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Razkritje modificiranja evtektskega Si v zlitini Al z napredno elektronsko mikroskopijo

Revealing the modification of eutectic Si in Al alloy by advanced electron microscopy

Izvleček

Sprememba evtektičnega Si iz kosmičaste v vlaknasto obliko je ključni dejavnik za izboljšanje lastnosti zlitin Al-Si. Mehanizem dvojčičenja zaradi nečistoč (ITT – impurity-induced twinning) in mehanizem povratnega roba dvojčične ploskve (TPRE – twin plane re-entrant edge) kot tudi zastrupitev mehanizma TPRE so na splošno sprejemljivi pod določenimi pogoji. Vendar pa IIT, TPRE ali zastrupitve mehanizma TPRE ni mogoče uporabiti za interpretacijo vseh opazovanj, ki spremljajo spreminjanje, kar pomeni, da lahko veljajo tudi drugi dejavniki. Ta članek ponuja pregled napredka sprememb evtektičnega Si s posebnim poudarkom na uporabi napredne elektronske mikroskopije. Več kot jasno je, da so lahko napredna elektronska mikroskopija vključno z visokokotnim obročastim detektorjem v temnem polju (HAADF) in spektroskopijo z izgubo energije elektronov (EELS) pri vrstični transmisijski elektronski mikroskopiji (STEM) ter tomografijo na atomsko sondo (APT) odlična orodja za pojasnitev mehanizma sprememb evtektičnega Si. Poleg uporabe napredne elektronske mikroskopije je zelo učinkovita tudi atomska simulacija, ki temelji na izračunu teorije gostotnega funkcionala (DFT), za pojasnitev lastnosti vezanja spreminjajočih elementov pri dvojčkih Si in učinka na dvojčičenje Si. Tako pri eksperimentalni kot simulacijski raziskavi smo odkrili, da imajo spreminjajoči elementi štiri različne vloge: (i) adsorpcija na presečišču faset Si, ki sproža mehanizem tvorbe IIT, (ii) adsorpcija na povratnem robu dvojčične ploskve, ki sproža mehanizem rasti TPRE, (iii) adsorpcija pred rastjo dvojčkov Si, ki sproža prehajanje snovi znotraj evtektičnega Si in (iv) segregacija na fronti med evtektičnim Si in evtektičnim Al, ki zavira rast evtektičnega Si. Prav tako je poudarjen pomen napredne elektronske mikroskopije (HAADF-STEM, EELS in APT) na področju strjevanja.

Ključne besede: zlitina Al-Si; nukleacije; rast; evtektično strjevanje; napredna elektronska mikroskopija; izračun teorije gostotnega funkcionala.

Abstract

Modifying the eutectic Si from flake-like to fibrous is a key factor to improve the properties of Al-Si alloys. The impurity-induced twinning (IIT) mechanism and the twin plane re-entrant edge (TPRE) mechanism as well as the poisoning of the TPRE mechanism are generally accepted to be valid under certain conditions. However, IIT, TPRE or poisoning of TPRE mechanism cannot be used to interpret all the observations accompanying modification, indicating that other factors may be also valid. In this paper, we overview the progress of modification of eutectic Si, which in particular focus on the application of advanced electron microscopy. It is very clear that advanced electron microscopy, including high angle annular dark field imaging (HAADF) and electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) as well as atom probe tomography

(APT), can provide a great tool to elucidate the modification mechanism of eutectic Si. Apart from the application of advanced electron microscopy, atomic simulation based on density functional theory (DFT) calculation was also found to be very efficient to elucidate the bonding behaviour of modifying elements within Si twins and its effect on the Si twinning. From both experimental and simulation investigation, it was found that modifying elements have four different roles: (i) the adsorption at the intersection of Si facets, inducing IIT growth mechanism, (ii) the adsorption at the twin plane re-entrant edge, inducing TPRE growth mechanism, (iii) the adsorption ahead of the growing Si twins, inducing a solute entrainment within eutectic Si, and (iv) the segregation at the interface between eutectic Si and eutectic Al, suppressing the growth of eutectic Si. The importance of advanced electron microscopy (HAADF-STEM, EELS and APT) in the field of solidification is also highlighted.
Keywords: Al-Si alloy; Nucleation; Growth; Eutectic solidification; Advanced electron microscopy; Density functional theory calculation.

1 Uvod

Da bi zmanjšali težo vozil in zagotovili skladnost s strožjimi predpisi v zvezi z učinkovitostjo goriv in emisijami CO_2, je v avtomobilski industriji vse več povpraševanja po oblikovanju lahkih ulitkov s še tanjšimi stenami. Za ta namen se za izdelavo lahkih ulitkov s tankimi stenami pogosto uporabljajo visokozmogljive hipoevtektične zlitine Al-Si, zahvaljujoč njihovi odlični zmogljivosti polnjenja in visoko specifični trdnosti. Hipoevtektične livarske zlitine Al-Si navadno vsebujejo med 5 in 12 wt. % Si skupaj z dodatki elementov Mg, Cu in Fe/Mn za izboljšanje mehanskih lastnosti [1]. Za nadzor strjevanja mikrostruktur in posledično lažje dovajanje se pogosto uporabljata dva postopka obdelave talin pri hipoevtektičnih zlitinah Al-Si. Prva obdelava taline je udrobnjevanje primarne a-Al, ki se navadno doseže z dodajanjem udrobnjevalnega sredstva, npr. udrobnjevalnega sredstva Al-Ti-B. Dobro je znano, da udrobnjevanje primarnega a-Al izboljšuje zmožnost polnjenja do točke koherence, s čemer se izognemo zvarom v hladnem. Vendar pa je treba opozoriti, da do napak pri litju navadno pride pri poznejših stopnjah strjevanja med

1 Introduction

To reduce vehicle weight and comply with more stringent regulations on fuel efficiency and CO_2 emissions, there is an increasing demand for light weight designs of even thinner walled casting parts in the automotive industry. For this purpose, high performance hypoeutectic Al- Si alloys have been widely used to produce light weight thin walled casting due to their excellent filling ability and high specific strength. Hypoeutectic Al-Si foundry alloys normally contain between 5 and 12 wt. % Si, together with additional Mg, Cu and Fe / Mn elements, to improve the mechanical properties [1]. Two very important melt treatments in hypoeutectic Al-Si alloys are very often employed to control solidification microstructure and thereby facilitate a better feeding. The first melt treatment is the grain refinement of primary α-Al, which is usually achieved by the addition of grain refiners, e.g. Al-Ti-B grain refiner. It is well-accepted that the grain refinement of primary α-Al improves the filling ability up to the coherency point, thus avoiding cold runs. However, it should be noted that casting defects are normally formed in latter stages of solidification during

tvorbo binarne evtektične strukture Al-Si in posledično morebitne ternarne evtektične strukture. Zato je druga pomembna obdelava taline sprememba strukture evtektičnega Si iz kosmičaste morfologije v morfologijo finega vlakna. Za spremembo evtektičnega Si se pogosto uporabljajo različni modifikatorji (npr. Na [2–4], Sr [5–9], Eu [10, 11]). Podrobno so bili proučeni mehanizmi sprememb (tj. mehanizem rasti dvojčičenja zaradi nečistoč (IIT) [5], mehanizmi rasti povratnega roba dvojčične ploskve (TPRE) [12, 13], zastrupitev TPRE [14] in odnašanje topljenca [7]). Vendar pa IIT, TPRE ali zastrupitev mehanizma TPRE ni mogoče uporabiti za interpretacijo vseh procesov, ki spremljajo spreminjanje, kar pomeni, da lahko veljajo tudi drugi dejavniki. Še pomembnejše je dejstvo, da sprememba evtektičnega Si v bližini določenih intermetalnih spojin tipa Al_2Si_2X (npr. X: Sr), pri evtektičnih kristalnih mejah pa ni vselej enotna. To postaja še pomembnejše za ulitke s tankimi stenami Al-Si. Zato so še vedno potrebne dodatne preiskave spremembe evtektičnega Si.

Da bi popolnoma pojasnili mehanizem sprememb evtektičnega Si, je izjemno pomembna podrobna karakterizacija porazdelitve spreminjajočih elementov na atomski ravni. Razvoj elektronske mikroskopije (zlasti mikroskopije z visokokotnim obročastim detektorjem v temnem polju (HAADF) in spektroskopija z izgubo energije elektronov (EELS) pri vrstični transmisijski elektronski mikroskopiji (STEM) ter tomografije na atomsko sondo (APT)) je imel izjemno vlogo med raziskovanjem sprememb evtektičnega Si.

Ta članek je pregled napredka sprememb evtektičnega Si s posebnim poudarkom na uporabi napredne elektronske mikroskopije. Zelo jasno je, da je lahko napredna elektronska mikroskopija, vključno z mikroskopijo HAADF in EELS pri

the formation of binary Al-Si eutectic and subsequently possible ternary eutectics. Thus, the second important melt treatment is the modification of the eutectic Si structure from a flake-like morphology to a fine fibrous morphology. Different modifiers (e.g. Na [2-4], Sr [5-9], Eu [10, 11]) have been widely used to modify the eutectic Si. The modification mechanisms (i.e. impurity-induced twinning (IIT) growth mechanism [5], twin plane re-entrant edge (TPRE) growth mechanism [12, 13], poisoning of the TPRE [14], and solute entrainment [7]) have been investigated in detail. However, IIT, TPRE or poisoning of TPRE mechanism cannot be used to interpret all the observations accompanying modification, indicating that other factors may be also valid. More importantly, the modification of the eutectic Si is not always uniform in the vicinity of certain intermetallics of the type Al_2Si_2X (e.g. X: Sr) and at eutectic grain boundaries. This becomes even more relevant for the thin walled Al-Si casting. Further investigations on the modification of eutectic Si are therefore still required.

In order to fully elucidate the modification mechanism of eutectic Si, a detailed characterisation on the distribution of modifying elements at atomic scale is of great necessity. Indeed, the development of electron microscopy (in particular high angle annular dark field imaging (HAADF) and electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) as well as atom probe tomography (APT)) has played a very important role during the investigation on the modification of eutectic Si.

In this paper, we overview the progress of the modification of eutectic Si, which in particular focus on the application of advanced electron microscopy. It is very clear that advanced electron microscopy, including HAADF and EELS in STEM as

STEM in APT, odlično orodje za pojasnitev mehanizma sprememb evtektičnega Si. Poleg uporabe napredne elektronske mikroskopije je zelo učinkovita tudi atomska simulacija, ki temelji na izračunu teorije gostotnega funkcionala (DFT), za pojasnitev lastnosti vezanja spreminjajočih elementov pri dvojčkih Si in učinka na dvojčičenje Si. Tako pri eksperimentalni kot simulacijski raziskavi smo odkrili, da imajo spreminjajoči elementi štiri različne vloge:

(i) adsorpcija na presečišču faset Si, ki sproža mehanizem tvorbe IIT,
(ii) adsorpcija na povratnem robu dvojčične ploskve, ki sproža mehanizem rasti TPRE,
(iii) adsorpcija pred rastjo dvojčkov Si, ki sproža prehajanje snovi znotraj evtektičnega Si, in
(iv) segregacija na fronti med evtektičnim Si in evtektičnim Al, ki zavira rast evtektičnega Si.

2 Napredek pri modificiranju evtektskega Si

Odkritje spremembe evtektičnega Si izvira iz leta 1921 [2]. Od takrat so bili objavljeni številni članki o spremembi evtektičnega Si. Vendar pa natančen mehanizem sprememb še ni čisto pojasnjen kljub pogosti uporabi obdelave s spreminjanjem v livarski industriji. To je predvsem posledica pomanjkanja visokoločljivostnih opazovanj porazdelitve spreminjajočih elementov v evtektičnem Si. Hitri razvoj elektronske mikroskopije, zlasti HAADF-STEM, EELS in APT, je omogočil določitev porazdelitve spreminjajočih elementov v evtektičnem Si celo na atomski ravni.

Na Sliki 1 je prikazan sestavljeni evtektični Si v zelo čisti zlitini Al-5Si pri brizganju taline na hlajeno podlago z dodatkom 100 ppm Sr in 55 ppm Fe [6].

STEM and APT, as well as APT, can provide a great tool to elucidate the modification mechanism of eutectic Si. Apart from the application of advanced electron microscopy, atomic simulation based on density functional theory (DFT) calculation was also found to be very efficient to elucidate the bonding behaviour of modifying elements within Si twins and its effect on the Si twinning. From both experimental and simulation investigation, it was found that modifying elements have four different roles:

(i) the adsorption at the intersection of Si facets, inducing IIT growth mechanism,
(ii) the adsorption at the twin plane re-entrant edge, inducing TPRE growth mechanism,
(iii) the adsorption ahead of the growing Si twins, inducing a solute entrainment within eutectic Si, and
(iv) the segregation at the interface between eutectic Si and eutectic Al, suppressing the growth of eutectic Si.

2. The Progress of Modification of Eutectic Si

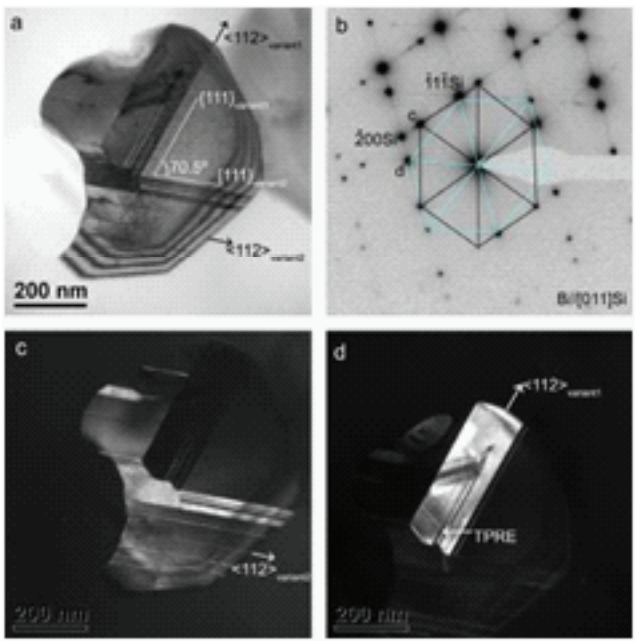
The discovery of the modification of eutectic Si can be dated back to 1921 [2]. Since then, a number of papers about the modification of eutectic Si have been published. But, the exact modification mechanism was still not clear yet, although the modification treatment has been widely used in foundry industry. This is mainly due to the lack of high resolution observation on the distribution of modifying elements within eutectic Si. With the rapid development of electron microscopy, in particular HAADF-STEM, EELS and APT, it becomes possible to determine the distribution of modifying elements within eutectic Si even at atomic scale.

V primerjavi z zelo čisto zlitino Al-5Si pri brizganju taline na hlajeno podlago z dodatkom 200 ppm Sr je številska gostota pri dvojčičenju Si mnogo višja. Še bolj zanimivo je to, da so bili atomi Sr določeni na presečišču dvojčičenja evtektičnega Si, kot je prikazano na Sl. 2. To je zelo neposredna poskusna podpora za mehanizem rasti IIT [6–8].

Zaradi velike razlike med atomskima številoma Sr (38) in Si (14) je mogoče določiti atomski stolpec Sr in Si s pomočjo mikroskopije HAADF-STEM. Vendar pa zaradi zelo majhne razlike med atomskimi števili Na (11) in Si (14) ni mogoče določiti Na v evtektičnem Si s pomočjo mikroskopije

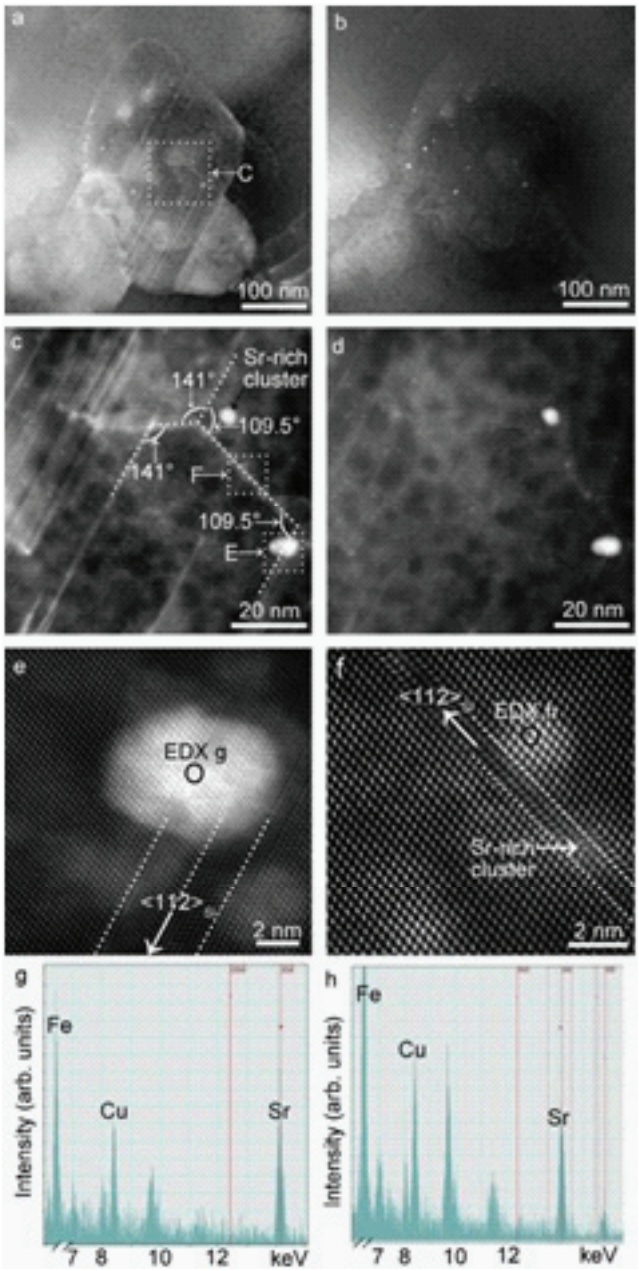
Figure 1 shows a multiple eutectic Si in high purity melt spun Al-5Si alloy with the addition of 100 ppm Sr and 55 ppm Fe [6]. Compared with high purity melt spun Al-5Si alloy without the addition of 200 ppm Sr, the number density of Si twinning is much higher. More interestingly, the Sr atoms were determined at the intersection of eutectic Si twinning, as shown in Figure 2. This is a very straightforward experimental support to IIT growth mechanism [6-8].

Due to the big difference of atomic numbers of Sr (38) and Si (14), it is possible to determine the Sr and Si atomic columns using HAADF-STEM. But, it is not possible to determine the Na within eutectic Si by



Sl. 1. (a) TEM-slika svetlega polja večkratnega dvojčnega delca Si, nagnjenega proti conski osi [011]$_{Si}$, v zlitini Al-5Si-100 ppm Sr-55 ppm, (b) ustrezno izbrano območje z vzorcem uklona, ki prikazuje dve možnosti, (c, d) centralne slike temnega polja, posnete na dveh {111} mestih Si pri obeh različicah, kot je označeno s črko (b) [6].

Fig. 1. (a) TEM bright field image of a multiple twinned Si particle, tilted to the [011]$_{Si}$ zone axis, in Al–5Si–100 ppm Sr–55 ppm Fe alloy, (b) corresponding selected area diffraction pattern showing two variants, (c, d) central dark field images taken from the two {111}$_{Si}$ spots of the two variants, as marked in (b) [6].

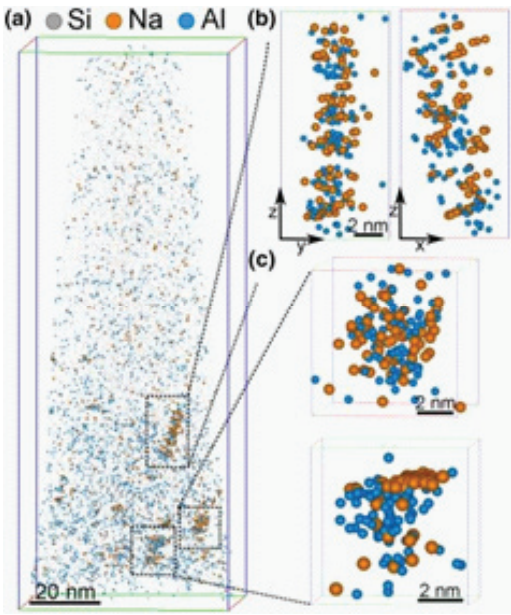


Sl. 2. Serija slik večkratnega dvojčnega delca Si, nagnjenega proti conski osi $[011]_{Si}$, v zlitini Al-5Si-100 ppm Sr-55 ppm Fe: (a) slika temnega polja pri majhni povečavi, (b) zadevno izbrano območje slike STEM-HAADF pri majhni povečavi, (c) povečana slika temnega polja s prikazom sestavljenih dvojčkov Si, vzeto iz območja (C) (označeno z belim kvadratkom v (c)) s prikazom grozda, bogatega s Sr, na presečišču dvojčkov Si, (f) povečana slika območja STEM-HAADF (F) (označena z belim kvadratkom v (c)) s prikazom grozda, bogatega s Sr, vzdolž $[112]_{Si}$ smeri rasti Si, (g, h) analize EDX z območij, kot je označeno na slikah (e, f). Grozd, bogat s Sr, na presečišču dvojčkov Si je na sliki (c) označeno tudi s črno puščico [6].

Fig. 2.. A series of images taken from a multiply twinned Si particle, tilted to the $[011]_{Si}$ zone axis, in Al–5Si–100 ppm Sr–55 ppm Fe alloy: (a) a dark-field image at a low magnification, (b) a corresponding STEM–HAADF image at a low magnification, (c) an enlarged dark-field image showing multiple Si twins, taken from the area (C) (marked with a white box in (a)), (d) a corresponding STEM–HAADF image, (e) an enlarged STEM–HAADF image taken from the area (E) (marked with a white box in (c)) showing a Sr-rich cluster at the intersection of Si twins, (f) an enlarged STEM–HAADF image taken from the area (F) (marked with a white box in (c)) showing a Sr-rich cluster along the $[112]_{Si}$ growth directions of Si, (g, h) EDX analyses taken from the areas as marked in (e, f), respectively. A Sr-rich cluster at the intersection of Si twins is also marked with a black arrow in (c) [6].

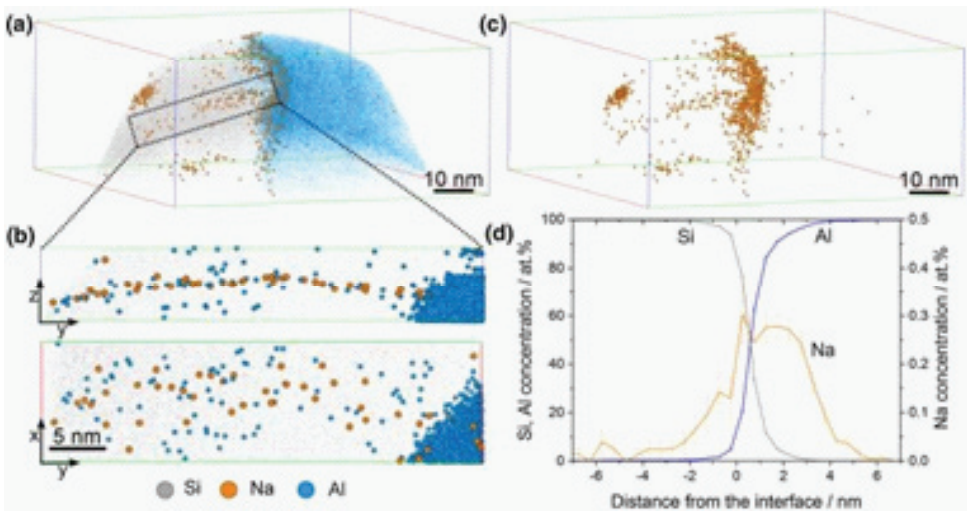
HAADF-STEM. Posledično je bila za določitev porazdelitve Na v evtektičnem Si uporabljena tomografija APT [3, 4].

using HAADF-STEM, which is due to its very close atomic numbers of Na (11) and Si (14). APT was therefore used to determine the distribution of Na within eutectic Si [3, 4].



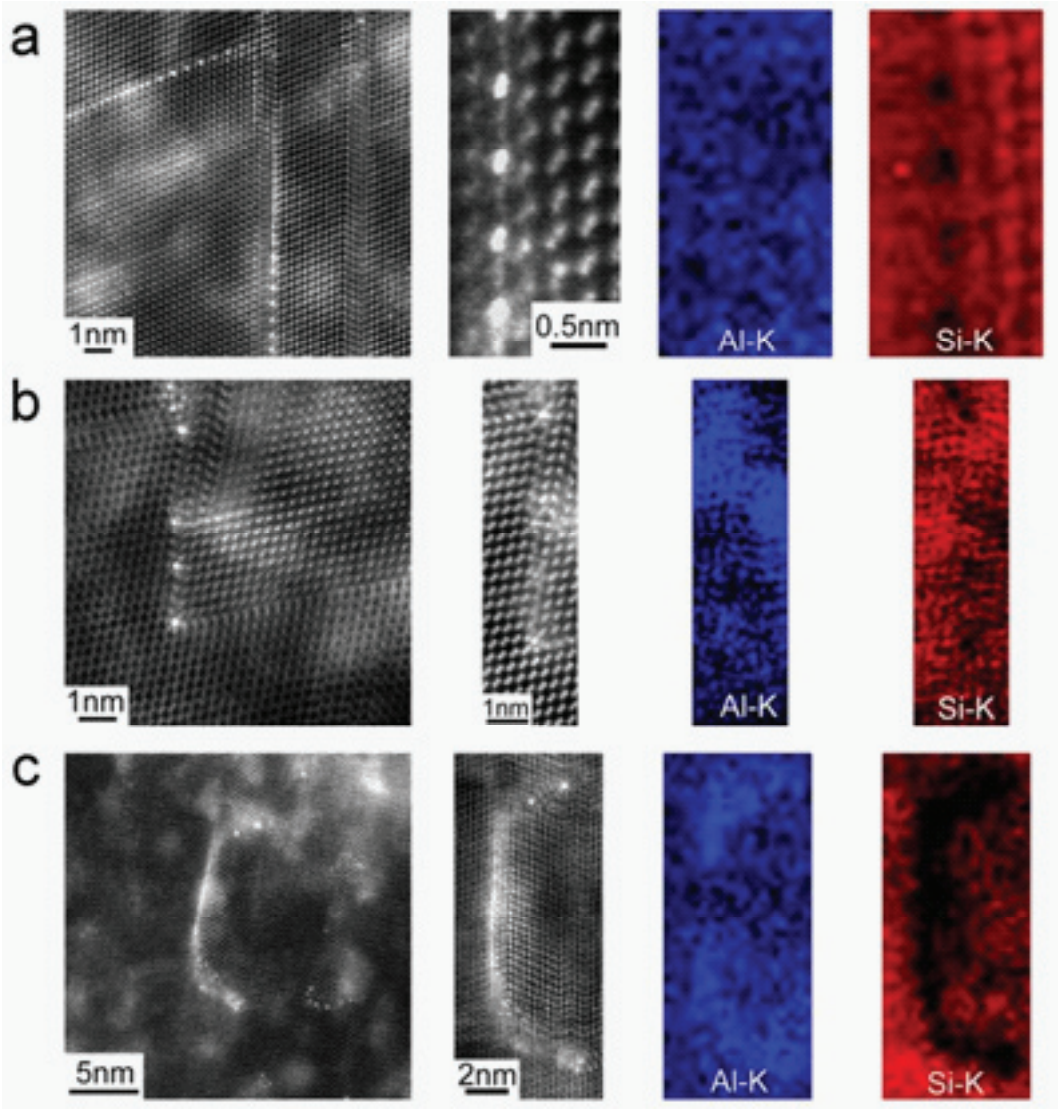
Sl. 3. Tomografija na atomsko sondo evtektičnega Si v zlitini Al-5Si z dodatkom 160 ppm Na, (a) popolna 3D-rekonstrukcija podatkov (atomi vsakega elementa so za namene prikaza prikazani v različnih velikostih), (b) povečana slika gnezda v obliki cevi, (c) povečani sliki dveh grozdov v obliki delcev [3],

Fig. 3. Atom probe tomography of eutectic Si in Al-5Si alloy with 160 ppm Na addition, (a) complete 3D reconstruction of the data (atoms of each element are shown in different sizes for visualization purposes), (b) magnified image of a rod-like cluster, (c) magnified images of two particle-like clusters [3].



Sl. 4. Tomografija na atomsko sondo evtektičnega Al in evtektičnega Si v zlitini Al-5Si z dodatkom 160 ppm Na, (a) popolna 3D-rekonstrukcija podatkov z atomi Na, prikazanimi v sferični obliki, (b) subvolumenska označitev grozda v obliki cevi, sestavljenega iz enoatomske plasti, (c) atomska preslikava atomov Na, ki prikazuje obogatitev Na na fronti med evtektičnim Al in evtektičnim Si, (d) koncentracija profila po fronti, izdelana s pomočjo histograma bližine, ki prikazuje obogatitev Na na fronti [3].

Fig. 4. Atom probe tomography of eutectic Al and eutectic Si in Al-5Si alloy with 160 ppm Na addition, (a) complete 3D reconstruction of the data with Na atoms represented as sphere, (b) a sub-volume highlighting a rod-like cluster composed of an atomic monolayer, (c) atomic map of Na atoms showing Na enrichment at the interface between eutectic Al and eutectic Si, (d) concentration profile across the interface constructed using proximity histogram, showing the enrichment of Na at the interface [3].

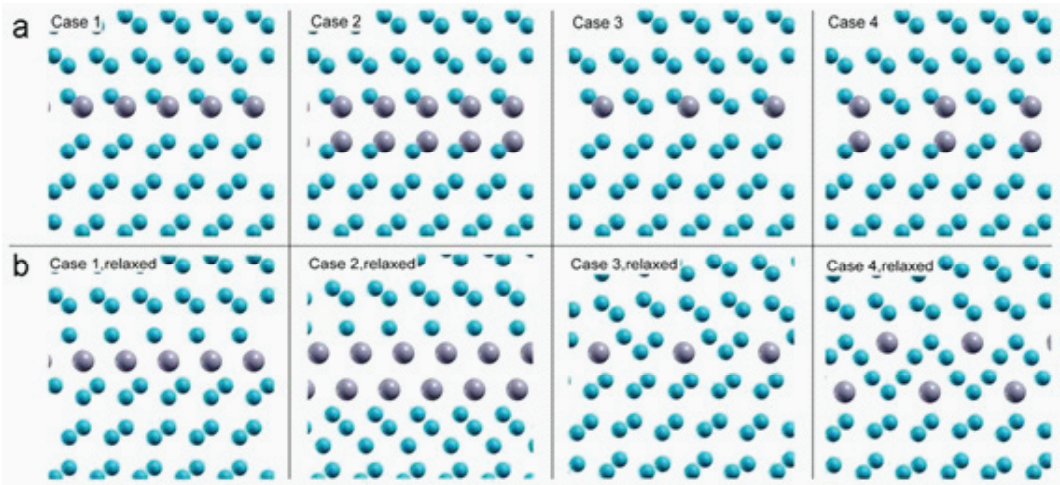


Sl. 5. Slike HAADF-STEM v visoki ločljivosti in preslikave EELS Al, Si in Eu v zlitini Al-5Si-0.05Eu. (a) prikazuje atome Eu med vsakima atomskima stolpcema Si na povratnem robu dvojčične ploskve, kar kaže na aktivno zastrupitev mehanizma TPRE. (b) prikazuje, da so atomski stolpci, bogati z Eu, na fronti faset Si in njihovih dvojčkov, kar kaže na aktivnost mehanizma IIT. (c) prikazuje, da so atomi Eu pred rastočimi dvojčki Si, ki tvorijo neprekinjeno plast, obogateno z Eu, kar kaže, da se segregacija na fronti odvija v okviru evtektičnega Si [11].

Fig 5. High resolution HAADF STEM images and EELS maps of Al, Si and Eu in Al-5Si- 0.05Eu alloy. (a) shows Eu atoms between every two Si atomic columns being located at the twin plane re-entrant edge, indicating that poisoning of the TPRE mechanism is active. (b) shows Eu-rich atomic columns are located at the intersection of Si facets and respectively twins, indicating that the IIT mechanism is active. (c) shows Eu atoms are located ahead of the growing Si twins, forming a continuous Eu-rich layer, indicating that a solute entrainment occurs within eutectic Si [11].

Slika 3 prikazuje distribucijo atomov Na v evtektičnem Si [3]. Jasno se je za Na izkazalo, da se nahaja vzdolž TPRE in na presečišču dvojčičenja Si, ki je zelo podobno Sr, kar nakazuje, da bi lahko bila mehanizma sprememb Na in Sr tudi podobna in se zato lahko interpretirata na podoben način. Nadalje so bili vzdolž fronte med matriko evtektičnega Si in Al določeni tudi atomi Na, kot prikazuje Sl. 4 [3]. To kaže, da se lahko Na difundira iz evtektičnega Si med postopkom strjevanja in se izceja pred strjevalnimi frontami, kar ovira nadaljnjo rast evtektičnega Si [3, 4]. O zelo podobnih opažanjih z mikroskopiranjem HAADF-STEM so poročali tudi pri zlitini Al-5Si s

Figure 3 shows the distribution of Na atoms within eutectic Si [3]. Clearly, Na was found to be located along TPRE and at the intersection of Si twinning, which is very similar to Sr, indicating that the modification mechanism of Na and Sr may also be similar and therefore can be interpreted in a similar manner. Furthermore, Na atoms were also determined along the interface between eutectic Si and Al matrix, as shown in Figure 4 [3]. This indicates that Na may diffuse out the eutectic Si during solidification and segregate ahead of solidification fronts, hampering the further growth of eutectic Si [3, 4]. A very similar observation was also reported in Al-5Si alloy with 500 ppm Eu



Sl. 6. (a) Začetne strukture in (b) sproščene strukture za štiri različne primere atomov Eu v evtektičnem Si. V primeru 1 so bili vsi atomi Si na eni strani TB zamenjani z atomi Eu, kar ustreza celotnemu pokritju atomov Eu na eni strani dvojčka Si. V primeru 2 so bili vsi atomi Si na obeh straneh TB zamenjani z atomi Eu, kar ustreza celotnemu pokritju atomov Eu na obeh straneh dvojčka Si. Podobno primer 3 prikazuje polovično pokritost atomov Eu na eni strani dvojčka Si, primer 4 pa prikazuje polovično pokritost atomov Eu na obeh straneh dvojčka Si [11].

Fig 6. (a) Starting structures and (b) relaxed structures for four different cases of Eu atoms within eutectic Si. In Case 1, all Si atoms on one side of the TB have been substituted with Eu atoms which corresponds to a full coverage of Eu atoms on one side of the Si twin. In Case 2, all Si atoms on both sides of the TB have been substituted with Eu atoms which corresponds to a full coverage of Eu atoms on both sides of the Si twin. Similarly, Case 3 corresponds to half coverage of Eu atoms on one side of the Si twin, and Case 4 corresponds to half coverage of Eu atoms on both sides of the Si twin [11].

dodatkom 500 ppm Eu, kot je prikazano na Sl. 5 [10, 11]. Treba je opozoriti tudi, da je mogoče tovrstna opažanja pri visokoločljivostnih preizkusih dodatno potrditi s simulacijo DFT, kot je prikazano na Sl. 6 [11].

Tako pri eksperimentalni kot simulacijski raziskavi smo odkrili, da imajo spreminjajoči elementi štiri različne vloge: (i) adsorpcija na presečišču faset Si, ki sproža mehanizem tvorbe IIT, (ii) adsorpcija na povratnem robu dvojčične ploskve, ki sproža mehanizem rasti TPRE, (iii) adsorpcija pred rastjo dvojčkov Si, ki sproža prehajanje snovi znotraj evtektičnega Si in (iv) segregacija na fronti med evtektičnim Si in evtektičnim Al, s čimer zavira rast evtektičnega Si.

3 Sklep

Razvoj napredne elektronske mikroskopije, vključno z vključno z mikroskopijo HAADF in EELS pri STEM in APT, prinaša odlično orodje za pojasnitev mehanizma sprememb evtektičnega Si. Nadalje bi bilo treba za popolno osvetlitev vedenja vezave treba upoštevati tudi atomsko simulacijo, ki temelji na izračunu teorije gostotnega funkcionala (DFT) spreminjajočih elementih v dvojčkih Si in njen učinek na dvojčičenje Si. Iz predhodnega raziskovalnega dela je jasno razvidno, da igra napredna elektronska mikroskopija (HAADF-STEM, EELS in APT) zelo pomembno vlogo pri poglobljenem raziskovanju na atomarni ravni na področju strjevanja.

addition by HAADF-STEM, as shown in Figure 5 [10, 11]. It should also be noted that such type of high resolution experimental observation can be further confirmed by DFT simulation, as shown in Figure 6 [11].

From both experimental and simulation investigation, it was found that modifying elements have four different roles: (i) the adsorption at the intersection of Si facets, inducing IIT growth mechanism, (ii) the adsorption at the twin plane re-entrant edge, inducing TPRE growth mechanism, (iii) the adsorption ahead of the growing Si twins, inducing a solute entrainment within eutectic Si, and (iv) the segregation at the interface between eutectic Si and eutectic Al, suppressing the growth of eutectic Si.

3 Conclusion

The development of advanced electron microscopy, including HAADF and EELS in STEM as well as APT, provides a great tool to elucidate the modification mechanism of eutectic Si. Furthermore, atomic simulation based on density functional theory (DFT) calculation should be also taken into consideration in order to fully elucidate the bonding behaviour of

modifying elements within Si twins and its effect on the Si twinning. From our previous research works, it is very clear that advanced electron microscopy (HAADF-STEM, EELS and APT) play a very important role for the in-depth atomic scale investigation in the field of solidification.

Viri / References

[1] D.G. McCartney (1989) Grain refining of aluminum and its alloys using inoculants, International Materials Reviews 34: 247–260.
[2] A. Pacz (1921) Alloy, U S Patent No. 1387900.

[3] J. H. Li, J. Barrirero, M. Engstler, H. Aboulfadl, F. Mücklich in P. Schumacher (2015) Nucleation and growth of eutectic Si in Al-Si alloys with Na additions, Metall. Mater. Trans. A, 46A: 1300–1311.
[4] J. Barrirero, J.H. Li, M. Engstler, N. Ghafoor, P. Schumacher, M. Oden in F. Mücklich (2016) Cluster formation at the Si/liquid interface in Sr and Na modified Al-Si alloys, Scripta Mater. 117: 16–19.
[5] Shu-Zu Lu in A. Hellawell (1987) The mechanism of silicon modification in aluminum-silicon alloys: Impurity induced twinning, Metall. Mater. Trans. A, 18: 1721–1733.
[6] J. H. Li, M. Zarif, M. Albu, B. McKay, F. Hofer in P. Schumacher (2014) Nucleation kinetics of entrained eutectic Si in Al-5Si alloys, Acta Mater., 72: 80–98.
[7] J. H. Li, M. Albu, F. Hofer and P.Schumacher (2015) Solute adsorption and entrapment during eutectic Si growth in Al-Si based alloys. Acta Mater., 83: 187–202.
[8] J. H. Li, M. Zarif, G. Dehm and P. Schumacher (2012) Influence of impurity elements on the nucleation and growth of Si in high purity melt-spun Al-Si based alloys, PHIL. Mag., 92: 3789–3805.
[9] M. Timpel, N. Wanderka, R. Schlesiger, T. Yamamoto, N. Lazarev, D. Isheim, G. Schmitz, S. Matsumura in J. Banhart (2012) The role of strontium in modifying aluminium-silicon alloys, Acta Mater., 60: 3920–3928.
[10] J. H. Li, X. D. Wang, T. H. Ludwig, Y. Tsunekawa, L. Arnberg, J. Z. Jiang in P. Schumacher (2015) Modification of eutectic Si in Al-Si alloys with Eu addition, Acta Mater., 84: 153–163.
[11] J. H. Li, F. Hage, M. Wiessner, L. Romaner, D. Scheiber, B. Sartory, Q. Ramasse in P. Schumacher (2015) The roles of Eu during the growth of eutectic Si in Al-Si alloys. Scientific reports. 5, 13802. DOI: 10.1038/srep13802.
[12] R. S. Wanger (1960) On the growth of germanium dendrites, Acta Metall., 8: 57–60.
[13] R. D. Hamilton in R. G. Seidensticker (1960) Propagation mechanism of Germanium dendrites, J. Appl. Phys., 31: 1165.
[14] M. G. Day in A. Hellawell (1968) The microstructure and crystallography of aluminum-silicon eutectic alloys, Proc. R Soc. Lond A, 305: 473–491.