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Effect of processing temperature on the microstructure of Al-7Ti master alloy and on refinement of α-Al dendrites in Al-7Si alloys

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ABSTRACT

The present work aims at evaluating the grain refining performance of Al-7Ti master alloys with different microstructures on Al-7Si alloys. Al-7Ti master alloys were prepared in an induction furnace by salt route involving the reactions between K_2TiF_6 and molten Al. Reaction temperatures chosen for producing Al-7Ti master alloys were 800^0C, 900^0C and 1000^0C while reaction time was kept constant at 60min..These indigenously prepared master alloys at different temperatures were characterized by chemical analysis; particles size analysis, XRD and SEM/EDX microanalysis. Results of particle size analysis suggest that mean size of Al_3Ti intermetallic particles in Al-7Ti master alloys were increased from 15.8µm to 22.4 µm as temperature is increased from 800^0C-1000^0C. SEM/EDX studies revealed fine blocky morphology, large blocky and flaky/petal morphologies of Al_3Ti intermetallic particles in Al-7Ti master alloys at 800^0C, 900^0C and 1000^0C respectively. Results of grain refinement studies suggest that, Al-7Ti master alloy prepared at reaction temperature of 800^0C shows better grain refinement performance on Al-7Si alloy when compared to the Al-7Ti prepared at 900^0C and 1000^0C. In future, the influence of reaction time on microstructural and grain refining behaviour of Al-7Ti master alloys will be evaluated and the performance of these Al-7Ti master alloys will be compared with Al-B and Al-Ti-B master alloys. Copyright © 2015 VBRI press.

Keywords: Master alloy; grain refinement; Al-7Si alloy; microstructure.

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Introduction

Grain refinement has been an important method for improving the soundness of aluminium products which produces fine, equiaxed grain structure after solidification **[1-5]**. In case of aluminium alloys, though there exists many new techniques of grain refinement, such as melt agitation and electromagnetic vibration, mould coating rapid solidification **[1, 6-8]** still adding grain refiners as nucleant (or inoculant) is the preferred method for refining **[9-11].** In aluminium and its alloys, grain refinement involves introducing Al-Ti, Al–Ti–B, Al-B master alloys into the melt **[12-14].** The addition of these master alloys introduces nucleating particles, which promote formation of a fine equiaxed structure by deliberately suppressing the growth of columnar and twin columnar grains **[1, 7, 14-15].** Presence of fine, equiaxed grains in Al and its alloys result in improved toughness, yield strength, excellent formability, good surface finish and improved

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machinability **[1, 6, 7, 15, 16].** The production of these master alloys involves addition of inorganic halide salts like potassium flourotitanate (K_2TiF_6) and/or potassium fluoborate (KBF_4) to molten Al at temperature excess of 700^0C **[17-19].** Much attention has been given to Al–Ti master alloys for the improvement of properties in Al alloys due to the fact that mechanism of grain refinement in aluminum by Al–Ti is clear which can be best explained by heterogeneous nucleation and peritectic theory. Due to which, in certain areas, Al–Ti master alloys having Ti content between 3-10% are used as an alternative to Al–Ti–B grain refiner **[20-23].** In spite of a vast amount of work in the field of Al grain refinement, the production of master alloys has received very limited attention. Much of the research efforts have been focused on the studying the effect of Ti/B ratio and the presence of other alloying elements on the performance of a master alloy, whilst less attention has been given to the possible effects of other processing parameters. It is believed that microstructure and performance of a grain refiner are known to be highly sensitive to the processing parameters used in the production of these master alloys **[13, 23-27]**. Recently, it has been reported that holding the master alloy melt at approximately at 750^0C for several hours after the salt reaction, produces master alloys having very good grain refining properties **[16].** Thus, processing parameters such as reaction temperature, time and composition were found to have a strong influence on the size, size distribution and morphology of the intermetallic particles present in these master alloys and inturn on the grain refining efficiency **[28-30].**

With this backdrop, the present work is undertaken to identify the role of reaction temperature (800^0C, 900^0C and 1000^0C) on the microstructural features such as morphology, size and distribution of Al_3Ti intermetallic particles present in Al-7Ti master alloy produced by salt route indigenously. However, few reports have been given to study the grain refining performance of Al-Ti master alloys with different microstructures on Al-Si alloy; still the influence of reaction temperature is not clear. The intention of the present study is to identify an efficient grain refiner for hypoeutectic Al-7Si alloy amongst all the Al-7Ti master alloys produced.

Experimental

Preparation of Al-7Ti master alloys

Al-7Ti master alloys were prepared in an induction furnace (M/s Cera-therm International, Bangalore) by the reaction of preheated halide salt of Ti [K_2TiF_6 as received from Madras Fluorine Pvt. Ltd. in the powder form (≤74μm)] and molten Al. The charge containing Commercial purity aluminium (99.7% purity, Hindalco, India) metal is heated to reaction temperature using an induction furnace containing neutral refractory lining. The furnace temperature was controlled to an accuracy of $\pm5^0$C using a digital temperature controller. Once the molten Al reaches the required temperature, the halide salt weighed in required proposition was added to the melt after preheating at 150^0C. The temperature at which salt addition is made is taken as reaction temperature. Three reaction temperatures were chosen namely 800^0C, 900^0C and 1000^0C, while the reaction time was kept constant at 60min. After completion of the reaction time the unspent salt is decanted and melts were poured into a split cylindrical graphite mould [Graphite India, Pvt. Ltd, Bangalore]. **Table 1** shows the chemical compositions of Al-7Ti master alloys prepared at different reaction temperatures, Al-7Si alloy and commercial purity Al used in the present study. Chemical compositions were assessed using Atomic Absorption Spectrophotometer (model AA-670, Varian, The Netherlands). The indigenously prepared master alloys were taken for grain refinement studies of Al-7Si alloy in order to assess their grain refining potency.

Table 1. Chemical compositions of the Al-7Ti master alloys prepared at different reaction temperatures and cast alloys used in the present study.

Alloy Code	Conditions		Composition (wt%)			
	Temp (^{0}C)	Time (min.)	Ti	Si	Fe	Al
860M70	800	60	6.75	0.13	0.15	Bal
960M70	900	60	6.22	0.13	0.14	Bal
160M70	1000	60	6.07	0.13	0.15	Bal
CPAl	-	-	-	0.09	0.11	Bal
Al-7Si	-	-	-	6.97	0.15	Bal

860M70; 1st digit temperature, 2nd and 3rd digit reaction time, M for master alloy, next digit -% of Ti and last digit -% of B. For eg. 860M70 is 800^0C-60min. Master alloy Al-7%Ti.

Grain refinement studies

Al-7Si alloy was prepared using commercial purity Al and Al-20%Si master alloy. Grain refinement studies of Al-7Si alloy have been carried out in a resistance furnace under a cover flux (45% NaCl + 45% KCl + 10% NaF) and the melt was held at 720^0C. After degassing with solid hexachloroethane (C_2Cl_6-Fenfee Metallurgicals Bangalore) master alloy chips were added to the melt for grain refinement. The addition level of the master alloy is being kept constant at 0.01%Ti. The melt is stirred for 30 seconds with zirconia coated iron rod after the addition of grain refiner, after which no further stirring is carried out. Parts of the melts were poured at regular intervals of 0, 2, 5, 30, 60, 120 and 120 min into a cylindrical graphite mould (25mm dia and 100 mm height) surrounded by fireclay brick with its top open for pouring. The sample designated as 0 min. refers to that part of the melt to which no grain refiner was added. Further, after 120 min. casting, the melt was stirred again with zirconia coated steel rod for a period of 10sec and poured into a cylindrical graphite mould and is designated as 120smin. Stirring after 120min. casting is carried out to study the settling of the intermetallic particles by the action of gravity.

Characterization of Al-7Ti master alloys particle size analysis

Al-7Ti Master alloys prepared by salt route are characterized for particle size analysis using image analyzer [METATECH (MIM-I), Pune inverted metallurgical microscope attached with ccd camera]. For optical microscopy the master alloy samples were cut to 5x10x5mm size. The cut samples were initially held on a belt grinder to achieve flat surface. Then the samples were polished on a series of water proof SiC emery papers with increasing grit size of 300, 600, 800 and 1000. Final

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polishing is carried out on a disc polisher using colloidal silica until a scratch free mirror finish surface was obtained. Polished samples were cleaned in hot water and alcohol, followed by drying and then studied under the microscope. The longest and shortest dimensions of the Al_3Ti particles were measured and the square root of their product was taken as the particle size. Total of 100 measurements were carried out for each master alloy at different locations to avoid any errors. Mean standard deviation and size distribution of the particles were obtained using statistical methods.

X-ray diffraction studies

X-ray diffraction studies were performed on Al-7Ti master alloys in order identify the different phases present in these master alloys. For XRD studies Al-7Ti master alloys prepared at 800^0C-60min., 900^0C-60min. and 1000^0C-60min. were selected in order to identify the second phase particles. For this purpose the master alloy samples were cut to 5x10x5mm in size and the similar polishing technique is employed as in the case of particle size analysis. XRD studies were carried out using a JEOL X-ray diffractometer using CoKα/CuKα radiation. The 2θ range was selected such that all the major intense peaks of the phases expected were covered.

Scanning electron microscopic (SEM) /energy dispersive x-ray (EDX) analysis

Analysis of microstructural features such as morphology, size, shape and distribution of intermetallic particles present in Al-7Ti master alloys were carried out using scanning electron microscope (JEOL, JSM 5800 and JSM 6380 Japan)/EDX microanalyser, 6380 LA, Japan). The machine is interfaced with link JED 2300 Analysis station software for EDX analysis. For SEM studies master alloy samples were cut to 5x10x5mm in size, polished using increasing grits of SiC papers and final polishing is done on disc polisher using colloidal silica. Later the samples were electropolished in an electrolytic bath comprising of 39% of orthophosphoric acid, 37% ethanol and 24% water by volume. The electropolished samples are etched using Keller's reagent (2.5%HNO_3+1.5%HCl+1%HF+95%H_2O) before SEM/EDX studies

Characterization of grain refined samples macroscopic studies

The castings with and without grain refinement were sectioned at a height of 25mm from bottom and the freshly cut surface of the bottom portion is taken for macroscopic studies. The sectioned surfaces so obtained were initially polished on a belt grinder and then on a series of SiC water proof emery papers with increasing grit size. Final polishing is done on a disc polisher using 75µm Al_2O_3 powder with water until a scratch free surface is obtained. The samples so obtained were etched by Poulton's reagent (30%HNO_3 + 30%HCl + 35%H_2O + 5%HF by volume) for about 30-45sec in order to develop the macrostructure. Finally the etched samples were washed in 1:1 HNO_3: HF solution to obtain the shining surface. The macroetched samples were directly scanned to computer using a scanner at a resolution of 600dpi for taking the macrophotographs. Macroscopy was performed on all the samples with and without grain refinement.

Secondary dendrite arm spacing (SDAS)

Measurement of Secondary Dendrite Arm Spacing (SDAS) in Al-7Si alloys is carried out using METAVISION Automatic Image Analyzer (Metatech, Pune) at a magnification of 100x. METAVISION is a semi-automatic image analysis system. The system uses a high performance CCD camera to provide direct imaging of the samples viewed with a microscope. Measurements were carried out for the Al-7Si alloys before and after the addition various Al-7Ti master alloys. The length and breadth of the secondary dendrites were obtained as an average of 100 readings horizontally and 100 vertically. SDAS is represented as square root of the mean product of the length and breadth readings obtained from vertical and horizontal intercepts.

SEM/EDX microanalysis

Microstructural evaluations of the grain refined samples were carried out by SEM/EDX X-ray microanalyser (JEOL, JSM-6380, Japan). For SEM studies, the grain refined samples were cut to a size of 5x10x5 mm. The samples were polished in the similar manner as in case of microscopic sample preparation. Polished samples were cleaned with soap solution, distilled water and ethyl alcohol followed with drying. The polished samples were etched using Keller's reagent having a chemical composition of 2.5%HNO_3+1.5%HCl+1%HF+ 95%H_2O by volume. The samples thus prepared were taken for SEM and EDX microanalysis.

Results and discussion

Ti recovery and particle size analysis

Table 2 shows the processing conditions used for the preparation of Al-7Ti master alloys and the associated Ti recoveries in each case. While preparing Al-Ti master alloys, an amount of K_2TiF_6 salt is added assuming 20% loss. The master alloys so prepared were analyzed for Ti and the recovery was calculated as below **[21].**

Table 2. The particle size analysis of Al_3Ti particles present in Al-7Ti master alloys prepared in an induction furnace at different reaction temperatures.

Alloy Code	Ti Pick up (%)	Ti Recovery (%)	Particle size <10µm (%)	Statistical Data Range in µm Min.	Max.	Mean particle size in µm
860M70	6.75	80.37	67.5	6.6	27.0	15.8
960M70	6.22	74.04	63.3	8.4	32.6	18.9
160M70	5.98	70.71	53.4	9.4	37.9	22.4

$$\% \text{ Ti Recovery} = \left[\frac{\%\text{Ti in the master alloy}}{\%\text{Ti added to prepare the master alloy}}\right] \times 100$$

The microstructural features of the Al-7Ti master alloys prepared at different processing conditions were first observed under metallurgical microscope and measurement

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of particle size analysis were performed using image analyzer. The technique used gives an idea of the size of the Al_3Ti particles in Al-7Ti master alloys. Statistical data obtained from particle size analysis are shown in **Table 2.**

It is clear from **Table 2** that the recovery of Ti in various Al-7Ti master alloy decreases with increase in reaction temperature from 800^0C-1000^0C. From **Table 2**, it is apparent that the Al-7Ti master alloys prepared at 800^0C-60min. shows higher Ti recoveries when compared to other reaction temperatures. However, the size of the Al_3Ti particles in binary Al-7Ti master alloys increases with increase in reaction temperature (from 800-1000^0C). The mean particle sizes of 15.8 μm, 18.9 μm and 22.4 μm were obtained in Al-7Ti master alloys at reaction temperatures of 800, 900 and 1000^0C respectively. Further, from **Table 2** it is also clear that the population of particles having sizes less than 10μm decreases with increase in reaction temperature. The population of finer intermetallic particles (<10μm) at 800^0C was 67.5% and is decreased to 53.4% at 1000^0C. It is believed that the reaction between molten Al and K_2TiF_6 is intense and exothermic in nature. The intensity of the exothermic reaction is further increased with increase in reaction temperature from 800^0C – 1000^0C and is possibly leading to loss of K_2TiF_6 salt thereby lower Ti recovery as well as increase in mean size of the intermetallic particles. These results are in good agreement with the results of Kori **[29]** obtained a Ti recovery of 83.33% during the preparation of Al-3Ti master alloy prepared at 800^0C-60min. Thus, the results clearly suggests with increase in reaction temperature the recovery of Ti in the prepared master alloy decreases also mean size of the intermetallic particle increases.

XRD analysis

X-ray diffraction patterns were obtained from Al-7Ti master alloys prepared at reaction temperatures of 800, 900 and 1000^0C with constant reaction time of 60min. and are shown in **Fig. 1a-c.** Indexing of the XRD peaks has shown the presence of α-Al and Al_3Ti phases. The phases observed in Al-7Ti master alloy are in confirmation with binary Al-Ti phase diagram. The reaction of K_2TiF_6 with the molten Al releases titanium into aluminium, which when crosses the solubility limit as decided by the Al-Ti phase diagram at the reaction temperature, Al_3Ti precipitates according to the Al-Ti phase diagram. The reaction between Al and K_2TiF_6 is expected to release Ti in the solid form according to the following reaction **[30].**

$$3K_2TiF_6 + 13Al \rightarrow 3Al_3Ti + 3KAlF_4 + K_3AlF_6 \text{ ----- (1)}$$

This reaction is expected to be at the interface of K_2TiF_6 particle and liquid Al. The Ti thus released is dissolved in liquid Al at the reaction temperature in the following way.

$$3Al + Ti \rightarrow Al_3Ti \text{ ---- (2)}$$

However, at higher reaction temperatures (900^0C and 1000^0C) decrease in relative intensities of the Al_3Ti peaks were observed as clearly seen in **Fig. 1b-c**. The decrease in intensities of peaks supports the decrease in Ti recovery with increasing temperature **(Table 2)**. Probably at higher reaction temperature the extent of exothermic reaction between molten Al and K_2TiF_6 is more intense and is expected to increase further during reaction and possibly leading to loss of K_2TiF_6 salt, thereby resulting in the lower recovery of Ti. Jonas **[31]** evaluated the heat of reactions between Al and K_2TiF_6 at reaction temperatures of 800^0C and 1000^0C, shown in **Table 3**. From **Table 3** it is clear that the heat of reaction between molten Al and K_2TiF_6 salt is more at a reaction temperature of 1000 ^{0}C when compared to the heat of reaction at 800^0C, which clearly reveals the intense exothermic nature of the reaction.

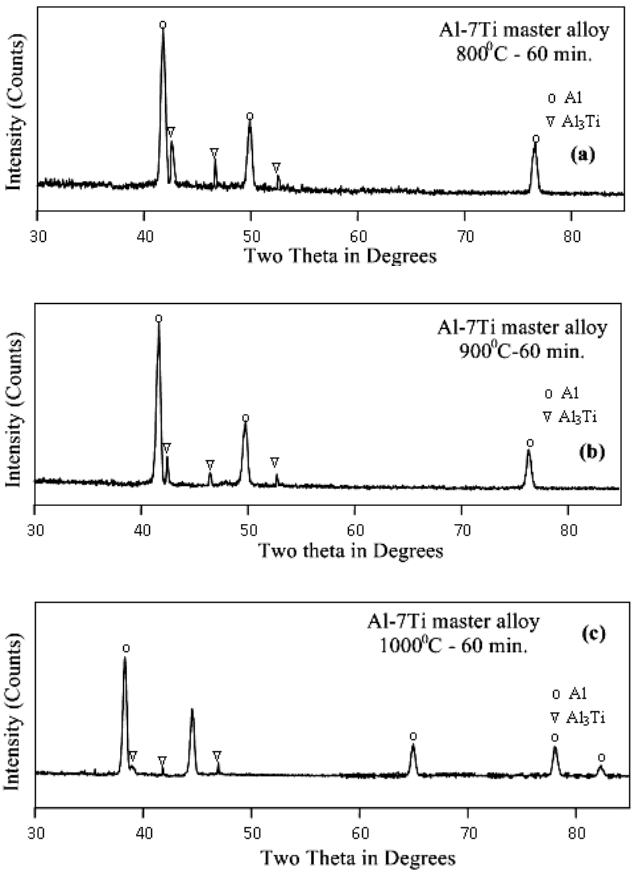

Fig. 1. X-ray diffraction patterns (using CoKα) of Al-7Ti master alloys prepared at (a) 800 ^{0}C-60 min. (b) 900 ^{0}C-60 min. and (c) 1000 ^{0}C-60 min.

Table 3. Evaluated heat of reactions between molten Al and K_2TiF_6 salt (Jonas, 2001).

Reaction / Temperature	$H_{Reaction}$ [J/mol]x10^{-5} 800^0C	$H_{Reaction}$ [J/mol]x10^{-5} 1000^0C
K_2TiF_6 addition to Al	-8.3	-9.2

Scanning electron microscope (SEM) and/EDX microanalysis

Table 4 shows the intermetallic particles present in various Al-Ti master alloys along with their morphologies.

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Table 4. Type and morphologies of intermetallic particles formed by the reaction of molten Al with K_2TiF_6 under different conditions in Al-7Ti master alloys prepared.

Processing Conditions ^{0}C-min.	Intermetallic particles	Morphology
800^{0}C-60min.	$TiAl_3$	Fine blocky Agglomerates/
900^{0}C-60min.	$TiAl_3$	Large blocky
1000^{0}C-60min.	$TiAl_3$	Flaky and petals

Fig. 2a-b shows SEM microphotographs of Al-7Ti master alloy prepared at 800^{0}C and with reaction time of 60min. showing the morphology and distribution of Al_3Ti particles. Blocky morphology of Al_3Ti particles is observed with a size range of 3 to 25µm and the confirmation of Al_3Ti particle is done through EDX which is shown in **Fig. 2c.**

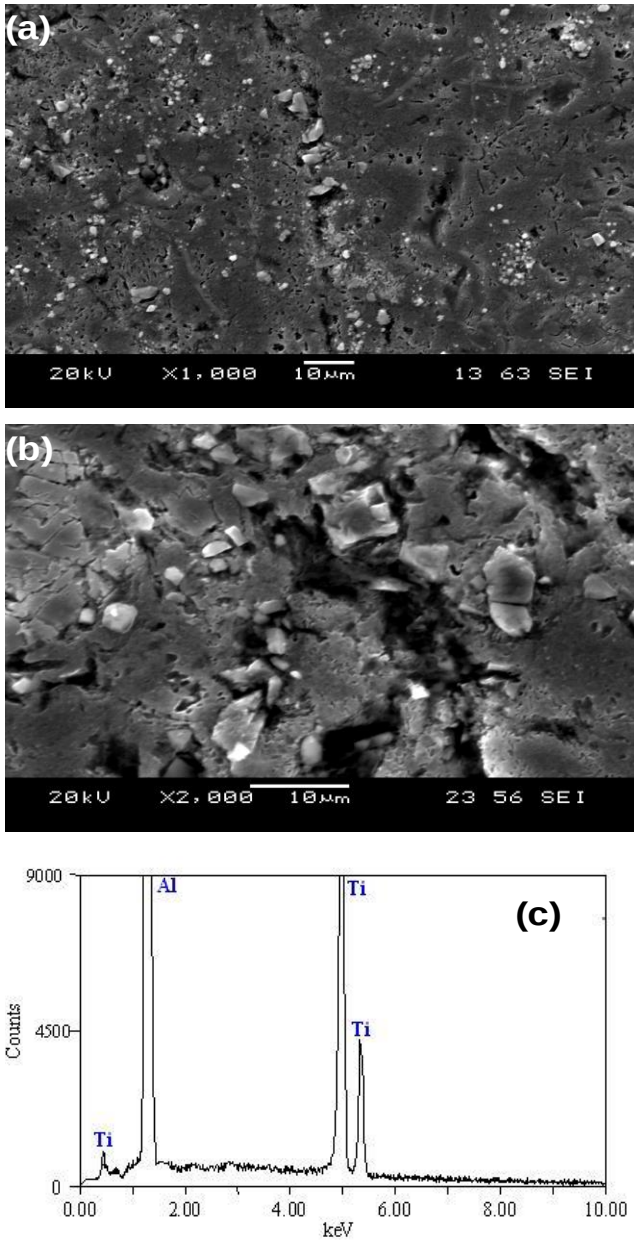

Fig. 2 a-b. SEM microphotographs of Al-7Ti master alloy prepared at 800 ^{0}C-60 min. (c) EDS spectrum of Al-7Ti master alloy.

From above figures it is clear that the processing conditions of 800^{0}C-60 min. have resulted in formation of relatively large number of blocky Al_3Ti particles with wide size ranges in Al-7Ti. Fair and uniform distribution of Al_3Ti particles observed is also evident from the microphotographs.

Fig. 3 a-d shows the SEM microphotographs of Al-7Ti master alloys prepared at reaction temperatures of 900^{0}C and 1000^{0}C with reaction time of 60min. Figures clearly revealed the changes in the morphology of Al_3Ti particles. Larger agglomerations of Al_3Ti particles were observed at 900^{0}C **(Fig. 3 a-b)** while flake like Al_3Ti particles were observed in case of Al-7Ti master alloy prepared at 1000^{0}C-60min. **(Fig. 3c-d)**. A possible explanation for the formation of blocky or flaky aluminides proposed by *Lee et al.* **[32]** is that, the blocky particles have a high volume/surface area ratio, suggesting that these particles were formed in the two-phase liquid + solid region of the phase diagram. In this region, the strain energy between the aluminide particle and the aluminium present as a liquid is of no relevance in determining the aluminide morphology.

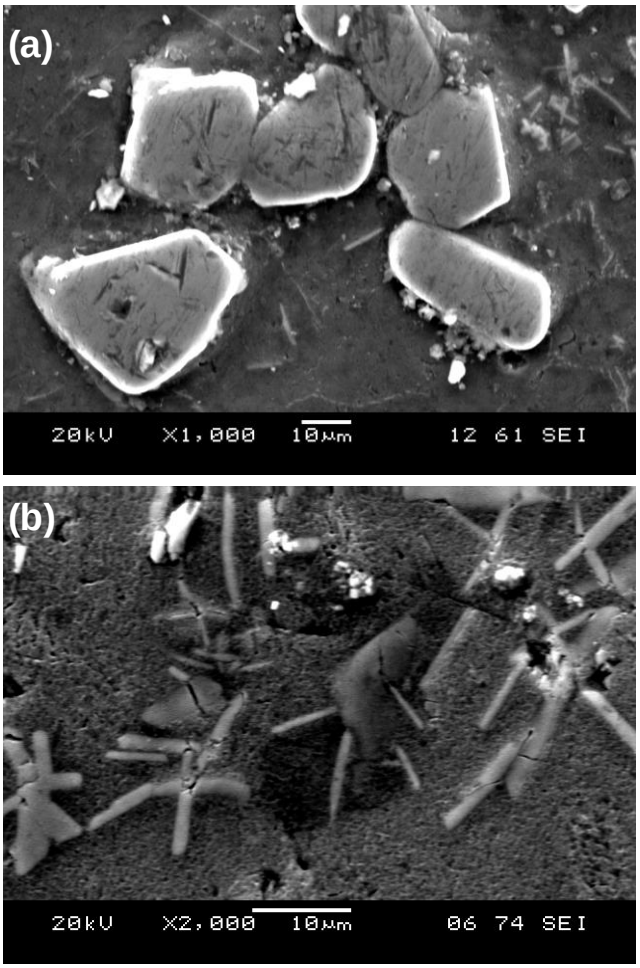

Fig. 3. SEM microphotographs of Al-7Ti master alloy prepared at (a) 900^{0}C-60min. showing the agglomerates/large blocky morphology of titanium aluminide intermetallic particles (b) 1000^{0}C-60min. showing the Flake/petal morphology of titanium aluminide intermetallic particles.

The aluminide particle will therefore grow so as to minimize its surface energy i.e low aspect ratio blocks will be formed. Therefore, it may be predicted that aluminide

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particles formed in the liquid + solid region of the phase diagram will adopt a blocky morphology. Al-Ti phase diagram reveals that at relatively low temperatures most of the alloy compositions are in this two-phase region. Flakes have a low volume/surface area ratio, suggesting that the growth of these particles has been influenced by strain energy considerations. A probable explanation is that the flakes are formed in the solid phase by precipitation from a supersaturated solid solution of titanium in aluminium. Thus, if an alloy solidifies from the single-phase liquid region, then the flaky particles will be expected to form, since if the cooling rate is sufficiently fast the liquid will solidify to give a supersaturated Al-Ti solution. Alloys, which falls, in the single-phase liquid region are generally those produced at high temperatures.

Therefore, it can be said that if the aluminide particles are produced in the two phase liquid + solid region then they have time to grow into blocks. On the other hand, for an alloy cooled from the single phase liquid region formation of $TiAl_3$ occurs quickly and flake morphology is observed. Thus, it is evident from SEM microphotographs that increase in reaction temperature has not only resulted in decrease of number of particles, also resulting in the change in morphology of Al_3Ti particles. In addition, processing temperature of 800^0C and reaction time of 60min. were suitable for complete reduction in K_2TiF_6 and formation of the Al_3Ti particles in an α-Al matrix without any constraint.

Grain refinement studies of Al-7Si alloy using Al-7Ti master alloys

The grain refining response of Al-7Si alloy towards indigenously developed Al-7Ti master alloys prepared at different reaction temperatures have been investigated by macroscopic studies, DAS analysis and SEM/EDX microanalysis. **Fig. 4a-c** shows the macrophotographs and **Fig. 5** shows DAS analysis of Al-7Si alloy before and after the addition of 0.01%Ti using Al-7Ti master alloys prepared under different processing conditions.

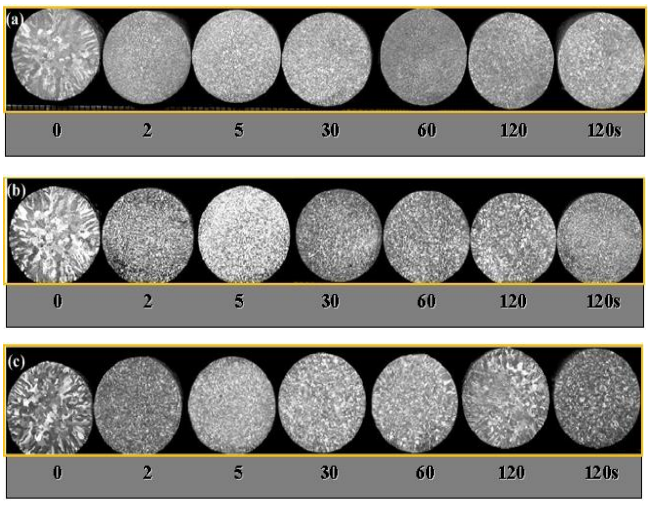

Fig. 4a-c. Macrophotographs of Al-7Si alloy before and after addition of (0.01%Ti) Al-7Ti master alloy prepared 800 ^{0}C-60 min., 900 ^{0}C-60 min. and 1000 ^{0}C-60 min., respectively.

From figures it is clear that Al-7Si alloy shows coarse columnar dendritic structure (0 min.) with a DAS value of 90μm, when no grain refiner was added to the melt. However, with the addition of 0.01%Ti using Al-7Ti master alloy, prepared at 800^0C-60 min., 900 ^{0}C-60 min. and 1000 ^{0}C-60 min., Al-7Si alloy has shown response towards grain refinement with structural transition from coarse columnar to equiaxed structure at shorter holding periods in all the cases. Such structural changes could be due to the presence of Al_3Ti particles present in the Al-7Ti master alloy, which acts as heterogeneous nucleating sites during solidification. However, on holding the melt beyond 30 min. (DAS of 71.4 μm) and 5min.(DAS of 71.3 μm), in case of Al-7Si with Al-7Ti master alloy prepared at 900^0C-60min. and 1000^0C-60min. respectively, the coarsening of the structure was observed suggesting fading/poisoning due to the settling/dissolution of the Al_3Ti nucleating particles present in Al-7Ti master alloys **[33].**

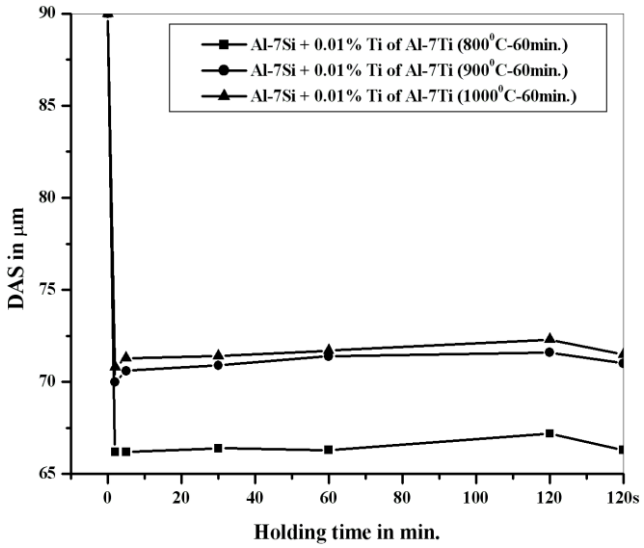

Fig. 5. Shows the DAS analysis of Al-7Si alloy grain refined with conventional addition level of (0.01%Ti) Al-7Ti master alloys prepared at different reaction temperatures.

The fading/poisoning effect can be observed from 120s min. sample, which resulted in equiaxed structure because of stirring for a period of 10sec. after 120min. pouring. Stirring after 120min. casting resulted in recovery of some of the settled Al_3Ti particles and these recovered Al_3Ti particles again taking part in the process of refinement by acting as nucleating sites which in turn lead to the equiaxed structure. However, an equiaxed structure in Al-7Si alloy was observed up to holding time of 60 min. (DAS of 66.2μm) with the addition of Al-7Ti master alloy prepared at 800^0C-60min. **(Fig. 4a)** beyond which grain coarsening was seen (DAS of 67.4μm). Stirring for period of 10 sec after 120 min. casting has resulted in decrease in DAS from 67.4μm to 66.2μm clearly suggesting the settling of nucleating particles present in the Al-7Ti master alloy. Therefore, present results suggest that Al-7Ti master alloy prepared at reaction temperature of 800^0C has shown better grain refining response on Al-7Si alloy compared to other two reaction temperatures with constant reaction time in all the cases studied. Such equiaxed structure achieved up to longer holding times could be due to the homogeneous

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distribution of wide size range blocky Al_3Ti particles as observed and discussed in SEM/EDX studies. These results are in good agreement with the results of Li et al. **[34]** and Arnberg et al. **[35].** Li et al. **[34]** suggested that the grain refinement effect is revealed to fade away markedly for master alloys with larger needle and blocky Al_3Ti crystals, while for the master alloy with finer blocky Al_3Ti crystals the effect did not fade away even at longer holding periods. Arnberg et al. **[35]** thought that blocky aluminides are probably more efficient nucleating sites than flaky and petal like crystals with their (011) surfaces providing suitable substrates on which the (012) planes of aluminium can nucleate. As blocky $TiAl_3$ particles are usually faceted, the number of faces on which aluminium can nucleate would be expected to be larger compared to plate like particles, which have a limited number of faces for nucleation. Further, according to stoke's law the settling behavior is influenced by the particle characteristics, size and density. The size of the intermetallic particles will impact on the settling rate and stoke's law predicts that larger particles settle more quickly than smaller particles **[35].** Blocky and needle like Al_3Ti particles have larger in size and because of their higher aspect ratio larger particles exhibit higher density and have greater tendency to settle at the bottom of the melt due to the action of gravity, while finer blocky Al_3Ti particles have smaller aspect ratio and higher tendency to stay in the melt and take part in nucleation events thereby obeying the stoke's law.

Fig. 6a shows SEM microphotographs of Al-7Si alloy in the absence of grain refiner (0min.). It is clear from **Fig. 6a** that the alloy solidifies with columnar dendritic structure in the absence of grain refiner with large eutectic Si needles/flakes at the grain boundaries of columnar α-Al dendrites. The addition of 0.01%Ti of Al-7Ti master alloy prepared at 800^0C-60 min. resulted in refinement of α-Al dendrites and converts them from columnar to fine equiaxed dendrites as evident from **Fig. 6b.** Such structural conversion from columnar to equiaxed dendrites is due to the presence of Al_3Ti intermetallic particles present in Al-7Ti master alloy, which acts as nucleating sites during solidification of α-Al. **Fig. 6c** clearly shows the presence of an unreacted Al_3Ti particle and an EDX spectrum **(Fig. 6d)** taken on the unreacted Al_3Ti particle clearly revealing Ti and Al peaks thus confirming the particle to be Al_3Ti. **Fig. 6e** shows SEM microphotographs of Al-7Si alloy grain refined with 0.01%Ti using Al-7Ti (800^0C-60 min.) master alloy at holding time of 120 min. Fig. clearly shows the mixture of coarse and equiaxed structure which are in good agreement with DAS results **(Fig. 5).** The mixture of coarse and equiaxed structure clearly points out the fading phenomena and poisoning effect of Si. On longer holding the melt, some of the blocky Al_3Ti particles which are introduced in the melt tend to settle at the bottom due to the action of gravity and among rest, some of the Al_3Ti particles will probably react with Si from melt thereby becoming less potent nucleating sites for Al. Work on Al-Si-Ti phase diagram has shown strong interaction between Si containing Al melt and the Al_3Ti particles. Therefore, at longer holding periods with conventional additional level of Al-7Ti master alloy, only few particles are available for nucleating action thereby resulting in mixture of equiaxed and columnar structure.

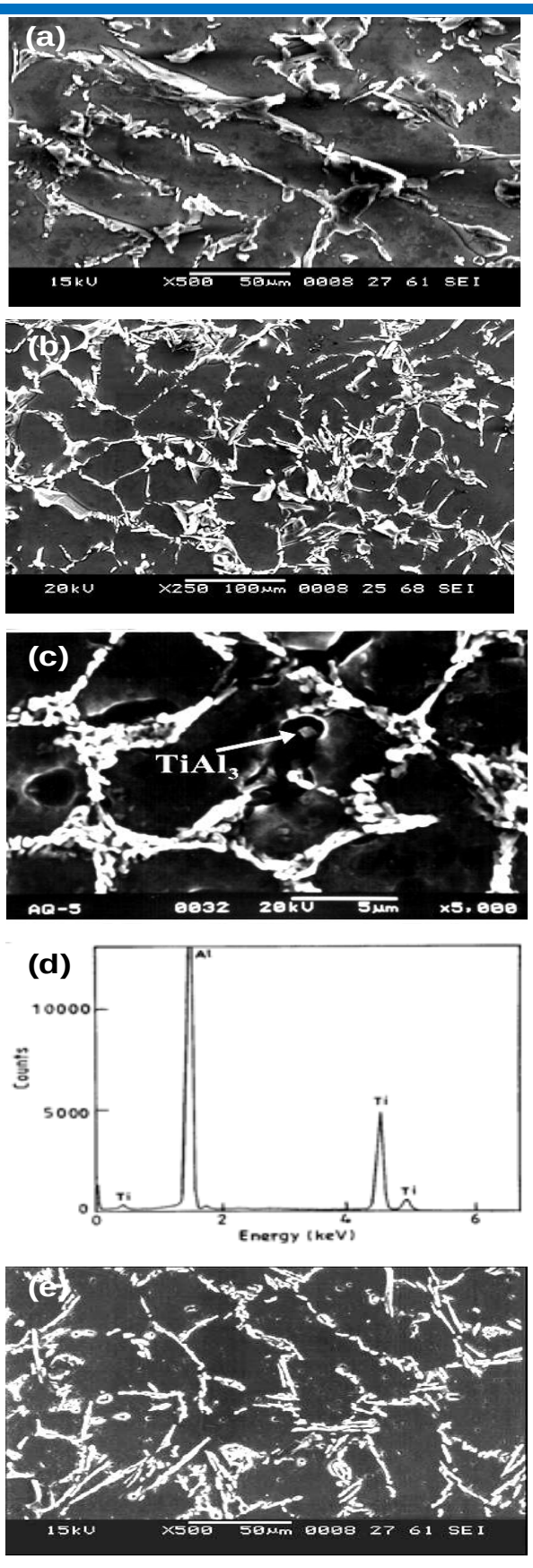

Fig. 6. SEM microphotographs of Al-7Si alloy (a) without grain refiner (b) with 0.01%Ti of Al-7Ti prepared at 800^0C-60 min. (c) unreacted Al_3Ti particle at the centre of the α-Al dendrite (d) EDX spectrum on Al_3Ti particle showing Al and Ti peaks (e) showing mixture of coarse and equiaxed grain structure at a holding time of 120min.

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Conclusion

The present work on effect of processing temperature on the microstructure and grain refining behavior of Al-7Ti master alloy has led to following conclusions. Reaction temperature used for processing master alloy has greater effect on size, size distribution and morphology (shape) of the intermetallic nucleating particles (Al_3Ti) present in the Al-7Ti master alloys. Processing temperature of 800^0C has resulted in higher population of intermetallic particles having sizes less than 10µm (67.5%) when compared to other two processing temperatures i.e 900^0C (63.3%) and 1000^0C (53.4%). At reaction temperature of 800^0C, fine blocky morphology of Al_3Ti particles while at 900^0C and 1000^0C large blocky/agglomerates and flake/ petal morphologies of Al_3Ti intermetallic particles were observed in Al-7Ti master alloys. Further, minimum DAS of 66.2µm upto holding time of 60 min. was obtained in Al-7Si alloy when grain refined with (0.01%Ti) Al-7Ti master alloy prepared at 800^0C compared to the addition of same master alloy prepared at 900^0C (71.4 µm upto 30 min.) and 1000^0C (71.3 µm upto 5 min.). Stirring of the melt after 120 min. casting has led to decrease in DAS of Al-7Si alloy (120s min.) clearly brings out the fact that agitation of the melt after prolonged holding will result in recovery of some of the nucleating particles which are settled due to the action of gravity. However, in future by studying the influence of reaction time, optimizing the addition level for complete grain refinement these master alloys can be made suitable for mass production for the benefit of Al industries.

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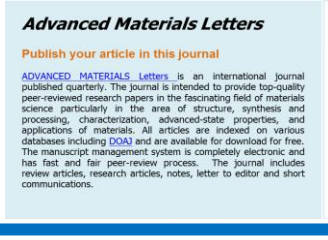
Reference

1. Murty, B. S.; Kori, S. A.; Chakraborty, M., *Int. Mater. Rev.*, **2002,** *47*, 3. **DOI:** 10.1179/095066001225001049
2. Cahoon, J. R.; Tandon, K. N.; Chaturvedi, M. C.; *Metall. Trans. A*, **1992**, *23A*, 3399. **DOI:** 10.1007/BF02663452
3. Krishnamurthy, S.; Khobaib, M.; Robertson, E.; Froes, F. H. *Mater. Sci. Eng.*, **1998**, *99*, 507. **DOI:** 10.1016/0025-5416(88)90386-2
4. Houshang, D. Alamdari.; Dominique, Dube.; Pascal, Tessier, *Met. and Mater. Trans A.*,**2013,** *44A*, 388. **DOI:** 10.1007/s11661-012-1388-x
5. Zongning, Chen.; Tongmin, Wang.; Lei, Gao.; Hongwang, Fu.; Tingju, Li., *Mater. Sci. and Engg. A*, **2012,** *553*, 32. **DOI:** 10.1016/j.msea.2012.05.088
6. McCartney, D. G. *Int. Mater. Rev.*, **1989,** *34*, 247. **DOI:** 10.1179/imr.1989.34.1.247
7. Cibula, A., *J. Inst. Met.*, **1949,** *76*, 321.
8. Reddy, N. S.; Prasada, Rao. A. K.; Krishnaiah J. ; Chakraborty, M.; Murty, B. S., *J. Mater. Eng. Perform.*, **2013**, *22(3)*, 696. **DOI:** 10.1007/s11665-012-0334-9
9. Spassove T, Rangelova V, Neykov N, *J. Alloys Comp*, **2002,** *334*, 219. **DOI:** 10.1016/S0925-8388(01)01745-5
10. Zhang, M. X., Kelly, P. M., Easton, M. A., Taylor, J. A., *Acta Materialia*, **2005,** *53(5)*, 1427. **DOI:** 10.1016/j.actamat.2004.11.037
11. Xiaowu HU, Fanrong A.I and Hong. YAN, Acta *Metall. Sin. (Engl. Lett.)*, **2012**, *25(4)*, 272. **DOI:** 10.11890/1006-7191-124-272
12. Tongmin, Wang.; Zongning, Chen.; Hongwang, Fu.; Lei, Gao.; Tingju, Li., *Mater. Sci. and Engg. A*, **2012,** *549*, 136. **DOI:** 10.1016/j.msea.2012.04.019
13. Ömer, Savas.; Ramazan, Kayikci., *J. Alloys Comp.*, **2013,** *580*, 232 **DOI:** 10.1016/j.jallcom.2013.05.112
14. Birol, Y., *Mater. Sci. Technol.*, **2012,** *28(3)*, 363. **DOI:** 10.1179/1743284711Y.0000000041
15. Easton, M.; St. John D. *Met. and Mater. Trans A.*, **1999**, *30A*, 1613. **DOI:** 10.1007/s11661-999-0098-5
16. Birol, Y.; *J. Alloys Comp*, **2006**, *420*, 207. **DOI:** 10.1016/j.jallcom.2005.11.010
17. Tongmin, Wang.; Hongwang, Fu.; Zongning, Chen.; Jun, Xu.; Jing, Zhu.; Fei, Cao.; Tingju, Li.; *J. Alloys Comp.*,**2012,** *511*, 45. **DOI:** 10.1016/j.jallcom.2011.09.009
18. Wang, Jun.; He, Shuxian.; Sun, Baode.; Guo, Qixin.; Nishio, Mitsuhiro. *J. of Mater. Proces. Technol.*, **2003,** *141*, 29. **DOI:** 10.1016/S0924-0136(02)01007-5
19. Yuan, Liu.; Chao, Ding.; Yan-xiang, Li. *Trans. Nonferrous Met. Soc. China*, **2011,** *21*, 1435. **DOI:** 10.1016/S1003-6326(11)60878-9
20. Wanwu Ding.; Tiandong, Xia.; Wenjun, Zhao, *Materials*, **2014**, *7*, 3663. **DOI:** 10.3390/ma7053663
21. Sergio, Haro-Rodríguez.; Rafael, E. Goytia-Reyes.;, Dheerendra, Kumar. Dwivedi.; Víctor, H.; Baltazar, Hernández,; Horacio, Flores-Zúñiga.; María, J. Pérez-López., *Mater. Des.* **2011**, *32*, 1865. **DOI:** 10.1016/j.matdes.2010.12.012
22. Chu, M. G. *Mater. Sci. Engg.*, **1994**, *A179-180*, 669. **DOI:** 10.1016/0921-5093(94)90290-9
23. Murty, B. S.; Kori, S. A.; Venkateswralu, K.; Bhat, R. R; Chakraborty, M. *J. Mater. Process. Technol.*, **1999**, *89-90*, 152. **DOI:** 10.1016/S0924-0136(99)00135-1
24. Greer, A. L.; Cooper, P. S.; Meredith, M. W.; Schneider, W.; Schumacher, P.; Spittle, J. A.; Tronche A. *Adv. Eng. Mater*, **2003**, *5*, 81. **DOI:** 10.1002/adem.200390013
25. Mohanty, P. S.; Gruzuleski, J. E. *Acta. Metall. Mater.*, 1995, *43*, **2001**. **DOI:** 10.1016/0956-7151(94)00405-7
26. Wang, Tongmin.; Chen, Zongning.; Fu, Hongwang.; Li, Tingju.; *Met. Mater. Int.*, **2013**, 19, *2*, 367. **DOI:** 10.1007/s12540-013-2012-3
27. Jiang, Bin.; Yang, Qing-shan.; Zhang, Ming-xing.; Qiu, Dong.; Li, Rui-hong.; Pan, Fu-sheng., *Mater International*, **2011**, *21*, 236. **DOI:** 10.1016/S1002-0071(12)60036-7
28. Auradi, V.; Kori S.A. *J Alloys Comp*, **2008,** *453*, 147. **DOI:** 10.1016/j.jallcom.2006.11.119
29. Kori. S. A.; 'Grain refinement and modification studies of some hypoeutectic and eutectic Al-Si alloys', Ph.D. thesis, IIT Kharagpur, **2000.**
30. Mahallawy, N. E.; Taha, M. A.; Jarfors, A. E. W.; Fredrikson, H. *J. Alloys Comp*, **1999,** *292*, 221. **DOI:** 10.1016/S0925-8388(99)00294-7
31. Fjellstedt Jonas, *On crystallization processing of Al-base alloys*, Ph. D. thesis, The Royal Institute of Technology, Stockholm, **2001.**
32. Lee. M. S.; Terry, B. S. *Mater. Sci, Technol.*, **1991**, *7*, 608. **DOI:** 10.1179/026708391790184573
33. Kori. S. A.; Auradi. V.; Murty, B. S.; Chakraborty, M. "Poisoning and Fading mechanism of grain refinement in Al-7Si alloy", *Materials Forum*, **2005**, *29*, 387.
34. Li, Peijie.; Kandalova, E. G.; Nikitin, V. I. *Mater. Lett.* **2005**, *59*, 723. **DOI:** 10.1016/j.matlet.2004.06.073
35. Arnberg, L.; Backeraud, L.; Klang, H., *Met. Technol.*, **1982**, 9, 1. **DOI:** 10.1179/030716982803286205



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