the formation of Al_3Zr phase, which solidifies in the final solidification zone. On the basis of thermodynamic calculations it can be suggested that the addition of zirconium (from 0.1 to 0.25 wt. %) increases mechanical properties and increases temperature stability. To confirm these allegations, further laboratory and industrial testing should be made.

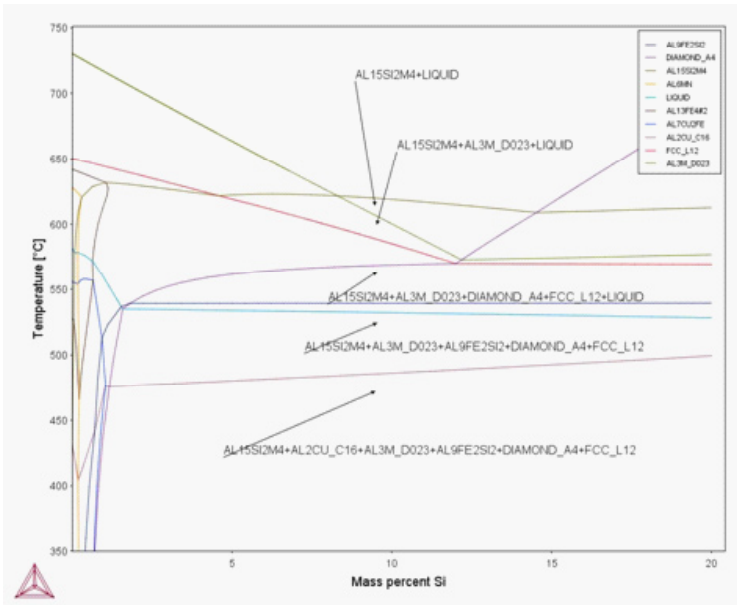
4 Conclusion

Synthesised and characterised were two aluminium alloys A1 (with Zr) and A2. From chemical composition and thermodynamic calculations the path of solidification was predicted. The main phases, that are present in the alloy, are: α_{Al} and $Al_{13}Fe_4$ which is solidified in the form of a eutectic and phase on the base of Zr (Al_3Zr). These microstructural constituents were also analysed by metallographic analysis.



Slika 5: Izračunani izopletni fazni diagram za zlitino AlSi9Cu3 z dodatkom Zr

Figure 5: Calculated isopleth phase diagram for AlSi9Cu3 alloy with Zr



Slika 6: Izračunani izopletni fazni diagram za zlitino AlSi10Mg z dodatkom Zr

Figure 6: Calculated isopleth phase diagram for AlSi10Mg alloy with Zr

opisan potek strjevanja preiskovanih zlitin. Prisotne so bile naslednje faze: α-Al, $Al_{13}Fe_4$, ki se strdi v obliki evtektika, ter faza na osnovi Zr (Al_3Zr). Te mikrostrukturne sestavine so bile analizirane tudi z metalografsko analizo. Preiskave mehanskih lastnosti so pokazale, da je natezna trdnost zlitine A1 višja kot zlitine A2, vendar pa je raztezek zlitine A2 višja od zlitine A1.

Rezultati in podatki iz literature podajajo, da dodatek cirkonija v koncentracijah od 0,1 do 0,25 mas. % izboljša mehanske lastnosti zlitine, kar bi se lahko uspešno uporabilo tudi pri izboljšanju kakovosti aluminijevih livarskih zlitin.

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This work was financially supported by a project of the Slovene human resources development and scholarship fund “Po kreativni poti do znanja”. The authors also wish to thank the graduate students at Faculty of Natural Sciences and Engineering that contributed to the experimental work done in this research.

Investigations of mechanical properties have shown that the tensile strength of the alloy A1 is higher than of the alloy A2, whereas the elongation at the alloy A2 is higher than that in the alloy A1.

The results and the literature data show the addition of Zr of 0.1 to 0.25 % improves the mechanical properties of the alloy, which may successfully be used in aluminium foundry alloys.

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