

FIB Cross-Sectioning of a Single Rapidly Solidified Hypereutectic Al-Si Powder Particle for HRTEM

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ABSTRACT A creative technique of in-situ focused ion beam (FIB) extraction was introduced to prepare a gas atomized rapidly solidified hypereutectic Al-Si single particle's cross-section for High Resolution Transmission Electron Microscopy (HRTEM) analysis. This preparation technique may be employed to characterize very inimitable samples that are abnormally wrought or intricate to prepare through traditional techniques. TEM results revealed that a gas-atomization/rapid solidification process leads to a homogeneous dispersion of 50–100-nm Si phase in the Al matrix. Stacking faults and dislocations are observed in the microstructure and will ultimately lead to the increased strength in a resultant bulk material manufactured from this powder to be further examined. *Microsc. Res. Tech.* 66:10–16, 2005. © 2005 Wiley-Liss, Inc.

INTRODUCTION

Controlling the size, shape, density, and composition of particles prior to any powder metallurgical synthesis, specifically plasma spray forming, is key due to the multitude of situations that can arise during the flight of the particles in the plasma flame (Bertrand et al., 2003; Boulos, 2004). The characterization of the feedstock powder is paramount and cannot be underemphasized due to its bearing impact on the microstructure of a resulting bulk component. This preparatory research focuses on the feedstock powder analysis and reports the microstructure analysis of a single particle. Similar particles will be the feedstock for commercially manufactured bulk nanostructured metal matrix and ceramic components, another key feature of our further research (Seal and Baraton, 2004). In the present study, it has been mentioned that plasma spray forming has been to “consolidate” gas atomized spherical Al-Si powder. Plasma spray technique involves rapid solidification (cooling rates of the ~10 exp 6–10 K/sec) resulting in a very fine grain structure. Due to such kinetics of the process, there is not enough time for diffusion to occur and hence nano phases and grains of as-received powders are retained. We have shown this successfully in our previous work (Agarwal and McKechnie, 2001). The intent of the present article was to characterize the as-received powder using a novel technique. The consolidation by plasma spray forming and subsequent properties will be presented elsewhere.

To further narrow the field of this specific research, the hypereutectic aluminum-silicon system was chosen for investigation by its intrinsic properties. Aluminum-silicon alloys share a favorable dichotomy of properties that would be beneficial for applications in automotive, aerospace, electronics, and optics industries (Chen and Chung, 1994; Estrada and Duszczuk, 1990). Namely, silicon has a low coefficient of thermal expansion (CTE) and good wear resistance relative to its high Poisson's Ratio and bulk modulus. Aluminum is

readily machinable and facilitates the alloy in choice addition compositions during manufacturing (Chen and Chung, 1994). The wear resistance and lowered CTE of this system are mainly due to the high volume fraction of silicon, above that of the eutectic composition (Kuroishi et al., 1986). Typically, ingot-type powder metallurgical approaches to manufacturing of similar alloys often incur a microstructure burdened with the generation of eutectic and the coarse primary silicon phases. These phases, created and typically during casting metallurgy manufacturing, cause porosity nucleation and cracking, which tends to debilitate the mechanical properties of the material (Kuroishi et al., 1986). The means is to maintain, to the extent possible, the mechanical properties of the primary Al matrix with the increased benefits of adding the particulate Si beyond that of the eutectic composition.

The current procedures for preparing TEM samples including the use of dicing saws and ex-situ micro-manipulator removals (Subramanian et al., 1998; Tsung et al., 2000; Young et al., 1998) are not sufficient to produce the same results with a single particle of a powder. In the case of the dicing saw, there is not enough specificity or stability in an array of particles to mill a cross-section. An overview and comparison of conventional sample preparation techniques including ion milling was extensively performed and reported

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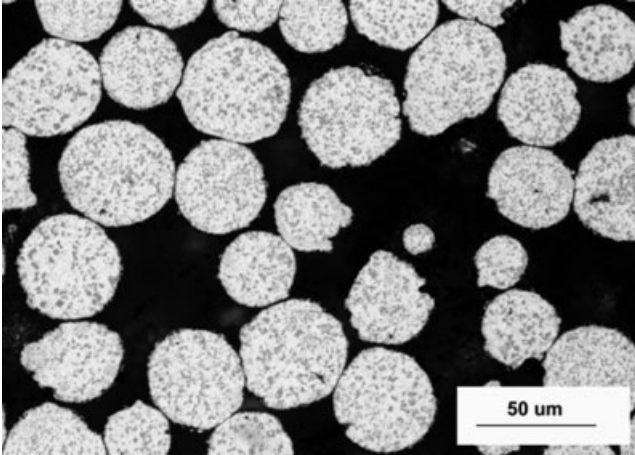


Fig. 1. SEM of starting powder showing size and spherical shape after mounting & polishing.

previously (Shannon, 2000)]. We have tried and succeeded in the case of ex-situ micromanipulator removals; however the failure rate and time consumption are both above the tolerable range of efficiency. A new and creative technique was used to enable a sample to be procured of the dimensions necessary for characterization in the transmission electron microscope (TEM). Knowledge of the microstructure of the powder will allow us the ability to control, through planned manipulation, the nanostructured homogeneous reinforcement and strengthening mechanisms of the resultant material during deposition, all further directing the final goal to form a large and useful monolithic part through the ascribed synthesis method.

We have characterized a hypereutectic Al-Si powder, which is subsequently used for plasma spray forming bulk parts (Agarwal et al., 2003; McKechnie, 2000), using advanced techniques such as FIB and HRTEM to determine the internal substructure of the powder.

MATERIALS AND METHODS

Powder History

The starting powder for characterization was custom gas atomized hypereutectic Al-Si powder procured from Valimet Inc. Inert Gas atomized powder was chosen for a multitude of benefits. The average powder size $\sim 20\text{--}45\ \mu\text{m}$ (Fig. 1) was synthesized with the aim of using it as feedstock for thermal spray processes. Spherical morphology provides the excellent flow characteristics through the plasma gun and flame resulting in a higher degree of melting and subsequent dense spray deposits (Bertrand et al., 2003). Furthermore, spheroidization of the powder enhances handling characteristics and enables strict management of feed rates in the plasma-forming application (Boulos, 2004). Through the gas atomization and melting of the individual particles, the internal porosity and cavities are dramatically reduced thereby yielding a higher bulk density of the powder (Boulos, 2004). The particular composition of the Al-Si powder chosen for investigation is given in Table 1. The customization of the powder's composition was also pertinent to the particular

TABLE 1. Vanasil powder composition as requested from vendor

Element	Vanasil powder composition (wt %)
Silicon	21.1
Zinc	<0.10
Copper	1.19
Iron	0.16
Titanium	0.19
Nickel	2.13
Magnesium	0.98
Vanadium	0.11
Aluminum	>74.04

desire for Ni-Al and Al-Si-X (where X = Cu, Mg) inter-metallic compounds for possible improved mechanical properties (Estrada and Duszczyk, 1990; Gloriant and Greer, 1998; Jain and Gupta, 2003; Park et al., 1996; Salvador et al., 2003; Satyanarayana et al., 2001; Srinivasan and Chattopadhyay, 2004; Srivastava et al., 2002; Srivatsan et al., 1995; Wang et al., 2004).

Analytical Methods

The selection and characterization of the powders were performed with the scanning electron microscope. A JEOL 4600 Scanning Electron Microscope (SEM) was used at 5 kV acceleration voltage to obtain images of the powders with composition Al-21-wt% Si. Powder with particle diameters in the range of $20\text{--}45\ \mu\text{m}$ was further selected for analysis by Optical Microscopy (OM), Transmission Electron Spectroscopy (TEM), Energy Dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). A Philip Norelco X-Ray Diffractometer (XRD) using Cu K_{α} radiation operated at 40 kV and 20 mA was employed for phase identification in the powder. This powder was mounted, polished, etched, and examined for cross-sectional, shape, and size properties under the same settings. Optical microscopy of the mounted and polished powder yielded the possible appearance of a homogenous dispersion of the primary silicon phase within the α -aluminum phase (Trivedi et al., 2003), which led to the desire for further and more precise characterization (Fig. 1). Furthermore, single particle characterization was performed using focused ion beam and transmission electron microscopy techniques as described further.

Focused Ion Beam

For sample extraction from the powder, an FEI Focused Ion Beam 200 TEM field emission magnum column workstation with a gallium liquid metal ion source (LMIS) was used. Ion emission of a LMIS is achieved with a current density of $\sim 10^8\ \text{A cm}^{-2}$ at the surface. The physical sputtering process undertaken during this sample preparation procedure can reach a lateral resolution of approximately 5 nm. This ion milling workstation is very useful for varying applications of sample characterization preparation including non-charging Auger electron spectroscopy (Wannaparhun et al., 2001), whereby this specific sample extraction is a creative spin-off of the previous and similar route. Typical damage during FIB milling occurs as lattice defects and amorphization of the target structure (Shannon, 2000). The amorphization of the surface is proposed to be a function of FIB operating parameters during active milling. These parameters include beam

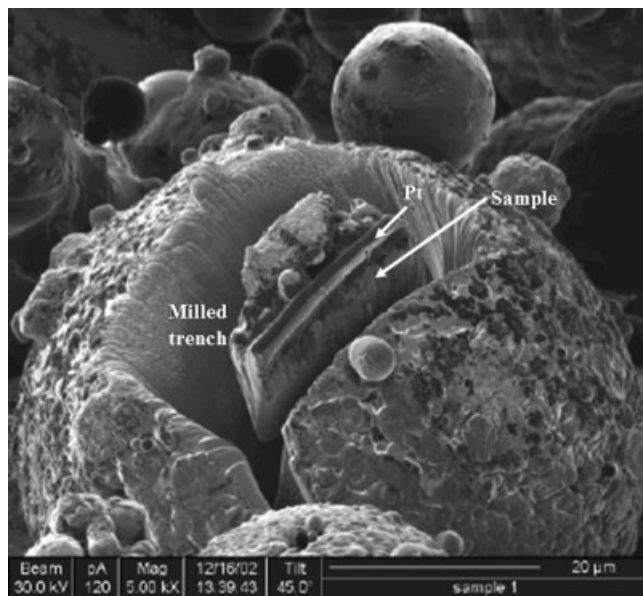


Fig. 2. Focused ion beam milling procedure showing and labeling the protective platinum layer and the trenches that are used to enable the sample extraction.

current, accelerating voltage, and gas-assisted etching (Shannon, 2000). Understanding the possible sources of surface amorphization and to minimize damage during the Focused Ion Beam milling procedure, we used a low-beam current (30–50 pA). To further lessen the possible damage, we also calibrated the apertures and eucentric height multiple times during both the initial and final in-situ processes.

In situ Preparation by FIB Milling

A specific technique of in situ removal was used in order to remove a cross-section of material. As is customary in these procedures (Young et al., 1998), a thin layer of platinum is deposited on the surface via an in situ needle platinum aspirator that is positioned $\sim 80 \mu\text{m}$ above the region of interest. Chemical vapor deposition occurs through a sputtering process where the transfer of energy and momentum from the incoming Ga^+ ions to the target ions (platinum and the sample surface) forms a CVD thin film. This thin film layer serves to protect the underlying material. Subsequently, small trenches were milled on either side of this deposition to enable the removal of the cross-section sample, as shown in Figure 2. To diverge from traditional ex-situ techniques, a mechanical probing manipulator is then inserted (all the while inside the vacuum chamber/milling vacuum environment) and maneuvered so that it is carefully touching the sample of interest. After these two surfaces are adjoining, a similar chemical vapor deposition technique per the operator's manual (Focused Ion Beam xP Workstation User's Guide 1997) and is utilized to deposit platinum on the adjoining surfaces, whereby the adsorbed gas and the sputtered material create a temporary "weld" of the probe and the sample of interest (see Fig. 3). The sample is then milled loose at its remaining edge, thus separating the sample from the

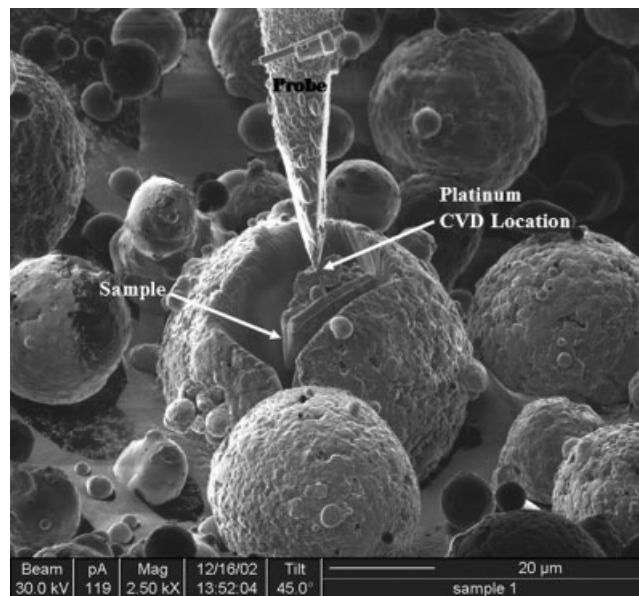


Fig. 3. In situ probing manipulator used to weld to the sample and subsequently extract for TEM examination.

particle. Attached to the manipulator, the cross-section in its entirety is moved in situ to the specially prepared horseshoe-shaped Copper TEM grid that is already positioned vertically in the vacuum FIB chamber. A special trench is milled specific to the sample's shape and size on the grid to enable its proper situation to become visible orthogonally in the TEM. Next, as if in the machine shop, the $\sim 20\text{-}\mu\text{m}$ -wide wedge-shaped sample is again spot welded in its custom trench to the grid and then cut from the manipulator, leaving the sample ready for further preparation. The next steps were used implicitly to finalize the sample for electron opacity.

To get the cross-section to the desired thickness of $<250 \text{ nm}$, at zero tilt, the extraneous material on either side of the protective platinum layer is carefully milled away at a decreasing beam current (1,000–100 pA). Once the cross-section is thin enough to continue without loss of sample integrity (Pt layer still visible and providing protection), the stage is tilted at $\pm 1^\circ$ -intervals from the horizontal and milled orthogonal at even lower beam currents ($\sim 30\text{--}50 \text{ pA}$, this is done to minimize damage of ion milling) until the thinnest portion (at about 100–150 nm thickness) of the sample remains farthest from the visible platinum layer, but above the custom trench (visible base) of the TEM grid.

High Resolution Transmission Electron Microscopy

A Philips/FEI Tecnai F30 field emission transmission electron microscope at an acceleration voltage of 300 keV and extraction voltage between 4.3 and 4.4 keV was used for the investigation of the aforementioned prepared powder sample. Energy Dispersive X-ray Analysis High-Angle Annular Dark Field Detector (HAADF) was used to identify chemical species

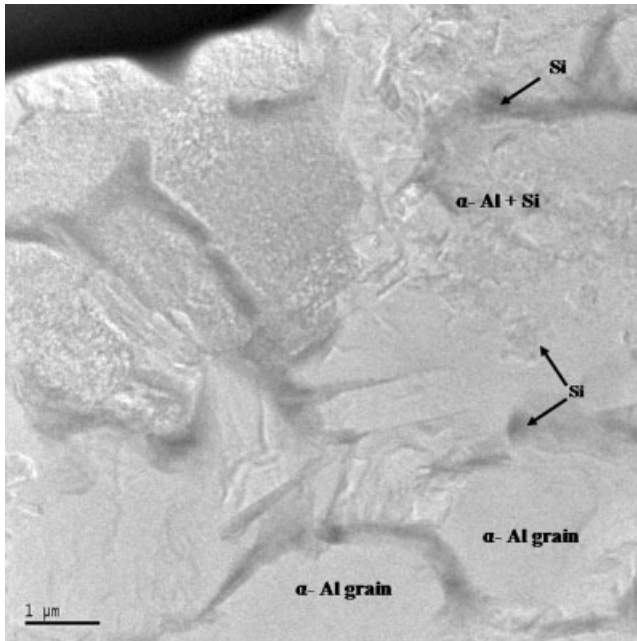


Fig. 4. TEM bright field image taken from a cross-section of pre-sprayed powder of about 50 μm in diameter.

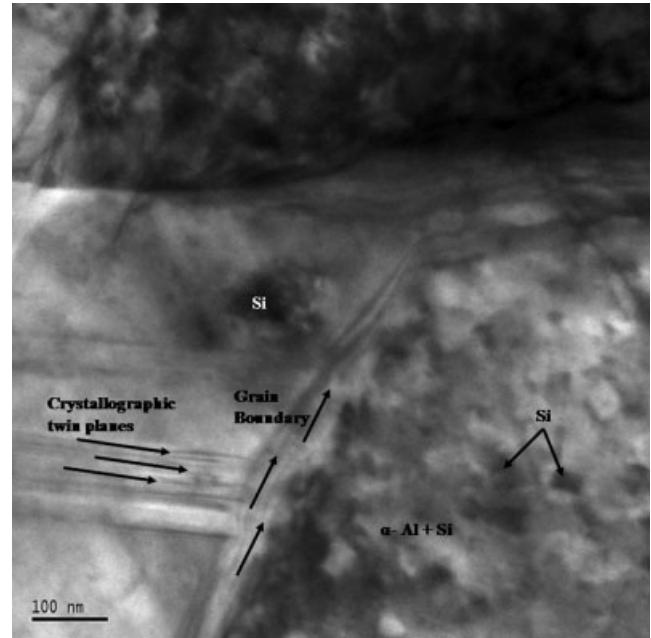


Fig. 6. HRTEM image of pre-sprayed powder elaborating fine distribution of Si and the intersections of twin planes impeding dislocation motion.

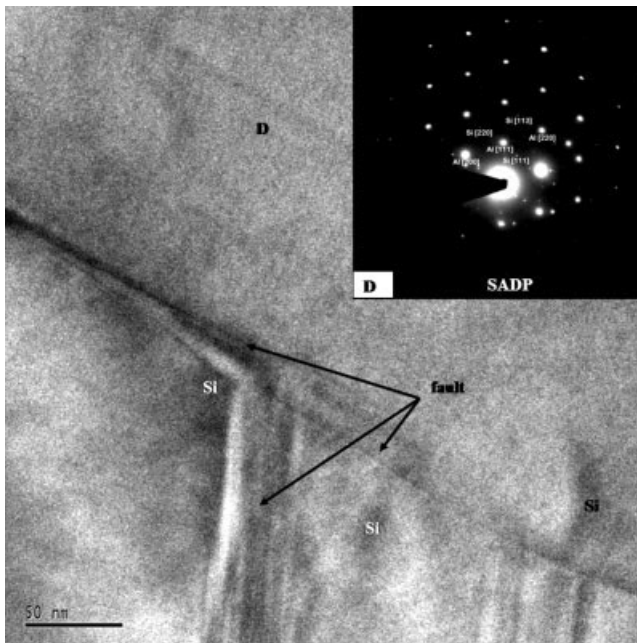


Fig. 5. TEM image of pre-sprayed powder of about 50 μm with SADP taken away from the fault.

present at specific areas of interest by the relation of proportional intensity count return.

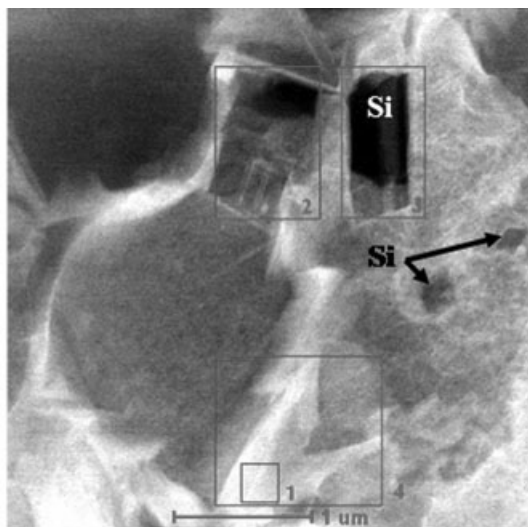
RESULTS AND DISCUSSION

The technique used in this characterization experiment was very successful and efficient to characterize a single particle's cross-section and microstructure.

The twofold significance of this technique was to enable the characterization of a particle's cross-section and then document these findings to relate to the microstructure of the final bulk spray-formed part that will be published following further experimentation. As can be seen in the transmission electron microscope images (Figs. 4–7), the microstructure is typical of Al-Si alloys in a rapid solidification environment (Anand et al., 1996) and shows little or unnoticeable contamination from the ion beam milling procedures as described above. Time is a valuable parameter in characterization and leads to another key benefit of this particular in situ sample removal procedure whereby the final sample for investigation was produced in a few hours.

The primary reason for starting the characterization with the pre-spray powder was to investigate the outcome of the solid-solubility and microstructure properties of the hard Si precipitates in the Al matrix proceeding gas atomization. The starting powders were analyzed using optical microscopy and showed a fine homogenous dispersion of primary Si in the α-aluminum matrix (see Fig. 1). This was confirmed by SEM-EDS and crystallographic orientation differences via selected area diffraction pattern (SADP) analysis as seen in Figure 5.

Transmission electron microscopy (Figs. 4, 6) revealed a typical grain size of Al and particulate Si as 3 μm and 50 nm, respectively. The proposed strengthening and the improved properties of the powder (and subsequent bulk component) are inherently attributable to the finely embedded and dispersed hard particulate Si throughout the Al matrix by the advantage of dislocation pinning (see Figs. 4, 5) (Agarwal and McKechnie, 2000; Lavernia and Wu, 1996). Al-Si-X (where X = Ni, Cu, Fe) intermetallic phases might



EDX HAADF DETECTOR RESULTS

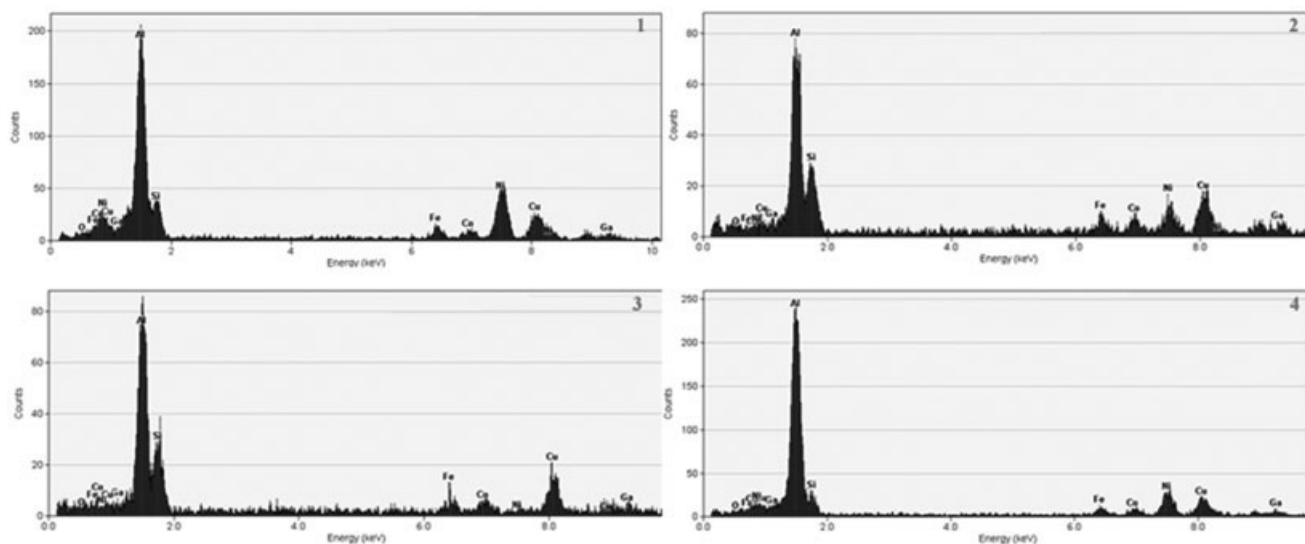


Fig. 7. EDX high annular angular dark field detector results showing the particulate distribution of silicon throughout the particle (darker region [top] is silicon by count concentration [bottom]).

have been present, but were not observed by EDX HAADF in Figure 7. At specific compositions and under rapid solidification environments, these ternary phases form ultra-fine intermetallic particles and structures that provide a variety of favorable mechanical properties most notably high temperature strength, creep resistance, oxidation resistance, and room temperature strength (Fig. 7) (Estrada and Duszczek, 1990; Gloriant and Greer, 1998; Jain and Gupta, 2003; Park et al., 1996; Salvador et al., 2003; Satyanarayana et al., 2001; Srinivasan and Chattopadhyay, 2004; Srivastava et al., 2002; Srivatsan et al., 1995; Wang et al., 2004). During rapid solidification, the “crystallization and precipitation of intermetallic compounds is inhibited” (Estrada and Duszczek, 1990). X-ray diffraction was employed to characterize these phases, but due to the trace amounts and underdevelopment of

these intermetallics, they were most probably beyond the detection range of X-rays (Fig. 8).

The microstructure findings of our experiment led to further characterization when we noticed the Si precipitates themselves contained defects within their multi-crystal structures. The presence of intersecting stacking fault regions was also examined (see Fig. 6). These stacking faults, found near high concentrations of Silicon, would tend to impede dislocation movement, moreover increasing the strength through “dispersion strengthening” of a proposed material (Kim et al., 2001). The grain refinement is caused during the gas atomization evolution when the fragmented dendrites create numerous nucleation sites (Anand et al., 1996; Lavernia and Wu, 1996). The phenomenon of fine equiaxed grain structure and homogenous dispersion of the secondary phase Si particle precipitates are

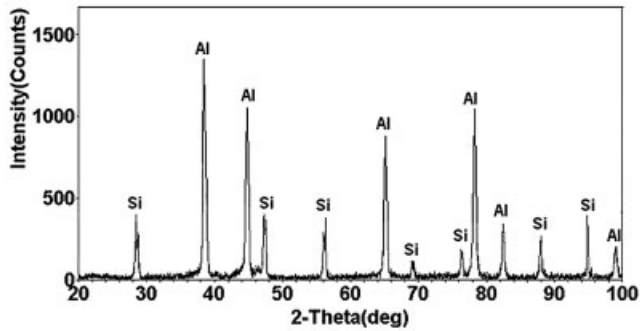


Fig. 8. X-ray diffraction of Al-Si powder.

microstructural features characteristic of gas atomization and rapid solidification processes (Anand et al., 1996; Lavernia and Wu, 1996). Atomization of liquid droplets promotes a rapid solidification environment with cooling rates in the range of 10^3 – 10^5 K s⁻¹ (Lavarnia and Wu, 1996). The stacking faults that are visible in Figures 4 and 6 are the amalgamation of the difference in the coefficient of thermal expansion of Al versus Si in this rapidly solidified particle (Lavarnia and Wu, 1996). As seen in the TEM micrographs provided in Figures 5–7, rapidly solidified Al-Si alloy can be characterized by its dendrite arm spacing, small and homogenous grain size distribution, decreased microsegregation of alloying elements, and broad metastable solid solubility (Estrada and Duszczek, 1990; Lavarnia and Wu, 1996). As seen by Kim et al. (2001), the relationship orientation between the particulate Si and the Al matrix was determined by SADP as $\langle 111 \rangle_{\text{Si}} \parallel \langle 111 \rangle_{\text{Al}}$ (Fig. 5, top). TEM investigation, coupled with EDX High Annular Angular Dark Field Detector (HAADF), clearly identified the twinning effects and dislocations near high concentrations of Si (Fig. 7). Using the information obtained from this initial characterization, we envisage that rapid solidification during plasma forming and deposition procedures would lead to additional refinement and the homogeneous dispersion of Si precipitates within the aluminum matrix in hypereutectic Al-Si alloy.

CONCLUSIONS

An in situ FIB sample preparation technique has been developed to characterize a single powder particle cross-section microstructure in only a few hours as compared to conventional polishing techniques, which are very hard to apply to an individual particle. The FIB ion milling technique did not leave behind any noticeable contamination or detrimental flaws in the characterization at the nanoscale and is specifically useful for retrieval of an electron transparent sample of <250-nm thickness from a single, small, circular-shaped dense agglomerate for further characterization.

The TEM analysis of this hypereutectic Al-Si powder revealed multiple mechanical strengthening mechanisms that are beneficial to this particular application of maintaining the nanophase at the pre-sprayed bulk component stage of production to specifically tailor the

mechanical properties of a material by constituent composition and microstructure interactions.

Although this preliminary characterization research is quite promising, it leaves a large realm to the imagination. Other novel material combinations, different enhanced methods of powder agglomeration, and rapid solidification deposition processes like plasma spraying will ultimately lead to further improvements in this expeditious nanostructured bulk component synthesis technique.

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