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Formation of Primary TiAlSi Intermetallic Compounds in Al-Si Foundry Alloys

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Abstract

It is common practice to add Ti to Al-Si foundry alloys because of its potential grain refining effect. However, an excess of Ti may cause the precipitation of primary TiAlSi coarse particles in the cast microstructure. The present paper describes work conducted to better understand the formation of primary TiAlSi compounds and the resulted cast microstructure. The precipitation temperature of primary TiAlSi intermetallics and the solubility limit of Ti in Al-Si alloys were investigated using thermodynamic calculation, metallographic examination and by LiMCA detection. The impact of the Ti level and cooling rate on the formation and growth of intermetallic particles was experimentally evaluated. The variation of the particle morphology and composition in the cast microstructure were described. The growth of TiAlSi intermetallics in a DC casting of alloy A356 was demonstrated by a decanting method.

1. Introduction

It is common practice to add Ti as an alloying element to Al-Si foundry alloys because of its potential grain refining effect. However, an excess of Ti may cause problems in the liquid metal process and defects in the casting [1], due to the precipitation of primary TiAlSi coarse particles above the liquidus temperature. Although there is ample information on the formation of TiAl intermetallics in the binary Al-Ti system mostly related to the grain refining mechanism, little published literature exists describing the formation and growth of TiAlSi intermetallics in widely used Al-Si foundry alloys.

1.1 Binary Al-Ti System.

The formation and growth of $TiAl_3$ intermetallics were studied in the binary Al-Ti system by various authors [2-8]. These studies mainly focused on the grain refinement capabilities of titanium aluminides. In its binary form, the alloy, composed of aluminum and titanium at the aluminum-rich part, presents a peritectic reaction at a composition of approximately 1.2% Ti and a temperature of 665°C ($L + TiAl_3 \Leftrightarrow \alpha$-Al). $TiAl_3$ intermetallics have an existence range of 36.5 to 37.5 wt.% Ti and a 3370 kg/m^3 density [9]. Because of the large difference of density with aluminum, $TiAl_3$ particles in liquid aluminum always tend to settle at the bottom.

The solubility limit of titanium in liquid aluminum is situated between 0.12 and 0.15%Ti, depending on the chosen reference [3,9].

It is reported that $TiAl_3$ intermetallics can have three different morphologies (flakes, petals and blocks) depending on the solidification conditions and the temperature history of the alloy [4,10]. Slow cooling from high temperature produces flakes. Rapid cooling and high thermal gradients form a petal-like shape. If the alloy is produced at a relatively low temperature and at a high Ti saturation, faceted blocky aluminides form, which may range from nearly cubic to long flat plates.

1.2 Ternary Al-Si-Ti System

Because of the excellent castability, Al-Si alloys are mainly used as foundry alloys for shape casting. It is common practice to add Ti up to 0.2 wt% in foundry alloys in order to promote the grain refining effect. At the aluminum-rich corner of ternary Al-Si-Ti system, three possible types of titanium aluminides could be present [11].

1. $TiAl_3$. Up to 15% Al can be replaced by silicon in $TiAl_3$ lattice structures, resulting in various chemical compositions and a range of lattice parameters [9]. It can be commonly written as $Ti(AlSi)_3$.
2. τ_1. Commonly written as $Ti_7Al_5Si_{12}$. This phase is stable below 900^{o}C.
3. τ_2. Commonly written as $Ti(AlSi)_2$. This phase forms at a higher amount of silicon and has an existence range from 46% to 38% Si.

Table 1 summarises the possible phases existing in the aluminum-rich corner. As each ternary phase has a range of chemical compositions and lattice parameters, this causes great difficulties for the identification of these ternary intermetallic phases. The morphology of TiAlSi intermetallics in Al-Si foundry alloys has been reported to be similar to $TiAl_3$ in binary alloy, i.e. flakes and blocks [12,13]. However, the favourite conditions under which either of these morphologies would form are still unknown.

In general, when dealing with titanium in Al-Si foundry alloys, limited information exists in open literature. Thus, it is of great interest to understand the precipitation behaviour of primary TiAlSi intermetallics from liquid metal. The aim of the present study is to investigate the formation of these particles using thermodynamic calculation, metallographic examination and by LiMCA (Liquid Metal Cleanliness Analyser) detection.

Table 1: Possible phases existing in the Al-rich part of the ternary Al-Si-Ti system [11].

Common Name	Phase ID	Structure Type	Chemical Range
$Ti(AlSi)_3$	$Ti(Al_{1-X}Si_X)_3$	$TiAl_3$ (tI8)	$0 \leq x \leq 0.15$
τ_1 or $Ti_7Al_5Si_{12}$	$(Ti_{1-x}Al_x)_8(Al_ySi_{1-y})_{16}$	$Zr_3Al_4Si_5$ (tI24)	$x \approx 0.12$, $0.06 \leq y \leq 0.25$
τ_2 or $Ti(AlSi)_2$	$Ti(Al_XSi_{1-X})_2$	$ZrSi_2$ (oC12)	$0.15 \leq x \leq 0.30$

2. Experimental

A batch of 5-20 kg of commercial purity aluminum was melted at 750-770°C and alloyed to the desired composition. Titanium additions were achieved using an Al-6%Ti master alloy. Three alloys were studied at different titanium contents ranging from 0.10 to 0.26% and their chemical composition is given in Table 2.

For the evaluation of the precipitation temperature of titanium aluminides, a melt quenching method was used. For each alloy, the metal was transferred into a small crucible (100 g) and placed into a furnace at 800°C. The furnace temperature was then gradually lowered to reach the desired temperature and the crucible was allowed to stabilise for five minutes. The crucible was then quenched directly into cold water to rapidly solidify the molten metal and prevent further particle precipitation. The quenched samples with different Ti contents were sectioned, polished and observed under optical microscopy to detect the possible presence of intermetallic particles.

For the determination of the impact of the Ti level and cooling rate on the particle quantity and morphology, the crucibles were left to solidify at different cooling conditions. Samples were also metallographically analysed to quantify the titanium aluminide particles. For the validation of the precipitation temperatures at various Ti levels, another method using LiMCA (Liquid Metal Cleanliness Analyser) detection [13] was employed.

Table 2: Chemical composition of the investigated alloys (wt.%).

	%Si	%Mg	%Ti	%Fe
Al-4.5%Si	4.5	0.35	0.1-0.26	0.1
Al-7%Si	7.0	0.35	0.1-0.26	0.1
Al-9.5%Si	9.5	0.35	0.1-0.26	0.1

3. Results and Discussions

3.1 Thermodynamic Calculation

Thermo-Calc [14] was used to predict TiAlSi intermetallic phase formation in Al-Si foundry alloys. Unfortunately, no thermodynamic data of ternary TiAlSi intermetallic phases is available. The data of the binary $TiAl_3$ phase was used instead. Figure 1 shows the predicted phase diagram of an Al-7.2%Si-0.36%Mg-Ti alloy, which has a typical chemical composition of commercial alloy A356. It can be seen that the liquidus temperature is 610^{o}C and the solubility limit of Ti is around 0.11 wt.%. When a molten A356 alloy with a certain Ti content of say 0.18 wt.% is cooled down to ~635^{o}C, primary $TiAl_3$ compounds will first precipitate. As the melt temperature continues to decrease to 610^{o}C (liquidus temperature), the α-Al dendrites start forming and growing and then Al-Si eutectic follows at 575^{o}C. The solidification ends shortly afterwards at 570^{o}C.

3.2 The Precipitation Temperatures

The precipitation temperature curves of titanium aluminides, experimentally obtained for three alloys, are presented in Figures 2 to 4 as a function of titanium content. Most results are validated using both melt quenching and LiMCA measurements. For comparison purposes, the precipitation temperatures predicted by thermodynamic calculation are also included in Figure 3 for Al-7%Si (A356 alloy). It is found that the calculated temperatures are much lower than the measured temperatures. The difference is probably due to the fact that there is a lack of thermodynamic data for ternary TiAlSi intermetallic phases calculations.

The precipitation temperatures of the titanium aluminide were found to be influenced by the titanium and silicon content of the alloy. As can be seen in Figures 2 to 4, as the titanium content of the alloy increases, so does the precipitation temperature. Also, as the silicon content is increased, the slope of the precipitation temperature curve is also increased.

Results also indicate that the solubility limit of titanium in liquid Al-Si alloys is around 0.10-0.11 wt.%. If the titanium level in the alloy exceeds the solubility limit, the primary TiAlSi intermetallics may form from the liquid metal. It is clearly seen that as the Ti level increases, primary TiAlSi intermetallic particles precipitate well above the liquidus temperature of the alloy and may be present at melt temperatures generally used in liquid processes and during casting. It becomes obvious that the titanium addition level plays an important role in the presence of such intermetallic particles as well as the particle quantity.

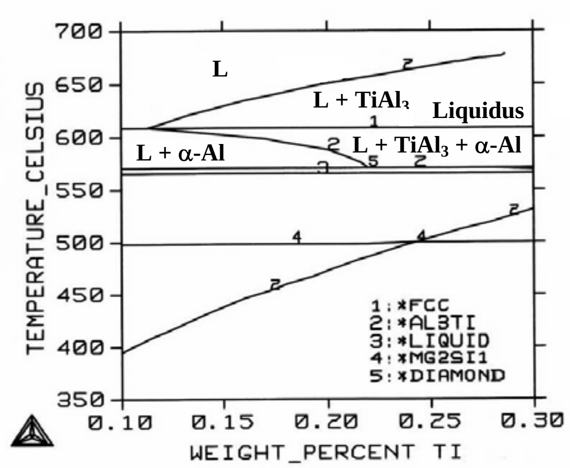

Figure 1: A calculated phase diagram of Al-7.2%Si-0.36%Mg-Ti (A356).

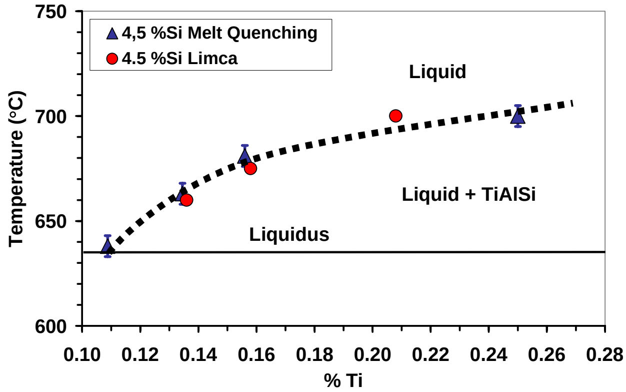

Figure 2: TiAlSi precipitation temperatures for Al-4.5%Si.

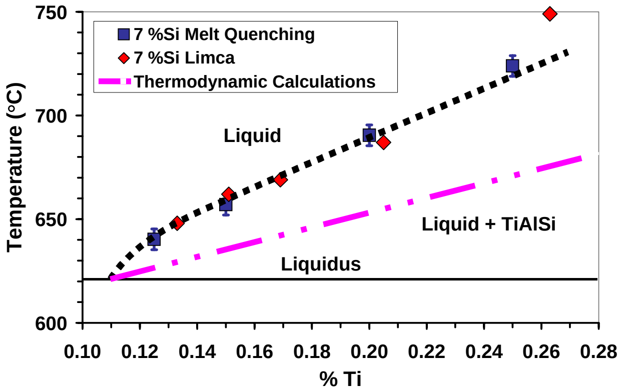

Figure 3: TiAlSi precipitation temperatures for Al-7%Si.

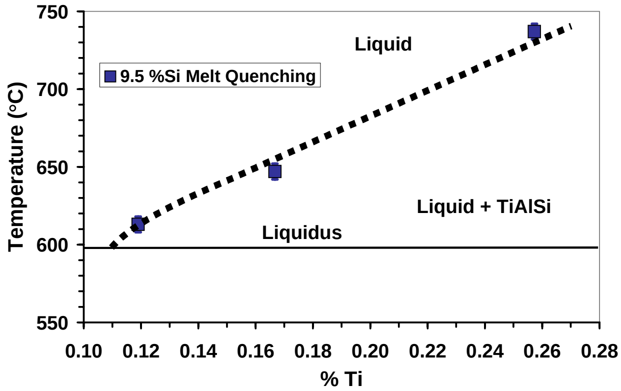

Figure 4: TiAlSi precipitation temperatures for Al-9%Si.

3.3 The Impact of Ti Level and Cooling Rate.

The effect of the titanium level and the cooling rate on the formation of TiAlSi particles has been evaluated for the Al-7%Si alloy (A356). As can be seen in Figure 5, for a fixed cooling rate, the size and density of particles increases with increasing titanium content. It is evident that as the cooling rate decreases the particles become larger. Because of the quick settling of the TiAlSi particles during holding and cooling, the density of the particles is different for the top, middle and bottom sections of the sample (Figure 6). It can also be seen that the formation of titanium aluminide particles can be suppressed at lower titanium levels using a high cooling rate.

3.4 The Phase Morphology and Type

In all the examined samples, most TiAlSi intermetallic particles had either a flake-like or a blocky morphology. On a rare occasion, a few petal-like particles were found in the cast microstructure. It is therefore reasonable to believe that the morphology of TiAlSi particles in ternary Al-Si alloys is similar to that of $TiAl_3$ in binary alloy, which was reported as having three distinct morphologies [10].

However, it is observed that although the particles can have the same morphology, they may have very different compositions. The back-scattered image and EDS detection of SEM revealed that the particles with the same morphology, mostly flake-like particles, may have completely different compositions. As shown in Figure 7 as an example, the brighter parts in the picture have high Si (~37 wt.%) and low Al (~10 wt.%) while the darker parts have low Si (~8 wt.%) and high Al (~40 wt.%) contents. This fact may suggest that several types of ternary TiAlSi intermetallics can co-exist in an as-cast structure. Using the EDS technique in SEM, the composition of a large number of particles of Al-7%Si alloy was quantitatively analysed. It is found that there are three types of ternary TiAlSi intermetallics with the following range of composition co-existing in the microstructure.

I. $TiAl_3$ type, Ti 36-37% - Al 52-54% - Si 9-11%

II. Low Si type, Ti 50-55% - Al 37-43% - Si 7-9%

III. High Si Type, Ti 50-55% - Al 5-15% - Si 35-39%

It is clear that the formation of titanium aluminides in the ternary system is complex and it is beyond the scope of this paper to identify the exact type and composition of the primary TiAlSi intermetallics. For this reason, the titanium aluminides in the microstructure are thus referred to as TiAlSi intermetallic particles.

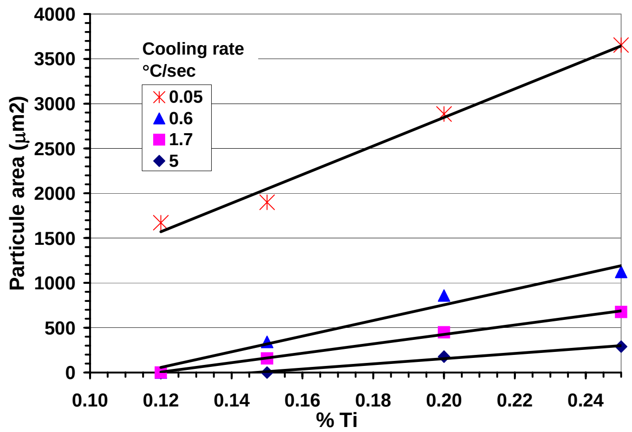

Figure 5: Effect of titanium level on particle size.

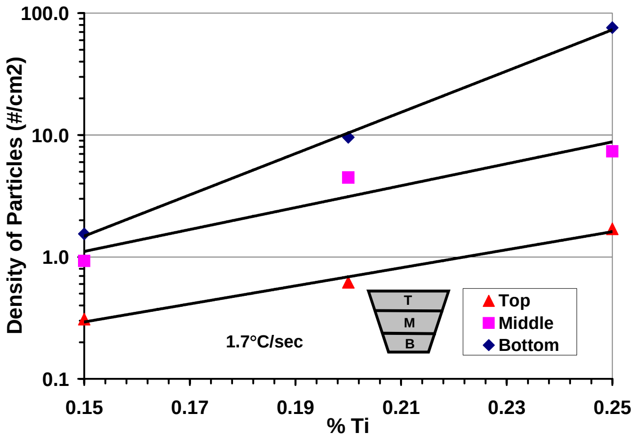

Figure 6: Effect of titanium level on particle density on different sections of the sample.

3.5 The Growth of TiAlSi Intermetallics in a DC Casting.

In continuous or semi-continuous DC casting of Al-Si alloys, it is observed that primary TiAlSi intermetallics tend to precipitate into a cooler location and then grow towards the liquid sump where titanium is supersaturated at certain melt temperatures. In a favourable condition, some intermetallic particles can reach up to several centimetres in length for an extended period of time. Such large and coarse particles can be revealed by decanting (Figure 8). Two distinct forms of particles are noticed in the cast structure. The blocky particles tend to form clusters and are often found inside and close to the wall where all intermetallic particles initially precipitated (Figure 9). In the direction towards the liquid sump, the dominating particles are flake-like (Figure 10), they continuously grow in an unidirectional manner and are prone to form a network with neighbouring particles. To characterise the particle morphology, 3-D views of these particles were taken under SEM. Figures 11 and 12 show the nature of both blocky and flake-like particles. For the blocky particles, the growth seems to be restricted to a certain size limit. Contrarily, the very large size of the flake-like particles, ranging between several millimeters to centimeters, may indicate that the growth will only interrupt when the intermetallic particles are starved of Ti in the liquid.

Figure 7: Back-scattered image of SEM showing flake-like particles with different compositions.

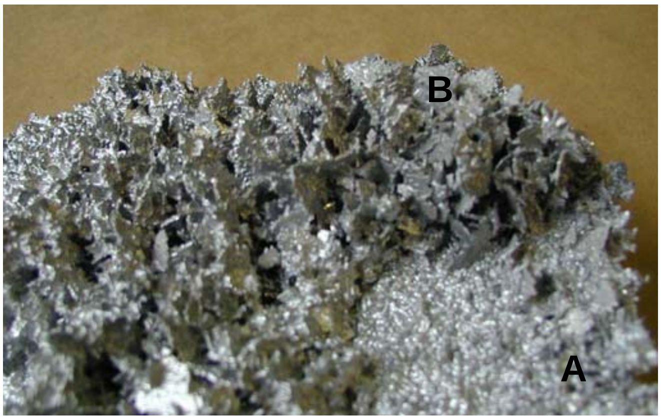

Figure 8: Macrograph of a decanted sample of A365 alloy (~1:5).

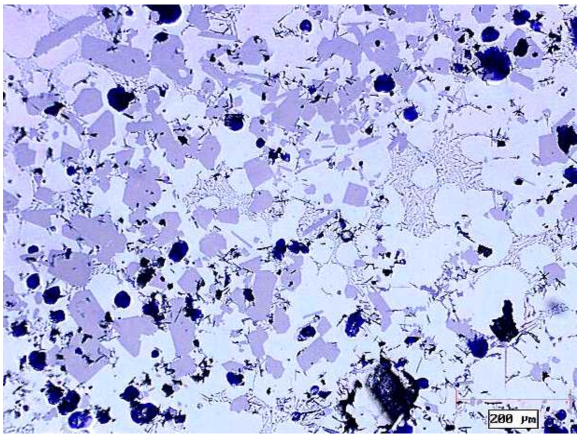

Figure 9: Blocky TiAlSi particles (location A of Figure 8).

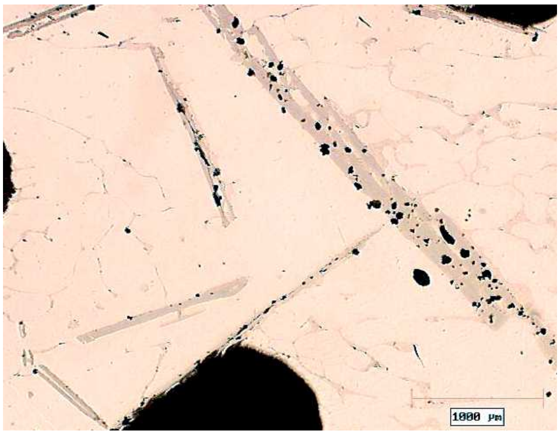

Figure 10: Flake-like TiAlSi particles (location B of Figure 8)

4. Conclusions

- The precipitation temperatures of primary TiAlSi intermetallics in three Al-Si foundry alloys have been determined using the melt quenching and LiMCA measurements.
- The formation of primary TiAlSi intermetallics takes place at higher temperatures as the titanium content increases. The slope of the precipitation temperature curve becomes steeper as the silicon content increases.
- The solubility limit of Ti in liquid Al-Si alloys is around 0.10 - 0.11 wt.%.
- The ternary TiAlSi intermetallics have three morphologies: flake-like, blocky and petal-like, which are similar to the binary $TiAl_3$ phase. It is found that several types of TiAlSi intermetallics with different chemical compositions can co-exist in the Al-Si foundry alloys.

- The growth of primary TiAlSi intermetallics in DC casting of Al-Si alloys has been demonstrated by decanting. The blocky and flake-like particle morphologies are the most common in the cast microstructure.

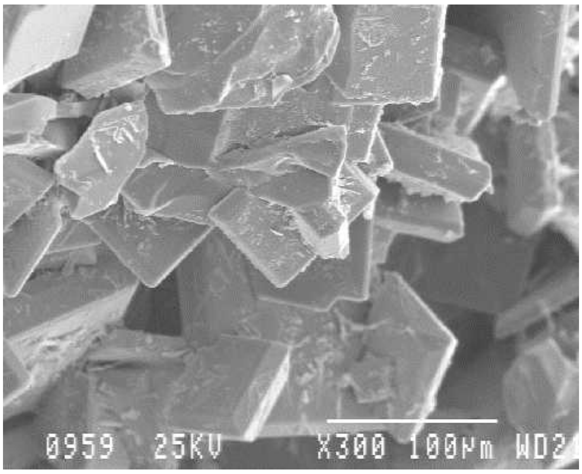

Figure 11: SEM micrograph showing a 3-D view of blocky particles from the decanted sample.

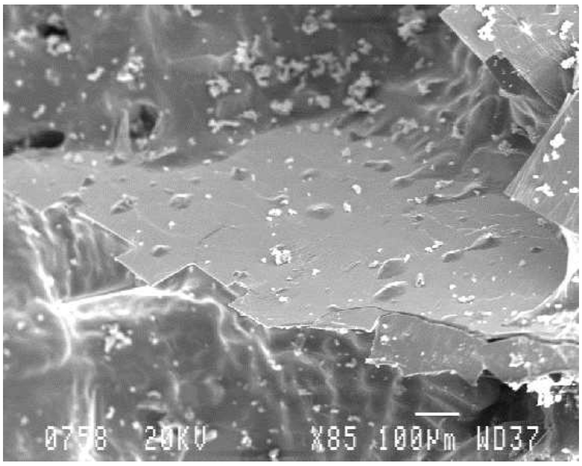

Figure 12: SEM micrograph showing a 3-D view of flake-like particles from the decanted sample.

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