Materials and Design 56 (2014) 542–548

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Ultra-fine Al–Si hypereutectic alloy fabricated by direct metal deposition

L.Z. Zhao [a,b,c,*], M.J. Zhao [a], L.J. Song [b], J. Mazumder [b]

[a] Key Laboratory of Ministry of Education for Conveyance and Equipment, East China Jiaotong University, Nanchang 330013, People's Republic of China
[b] Center for Laser-Aided Intelligent Manufacturing, University of Michigan, Ann Arbor, MI 48109, USA
[c] Key Laboratory of Super-light Materials & Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, People's Republic of China

ARTICLE INFO

Article history:
Received 28 August 2013
Accepted 24 November 2013
Available online 1 December 2013

Keywords:
In situ hypereutectic alloy
Microstructure
Microhardness
Direct metal deposition
Scanning speed
Laser power

ABSTRACT

Ultra-fine Al–Si hypereutectic alloy with <10 μm primary Si phase was fabricated by direct metal deposition (DMD). The microstructure and microhardness of the hypereutectic alloys manufactured under different scanning speeds and laser powers during DMD were investigated. Compared with the conventional modified hypereutectic alloy whose primary Si phase is around 40 μm, the primary Si particle obtained by DMD has a much smaller size of about 5–10 μm. With increased scanning speed and laser power, the volume fraction and size of the primary Si increase. The unique hypoeutectic microstructure can be found around the primary Si phase in the hypereutectic alloy. With increased scanning speed, the size of eutectic Si grain decreases and the microhardness of deposition increase. However, the size of eutectic Si reaches the minimum value at a certain power level, and the microhardness of deposition reaches the maximum value at 850 W laser powers. The mircohardness of the deposited hypereutectic alloy is approximately 2.5 times of that of the raw eutectic alloy.

1. Introduction

Hypereutectic Al–Si alloys are attractive materials for aeronautical, automobile, and military applications because of their excellent combined properties, such as low coefficient of thermal expansion, low density, good corrosion resistance, high wear resistance, and good casting ability [1,2]. Hypereutectic Al–Si alloys have a higher volume fraction of the primary silicon than conventional hypoeutectic Al–Si alloys. Thus, hypereutectic Al–Si alloys are candidate materials for high-quality pistons and optical modules [3]. However, the large size of the coarse primary silicon in hypereutectic Al–Si alloys obtained by conventional casting technology can reduce the anti-wear property and ductility of alloys [4]. Therefore, the primary silicon of hypereutectic alloys must be refined to improve their mechanical properties and thus increase their industrial applications.

Various methods have been used to refine primary silicon phases, such as the addition of modification agent, heat treatment, ultrasonic vibration treatment and rapid cooling [4–11]. Modification can change the morphology and size of both primary and eutectic silicon at the same time. However, modification is not stable and green because upon heating, phosphorus modification agents can be volatile, which causes agent burning loss and possible environment pollution [4,5]. Moreover, the most common modification agents are costly rare earths. Furthermore, the modification effects are also limited for >40 μm-sized primary silicon in modified alloys, which limit the improvement of the mechanical properties. During heat treatment, eutectic silicon in hypereutectic Al–Si alloys disintegrated and spheroidized [6], but the primary silicon almost keep stable, very limited information is available regarding the effects of heat treatment on the hardness of hypereutectic alloy.

The introduction of ultrasonic vibration into the alloy melt can refine grains and produce globular non-dendritic grains. During the vibration process, the amplitude transformer immersed in the melt needs to endure the severe high temperature of 970 K for a long time, which results in the discontinuous industry production. In addition, the limit vibration power cannot refine the melt needed in industry [7].

The microstructure of hypereutectic Al–Si alloys such as size, shape, and morphology of primary Si strongly depends on the cooling rate of solidification [8]. Numerous studies have reported on the rapid solidification of Al–Si alloys by melt spinning, surface treatment with high-energy beams, and metal mold casting [9–11]. The melt spinning technology can only be used to fabricate the thin strip; the morphology of surface layer with short lifetime is obtained in the surface treatment technology and the primary silicon in aluminum alloy is not affected in metal mold casting. Furthermore, all these methods are difficult to use in the industrial fabrication of certain components. DMD technology features a rapid cooling rate as well as the abilities to produce net-shaped

* Corresponding author at: Key Laboratory of Ministry of Education for Conveyance and Equipment, East China Jiaotong University, Nanchang 330013, People's Republic of China. Tel.: +86 79187046157; fax: +86 79187046122.
E-mail addresses: zhaolz@ecjtu.edu.cn, zhaolongzhi@163.com (L.Z. Zhao).

0261-3069/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.matdes.2013.11.059

components and synthesize materials. DMD is a new rapid manufacture technology, the deposited material has a high cooling rate of 10^6 K/s, thus, DMD is suitable for fabricating fine-grained hypereutectic Al–Si alloy [9,12].

During DMD, raw powders are delivered to the substrate through small pipes and a cladding nozzle with the aid of a delivery gas. However, Si particles are difficult to deliver because of their static electricity that often blocks delivering pipes. Silicon carbide tends to react with molten Al and form silicon at 1670 K, thereby providing elemental silicon for the formation of hypereutectic alloys [13,14]. In this study, the mixture powder is composed of Al–11.28 Si alloy powder and the easily flowing silicon carbide powder instead of Si powder. The microstructure and microhardness of the hypereutectic Al–Si alloy produced by DMD are reported.

2. Materials and methods

The substrate, which was multipurpose 6061 aluminum alloy with dimensions of 100 mm × 80 mm × 10 mm, was sandblasted prior to deposition. Gas-atomized 4047 eutectic Al–Si alloy powder (100 μm) and silicon carbide powder (70 μm) were used. The alloy powder comprised 88.51 Al, 11.28 Si, 0.18 Fe, and 0.03 Cu (in weight percentage).

A DMD 105D machine (developed by the POM Group, Auburn Hills, MI, USA) with a disk laser beam diameter of 1.0 mm was used in the experiments. Ten successive layers of a single-wall sample (50 mm long × 2 mm wide × 3 mm high) were deposited. During deposition, a laser was scanned back and forth over the previous layer. A coaxial nozzle was used to deliver powders at a feeding rate of 4.9 g/min. The process parameters including laser power and scanning speed are shown in Table 1.

Transverse sections of the samples were cut, metallographically polished, and etched with Keller's reagent (containing 95 ml of H_2O, 2.5 ml of HNO_3, 1.5 ml of HCl, and 1.0 ml of HF).The samples were then immersed in Keller's reagent for 15–20 s, immersed in HCl for 1–2 s, rinsed with water, and then dried. The microstructure of the samples was characterized by scanning electron microscopy (SEM) on a Philips XL30 FEG SEM system and by energy-dispersive spectrometry (EDS). Different phases in the deposited samples were examined by X-ray diffraction (XRD) using a Rigaku rotating anode X-ray diffractometer with Cu Kα radiation at 40 kV and 100 mA. All samples were scanned within the standard θ–2θ geometry from 17° to 90° with a 0.015° step size and 1 s dwell time. Microhardness measurements were performed on the cross-section of samples using a CM-400AT automatic microhardness tester with a 200 g load for a dwell time of 15 s based on ISO 6507 standard [15]. The final hardness value was calculated using average data from 10 indentations.

3. Results and discussion

3.1. Microstructure

The microstructure of hypereutectic Al–Si alloy obtained by DMD is shown in Fig. 1. The phases were identified based on morphological, XRD, and EDS analyses. Silicon is mainly distributed in the plate-like phase with a small portion in the stripe-like phase.

Table 1
Parameters of DMD.

Sample number	1	2	3	4	5	6	7
Laser power (W)	500	700	900	1200	700	700	700
Scanning speed (mm/min)	450	450	450	450	400	500	300

The carbon element was presented in the stripe-like phase. To further understand the composition of different-shaped phases, the energy-dispersive spectrum analysis in hypereutectic-alloy is shown in Fig. 2. The white needle-like or dot-like eutectic Si and the gray α-Al form the eutectic master alloy (spot A). The stripe-like phase is ternary carbide consisting of elemental carbon, aluminum, and silicon (spot B). The plate-like phase is mainly silicon (spot C). The XRD pattern in Fig. 3 shows that the phases present in the structure are α-Al, Si, and Al_4SiC_4 ternary carbide, in good agreement with the EDS elemental distribution spots. Therefore, the hypereutectic Al–Si alloy is composed of needle-like or dot-like eutectic Si, stripe-like Al_4SiC_4 ternary carbide, and plate-like primary Si.

The size of the primary Si phase is approximately 5–10 μm, which is much smaller than that of primary Si in the modified hypereutectic alloy (40 μm) and the primary Si phases (100 μm) in conventional hypereutectic Al–Si [10]. During DMD, SiC particles fly through the laser beam, absorb laser energy, and undergo a temperature increase to 3273 K [16]. This temperature is much higher than the minimum temperature (940 K) needed for SiC and aluminum to react. The reaction products strongly depend on the temperature. From 940 K to 1620 K, the products are Si and Al_4C_3. Beyond 1670 K, the reaction product is Al_4SiC_4 ternary carbide and Si [17]. Given that Al_4C_3 is brittle and easily reacts with water, Al_4C_3 should be avoided by increasing the temperature of SiC particles to >1670 K.

The size of ultra-fine primary Si in the alloy depends on the cooling rate of alloy deposited during DMD. The cooling rate of part deposited by DMD ranges from 10^5 K/s to 10^6 K/s [18], which are much higher than those of the conventional casting method. The nucleation drive of liquid Si during DMD is also much higher than that during conventional casting because of the high under-cooling rate. Consequently, ultra-fine primary Si in hypereutectic alloy can be obtained from the high nucleation rate of Si crystal.

The morphologies of primary Si in hypereutectic alloys deposited by DMD at different scanning speeds and laser powers are shown in Figs. 4 and 5, respectively. Plate- and star-like white primary Si phases are uniformly distributed in the hypereutectic alloys. With increased scanning speed, the volume fraction of the primary Si phase and the ratio of the massive star-like phase to the star phase decrease. With increased laser power, the change in morphology of primary Si is opposite to the change in scanning speed. The morphology of primary Si can be correlated with the temperature field in the molten pool. To further understand the morphology of primary Si, the energy density ρ was used (Eq. (1)) [19]:

$$\rho = \frac{P}{v \cdot d} \tag{1}$$

where P, v, and d refer to the laser power, scanning speed, and diameter of the laser beam, respectively. The energy density is proportional to the laser power and inversely proportional to the scanning speed. During DMD, the laser power is mainly used to create a molten pool on the substrate or previous deposition and heat the powder passing through the laser beam. At a low energy density, the temperature of the SiC particles and the liquid pool are low. At a low temperature, SiC difficultly reacts with aluminum; thus, the content of Si product in the alloy is low when the energy density of the laser is low. Compared with aluminum, SiC absorbs much higher laser power when the temperature is low. Hence, only a small amount of aluminum around the high-temperature SiC particles can react with SiC. The ultra-fine Si product is then distributed around the SiC particles (Fig. 6). SiC particles with a low coefficient of thermal expansion remain in the bulk, which makes the product Si surrounds the SiC surface. Molten aluminum has a high viscosity at a low temperature. Therefore, the Si product cannot be easily