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DSC ANALYSIS OF THE EFFECT OF PROCESSING TECHNIQUE ON THE DISSOLUTION/PRECIPITATION REACTIONS IN A HYPEREUTECTIC Al–Si ALLOY

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Abstract

In the present study, the effect of primary processing route on the dissolution and precipitation reactions in a commercial Al–Si alloy (designated as A390) is investigated using differential scanning calorimetry (DSC). The Al–Si alloy selected for the present investigation was processed using conventional casting and spray atomization and deposition routes. The results of differential scanning calorimetry conducted on the as-processed samples indicated no significant dissolution reaction for the as-cast A390 alloy when compared to the similar results obtained for as-spray atomized and deposited samples. However, the thermal analysis conducted on the solutionized cast and spray deposited samples exhibited no significant difference in the kinetics of precipitation reactions. The results of the differential thermal analyses were finally rationalized in terms of observed microstructural features.

Keywords: Al–Si alloy, DSC

Introduction

The low coefficient of thermal expansion and high thermal stability associated with high Si containing aluminum alloys have made them attractive candidates for automotive and aerospace applications [1]. A390 is one such alloy which is extensively used in engine parts of the automobiles [2]. This alloy is conventionally processed using casting route [3].

It has been extensively documented that the properties of a particular material depend largely on the selection of processing type and the resultant microstructural features. Ingot metallurgy (*IM*) route is usually associated with low solidification front velocities that lead to the formation of intermetallics, macrosegregation and coarse primary phases. In order to circumvent the problems as-

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sociated with the ingot metallurgy processing route, researchers investigated several processing techniques that uses high cooling rates and corresponding faster solidification front velocities. Spray atomization and deposition processing (*SPD*) is one such technique that uses rapid solidification to increase solid solubility; minimize segregation; and produce a refined, equiaxed microstructure [4].

For the materials synthesized using different processing routes, it is imperative that the corresponding microstructural features will be different in their morphological characteristics even after keeping the same chemical composition. These microstructural features, characteristics of the type of processing technique used, can significantly affect the nature of the dissolution and precipitation reactions. The knowledge of dissolution and precipitation of the phases in the matrix is important in order to achieve an optimum synergism between the microstructure and mechanical properties of the alloy [5]. In addition, the information thus obtained can be successfully utilized to optimize T6 heat treatment, commonly used for Al-base alloys, as a function of the processing technique utilized to synthesize the material.

Accordingly, the objective of the present study was to investigate the effect of different processing routes on the nature of dissolution and precipitation reactions in an Al–Si (A390) alloy. Conventional casting (also designated as *IM* route) and spray atomization and deposition were selected as two different processing routes. Thermal analysis was carried out using differential scanning calorimetry. Particular emphasis was placed in correlating the microstructural features (characteristic of the processing technique) with the thermal analysis results.

Experimental

Material

The starting material used in the present study was an Al–Si alloy designated as A390. The nominal composition of the alloy was (in wt. %): 17Si – 4.5Cu – 0.6Mg – 0.5Zn – 0.5Fe (max.) – Al (bal.). The alloy was provided, in the form of ingot bars by Reynolds Metal Company (Richmond, Virginia, USA).

Spray atomization and deposition processing of A390 alloy was carried out according to the following procedure. The starting material was superheated to a melt temperature of 1073 K and disintegrated into a fine dispersion of micron-sized droplets using nitrogen gas at a pressure of 3.1 MPa. Following atomization, the gaussian distribution of partially solidified droplets was deposited on a water cooled Cu substrate. The selection of the processing parameters was made to ensure that most of the droplets impacting the substrate consist of both solid and liquid phases. A detailed study regarding the selection of the processing parameters is presented elsewhere [6]. The experiment was carried out in Nitrogen atmosphere in order to minimize the oxidation of the Al-alloy. Figure 1 shows a schematic diagram of a typical experimental arrangement illustrating the salient features associated with the spray deposition processing used in the present study. Table 1 shows the primary processing variables used in the present study.

Table 1 Experimental parameters used for spray atomization and deposition processing

Atomization pressure / MPa	Superheat temperature / K	Flight distance / m	Metal/Gas flow rate
3.1	1073	0.46	1.3

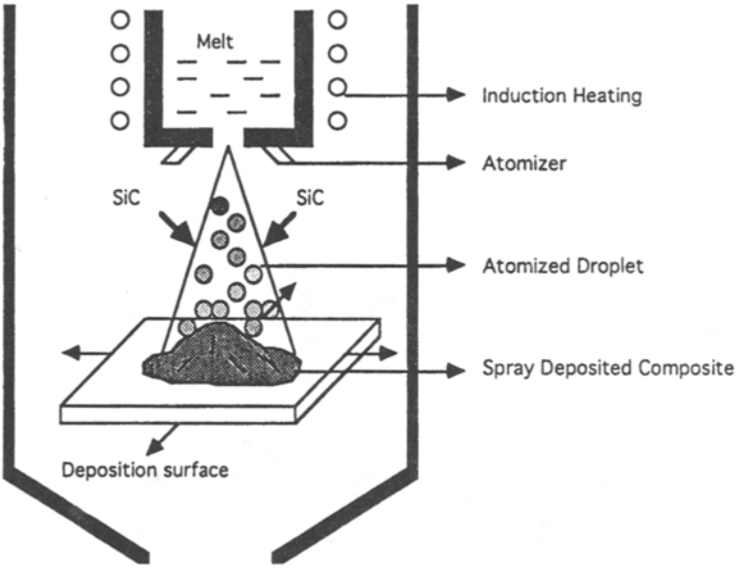

Fig. 1 Schematic diagram of experimental arrangement used for spray deposition processing of Al–Si alloy

Microstructural analysis

Microstructural characterization studies were conducted on the as-cast and as-spray deposited samples in order to investigate the grain size, and the morphological characteristics of the secondary phases.

Optical microscopy was carried out on the polished and etched as-cast and as-spray deposited samples. Keller's reagent [0.5Hf – 1.5HCl – 2.5HNO_3 – 95.5H_2O] was used in the present study to reveal the grain boundaries for microstructural analysis. The grain size was measured from the optical micrographs using the linear intercept method, as described in ASTM E 112-84 standard.

Scanning electron microscopy (SEM) studies were carried out using a JEOL Scanning Electron Microscope equipped with EDS [Energy Dispersive Spectroscopy] to examine the chemistry and morphological characteristics of the secondary phases in the as-cast and as-spray deposited samples. Image analysis was performed using Leica Quantimet image analysis system to determine the morphological characteristics of the secondary phases.

Heat treatment

Solutionizing heat treatment was carried out on the as-cast and as-spray deposited samples to investigate the precipitation behaviour of these samples. As-cast samples were heat treated at 500°C for 3 h while the as-spray deposited samples were heat treated at 500°C for 1 h in order to provide the optimized solutionizing heat treatment [7].

Differential scanning calorimetry

DSC analysis was carried out on the cast and spray deposited samples in the as-processed and solutionized conditions in order to provide insight into the characteristics of the dissolution and precipitation reactions. The analysis was performed on a Du Pont 2100 calorimeter and carried out over a temperature range of 25 to 505°C with a heating rate of 4 deg·min^{-1}. The results thus obtained were plotted in terms of heat flow and temperature.

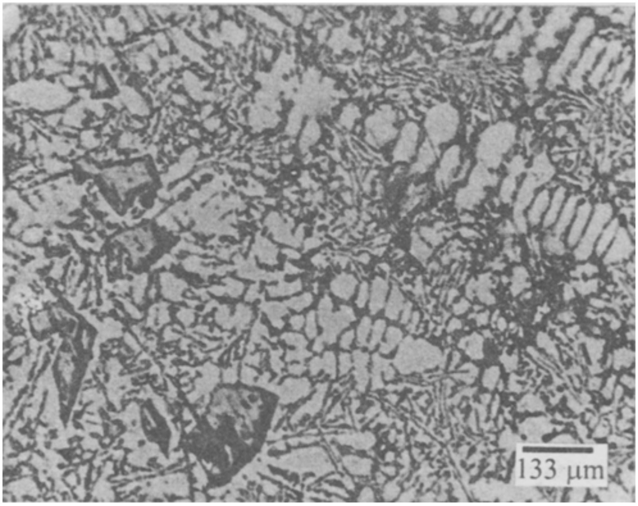

Fig. 2 SEM micrograph showing the microstructural characteristics of the as-cast samples

Results

Microstructural characterization

The optical microscopy studies revealed the presence of equiaxed grains in the as-spray deposited samples, with an average size of 15.6±0.4 μm. For the

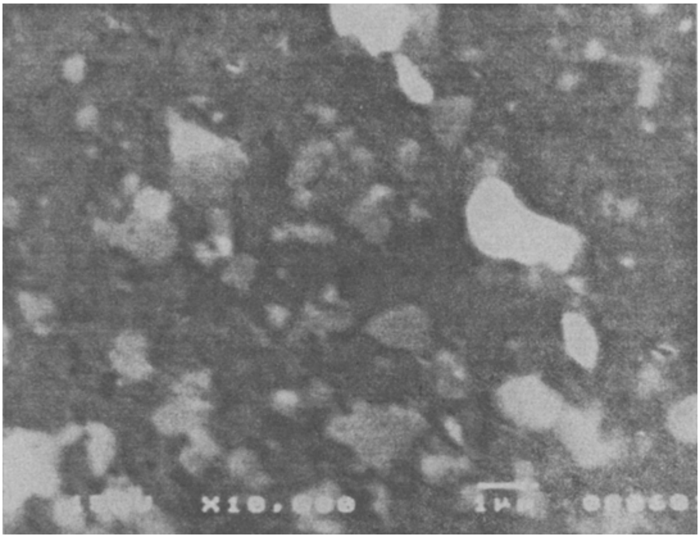

Fig. 3 SEM micrograph showing the microstructural features of the as-spray deposited material

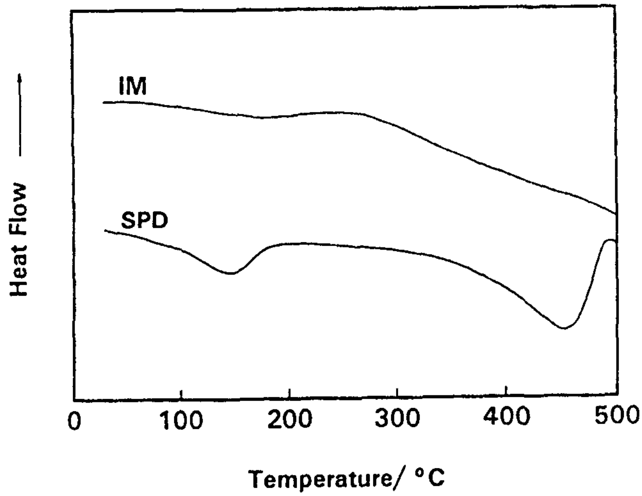

Fig. 4 DSC curves of ingot metallurgy (*IM*) and spray deposited (*SPD*) samples in the as-received condition

as-cast samples, microstructure revealed the presence of α-Al dendrites instead of well defined grains. The presence of dendritic microstructure precluded the determination of the grain size in the as-cast material.

SEM studies carried out on the as-cast samples revealed the presence of primary silicon, eutectic silicon, Al–Cu eutectic phase and needle shaped intermetallic phases (Fig. 2). The identities of these phases were determined using EDS analysis. SEM/EDS studies carried out on the as-spray deposited samples revealed the presence of spheroidal primary silicon, eutectic silicon and Al–Cu phases, however, no needle shaped intermetallics were found (Fig. 3). The results of computerized analysis of the SEM micrographs carried out in order to provide insight into the various characteristics of the secondary phases evolved during casting and spray deposition processing techniques are summarized in Table 2.

Table 2 Results of SEM/EDS and image analysis techniques

Microstructural feature	Shape	Average size / μm
As-cast material		
Primary Si	Cuboidal	72.80
Eutectic Si	Needle	*
Al–Cu phase	Plate	10.10
Intermetallis	Needle	**
As-spray deposited material		
Primary Si	Spheroidized	0.56
Eutectic Si	Spheroidized	**
Al–Cu phase	Spheroidized	0.53
Intermetallis	Not observed	–

* Could not be identified separately from the needle shaped intermetallics on the contrast basis

** Sparsely distributed and could not be identified on the contrast basis

DSC analysis

The results of DSC analysis carried out on the as-cast samples did not reveal the presence of any distinct dissolution peak (Fig. 4). However, the samples did show the absorption of heat initiating at a temperature of ~250°C. The as-spray deposited samples, on the other hand, exhibited two distinct endothermic peaks one at ~157°C and the other at ~457°C. The melting of the samples were observed at 505°C consistent with the results of earlier studies [2].

The results of DSC analysis performed on the cast and solutionized sample revealed two exothermic peaks at 222 and 263°C respectively (Fig. 5). Spray deposited and solutionized sample also exhibited the presence of two exothermic peaks, one each at a temperature of 216 and 263°C respectively.

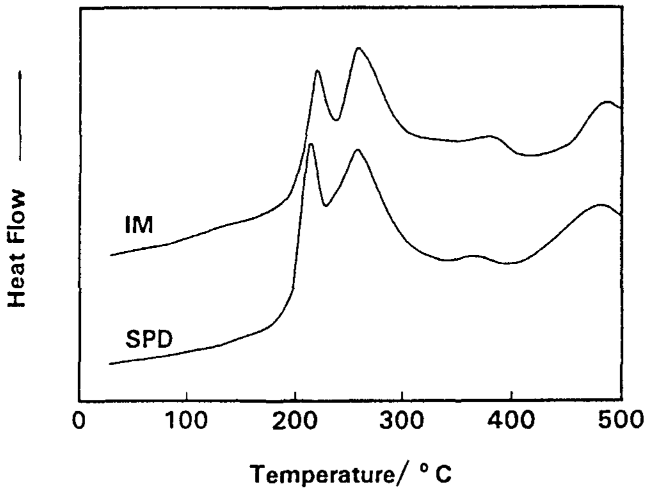

Fig. 5 DSC results of ingot metallurgy (*IM*) and spray deposited (*SPD*) samples obtained after solutionizing heat treatment

Discussion

Microstructure

The presence of α-Al dendrites, primary silicon, eutectic silicon, Al–Cu eutectic and intermetallic phases observed in the as-cast material can be attributed to the low solidification front velocity and the increased partition of the solute elements generally associated with the ingot metallurgy processed materials [4, 8, 9].

Regarding as-spray deposited samples, the equiaxed grain size and the presence of spheroidized Al–Cu phases, eutectic Si and primary Si phase is consistent with high cooling rates ($1\cdot10^3$ K/sec) and the relatively faster solidification front velocity associated with spray atomization and deposition processing technique [4, 6, 10, 11].

DSC analysis

DSC studies carried out on the as-cast samples did not exhibit any distinct dissolution peak. This observation may be attributed to the inability of the matrix to retain solute elements in excess of the limits set up by the equilibrium solidification conditions. Moreover, the manifestation of partitioned solute elements into the formation of intermetallic phases may also contribute to the observation made in the present study. The strong bonding and inherently high melting point associated with the intermetallics make it difficult for the dissolution of these phases to take place readily. The initiation of the dissolution (endothermic) reaction at a temperature of ~25°C in the as-cast samples can primarily be attributed to the dissolution of Si at sharp tips and edges of the primary Si due to the high solute concentration gradients in the regions in accordance with the Freundlich-Thomson equation [8, 12]. In addition, the enhanced ability of matrix to take alloying elements into solution and the gradual dissolution of Al–Cu based precipitates with increasing temperature may be considered as additional factors responsible for the onset of dissolution (endothermic) reaction at ~250°C. It may be noted that the solid solubility of Cu in Al at 250°C is 0.1–0.2 wt.% as compared to 0.45% at 300°C and 4.05 wt.% at 500°C [13]. The results of DSC analysis carried out on the as-cast samples thus indicates a strong correlationship with the characteristics of the microstructural state of the metallic matrix.

The as-spray deposited samples show two distinct dissolution peaks, one at 157°C and the other at 457°C. The endothermic peak at 157°C can be attributed to the dissolution of GP zones. This observation is consistent with the work of other investigators who reported the GP zone solvus temperature of 149°C for an Al–4.5 wt.% Cu alloy [14, 15]. The second dissolution peak at 457°C can be attributed to the significant dissolution of the θ phase and other high temperature phases in the matrix. The relative prominence of dissolution reactions exhibited by the as-spray deposited samples when compared with the as-cast samples may be attributed to the dissolution of significantly refined metastable Al–Si and Al–Cu based phases and the absence of thermally stable intermetallics (Table 2). This is consistent with the faster solidification kinetics associated with the as-spray deposited materials. In the related studies, investigators have reported that the Al–Cu phases (Al_2Cu type) gets refined to nanometric scale as a result of the dynamic solidification conditions present during spray atomization and deposition processing technique [16]. Moreover, it is well established that the thermodynamics favors the solubility of phases in the matrix which are associated with large surface area (significantly refined) and are coherent with the matrix [17]. In addition, the factors like enhanced solid solubility of the alloying elements with an increase in temperature may also be considered as added factors responsible for the prominent dissolution behavior exhibited by the as-spray deposited material. Thus the results of dissolution studies carried out on the as-spray deposited samples suggest a strong correlation with the processing-affected morphological characteristics of the observed microstructural features.

The results of DSC analysis carried out on the solutionized samples, however, revealed the similar trend of precipitation reactions. The initiation of heat liberation for solutionized as-cast and as-spray deposited samples at temperatures greater than 200°C can be attributed to the complex precipitation sequence involving:

a) precipitation and coarsening of primary Si particles [18],

b) precipitation of semicoherent β' (Mg_2Si) phase (temperature range: 200–260°C) [19],

c) precipitation of stable β (Mg_2Si) phases (at T>260°C) [19], and

d) precipitation of Al–Cu–X (Mg, Si, Fe) ternary phases.

The initiation of exothermic reactions at a slightly lower temperature (first peak, Fig. 5) for as-spray deposited and solutionized samples may be attributed to the larger supersaturation of the matrix material when compared to the as-cast material. This observation is in accordance with the results of earlier investigation carried out on binary Al–Si alloys [18].

The negligible difference in the heat liberation between the solutionized cast and spray deposited samples may be explained as follows. In spray deposited and solutionized samples the heat is liberated primarily as a result of: a) coarsening of fine Si particles in order to reduce the particle/matrix interfacial area and consequently to reduce the Gibbs free energy, and b) the relaxation of misfit strains in the matrix [18]. On the contrary, for as-cast and solutionized samples the presence of coarse secondary phases (primary Si, eutectic Si and intermetallic) may serve as the heterogeneous nucleation sites thus promoting the precipitation of binary and ternary phases accounting for the similar heat liberation as that observed for as-spray deposited and solutionized samples. The enhancement in the heterogeneous solid state nucleation in the as-cast may primarily be attributed to the coarse size and the variation in physical properties such as coefficient of thermal expansion (Al/Si: 3.1 [20]) of the secondary phases and the metallic matrix. On solid state quenching the differences in the physical properties will correspond to an increase in number of point defects (vacancies) and line defects (dislocations) in the vicinity of the secondary phase/matrix interface. This resultant increase in number of defects will be instrumental in increasing number of nucleation sites for the precipitates. The added advantage of the as-cast and solutionized samples over as-spray deposited and solutionized samples towards the nucleation of the precipitates is due to the inability of the submicron size phases (observed in spray deposited materials, Table 2) to significantly contribute towards producing defect structure after solid state quenching [21, 22].

In essence, the overall similarity in the precipitation trend observed using calorimetry studies (the onset temperature and the quantitative heat liberation) for the solutionized samples, suggests that the resultant effect of the various microstructural features arising due to various processing techniques used in the present study, counterbalances itself during the solutionizing heat treatment. It may however be noted that beside the negligible difference in the nature of precipitation reactions, the microstructure of the samples solidified under rapid solidification conditions promises enhanced properties due to its inherent microstructural refinement and homogeneity.

Conclusions

The primary conclusions that may be derived from this work are as follows:

1. Spray atomization and deposition processing leads to significant refinement of the microstructure as compared to its as-cast counterpart.

2. The absence of well defined dissolution peaks in case of the as-cast material can be attributed to the presence of coarse equilibrium phases and thermally stable intermetallics in the matrix.

3. The prominent dissolution peaks exhibited by the as-spray deposited Al–Si alloy can be attributed to the dissolution of significantly refined metastable phases in the matrix and the absence of thermally stable intermetallics.

4. The similarity observed in the DSC analysis results carried out on the solutionized cast and spray deposited materials suggests that the processing conditions and the corresponding microstructural features does not significantly affect the overall nature of precipitation reactions.

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Zusammenfassung — Vorliegend wurde mittels DSC der Einfluß des primären Herstellungsweges auf Auflösungs- und Prezipitationsreaktionen in einer handelsüblichen Al-Si-Legierung (bezeichnet als A390) untersucht. Die für vorliegende Untersuchung gewählte Legierung wurde über herkömmliche Guß- und Zerstäubungs- sowie Abscheidungsverfahren hergestellt. Die an den Proben durchgeführte DSC zeigte – im Vergleich zu den Zerstäubungs- und Abscheidungsproben – keine signifikanten Auflösungsreaktionen für die Gußlegierung A390. Die Thermoanalyse der aufgelösten Guß- und Zerstäubungsproben zeigt keinen signifikanten Unterschied in der Kinetik der Prezipitationsreaktionen. Das Ergebnis der DTA wurde letztlich unter dem Aspekt der beobachteten Mikrostrukturmerkmale betrachtet.