

Ocena kakovosti udrobnilnih sredstev

Assessing the Quality of Grain Refiners

Povzetek

Primarni cilj udrobnjevanja v aluminijevih zlitinah je zmanjšati velikost strjenih kristalnih zrn, s čimer se odpravi prisotnost velikih stebrastih zrn. Ta proces udrobnjevanja je ključen za izboljšanje mehanskih lastnosti in splošne učinkovitosti zlitine. Da bi dosegli odlične rezultate udrobnjevanja zrn, je bistvenega pomena uporaba visokokakovostnega udrobnilnega sredstva. To vključuje upoštevanje različnih dejavnikov, kot so ustrezno število delcev Al_3Ti in TiB_2 , primerna oblika in velikostna porazdelitev delcev ter optimalno razmerje Ti/B.

Za oceno kakovosti različnih udrobnilnih sredstev je bila izvedena raziskava z uporabo električne upornosti. Poleg tega so bile izvedene analize diferenčne vrstične kalorimetrije in mikrostrukture za potrditev in podporo pridobljenih rezultatov.

Med preiskovanimi udrobnilnimi sredstvi je najnižjo električno upornost izkazalo udrobnilno sredstvo B ($Al-3Ti-1B$). Rezultat je mogoče pripisati več dejavnikom. Prvič, udrobnilno sredstvo B je imelo nizko vsebnost nečistoč, kar kaže na visoko stopnjo čistosti in kakovosti. Nečistoče, kot sta Fe in Si, lahko negativno vplivajo na učinkovitost udrobnjevanja in prispevajo k večji električni upornosti. Poleg tega je udrobnilno sredstvo B pokazalo ustrezno število in velikostno porazdelitev delcev TiB_2 in Al_3Ti . Prisotnost ustrezne količine teh delcev spodbuja učinkovito nukleacijo, ki je bistvena za uspešno udrobnjevanje. Velikostna porazdelitev delcev ima prav tako ključno vlogo pri zagotavljanju njihove enakomerne disperzije po zlitini, kar vodi do doslednega in učinkovitega udrobnjevanja zrn. Poleg tega je imelo udrobnilno sredstvo B optimalno razmerje Ti/B 3,6. Razmerje Ti/B je kritičen parameter, saj vpliva na nastanek in porazdelitev nukleirajočih delcev. Optimalno razmerje zagotavlja prisotnost zadostnega števila nukleirajočih delcev, kar omogoča učinkovito udrobnjevanje zrn.

Nasprotno pa so druga udrobnilna sredstva pokazala večjo električno upornost. To lahko pripišemo različnim dejavnikom, kot sta povečana količina in velikost delcev TiB_2 in Al_3Ti ter prisotnost nečistoč, kot sta Fe in Si. Ti dejavniki lahko ovirajo proces udrobnjevanja in povzročijo večjo velikost zrn ter zmanjšano učinkovitost udrobnilnega sredstva. Poleg tega lahko prisotnost vključkov v zlitini prispeva k večji električni upornosti.

Ključne besede: udrobnilna sredstva Al-Ti-B, kakovost, delci TiB_2 , delci Al_3Ti

Abstract

The main objective of grain refinement in aluminium alloys is to reduce the size of solidified crystal grains, thereby avoiding the presence of large columnar grains. This refining process is critical to improving the mechanical properties and overall performance of the alloy. To achieve excellent grain refining results, a high-quality grain refiner must be used. Several factors must be considered, such as the appropriate number of Al_3Ti and TiB_2 particles, the appropriate shape and size distribution of the particles, and an optimal Ti/B ratio.

To evaluate the quality of different grain refiners, a study using electrical resistivity measurement was conducted to assess the quality of these grain refiners. In addition, analyses using differential scanning calorimetry and microstructure studies were carried out to validate and support the results obtained.

Among the grain refiners tested, grain refiner B (Al-3Ti-1B) exhibited the lowest electrical resistivity. This superior performance can be attributed to several factors. First, grain refiner B had a low content of impurities, indicating a high level of purity and quality. Impurities, such as Fe and Si, can affect the effectiveness of the grain refiner and contribute to higher electrical resistivity. In addition, grain refiner B had an adequate number and size distribution of TiB_2 and Al_3Ti particles. The presence of a sufficient amount of these particles promotes effective nucleation, which is essential for successful grain refinement. The size distribution of the particles also plays a crucial role in ensuring their uniform distribution in the alloy, resulting in a uniform and efficient grain refinement. In addition, grain refiner B exhibited an optimum Ti/B ratio of 3.6. The Ti/B ratio is a critical parameter because it affects the formation and distribution of nucleation particles. An optimum ratio ensures the presence of a sufficient number of nucleating particles, which facilitates effective grain refinement.

In contrast, the other grain refiners exhibited higher electrical resistance. This can be attributed to several factors, such as the larger amount and size of TiB_2 and Al_3Ti particles, and the presence of impurities such as Fe and Si. These factors can hinder the grain refining process and result in larger grains and lower refiner effectiveness. In addition, the presence of inclusions in the alloy can contribute to higher electrical resistivity.

Key words: Al-Ti-B grain-refiners, quality, TiB_2 particles, Al_3Ti particles

1 Uvod

Glavni cilj udrobnjevanja zrn v aluminijevih zlitinah je zmanjšati velikost strjenih kristalnih zrn, kar pomaga preprečiti velika stebrasta zrna, ki se lahko pojavijo, ko hitrost hlajenja ni optimalna. Namen tega postopka je zmanjšati površinske napake med transformacijo materiala, izboljšati mehanske lastnosti in povečati sposobnost ulivanja zlitine [1–3].

Predzlitine Al-Ti-B se običajno uporabljajo za udrobnjevanje zrn aluminijevih zlitin. Vendar rezultati raziskav [4] kažejo, da je za učinkovito udrobnjevanje zrn potrebna prisotnost raztopljenih delcev Ti in TiB_2 z optimalnim povprečnim polmerom in ozko porazdelitvijo polmera. Običajne metode udrobnjevanja zrn so omejeno primerne za proizvodnjo visokokakovostnih

1 Introduction

The main objective of grain refinement in aluminium alloys is to reduce the size of solidified crystal grains, which helps to avoid large columnar grains that can occur when the cooling rate is not optimal. This process aims to minimize surface defects during material transformation, improve mechanical properties, and increase alloy castability [1–3].

Al-Ti-B master alloys are commonly used for grain refinement of aluminium alloys. However, research results [4] show that effective grain refinement requires the presence of dissolved Ti and TiB_2 particles with a reasonable average radius and a narrow radius distribution. Conventional grain refinement methods have limited suitability to produce high-quality aluminium

aluminijevih zlitin zaradi večjega polmera in širše porazdelitve polmera delcev TiB_2 v osnovnih zlitinah [5].

Prisotnost raztopljenega Ti ovira heterogeno nukleacijo α -Al z delci TiB_2 in omejuje rast zrn α -Al zaradi ustavnega podhlajevanja. Ko je koncentracija raztopljenega Ti nizka, je zaviralni učinek na rast α -Al minimalen in vodi le do izboljšanja stebraste zrnate strukture. Ko pa se koncentracija raztopljenega Ti poveča, se izboljša udrobnjevanje zrn in opazimo prehod iz stebraste v enakoosno strukturo zrn. Nad kritično vrednostjo nadaljnje povečevanje koncentracije raztopljenega Ti le malo vpliva na udrobnjevanje zrn [5].

Trenutno je najpogosteje uporabljeno udrobnilno sredstvo Al-5Ti-1B. Vendar pa obstajajo poročila [4], ki kažejo, da se polmer delcev TiB_2 , ki se običajno sintetizirajo s halogenidnimi solmi, postopoma povečuje v teh udrobnilnih sredstvih, kar ima za posledico širšo porazdelitev velikosti delcev in omejeno sposobnost udrobnjevanja.

Na morfologijo delcev Al_3Ti v udrobnilnih sredstvih vplivata razmerje Ti/B v predzlitini in pogoji obdelave, ki določajo mehanizme rasti. Različna udrobnilna sredstva Al-Ti-B vsebujejo različne morfologije delcev Al_3Ti . Na primer, v udrobnilnih sredstvih, kot je Al-5 mas. % Ti-1 mas. % B, se delci Al_3Ti pojavljajo kot veliki kockasti delci v središčih zrn α -Al, medtem ko se manjši delci TiB_2 nahajajo na mejah zrn. Po drugi strani pa delci Al_3Ti prevzamejo kosmičasto obliko v udrobnilnih sredstvih z zmanjšanim razmerjem Ti/B, kot je Al-3 mas. % Ti-1 mas. % B [5–7].

Da bi zagotovili učinkovito nukleacijo α -Al, mora vsebnost titana v končni talini (z dodatkom udrobnilnega sredstva) preseči stehiometrično razmerje za tvorbo delcev TiB_2 . Rahel presežek titana zadošča za udrobnjevanje zrn, višje vsebnosti titana, ki omogočajo obstoj Al_3Ti v talini, pa ne

alloys due to the larger radius and wider radius distribution of TiB_2 particles in master alloys [5].

The presence of dissolved Ti hinders the heterogeneous nucleation of α -Al nuclei by TiB_2 particles and restricts the growth of α -Al grains due to constitutional supercooling. When the concentration of dissolved Ti is low, the inhibitory effect on α -Al growth is minimal and leads only to a refinement of the columnar grain structure. However, as the concentration of dissolved Ti increases, grain refinement improves and a transition from a columnar to an equiaxed grain structure is observed. Beyond a critical value, further increasing the concentration of dissolved Ti has little effect on grain refinement [5].

Currently, the most used grain refinement is the Al-5Ti-1B master alloy. However, there are reports [4] indicating that the radius of TiB_2 particles, which are usually synthesized using halide salts, is gradually increasing, resulting in a wider distribution of particle sizes and limited refining ability.

The morphology of Al_3Ti particles in grain refiners is influenced by the Ti/B ratio in the master alloy and the processing conditions, which determine the growth mechanisms. Different Al-Ti-B grain refiners exhibit different morphologies of Al_3Ti particles. For example, in grain refiners such as Al-5 wt.% Ti-1 wt.% B, the Al_3Ti particles appear as large blocky particles in the centers of the α -Al grains, while smaller TiB_2 particles are located at the grain boundaries. On the other hand, the Al_3Ti particles assume a flaky form in grain refiners with a reduced Ti/B ratio such as Al-3 wt.% Ti-1 wt.% B [5–7].

To ensure effective nucleation of α -Al, the titanium content in the final melt (with the addition of the grain refiner) must exceed the stoichiometry of TiB_2 . A slight excess of

izboljšajo učinkovitosti. Če pa se delovanje udrobnilnega sredstva poslabša zaradi bledenja ali vpliva nečistoč, je mogoče njegovo učinkovitost obnoviti z dodajanjem titana v talino. Masno razmerje Ti/B, ki ustreza stehiometriji TiB_2 , je 2,215 in učinkovitost udrobnjevanja se bistveno izboljša, ko je to razmerje preseženo. Vendar pa se zmogljivost zmanjša pri višji vsebnosti titana [6, 7].

Prisotnost določenih legirnih elementov ali nečistoč, kot so Zr, Cr, Li in visoka vsebnost Si v aluminijevih zlitinah, lahko znatno zmanjša učinkovitost osnovnih zlitin Al-Ti-B za udrobnjevanje zrn [8, 10–13]. Ta pojav je splošno znan kot „zastropitev“ [8]. Študije so pokazale, da lahko celo majhne količine Zr (nekaj sto ppm) v staljenem aluminiju naredijo komercialno dostopna udrobnilna sredstva Al-5Ti-1B neučinkovita, kar povzroči grobo in popolnoma stebrasto strukturo zrn po strjevanju. Zanimivo je, da na osnovni površini TiB_2 ni segregiranja Fe ali Si, čeprav se Fe tvori na prizmatični površini TiB_2 . Zdi se, da niti Fe niti Si nimata vloge nečistoč pri zastropitvi delcev TiB_2 z Zr v staljenem aluminiju ob prisotnosti Zr. Študije so pokazale, da lahko kemična segregacija izbranih zlitinskih elementov/nečistoč na vmesni površini tekoče-substrat učinkovito vpliva na heterogeno nukleacijo in spodbuja ali ovira proces [9].

Čistost aluminija je ključni dejavnik, ki vpliva na električno upornost. Večja vsebnost nečistoč povzroči višjo električno upornost. Silicij ima razmeroma majhen vpliv na električno upornost aluminija, če je njegova koncentracija do 0,006 mas. % in je razmerje Fe/Si med 0,8 in 3,8. Vendar pa povečanje vsebnosti silicija na 0,15–0,16 mas.% bistveno poveča ta učinek. Drugi elementi, kot so Cr, Sn, Mn in Ti, imajo močnejši učinek na povečanje električne upornosti aluminija. Za aluminij, ki se uporablja v elektroindustriji, skupna

titanium is sufficient for grain refinement, and higher titanium contents that allow Al_3Ti to survive in the melt do not improve performance. However, if the performance of a grain refiner degrades due to fading or the influence of impurities, it is possible to restore its effectiveness by adding titanium to the melt. The Ti/B weight ratio corresponding to the stoichiometry of TiB_2 is 2.215, and refining performance improves significantly when this ratio is exceeded. However, the performance decreases at higher titanium contents [6, 7].

The presence of certain alloying or impurity elements, such as Zr, Cr, Li, and high Si content, in aluminium alloys, can significantly reduce the effectiveness of Al-Ti-B master alloys in grain refinement [8, 10–13]. This phenomenon is commonly known as “poisoning” [8]. Studies have shown that even small amounts of Zr (a few hundred ppm) in molten aluminium can render commercially available Al-5Ti-1B grain refiners ineffective, resulting in a coarse and completely columnar grain structure upon solidification. Interestingly, there is no segregation of Fe or Si at the basal surface of TiB_2 , although Fe segregates at the prismatic surface of TiB_2 . Neither Fe nor Si appears to play a role as impurity elements in the Zr poisoning of TiB_2 particles in Zr-containing molten aluminium. Studies have shown that chemical segregation of selected alloy/impurity elements at the liquid-substrate interface can effectively influence heterogeneous nucleation and either promote or hinder the process [9].

The purity of aluminium is a critical factor affecting electrical resistivity. Higher impurity content results in higher electrical resistivity. Silicon has a relatively small effect on the electrical resistivity of aluminium when its concentration is up to 0.006 wt.% and the Fe/Si ratio is between 0.8 and 3.8. However, increasing the silicon content to

koncentracija teh štirih elementov ne sme presegati 0,015 mas. %, ker vplivajo na električne lastnosti. Če je vsebnost silicija med 0,12 mas. % in 0,16 mas. %, skupna koncentracija teh štirih elementov ne sme preseči 0,01 mas. %, da bi izpolnili zahteve industrije. Kljub učinkovitemu udrobnjevanju, ki ga zagotavljajo predzlitine Al-Ti-B, presežek titana, vnesen v aluminijasto matriko po udrobnjevanju, neizogibno zmanjša električno prevodnost [14–16].

Cilj te študije je bil določiti najučinkovitejše udrobnilno sredstvo Al-Ti-B za aluminijeve zlitine. Cilj je bil oceniti kakovost udrobnilnih sredstev štirih različnih proizvajalcev, in sicer Al-5Ti-1B in Al-3Ti-1B.

2 Materiali in metode

Tabela 1 prikazuje sestavo proučevanih udrobnilnih sredstev, analiziranih z induktivno sklopljeno plazmo optičnega emisijskega spektrometra (ICP-OES). Ta udrobnilna sredstva so bila izbrana zaradi njihove pogoste uporabe pri udrobnjevanju livnih in preoblikovalnih aluminijevih zlitin.

Za izvedbo meritev električne upornosti smo na desetih različnih lokacijah izmerili polmer žic udrobnilnih sredstev in izračunali povprečni polmer. Poleg tega je bila izmerjena dolžina žic udrobnilnih sredstev in vključena v izračune za merjenje

0.15–0.16 wt.% significantly enhances this effect. Other elements such as Cr, Sn, Mn and Ti have a stronger effect on increasing the electrical resistance of aluminium. For aluminium used in the electrical industry, the total concentration of these four elements should not exceed 0.015 wt.% because they affect the electrical properties. When the silicon content is between 0.12 wt.% and 0.16 wt.%, the total concentration of these four elements should not exceed 0.01 wt.% to meet industry requirements. Despite the effective grain refinement provided by Al-Ti-B master alloys, the excess titanium introduced into the aluminium matrix after refinement inevitably reduces the electrical conductivity [14–16].

The objective of this study was to determine the most effective Al-Ti-B grain refiner for aluminium alloys. The objective was to evaluate the quality of grain refiners from four different manufacturers, namely Al-5Ti-1B and Al-3Ti-1B.

2 Materials and Methods

Table 1 shows the composition of the grain refiners studied, as determined by an inductively coupled plasma optical emission spectrometer (ICP-OES). These grain refiners were selected because of their frequent use in grain refining of cast and wrought aluminium alloys.

Tabela 1. Kemijska sestava in oznake preiskovanih udrobnilnih sredstev.

Table 1. Chemical composition and designations of investigated grain refiners.

Oznaka / Designation	Predzlitina / Master Alloy	Kemijski element, mas. % / Chemical element, wt.%						Razmerje Ti/B / Ti/B ratio
		Si	Cr	Fe	B	Ti	Al	
A	Al-3Ti-1B	0,13	<0,01	0,11	0,82	3,5	ostalo / rest	4,27
B	Al-3Ti-1B	0,13	<0,01	0,11	0,86	3,1	ostalo / rest	3,60
C	Al-5Ti-1B	0,16	<0,01	0,11	0,89	4,9	ostalo / rest	5,51
D	Al-5Ti-1B	0,19	<0,01	0,12	0,92	4,8	ostalo / rest	5,22

električne upornosti. Tehnika enosmernega toka s štirimi sondami, ki je podrobno opisana v [17], je bila uporabljena za merjenje električnega upora proučevanih žic. Meritve so potekale deset minut pri sobni temperaturi. Električno upornost (ρ) smo izračunali z uporabo enačbe $R = \rho \cdot L/A$, kjer je L dolžina in A prečni prerez žice udrobnilnih sredstev. Rezultati so podani kot električna upornost pri sobni temperaturi za dano žico udrobnilnega sredstva v $\Omega \cdot m$.

Dodatne analize so bile izvedene na vseh udrobnilnih sredstvih, da bi ocenili kredibilnost dobljenih rezultatov električne upornosti. Preizkusi diferenčne vrstične kalorimetrije (DSC) so bili izvedeni z uporabo naprave DSC 404 F1 Pegasus v dinamični atmosferi argona. Udrobnilna sredstva smo segreli na 720 °C s hitrostjo 10 K/min, vzdrževali pri tej temperaturi 10 minut in nato z enako hitrostjo ohladili na sobno temperaturo. Krivulje DSC so bile ovrednotene za opredelitev značilnih temperatur strjevanja ter strjevalnih entalpij.

Mikrostrukturalna analiza je bila izvedena na udrobnilnih sredstvih z uporabo vrstičnega elektronskega mikroskopa JEOL JSM -6500F (SEM), opremljenega z energijsko disperzijsko spektroskopijo (EDS) in difrakcijo povratnega sipanja elektronov (EBSD). Velikost, obliko in porazdelitev delcev Al_3Ti in TiB_2 smo preučevali s sistemom INCA ENERGY 400 EDS in kamero HKL Nordlys II s programsko opremo Channel 5.

Poleg tega smo uspešnost in učinkovitost preiskovanih udrobnilnih sredstev ocenili na aluminijevi zlitini Al99.7. Zlitino smo predhodno segreli na 700 °C, po procesu taljenja pa smo talini dodali predzlitino Al-Ti-B v deležu, ki ga priporoča proizvajalec. Talino smo zadržali 2 minuti in jo nato ulili pri temperaturnem območju 680–690 °C v Croning celico s hitrostjo hlajenja približno 7 K/min. Za določitev velikosti

To perform the electrical resistivity measurements, the radius of the grain refiner wires was measured at ten different locations and the average radius was determined. In addition, the length of the grain refiner wires was measured and included in the calculations for measuring electrical resistivity. The four-probe direct current technique described in detail in [17] was used to measure the electrical resistance of the wires studied. Measurements were made for a period of ten minutes at room temperature. The electrical resistivity (ρ) was calculated using the equation $R = \rho \cdot L/A$, where L is the length and A is the cross-section of the grain refinement wire. The results are given as the electrical resistivity at room temperature for a given grain refining wire in $\Omega \cdot m$.

Additional analyses were performed on all grain refiners to assess the validity of the electrical resistivity results obtained. Differential scanning calorimetry (DSC) tests were performed using a DSC 404 F1 Pegasus instrument in a dynamic argon atmosphere. Grain refiners were heated to 720 °C at a rate of 10 K/min, held at this temperature for 10 min, and then cooled to room temperature at the same rate. The DSC curves were evaluated to determine the characteristic solidification temperatures.

Microstructural analysis was performed on the grain refiners using a JEOL JSM -6500F scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD). The size, shape, and distribution of Al_3Ti and TiB_2 particles were studied using the INCA ENERGY 400 EDS system and HKL Nordlys II camera with Channel 5 software.

In addition, the effectiveness and efficiency of the investigated grain refiners

zrn so bili odvzeti vzorci iz srednjega dela ulitih vzorcev. Ti vzorci so bili pripravljene s standardnimi metalografskimi tehnikami in elektropolirani z Barkerjevim reagentom. Meje zrn so bile vizualizirane pod polarizirano svetlobo z uporabo mikroskopa Olympus BX61 s kamero DP70 pri 50-kratni povečavi. Velikost zrn je bila izmerjena z metodo srednje presečne razdalje po ASTM E112.

3 Rezultati in diskusija

Vrednosti električnega upora preučevanih udrobnilnih sredstev so prikazane v tabeli 2. Udrobnilno sredstvo B ima najnižjo električno upornost, kar kaže na najmanjšo vsebnost nečistoč, ki prispevajo k nižji upornosti [10,16]. Predvidevamo lahko, da to udrobnilno sredstvo vsebuje enakomerno porazdeljene kosmičaste delce Al_3Ti , skladne z analiziranim razmerjem Ti/B, kar omogoča optimalno udrobnjevanje. Za udrobnilni sredstvi C in D (Al-5 mas. % Ti-1 mas. % B) se električna upornost povečuje z razmerjem Ti/B, kar kaže na prisotnost delcev Al_3Ti različnih oblik, kot so t.i. kockasti in luskasti [5–7]. Masno razmerje Ti/B, ki ustreza stehiometriji TiB_2 , je 2,215, učinkovitost udrobnjevanja pa se občutno izboljša, ko je to razmerje nekoliko preseženo, vendar se zmanjša pri višjih vsebnostih titana [6,7], kot je bilo opaženo pri udrobnilnih sredstvih C in D. Udrobnilno sredstvo D naj bi vsebovalo večje količine Al_3Ti in faz s prisotnostjo silicija, ki dodatno prispevajo k zmanjšanju električne upornosti.

Rezultati analize DSC med ohlajanjem so prikazani na sliki 1. Krivulje DSC zagotavljajo informacije o procesih strjevanja različnih udrobnilnih sredstev, tako da je mogoče narediti korelacijo med fazno transformacijo in rezultati

were evaluated on Al99.7 aluminium alloy. The alloy was preheated to 700 °C, and after the melting process, the Al-Ti-B master alloy was added to the melt in the dosage recommended by the manufacturer. The melt was held for 2 minutes and then poured at a temperature range of 680-690 °C using a Croning cup, with a cooling rate of about 7 K/min. Samples were taken from the middle region of the cast specimens to determine the grain size. These samples were prepared by standard metallographic techniques and electropolished with Barker reagent. Grain boundaries were visualized under polarized light using an Olympus BX61 microscope with a DP70 camera at 50x magnification. The grain size was measured by the mean linear section method according to ASTM E112.

3 Results and discussion

The electrical resistivity values of the studied grain refiners are shown in Table 2. Grain refiner B has the lowest electrical resistivity, which indicates a lower content of impurities contributing to a lower resistivity [10,16]. It can be assumed that this grain refiner contains uniformly distributed flaky Al_3Ti particles, consistent with the analyzed Ti/B ratio, which allows optimal grain refinement. For grain refiners C and D (Al-5 wt.% Ti-1 wt.% B), the electrical resistivity increases with the Ti/B ratio, indicating the presence of Al_3Ti particles with different shapes, such as blocky and flaky [5–7]. The Ti/B weight ratio corresponding to TiB_2 stoichiometry is 2.215, and the refining efficiency improves significantly when this ratio is slightly exceeded but decreases at higher titanium contents [6,7], as was observed for grain refiners C and D. Grain refiner D is expected to contain higher amounts of Al_3Ti and Si-containing phases,

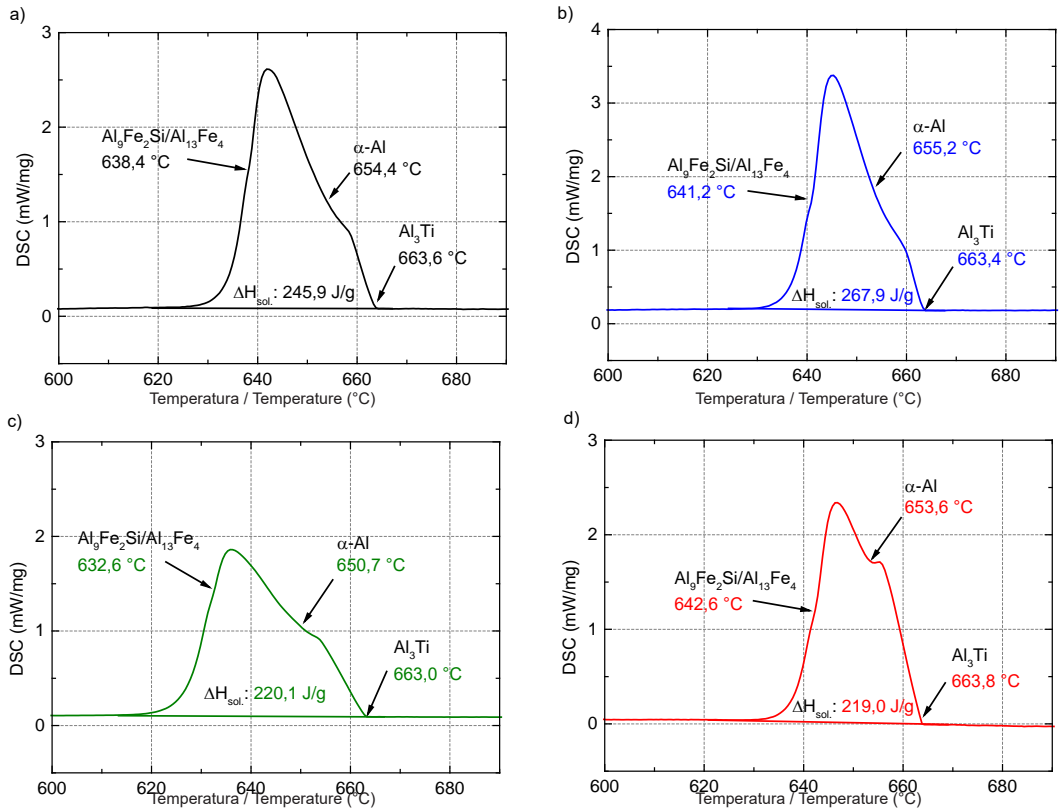
Tabela 2. Specifična električna upornost preiskovanih udrobnilnih sredstev**Table 2.** Specific electrical resistivity of investigated grain refiners

Oznaka / Designation	L, mm	A, mm ²	R, Ω	ρ, Ωm
A	800	0,76 ± 0,01	0,000368	3,48 · 10 ⁻⁸
B	1000	0,76 ± 0,01	0,000443	3,36 · 10 ⁻⁸
C	1000	0,77 ± 0,01	0,000454	3,48 · 10 ⁻⁸
D	700	0,24 ± 0,01	0,000341	3,53 · 10 ⁻⁸

električne upornosti. Pomembne razlike med udrobnilnimi sredstvi so vidne na ohlajevalnih krivuljah DSC. Temperature strjevanja ključnih faz (α -Al, Al_3Ti in $\text{Al}_9\text{Fe}_2\text{Si}/\text{Al}_{13}\text{Fe}_4$, navedene v [18]) se

which further contributes to a decrease in electrical resistivity.

The results of DSC analysis during cooling are shown in Figure 1. The DSC curves provide information on the



Slika 1. Ohlajevalne krivulje DSC preiskovanih udrobnilnih sredstev: A (črna), B (modra), C (zelena) in D (rdeča), z označenimi značilnimi temperaturami, fazami in entalpijami

Figure 1. Cooling DSC curves of the investigated grain refiners: A (black), B (blue), C (green), and D (red), with marking of the characteristic temperatures, phases, and enthalpies

razlikujejo med proučevanimi udrobnilnimi sredstvi, kar potrjuje njihove različne kemijske sestave. Sprememba strjevalne entalpije z najnižjo vrednostjo, opaženo pri udrobnilnih sredstvih C in D, kaže na večjo vsebnost nečistoč (nekovinskih vključkov), ki se talijo šele nad 720 °C in so manj učinkoviti udrobnjevalci. Poleg tega lahko nečistoče onesnažijo delce TiB_2 in vplivajo na učinkovitost udrobnjevanja udrobnilnih sredstev [19, 20].

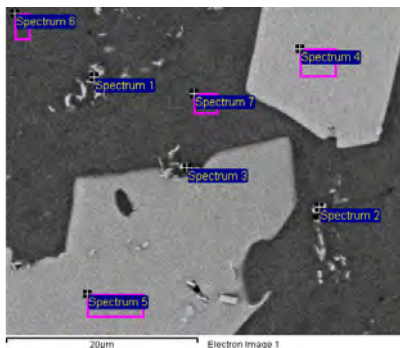
Slike 2a–h prikazujejo reprezentativne mikroposnetke udrobnilnih sredstev v litem stanju. Na slikah 2a in b, ki prikazujeta zlitino Al-3 mas. % Ti-1 mas. % B, so vidni kockasti ali luskasti veliki delci Al_3Ti , neenakomerno porazdeljeni v matrici, medtem ko so manjši razdrobljeni delci TiB_2 razpršeni. Sliki 2c in d prikazujeta zlitino Al-3 mas. %-Ti-1 mas. %-B z enakomerno porazdeljenimi kosmičastimi delci Al_3Ti različnih oblik. Pri udrobnilnih sredstvih C in D (sliki 2c in d), ki ustrezajo zlitini Al-5 mas. % Ti-1 mas. % B, se morfologija delcev Al_3Ti spremeni iz kockastih v luskaste z zmanjševanjem razmerja Ti/B. Ta opažanja dodatno potrjuje analiza EDS, predstavljena na sliki 2.

Izvedena je bila tudi SEM analiza več mikroposnetkov (48) za analizo delcev Al_3Ti in TiB_2 , s poudarkom na porazdelitvi velikosti. Rezultati, prikazani na sliki 3a in b, prikazujejo število delcev glede na njihovo velikost (površino delcev). Velikostna porazdelitev delcev TiB_2 igra ključno vlogo pri določanju učinkovitosti udrobnilnih sredstev. Najbolje se je izkazalo udrobnilno sredstvo B, saj je v primerjavi z ostalimi pokazal najugodnejše rezultate. Druga udrobnilna sredstva so imela večje število delcev TiB_2 v zelo majhnem območju velikosti, vendar so vsebovale tudi večje delce. Največje število delcev TiB_2 je bilo v udrobnilnem sredstvu D. Vendar pa zaradi neenakomerne porazdelitve velikosti in večje vsebnosti nečistoč, kot so Fe, Si in

solidification processes of the different grain refiners so that a correlation can be made between the phase transformation and the electrical resistivity results. Significant differences between the grain refiners can be seen in the DSC cooling curves. The solidification temperatures of the key phases ($\alpha-Al$, Al_3Ti , and $Al_9Fe_2Si/Al_{13}Fe_4$, reported in [18]) vary among the studied grain refiners, confirming their different chemical compositions. The variation in solidification enthalpy, with the lowest value observed for grain refiners C and D, indicates a higher content of impurities (non-metallic inclusions), which melt only at 720 °C and are less effective as inoculants. Moreover, impurities can contaminate the TiB_2 particles and affect the grain refining performance of the grain refiners [19,20].

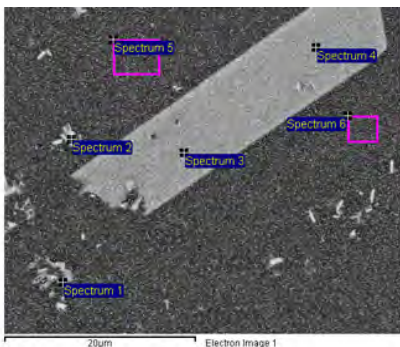
Figures 2a–h show representative micrographs of grain refinement in the as-cast state. In Figures 2a and b, which show the Al-3 wt.% Ti-1 wt.% B alloy, blocky or flaky large Al_3Ti particles are seen unevenly distributed in the matrix, while smaller fragmented TiB_2 particles are interspersed. Figures 2c and d show the Al-3 wt. %-Ti-1 wt. %-B alloy with uniformly distributed flaky Al_3Ti particles of different shapes. At grain refinement C and D (Figures 2c and d), corresponding to the Al-5 wt.% Ti-1 wt.% B alloy, the morphology of the Al_3Ti particles changes from blocky to flaky with decreasing Ti/B ratio. These observations are further confirmed by the EDS analysis presented in Figure 2.

SEM analysis of several microphotographs (48) was also performed to analyze the Al_3Ti and TiB_2 particles, focusing on the size distribution. The results, shown in Figures 3a and b, show the number of particles versus their size (particle surface area). The size distribution of TiB_2 particles plays a crucial role in determining the effectiveness of grain refinement. Grain



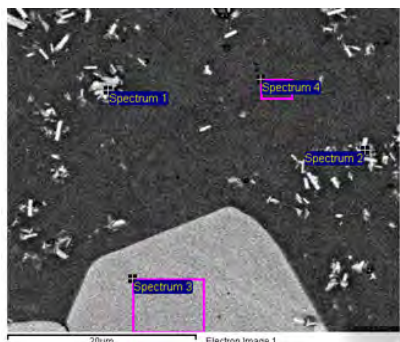
a)

Spectrum	B	Al	Si	Ti	Cr	Fe	Skupaj / Total
1	20,5	55,8	0,4	23,0	0,1	0,2	100,0
2	44,9	33,5	0,2	21,4	0,0	0,0	100,0
3	43,1	24,9	0,1	31,6	0,0	0,2	100,0
4	0,0	62,8	0,7	36,5	0,0	0,1	100,0
5	0,0	62,5	0,9	36,3	0,2	0,1	100,0
6	17,3	82,1	0,1	0,4	0,0	0,0	100,0
7	6,4	92,9	0,2	0,5	0,0	0,0	100,0



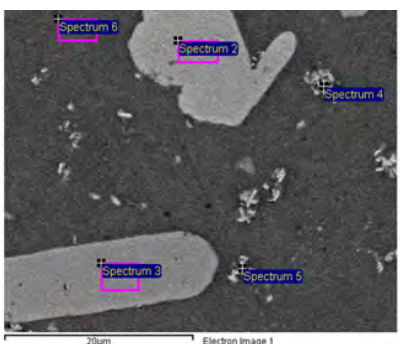
b)

Spectrum	B	Al	Si	Ti	Cr	Fe	Skupaj / Total
1	7.7	58.7	0	31.9	0.2	1.5	100,0
2	43.1	26	0	30.4	0.2	0.3	100,0
3	0	63.2	0.3	36.2	0.3	0	100,0
4	0	63.1	0.3	36.3	0.1	0.2	100,0
5	0	98.8	0.2	0.8	0.2	0.0	100,0
6	0	98.9	0	1.1	0.0	0.0	100,0



c)

Spectrum	B	Al	Si	Ti	Cr	Fe	Skupaj / Total
1	45.8	26.3	0.1	27.7	0.0	0.1	100,0
2	0.0	63.9	0.1	34.5	0.1	1.4	100,0
3	0.0	62.9	0.3	36.8	0.0	0.0	100,0
4	0.0	99.4	0.1	0.2	0.0	0.3	100,0



d)

Spec-tum	B	Al	Si	Ti	Mn	Fe	Cu	Skupaj / Total
1	0.0	63.5	0.5	35.5	0.0	0.2	0.3	0.3
2	0.0	64.0	0.5	35.0	0.1	0.1	0.3	0.3
3	40.8	28.3	0.0	30.4	0.1	0.4	0.0	0.0
4	0.0	64.8	0.3	25.2	0.1	9.6	0.0	0.0
5	0.0	98.9	0.1	0.9	0.0	0.1	0.0	0.0

Slika 2. SEM slike preiskovanih udobnilnih sredstev z ustreznimi rezultati EDS v mas. %: a) A, b) B, c) C in d) D.

Figure 2. SEM images of investigated grain refiners with corresponding EDS results in wt.%: a) A, b) B, c) C, and d) D

drugi elementi, potrjeni z analizo DSC, ni pričakovati, da bo najbolj učinkovito. Na drugi strani je udrobnilno sredstvo B imelo manjšo količino delcev TiB_2 , vendar bi moralo biti njegovo delovanje boljše zaradi enakomernije porazdelitve velikosti. Poleg tega je imela glede na analizo DSC udrobnilno sredstvo B najnižjo vsebnost nečistoč, kar je povzročilo najnižjo električno upornost. Večji delci in nečistoče, vključno z Fe, Si in vključki, prispevajo k povečanemu sipanju elektronov v matrici [15].

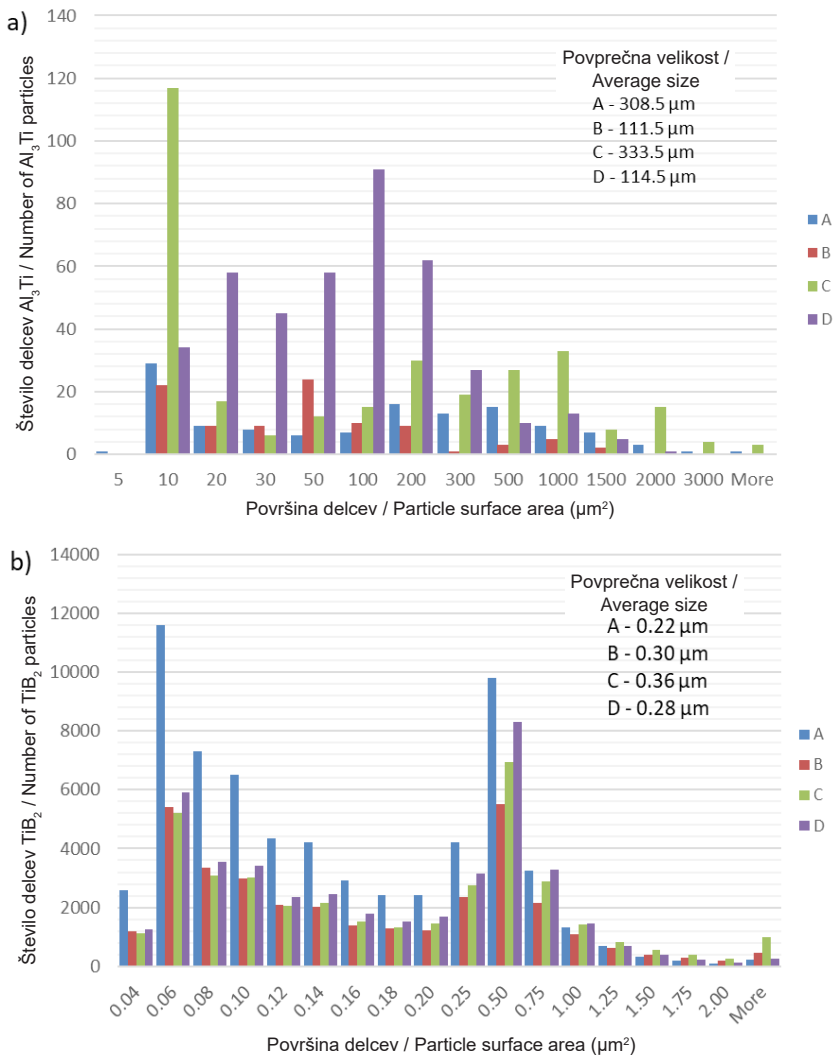
Slike 3a–h prikazuje različne oblike delcev Al_3Ti , ki jih je mogoče pripisati različnim mehanizmom rasti in pogojem obdelave. Za učinkovito udrobnjevanje morajo biti prisotni tako netopni delci TiB_2 kot topni delci Al_3Ti ustrežne velikosti in oblike. Delci TiB_2 delujejo kot substrat za nukleacijo Al_3Ti . Študije kažejo, da ima število delcev TiB_2 večji učinek na nukleacijo in udrobnjevanje v udrobnilnih sredstvih Al-Ti-B kot število delcev Al_3Ti [25]. To nakazuje, da TiB_2 predvsem poganja proces udrobnjevanja kot substrat za nukleacijo, medtem ko ima presežek Ti sekundarne učinke na površino TiB_2 . Vendar pa so za optimalno udrobnjevanje potrebne tudi primerne koncentracije in velikosti delcev Al_3Ti . V tem pogledu ima udrobnilno sredstvo B najbolj enakomerno porazdelitev velikosti delcev Al_3Ti , medtem ko udrobnilni sredstvi C in D kažeta večje razlike (slika 3).

Učinkovitost udrobnjevanja testiranih udrobnilnih sredstev je bila ovrednotena in pokazali so hitro delujoče in učinkovito udrobnjevanje, kot smo že poročali [20]. Prva slika na sliki 4a prikazuje mikrostrukturo lite aluminijeve zlitine Al99,7, strjene pri hitrosti hlajenja približno 7 K/min in kaže velikost kristalnih zrn približno 440 μm . Ko je bilo dodano udrobnilno sredstvo, se je velikost zrn znatno zmanjšala na 270–370 μm (slike 4b–e). Najboljše rezultate kažeta udrobnilni sredstvi B in C, kar bi lahko bila

refiner B exhibited the best performance as it showed the most favorable results compared to the others. The other grain refiners had a higher number of TiB_2 particles in the very small size range but also contained larger particles. Grain refiner D had the highest number of TiB_2 particles. However, due to the uneven size distribution and higher content of impurities such as Fe, Si, and other elements confirmed by DSC analysis, it is not expected to be the most efficient. Grain refiner B, on the other hand, had a lower amount of TiB_2 particles, but its performance should be better due to its more uniform size distribution. In addition, according to DSC analysis, grain refiner B had the lowest impurity content, resulting in the lowest electrical resistivity. The larger particles and impurities, including Fe, Si, and inclusions, contribute to enhanced electron scattering by the matrix [15].

Figure 4a–h illustrates the different shapes of Al_3Ti particles that can be attributed to different growth mechanisms and processing conditions. For effective inoculation, both insoluble TiB_2 particles and soluble Al_3Ti particles of appropriate size and shape must be present. TiB_2 particles act as a substrate for Al_3Ti nucleation. Studies show that the number of TiB_2 particles has a greater effect on nucleation and grain refinement in Al-Ti-B grain refiners than the number of Al_3Ti particles [25]. This suggests that TiB_2 primarily drives the grain refinement process as a nucleation substrate, while the excess of Ti has secondary effects on the surface area of TiB_2 . However, suitable concentrations and sizes of Al_3Ti particles are also required for optimal grain refinement. In this respect, grain refiner B exhibits the most uniform size distribution of Al_3Ti particles, while grain refiners C and D show larger variations (Figure 3).

The grain refining performance of the tested grain refiners was evaluated,

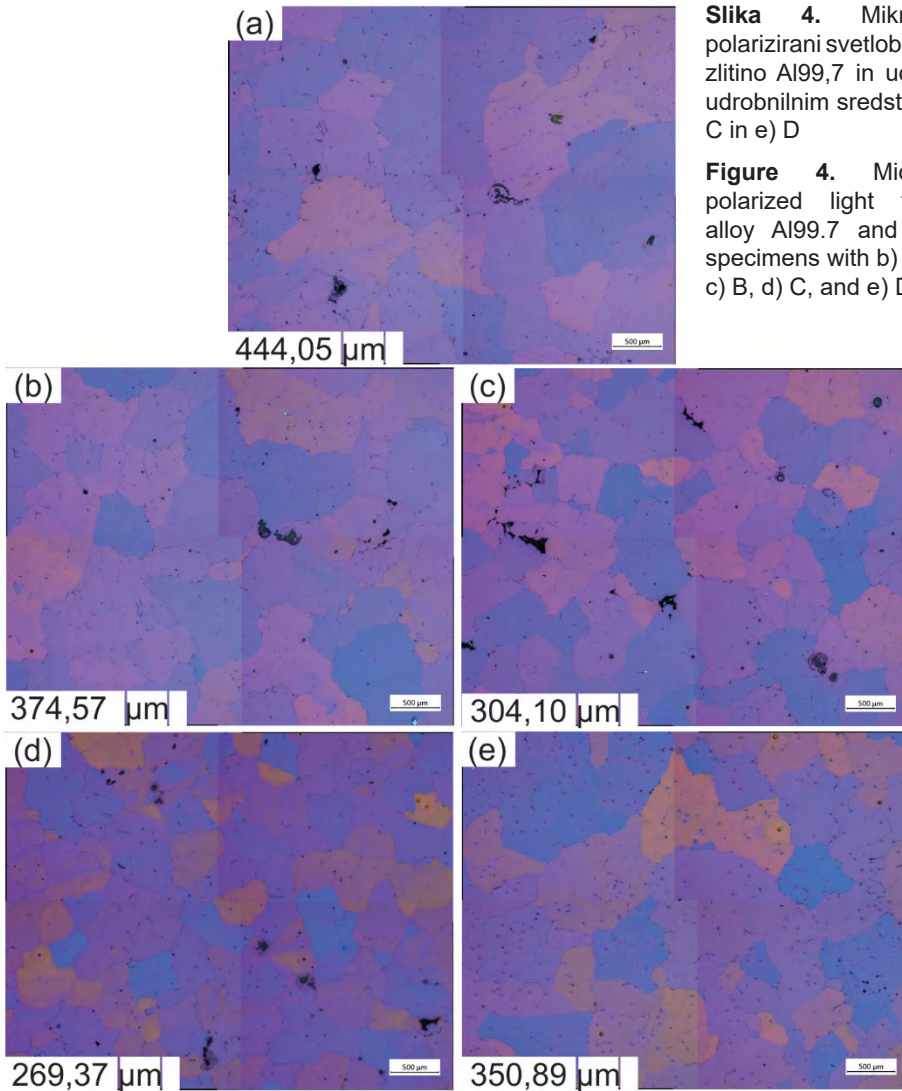


Slika 3. a) Velikostna porazdelitev delcev TiB_2 v preiskovanih udrobnilih sredstvih in b) velikostna porazdelitev delcev Al_3Ti v preiskovanih udrobnilih sredstvih

Figure 3. a) TiB_2 particle size distribution in various grain refiners and b) Al_3Ti particle size distribution in various grain refiners

posledica velikostne porazdelitve delcev, saj obe udrobnili sredstvi B in C sestojita iz ene same oblike delcev Al_3Ti , ki so bolj enakomerno porazdeljeni v matrici (slika 3).

and they showed fast-acting and efficient grain refining, as previously reported [20]. The first image in Figure 4a shows the microstructure of an $\text{Al}_{99.7}$ as-cast aluminum alloy solidified at a cooling rate of about 7 K/min and exhibited a large grain



Slika 4. Mikroposnetki v polarizirani svetlobi za aluminijevo zlitino Al99,7 in udrobnjene b) z udrobnilnim sredstvom A, c) B, d) C in e) D

Figure 4. Micrographs in polarized light for aluminum alloy Al99.7 and grain refined specimens with b) grain refiner A, c) B, d) C, and e) D.

4 Zaključki

Na podlagi predstavljenih rezultatov ima udrobnilno sredstvo B najnižjo električno upornost, kar kaže na nižjo vsebnost nečistoč in ugodno porazdelitev števila in velikosti delcev TiB_2 in Al_3Ti ter optimalno razmerje Ti/B. Nasprotno pa povečano število in velikost delcev TiB_2 in Al_3Ti ter prisotnost topnih elementov, kot sta Fe

size of about 440 μm . In contrast, when the experimental material was added for grain refinement, the grain size decreased significantly to a range of 270–370 μm (Figure 4b–e). The best results show grain refiners B and C, which could be due to the particle size distribution, as both grain refiners B and C consist of a single form of Al_3Ti particles that are more uniformly distributed in the matrix (Figure 3).

in Si ter njuni vključki, prispevajo k večji električni upornosti zaradi povečanega sipanja elektronov v matrici. Različne oblike delcev Al_3Ti lahko pripišemo različnim mehanizmom rasti in pogojem izdelave. Učinkovito udrobnjevanje zahteva kombinacijo netopnih delcev TiB_2 in topnih delcev Al_3Ti ustrezne velikosti in oblike, pri čemer TiB_2 služi kot nukleacijski substrat za Al_3Ti . Optimalno udrobnjevanje zahteva prisotnost ustrezne koncentracije in velikosti delcev Al_3Ti . Udrobnilno sredstvo B, izdelano iz Al-3Ti-1B z razmerjem Ti/B 3,6, ima optimalno število delcev TiB_2 in dobro velikostno porazdelitev delcev. Povprečna velikost delcev Al_3Ti je 111,5 μm , delcev TiB_2 pa 0,30 μm . Ko aluminijevi zlitini Al99,7 dodamo testirana udrobnilna sredstva, se velikost zrn zmanjša s približno 440 μm na 270–370 μm . Najboljše rezultate udrobnjevanja dosežemo z dodajanjem udrobnilnih sredstev B in C, saj imata najprimernejšo porazdelitev delcev.

4 Conclusions

Based on the results presented, grain refiner B exhibits the lowest electrical resistivity, indicating lower impurity content and favorable number and size distribution of TiB_2 and Al_3Ti particles, as well as an optimal Ti/B ratio. Conversely, an increased number and size of TiB_2 and Al_3Ti particles, as well as the presence of soluble elements such as Fe and Si and their inclusions, contribute to a higher electrical resistivity due to enhanced electron scattering by the matrix. The different shapes of Al_3Ti particles can be attributed to different growth mechanisms and processing conditions. Effective grain refining requires a combination of insoluble TiB_2 particles and soluble Al_3Ti particles of appropriate size and shape, with TiB_2 serving as a nucleation substrate for Al_3Ti . Optimal grain refinement requires the presence of a suitable concentration and size of Al_3Ti particles. Grain refiner B, made from Al-3Ti-1B with a Ti/B ratio of 3.6, has the optimum number of TiB_2 particles and well-distributed particle size. The average size of Al_3Ti particles is 111.5 μm and that of TiB_2 particles is 0.30 μm . When the tested grain refiners are added to the Al99.7 aluminum alloy, the grain size decreases from about 440 μm to a range of 270–370 μm . The best grain refining results are obtained by adding grain refiners B and C, as they have the most suitable particle size distribution.

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