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Multistep nucleation and multi-modification effect of Sc in hypoeutectic Al-Mg-Si alloys

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Abstract

Structure of Al₅Mg₂SiMn casting alloy with and without of Sc addition, morphology of primary phases and specifically morphology of the Sc-containing intermetallic compounds and nanoscale properties of the α -Al matrix of Al-Mg-Si-Mn alloys were observed. Morphology and chemical composition were investigated by scanning electron microscopy on polished and deep etched microsections.

It was found that addition of Sc changes morphology of α -Al, Al-Mg₂Si eutectic and intermetallic compounds with Mn. α -Al dendrites change their morphology to spherical, lamellar Al-Mg₂Si eutectic to fine fibrous eutectic. It was found that crystals Al₃Sc can act as nucleating particles of α -Al grains, as well as Mg₂Si eutectic fibrous. The mechanisms of nucleation can be attributed to heterogeneous nucleation.

Keywords: Materials science, Metallurgical engineering

1. Introduction

Higher mechanical properties are required for the Al alloys due to its wide application in the highly technological fields (automotive, marine, aerospace, chemical and

other industries). The mechanical properties of commercial Al casting alloys can be improved by heat treatment after solidification as well as during melting procedures. The general aim of melt treatments of Al alloys is to improve mechanical properties by reducing the grain size (in wrought alloys) or secondary dendrite arm spacing (in casting alloys), to modify eutectic (in eutectic alloys) and different intermetallic inclusions. It was reported [1, 2] that modified eutectic in Al-Si and Al-Mg₂Si alloys (fine platelets or fibers instead coarse angular eutectic particles) can improve strength and ductility. Additions of Li, Na, Sr and transition metals (such as Cr, Sc, Ni) to Al-Si and Al-Mg-Si eutectic alloys modify the morphology of eutectic (Al-Si, Al-Mg₂Si) from coarse angular eutectic particles (Al-Si) and eutectic lamellae (Al-Mg₂Si) into very fine plates or fibers as well as refine the primary Al grain size [1, 2, 3, 4, 5, 6, 7]. There are two possible modification mechanisms: heterogeneous nucleation (alloying element can form heterogeneous nucleus in the system) and poisoning effect (alloying element changes a surface energy of crystallizing phases during solidification). For the listed elements, added to the studied system, the authors currently favor the second explanation [2, 3, 6, 7]. However, in the case of Sc, both mechanisms are possible [8, 9].

Due to poor solubility of transition elements in Al alloys the precipitates or intermetallic phases can be formed. Thus even a small concentrations of transition elements have a large impact on the structure and properties of Al alloys. Sc has been successfully used as a minor alloying element not only as grain refiner, but also to prevent hot-cracking susceptibility and increase corrosion resistance in aluminum alloys [8, 9, 10, 11, 12]. Hence, among all transition elements, Sc is the most prospective addition to Al alloys.

Sc is relatively scarce and is commercially refined mainly in Ukraine, Russia and China. Until recently, Sc has been used as alloying addition to aluminum alloys for aircraft and aerospace applications in Russia [9, 13]. Recently, an interest in Sc as an additive to aluminum alloys for laser additive manufacturing (LAM) has appeared [14].

For the first time the addition of Sc as an effective alloying element for Al alloys (which increases the strength of Al-alloys) was proposed by Willey [15]. Researches carried out over the next 40 years show that Sc addition to pure aluminum and Al alloys enhances the mechanical properties and can refine Al grain sizes stronger than equivalent additions of Al–5Ti–1B refiner [8]. The mechanisms responsible for grain refinement by conventional methods (using Al–Ti and Al–Ti–B refiners) have been extensively studied [16, 17]. General ideas regarding mechanisms of grain refinement have mainly concluded that the titanium solute causing a growth restriction effect and Al₃Ti and TiB₂ (indirectly through the Al₃Ti adsorption layer) particles leads to the heterogeneous nucleation of Al grains.

A systematic study of Sc effect on a grain refinement in an Al–Mg–Si casting alloys has not yet been performed; only some limited reports regarding the modification effect of Sc in aluminium alloys have been found [8, 9, 18]. Sc leads to the modification of Al–Si eutectic in Al–Si–Mg and Al–Si alloys by changing its morphology to a rounded and fibrous shape, and refine Al grains [8, 18, 19, 20]. U. Patakhham et al. [18] reported that Al_3Sc particles also can act as nucleating particles for other intermetallic phases. The complex changes in the structure of the alloys after addition of Sc can be attributed to multi-modification effect [4].

However, there are no reports on the effect of Sc on grain refinement and eutectic modification of an Al–Mg–Si casting alloys. Thus, the main aim of the present study is to investigate the effects of Sc addition on the solidification behavior and morphology of Al5Mg2SiMn alloy.

2. Materials and methods

Alloys with nominal composition Al-5Mg-2Si-Mn with and without of addition of 0.65 wt.% Sc were studied. The chemical compositions was checked by the optical emission spectroscopy (OES) directly after each cast using SPECTROMAXx (Ametek, Germany) and represented in Table 1. All alloys were prepared in an electric resistant furnace using a graphite crucibles. As master alloys AlMg50, AlSi25, AlMn26, AlSc10 and high purity aluminum (A99.997 %) were used. The melt with the temperature $(720 \pm 5) ^\circ\text{C}$ was degassed under argon atmosphere during 10 minutes.

Samples for microstructure observations were prepared using conventional metallographic techniques. The metallographic specimens were examined in a SEM (MIRA 3XMH, FEG-SEM, TESCAN, Czech Republic) with Energy Dispersive Spectrometry systems (EDS). The chemical compositions of the phases were measured by quantitative EDX analysis at an accelerating voltage of 15 kV. For each phase five point analyses were conducted and the average values were taken.

Microstructural parameters such as the phase average size, secondary dendrite arm spacing (DAS), interlamella spacing (ILS) and the volume fraction of the phases were investigated and measured using ImageJ image analysis software. In order to obtain a statistical average of the distribution, a series of at least 10 micrographs

Table 1. Chemical composition of investigated alloys, wt.%.

Alloy	Si	Fe	Cu	Mn	Mg	Ti	Sc	Rest	Al
M59	1,90	0,02	0,02	0,53	4,86	0,05	-	0,06	Bal.
SC	1,96	0,03	0,03	0,55	4,92	0,05	0,65	0,08	Bal.

for each specimen were taken. Values of the volume fraction have been rounded to a larger integer.

A commercially available software package Thermo-Calc (TC) was used to perform thermodynamic and phase diagram calculations for multi-component systems, to investigate the possible effects of alloying elements on the equilibrium phases in the alloy, using the TCA12:Al-alloys v2.1 database. Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 404 instrument. During the DSC measurements, the samples were protected under an argon atmosphere with a flow rate of 75 ml/min. Measurements were taken in the temperature range from 20 to 750 °C at a heating rate of 5 K/min.

3. Results and discussion

The structures of the base alloy and after alloying by Sc are shown in Fig. 1. The structure of both of alloys has several phases, such as:

- α -Al solid solution (light-coloured fields);
- (α -Al)+(Mg₂Si) eutectic (dark, denoted 1);
- α -Al(Mn,Fe)Si phase (white, denoted 2);
- Sc-containing phase (white, denoted 3, 4, was found only in M59 + Sc samples);
- Mg₂Si primary crystal (black, denoted 5, was found only in M59 samples).

The predominant morphology of α -Al in alloys of Al-Mg-Si system is a dendritic structure with long primary arms (Fig. 1a–b). The (Al) + (Mg₂Si) eutectic has a lamellar morphology, where Mg₂Si plates nucleates on primary Mg₂Si crystals

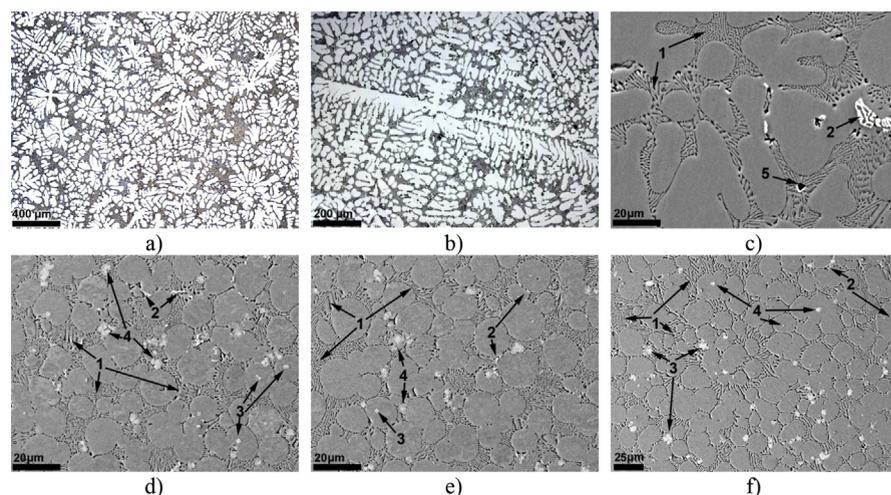


Fig. 1. General microstructure of Al-5Mg-2Si-Mn (a–c), and Al-5Mg-2Si-Mn-Sc (d–f) alloys in as-cast state (a, b – light microscopy images, c–f – SEM images).

(Fig. 1c). α -Al(Mn,Fe)Si phases have irregular, compact eutectic morphology [3, 16, 21].

Addition of Sc to the base alloy (M59) produces strong modification effect on all structural components of alloys:

- strong grain refinement effect, transforming Al grains from large dendrites (with arms from 100 μm to 500 μm) to small spheres (with diameter 10–30 μm) (Fig. 1);
- modification effect on eutectic lamellae, transforming them from plates into fine fibers (Fig. 2) which was observed on deep etched specimens. It also should be noted, that Sc addition change morphology of Al-Mg₂Si eutectic lamellae on the eutectic fibers arranged like a “cable harness” (Fig. 2).
- refinement and modification effects of Mn-containing phases that have been described in previous studies [16, 22].

Table 2 shows the grain size, the interlamellar space (ILS), size of the intermetallic phases and volume fraction of all phases in the investigated alloys.

The similar modification effect of Sc was described in the works [11, 19] for alloys of Al-Si and Al-Si-Mg systems. It was shown that addition of Sc modified irregular Al-Si eutectic into fine fibers.

In spite of the morphological difference caused by modification effect of Sc addition, the composition of the matrix of both alloys varies slightly (Table 3). The Mg content in solid solution measured in SEM using 15 kV acceleration voltage is 2.2–2.3 wt.%. The Mg distribution across the dendrite arm is not homogeneous and varies in the range from 2.0 to 2.5 wt.%. For all alloys the Mn content in α -Al solid solution is about 0.5 wt.%. The small Si content measured in case of EDX analysis obviously

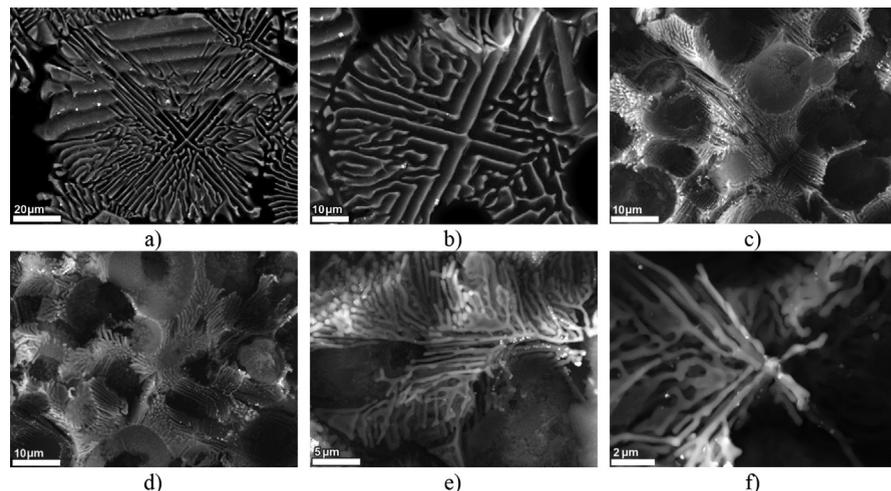


Fig. 2. Eutectic structure of Al-5Mg-2Si-Mn alloys a)–b) base alloy c)–f) alloy with 0,65 wt.% Sc.

Table 2. Results obtained from the image analysis.

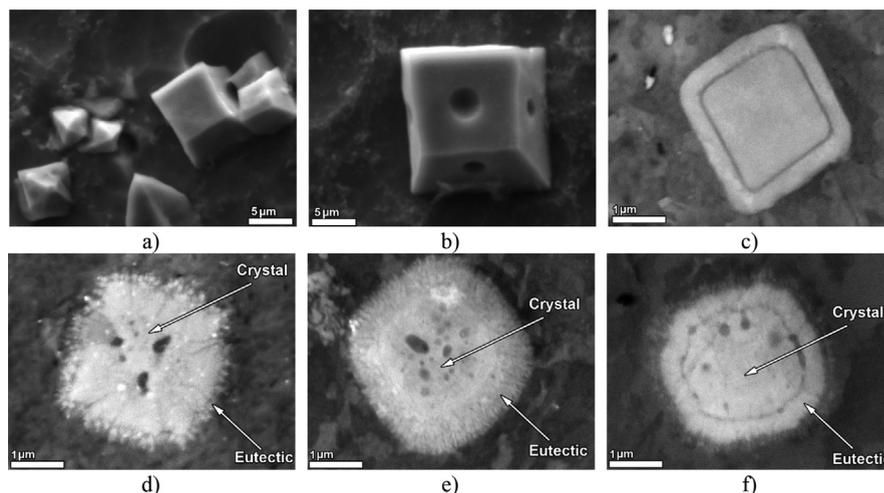
Alloy	Size and parameters of structure components, μm				Volume fraction, %			
	DAS	ILS	Size (thickness/length) $\alpha\text{-Al(Mn,Fe)Si}$	Size Al_3Sc	$V_{\alpha\text{-Al}}$	V_{eut}	V_{Mn}	V_{Sc}
M59	25.2 ± 5	2.1 ± 0.5	$1,1 \pm 0.3/7,2 \pm 2$	-	66	32	2	-
SC	12.4 ± 2	0.9 ± 0.2	$0,4 \pm 0.1/2,9 \pm 1$	2.2 ± 0.4	66	32	1	2

Table 3. EDX-analysis of $\alpha\text{-Al}$ grains of the alloys in as-cast state in wt. % (Al – bal.).

Alloy	Mg	Si	Sc	Ti	Mn
M59	2.2	0.3	-	0.1	0.5
SC	2.3	0.3	0.2	0.1	0.5
SC (after solution treatment)	2.2	0.2	0.4	0.1	0.5

originated from surrounding Mg_2Si lamellae or from those lying beneath the surface. The Si concentration in the $\alpha\text{-Al}$ grains of all alloys is about 0.3 wt%. The average composition of $\alpha\text{-Al}$ matrix for all samples is represented in Table 2. The solid solution of the alloy with Sc contains about 0.2 wt.% Sc. That is close to the solubility of Sc in Al. The remaining insoluble Sc constitutes with Al a stable phase Al_3Sc (Fig. 3).

The Al_3Sc particles can have a shape of octahedral, truncated octahedral and cube (solid (Fig. 3a) or hopper (Fig. 3b) morphology. Although it should be noted that the volumetric morphology of the Al_3Sc particles from Fig. 3a,b was found in an Al-2Sc alloy (the particles in Al-Mg-Si-Sc alloy after deep etching have not yet

**Fig. 3.** Morphology of Sc-containing phase in Al-2Sc alloy (a–c) and SC alloy.

been found). As it can be seen from Fig. 3(d–f) that Sc-containing particles in Al5Mg2SiMnSc alloy consist of two parts: “solid particle” with “micropores” (which suggests that the primary crystal has a hopper morphology) and very-fine fibrous eutectic (which hardly identified). The same results were shown by K. B. Hyde et al [23].

During solution treatment at 575 °C all Sc-containing particles decompose (Fig. 4) and partially dissolve in solid solution which lead to increase of Sc concentration in solid solution (Table 3). During process of decomposition of primary particles Al₃Sc dispersoids are formed.

A brighter particle, in the middle of the decomposed Al₃Sc particle, is visible in Fig. 4c. This particle according to EDX (Table 4) is an oxide. It was found only one such nucleation oxidic particle after decomposition of Al₃Sc phase due to its small size and close contrast to the Al₃Sc-phase. EDX analysis of this particle has a high amount of oxygen. Its composition consists of Al and Sc with a small amount of other elements (see Tab. 4), that allows us to conclude that this particle can be aluminum, scandium or complex oxides (such as Al₂ScO₄). K. B. Hyde reported that the Al₃Sc primary particles often nucleate heterogeneously on an aluminium, or Sc, oxidic particles floating in the melt [22]. Due to the fact that Sc forms a more stable oxide than aluminium, ($\Delta G_f(\text{Sc}_2\text{O}_3) = -1908.3 \pm 3.3 \text{ kJ/mol}$, $\Delta G_f(\text{Al}_2\text{O}_3) = -1675.5 \pm 1.3 \text{ kJ/mol}$ [22, 23]) it is possible to assume that the nucleating particles can be identified as Sc₂O₃. In this case Al which is appeared in the spectrum is from the matrix.

A lot of the Sc-containing particles were found in the middle of α -Al grains (Fig. 5a–c) as well as in the middle of the eutectic colonies (Fig. 5d–f). These particles, compared to those which were found in the eutectic zone, have similar average chemical composition (Tab. 4), and can be identified as Al₃Sc [9, 23].

It was reported [24] that eutectic reaction $L \rightarrow \alpha\text{-Al} + \text{Al}_3\text{Sc}$ at 655 °C with 0.38 wt.% Sc exists in Al side of Al-Sc binary system. In the current system (Fig. 6a) the eutectic reaction takes place at 591 °C and with concentration 0,12 wt.% Sc. With concentration 0,65 wt.% Sc the liquidus temperature rises to 730 °C. Fig. 6b

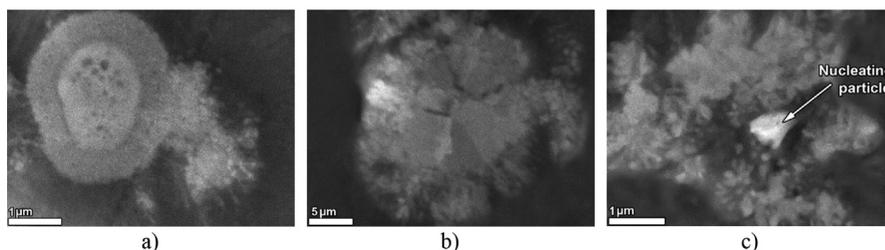


Fig. 4. Process of decomposition of Sc-containing phase during solution treatment at $T = 575 \text{ }^\circ\text{C}$ a) 30 min, b) 60 min, c) 90 min.

Table 4. EDX-analysis of Sc-containing particles in wt.%.

Sc-containing particles in:	O	Mg	Al	Si	Sc	Ti	Mn	Fe	Identified as
α -Al grains	0.9	1.2	70.5	0.3	24.0	2.7	0.3	0.1	Al_3Sc
Al- Mg_2Si eutectic	0.7	2.1	70.7	0.7	23.4	1.9	0.4	0.1	Al_3Sc
Oxidic particle (Fig. 4c)	39.6	1.8	38.1	0.2	19.1	1.2	-	-	Sc_2O_3

shows the calculated phase equilibria of the minor phases for the SC alloy. The major phases were liquid, Al-based FCC solid solution (the primary phase upon solidification). Amount of the Al_3Sc phase is near the same as $Al_{15}(Mn,Fe)_3Si_2$. Nevertheless, this amount is not enough to affect the thermal processes. The results of the DSC-

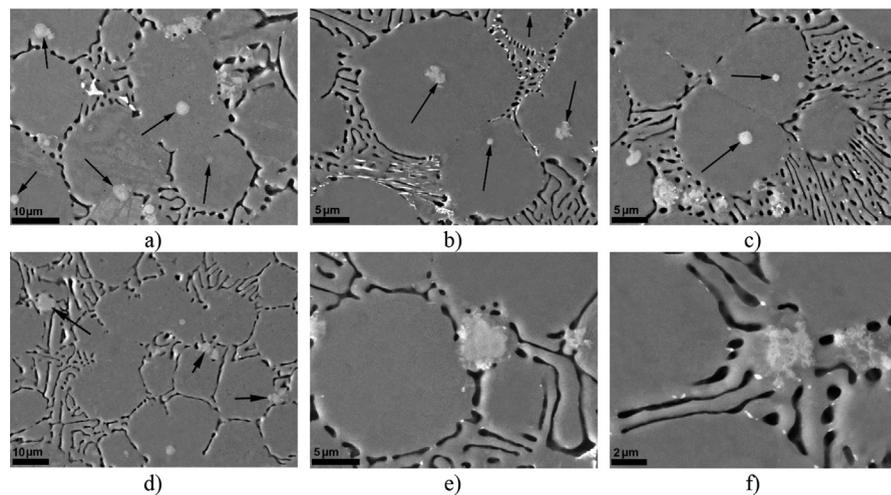


Fig. 5. Al_3Sc crystals as a nucleating particles of α -Al grains (SC) (a–c) and of Al- Mg_2Si eutectic (SC) (d–f).

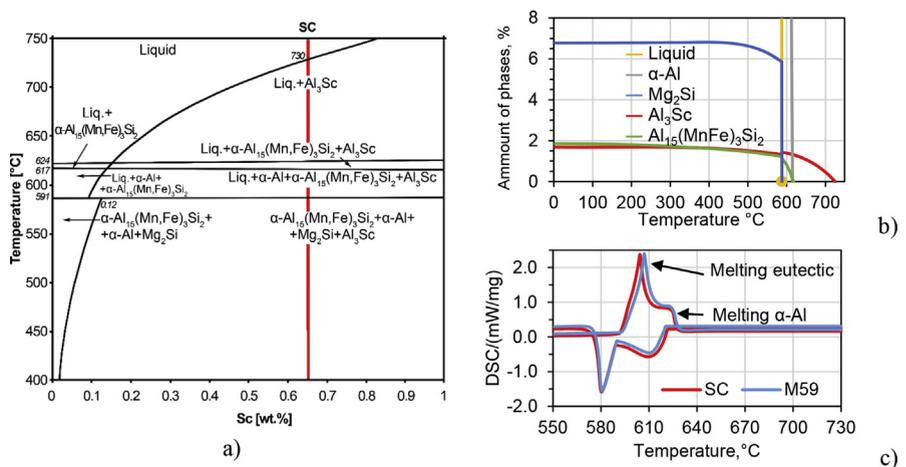


Fig. 6. Phase diagram of the proposed chemical composition $Al_5Mg_2SiMn + Sc$ (a); calculated phase equilibria (minor phases) for SC (b) and DSC-analysis of the investigated alloys (c).

analysis (Fig. 6c) show no changes during melting-crystallization processes after Sc addition to the base alloy.

According to the heterogeneous nucleation theory, the refinement of grain size of casting alloys is determined by the number and effectiveness of nucleating particles in melt. The effectiveness of the nucleating particle depends on the similarity in the lattice types and parameters of the nucleating particle and α -Al matrix [25]. It was reported [24, 25, 26] that with L12 type fcc lattice and $a = 0.4103$ nm, similar to that of α -Al ($a = 0.4088$ nm), Al_3Sc may serve as heterogeneous nuclei during solidification to refine the grain size in as-cast structure.

As it was reported earlier [16, 27] in hypoeutectic Al-Mg-Si alloys Mg_2Si lamella nucleate heterogeneously on primary Mg_2Si crystals. In case of present study we have not found any primary Mg_2Si crystals yet in alloy with Sc. Due to the facts that addition of Sc makes changes in diffusion processes, change energy on S-L interface during solidification that leads to changing structural components [8, 28], and also numerous Al_3Sc -particles detected inside of eutectic colonies it can be suggested that addition of Sc can inhibit the formation of Mg_2Si primary crystal and Al_3Sc particles act as heterogeneous nucleating particles of modified Mg_2Si eutectic fibrous.

4. Conclusions

The Al–Mg–Si alloy modified with Sc addition is studied and characterized.

Sc has the multi-modification effect on the microstructure of Al-Mg-Si casting alloys, including refinement of α -Al grains, modification of eutectic and refining of α - and β -(AlFeSi) phases.

The major grain refinement mechanism of primary aluminum with Sc addition is due to the heterogeneous nucleation. Thus, Al_3Sc can act as a substrate for α -Al grains and other intermetallic compounds (such as Mg_2Si), while the Al_3Sc particles are nucleated heterogeneously on oxide particles. Except nucleation, Sc produces modification effect on Mg_2Si eutectic which leads to the formation of a fine fibrous instead lamellae and “cable harness” instead eutectic colonies.

Declarations

Author contribution statement

Oleksandr Trudonoshyn: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Olena Prach: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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