Effect of ultrasonic treatment on formation of iron-containing intermetallic compounds in Al-Si alloys

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Abstract: Iron is generally regarded as an unavoidable impurity in Al-Si casting alloys. The acicular Al_3Fe and β-Al_5FeSi (or $Al_9Si_2Fe_2$) are common iron-containing intermetallic compounds (IMCs) in conventional structure which have a detrimental impact on the mechanical properties. In this paper, ultrasonic field (USF) was applied to modify acicular iron phases in Al-12%Si-2%Fe and Al-2%Fe alloys. The results show that the USF applied to Al-Fe alloys caused the morphological transformation of both primary and eutectic Al_3Fe from acicular to blocky and granular without changes in their composition. In the case of Al-Si-Fe alloys, ultrasonic treatment led to both morphological and compositional conversion of the ternary iron IMCs. When the USF was applied, the acicular β-$Al_9Si_2Fe_2$ was substituted by star-like α-$Al_{12}Si_2Fe_3$. The modification rate of both binary and ternary iron IMCs relates to the USF treatment duration. The undercooling induced by the ultrasonic vibration contributes to the nucleation of intermetallics and can explain the transformation effect.

Key words: ultrasonic treatment; Al-Si alloy; iron-containing intermetallics; modification

CLC numbers: TG146.21   **Document code:** A   **Article ID:** 1672-6421(2016)05-316-06

In general, iron is regarded as an unavoidable impurity in Al-Si cast alloys which is detrimental to the mechanical properties, especially the ductility [1]. Given that the solubility of Fe in liquid Al-Si alloys is high, it is natural that iron will interfuse into the melt from steel casting tools (e.g. de-slagging ladles and stirring lances) during the casting process. The solubility of Fe in solid Al-Si alloys is quite low, thus, a large amount of iron-containing intermetallic compounds (IMCs) will form in solidified structure as long as the iron content is above 0.7% [2, 3]. According to the Al-rich corner of the Al-Si-Fe phase diagram, iron-containing intermetallics include Al_3Fe (θ-phase), Al_8Si_2Fe (α-phase) and Al_5SiFe (β-phase) [4, 5]. Among those, Al_3Fe and Al_5SiFe phases are stable and always present in acicular shape, which has a poor bonding with the matrix, resulting in casting defects (e.g. shrinkage porosity) and a severe decrease in mechanical

properties (e.g. elongation) [6, 7]. It is therefore important to eliminate the harmful effect of the acicular iron-containing IMCs.

For the binary Al-Fe IMCs in the ternary Al-Si-Fe system, there is a simple eutectic reaction between α-Al and Al_3Fe under equilibrium conditions. It is well known that changes in cooling rate and alloy composition influence not only the size and distribution but also the type of Al-Fe IMCs [8-10]. During the non-equilibrium solidification, formation of $Al+Al_3Fe$ eutectic is suppressed by metastable $Al+Al_6Fe$ eutectic, with the conversion in the morphology of iron-containing constituent from acicular to granular. For this reason, rapid solidification is an optimal approach to modify the Al_3Fe phase. However, the industrial application of this method is limited by the difficulties in manufacturing equipment.

The ternary iron-containing IMCs appear in a great variety of shapes, among which the two most common phases have been designated as α-AlFeSi and β-AlFeSi. The α and β phases can be distinguished by the morphology and the Fe/Si ratio [11-14]. The β-phase only exhibits a needle shape, and is always denoted as Al_5SiFe or $Al_9Si_2Fe_2$, with a Fe/Si ratio of 1. By comparison, the α-phase appears in different

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shapes, such as Chinese script, fish bone, star or polygon. Its chemical formula is usually expressed as Al_8SiFe_2, $Al_{12}Si_2Fe_3$ or $Al_{20}Si_2Fe_5$, with a Fe/Si ratio of more than 1.5. In the conventional casting process, the α-AlFeSi is metastable, and only appears at some specific composition of Al-Si-Fe alloy. For other cases, it always converts to primary β-AlFeSi by a quasi-peritectic reaction, the β-AlFeSi therefore regularly presents in castings. Manganese is a common neutralizer, which can replace iron atoms without changing the crystal structure. With the addition of Mn, the hexagonal quaternary IMCs of compact shape are formed and the detrimental effect from acicular phase is reduced [15]. But the addition of manganese leads to an increase in the amount of IMCs, which is also harmful to Al-Si alloys' mechanical properties [16].

Therefore, it is very important to find a method to reduce the detrimental effect of both Al_3Fe and β-phase, without introducing new IMCs. Application of external fields is considered as a potential way to modify the iron-containing IMCs. It has been reported that physical fields, such as ultrasonic field (USF), and electromagnetic field, can refine the microstructure and modify secondary phases in Al-based alloys [17,18]. In the present work, the USF was applied during the solidification of Al-Fe and Al-Si-Fe alloys to study its influence on the iron-containing IMCs. By means of the microstructure evolution and changes in chemical composition, the effect of USF on the formation and conversion of iron-phases was investigated.

1 Experimental procedure

The alloys studied in this work, Al-2%Fe and Al-12%Si-2%Fe, were prepared from commercial purity Al (99.7%), pure Si (99.9%), and Al-20%Fe master alloy. All compositions quoted are in wt.% unless otherwise stated. The alloys were melted in a resistance furnace at 900 °C and held for 1 h in order to fuse thoroughly iron-compounds in the master alloy. After holding, the melt was transferred into a preheated cylindrical graphite crucible (60 mm in diameter and 80 mm in height) and the ultrasound was applied to the melt by the preheated ultrasonic probe, the temperature of which corresponded to the temperature of the melt. The ultrasonic treatment duration was 0 s, 60 s, 120 s and 300 s (until the melt was completely solidified). The detailed experimental parameters of USF treatment temperature are shown in Table 1. In addition, the whole process was performed in the air, but the graphite crucible was covered by asbestos felt to keep the treated Al melt in the designed temperature. After USF treatment, the melt was solidified under air cooling condition.

The ingots obtained in different experiments were 60 mm in diameter and 70 mm in height. Small samples taken from the cross-section of an ingot at 20 mm distance from the top were prepared for the microstructure observation by an optical microscope MEF-4A. The electron probe micro-analyzer (EPMA) was used to measure the chemical compositions of IMCs.

Table 1: Experimental parameters of USF treatment

Alloy	Treatment time	Initial temperature	Final
Al-2Fe	60 s and 120 s	720 °C	670 °C
Al-2Fe	300 s	720 °C	Solidification
Al-12Si-2Fe	60 s and 120 s	700 °C	650 °C
Al-12Si-2Fe	300 s	700 °C	Solidification

2 Results

2.1 Effect of USF on iron phase in Al-2Fe% alloy

Figure 1 shows the influence of USF on the microstructure evolution of iron-containing IMCs in the Al-2%Fe alloy. Without USF, the microstructure consists of coarse primary iron phase and eutectic $Al+Al_3Fe$ structure (Fig. 1a). Both primary and eutectic iron phases possess acicular shape (arrow 1) with the chemical formula Al_3Fe as concluded by the quantitative element analysis of EMPA (Table 2). When the USF is applied for 60 s, the Al_3Fe is refined. The morphology of primary Al_3Fe converts from acicular to blocky (Fig. 1b, arrow 2), but with little change in the composition. The amount of primary Al_3Fe phase, as well as the length and length-width ratio, decreases with prolonged duration of USF treatment. After treatment for 120 s, the primary Al_3Fe phase is further refined. However, the eutectic Al_3Fe phase still presents an acicular shape (Fig. 1c, arrows 3 and 4). It is a little difficult to distinguish primary and eutectic Al_3Fe phase due to their similar size. When the USF is applied to solidification (about 300 s), it is clearly observed in Fig. 1d that, the eutectic Al_3Fe is evenly distributed in the grain boundary of α-Al and completely refined to granular or short rod-like shape (arrows 5 and 6). The change of composition from Al_3Fe to $Al_{3.5}Fe$ (as listed in Table 2) is considered to result from the measured error, due to the similar size between the eutectic Al_3Fe phase and point analysis of EMPA (1 μm in dia.). The results of morphological analysis of iron-containing phases are presented in Fig. 2. It is clear that the size of primary Al_3Fe is obviously reduced with the USF treatment of any duration. On the contrary, the appearance of eutectic Al_3Fe changes greatly only in the case when the USF is applied for 300 s.

According to the aforementioned results and analysis, it can be concluded that the USF leads to morphological modification of the binary Al_3Fe phase without changing its composition.

2.2 Effect of USF on iron-containing phases in Al-12%Si-2Fe% alloy

The microstructure of the Al-12%Si-2%Fe alloy treated by the USF is shown in Fig. 3. The typical as-cast microstructure of the Al-12%Si-2%Fe alloy (Fig. 3a) consists of coarse acicular iron phases and Al+Si eutectic. When the USF is applied for 60 s, a number of star-like iron-containing IMCs appear in the microstructure (Fig. 3b). However, the acicular intermetallics are still present in the matrix, although their amount decreases with prolonged treatment duration, as shown in Fig. 3c. With the USF applied for 300 s, there is no acicular phase in the
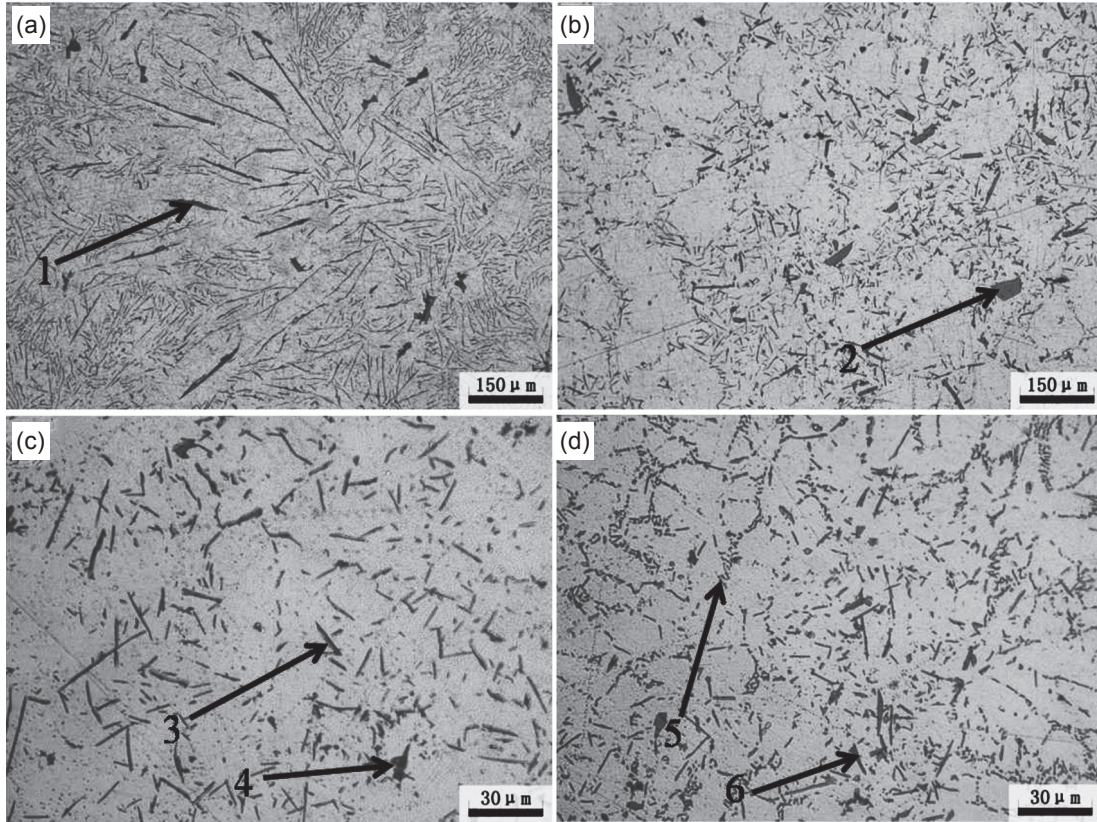
Fig. 1: Microstructures of Al-2%Fe alloy under USF with applied time of (a) 0 s, (b) 60 s, (c) 120 s (d) 300 s

Table 2: Composition analysis of iron phases by EPMA (at.%)

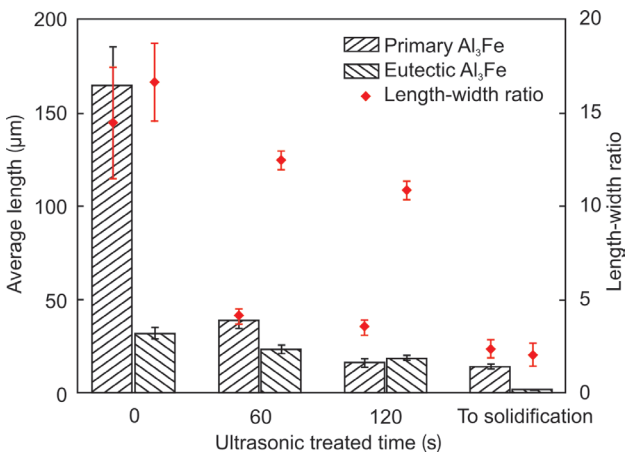| Point	Chemical composition		Chemical formula
	Fe	Al	
1	24.625	75.375	Al_3Fe
2	24.149	75.851	Al_3Fe
3	24.804	75.186	Al_3Fe
4	25.173	74.867	Al_3Fe
5	21.816	78.184	$Al_{3.5}Fe$
6	24.525	75.475	Al_3Fe

Fig. 2: Morphological analysis of iron-containing phases in Al-2%Fe alloy under USF

microstructure (Fig. 3d), only star-like iron-containing IMCs can be observed.

Figure 4 shows the morphological analysis of the iron-containing phases. It can be seen that the average length and length-width ratio of the iron-containing inclusions obviously decrease with the application of USF. Moreover, USF can change not only the morphology of iron phases, but also their composition. The average composition of iron phases measured by EPMA is listed in Table 3. The results indicate that the as-cast acicular iron phase is $Al_9Si_2Fe_2$, with no changes in the composition regardless of the USF treatment (as highlighted by the arrows 1, 2 in Fig. 3). In comparison, the star-like phase (as highlighted by the arrows 3–6 in Fig. 3) has a different composition and its chemical formula is $Al_{12}Si_2Fe_3$, corresponding to the α-AlSiFe as reported in the literature [12-14].

3 Discussion

As shown in Figs. 1 and 3, after the application of USF, both the primary and eutectic Al_3Fe are modified in Al-Fe alloy, and the metastable α-$Al_{12}Si_2Fe_3$ substitutes the stable β-$Al_9Si_2Fe_2$ in the Al-Si-Fe alloy. Furthermore, the modification rate increases with an increase in the USF applied duration.

The influence of USF on materials processing has been studied for several decades, and the cavitation is considered to be the most influential phenomenon of USF [19]. The cavitation is the formation, growth and immediate implosion of the cavitation bubbles in liquid, accompanied by a sharp increase in localized pressure to a peak value of 400 MPa [20]. According to the
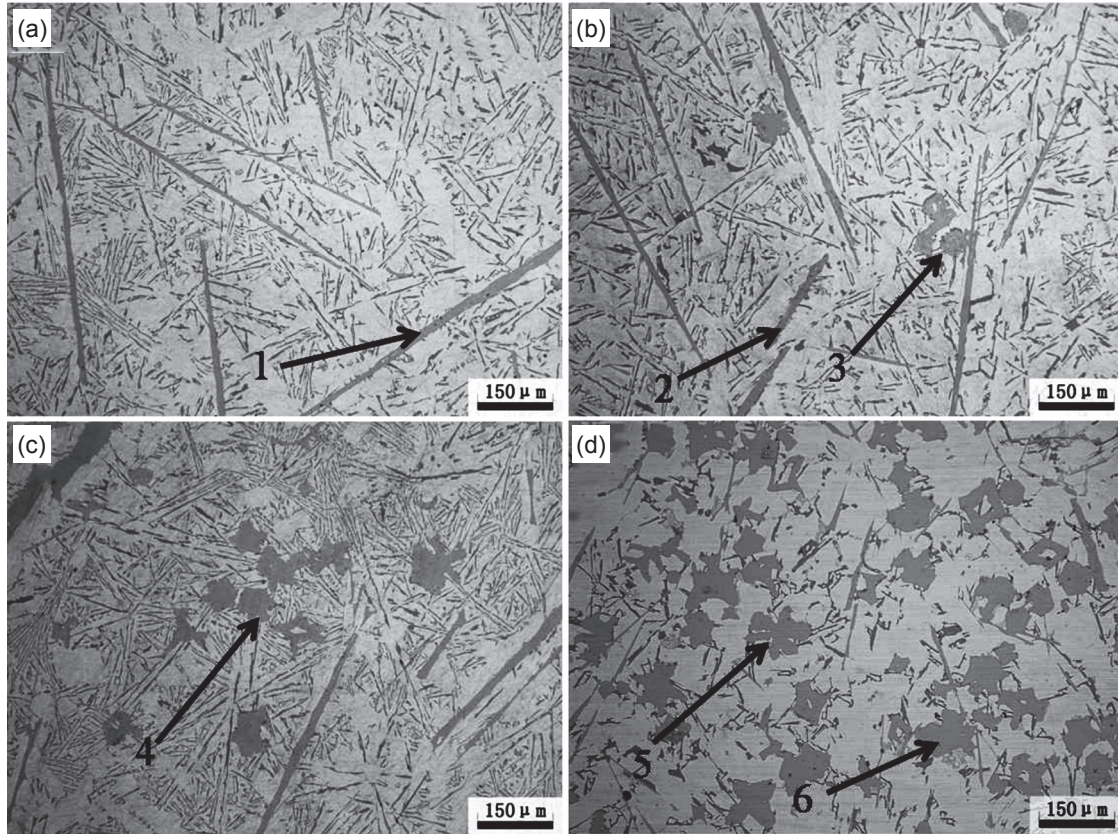
Fig. 3: Microstructures of Al-12%Si-2%Fe alloy under USF applied for (a) 0 s, (b) 60 s, (c) 120 s and (d) 300 s
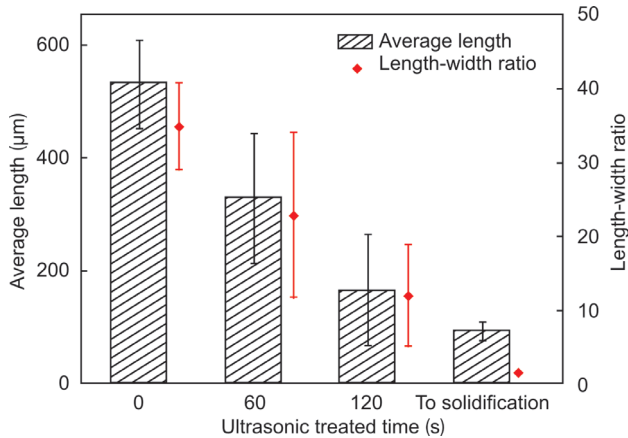

Fig. 4: Morphological analysis of iron-containing phases in Al-12%Si-2%Fe alloy under USF

Table 3: Composition analysis of iron phases by EPMA (at.%)

| Point | Chemical composition | | | Fe/Si | Chemical formula |
	Al	Fe	Si		
1	69.125	15.760	15.115	1.04	β-Al$_9$Si$_2$Fe$_2$
2	64.341	16.718	17.941	0.93	β-Al$_9$Si$_2$Fe$_2$
3	71.018	17.435	11.547	1.51	α-Al$_{12}$Si$_2$Fe$_3$
4	73.601	16.127	10.272	1.57	α-Al$_{12}$Si$_2$Fe$_3$
5	72.365	16.204	11.431	1.42	α-Al$_{12}$Si$_2$Fe$_3$
6	73.182	16.641	10.177	1.64	α-Al$_{12}$Si$_2$Fe$_3$

Clausius-Clapeyron equation, the increased local pressure will increase the local equilibrium melting point, suggesting that USF can bring about undercooling to the treated melts. In addition, the cavitation can clean the surface of insoluble inclusions and improve their wettability. The forced wetting of inclusions will increase the possibility of nucleation cores [21]. Thus, the application of USF can enhance not only the undercooling nucleation but also the heterogeneous nucleation.

In the case of the Al-2%Fe alloy, which is a typical binary eutectic system, occurrence of cavitation can lead to the formation of a large amount of nucleation sites in the melt for both, primary and eutectic Al$_3$Fe phases. When USF is applied for 60 s and 120 s, the corresponding temperature of the melt is about 670 ºC, which is lower than the liquidus temperature (685 ºC), but higher than the eutectic temperature (655 ºC), as shown in Fig. 5(a) of the Al-Fe binary phase diagram. The USF works in the liquid and the solid-liquid zone, during this duration only the nucleation of primary Al$_3$Fe happens, therefore, obvious modification of primary Al$_3$Fe can be observed in the corresponding microstructure. For the case of 300 s treatment, the temperature of USF termination was lower than the eutectic temperature, i.e., the application of USF lasts to the occurrence of the eutectic reaction. The eutectic structure is influenced by the ultrasonic cavitation induced nucleation. Thus, both primary and eutectic Al$_3$Fe are modified when USF is applied to solidification.

As for the ternary Al-Si-Fe system, the α-AlFeSi phase is metastable in the conventional casting process. It has been reported that the α-phase begins to crystallize at 751 °C and
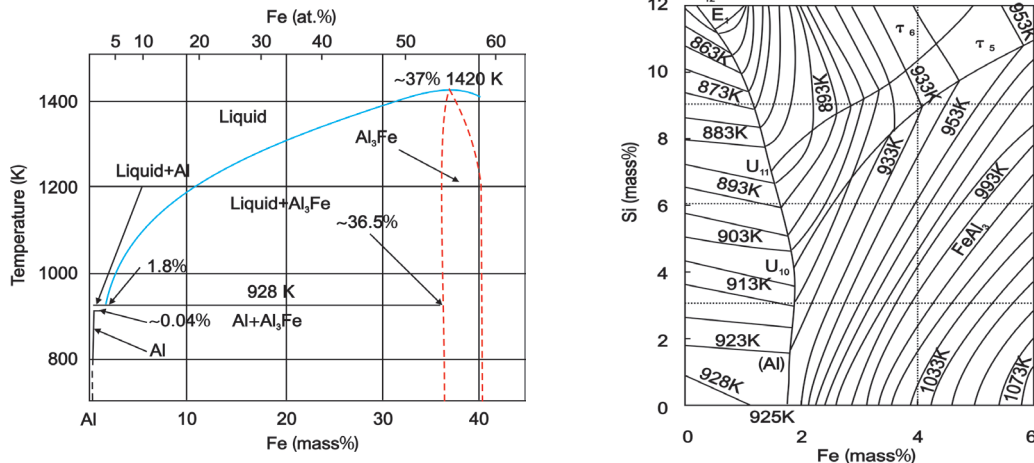
Fig. 5: In Al-rich region (a) Al-Fe phase diagram [22] and (b) liquidus surface of Al-Fe-Si [23]

continues to precipitate until the temperature drops to 628 °C. But it will convert to the primary β-AlFeSi phase by the quasi-peritectic reaction at 612 °C [4,12]:

$$\text{Liq.} + \alpha \rightarrow \text{Al} + \beta \qquad (1)$$

The formation of β-phase lasts till the Al-Si binary eutectic temperature of 577 °C. Hence, only acicular β-AlFeSi is presented in the solidification structure.

When USF is applied to the melt at 700 °C, the nucleation process of α-phase is promoted due to the cavitation-induced undercooling, and these nuclei then grow up. When the α-phase has grown to a certain size, its transformation to the β-phase is impeded due to lack of solute atoms in the surrounding melt. When the USF is applied for 60 s and 120 s, the treatment terminates at about 650 °C (which is higher than the liquidus of the Al-12Si-2Fe alloy as shown in Fig. 5b), and the size of the precipitated α-phase reached a critical value. These particles will therefore continue to grow to a star-like or blocky shape instead of the transformation into the acicular β-phase even without USF. At the same time, some of α-phase nucleated at the temperature range from 650 °C to 628 °C, grows without USF treatment and then participates in the quasi-peritectic reaction at 612 °C, resulting in the formation of acicular β-phase. Thus, both α-phase and β-phase can be observed in Figs. 3b and 3c. When the USF is applied for 300 s, i.e. till the melt solidifies, the improved effect of USF on the nucleation and growth of α-phase is persistent. In this case, most of iron atoms present in the melt are consumed and the growth of α- phase nuclei is facilitated while the transformation to β-phase is suppressed completely. For this reason, only star-like α-phase can be observed in the microstructure.

4 Conclusions

The influences of USF on the morphology and composition of binary and ternary iron-containing IMCs in Al-2%Fe and Al-12%Si-2%Fe alloys were studied, and the main findings can be concluded as follows:

(1) The application of USF leads to the morphological modification of both primary and eutectic Al_3Fe phases in Al-

2%Fe, with the relation of transition rate to the USF applied duration.

(2) The application of USF facilitates the formation of star-like α-$Al_{12}Si_2Fe_3$ phase and suppresses its conversion into the acicular β-$Al_9Si_2Fe_2$ phase in Al-12%Si-2%Fe alloy.

(3) The ultrasonic cavitation-induced undercooling facilitates the nucleation of iron phase, and is responsible for the morphological modification and phase transformation of iron-containing IMCs.

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