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Effect of (Mn + Cr) addition on the microstructure and thermal stability of spray-formed hypereutectic Al–Si alloys

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ABSTRACT

Microstructures and thermal stability of hypereutectic Al–Si alloys with or without (Mn + Cr) addition, prepared via Spray Forming technique, are studied and compared with traditional cast alloys with same composition, using scanning electron microscopy with energy diffraction spectrum, X-ray diffraction, transmission electron microscopy and differential scanning calorimeter. The results show that the Fe-bearing and primary silicon phases in SF-3C alloy can be refined to less than 10 μm, especially in SF-MC21 alloy the Fe-bearing phase is refined into uniformly distributed α-Al(Fe,Mn,Cr)Si phase particles with sizes smaller than 5–6 μm, contributing to the decrease/elimination of the deleterious effect of needle-like Fe-bearing phases. The results of different heat treatments show SF-MC21 alloy possesses excellent thermal stability than SF-3C alloy which is unstable below 750 K for the coarsening of β-Al_5FeSi phase and formation of Al_7Cu_2Fe phase. The study indicates that both the existence of thermodynamically stable α-Al(Fe,Mn,Cr)Si particles and the increase of solidus temperature of SF-3C alloy induced by adding (2Mn + 1Cr) elements contribute to the high thermal stability of SF-MC21 alloy. Contemporarily, combined the phase reactions or transformation occurred during the melting and solidification processes of both spray-formed hypereutectic Al–Si alloys, the microstructure formation of spray-formed alloys is discussed.

1. Introduction

With rapid development of new vehicles with preeminent properties, reducing the weight of new vehicles will undoubtedly become the most direct and beneficial way to reduce energy consumption [1]. Lightweight materials with low density, such as Al/Mg/Ti alloy, composites, *etc*., may become the main direction of research in materials science to reduce vehicles weight and energy consumption [2–4]. Al–Si alloys as the main cast Al alloys have been mainly applied in engine blocks, cylinder heads and wheels. Particularly, the traditional materials, cast irons and steels, used for heat- and wear-resistant parts (*e.g.* pistons, cylinder liners, rotors, *etc.* [5–11]), can be substituted by hypereutectic Al–Si (HEAS) alloys for its good castability, low density, low coefficient of thermal expansion (CTE) and excellent wear resistance [12,13].

Traditional cast (TC) HEAS alloys contain coarse primary Si and needle-like Fe-rich phases, both inducing fracture and failure for stress concentration effects [10,14,15]. Microstructural optimization, especially the coarse primary Si and needle-like Fe-bearing phases, becomes an important field of study and several strategies have been proposed in order to achieve high strength and good ductility. Firstly, adding some *modifiers* into alloy melts to increase the heterogeneous nucleation and depress the growth of primary Si phase so as to refine the primary Si phase, *e.g.*, Na [16,17], Sr [18], Nd [19], Ca [20], P [21–23], Sb [24], RE [21,25] elements, especially P and RE elements are more effective [21]. Secondly, adding some trace elements such as Mn [14,26–29], Cr [14,29–31], Be [32], Sr [33], Ca [20], Co [14,31], K [34], Li [35], named "*neutralizer*", can eliminate the negative effects of needle-like Fe-bearing phase in cast Al alloys [14,26,27,36,37]. These "*neutralizers*" have been already applied in cast 3000, 6000 series Al alloys [38–41] and can be effectively used in hypoeutectic and eutectic Al–Si alloys with low Fe content (<1 wt.%). But the mechanical properties of high-Fe HEAS alloys, manufactured by TC process, still cannot be improved fundamentally even though the morphology of Fe-bearing phase can be modified by adding "*neutralizer*". Thirdly, the increase of cooling rate during solidification can increase the number of nucleus and refine the microstructures. Rapid solidification technique, *e.g.*, Rapid Solidification Powder Metallurgy (RS/PM) [42,43], Semi-Solid Process (SSP) [44–46], Spray Forming (SF) [47–57], *etc.*, have been studied and applied in practice, particularly, the SF with high cooling rate (10^3–10^4 K/s) can refine the microstructures and eliminate the macrosegregation, accompanying uniformly distributed second phase particles [47]. Presently,

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SF process has become an important method for the preparation of HEAS alloys with outstanding properties [49–58]. With further densification process, the as-deposited HEAS alloys could be fully compacted and excellent properties can be obtained, such as high fracture toughness and high elevated temperature strength, good fatigue property and machinability, and applied in practice successfully in Germany, Japan and others.

Yang et al.'s research [58] showed that ternary Fe-bearing phases can be optimized via the composite effects of Mn addition and SF process. In addition, some researches showed that Cr can modify the morphology of needle-like Fe-bearing phase as Mn did in Al–Si alloys [14,31–33]. So, adding Cr to HEAS alloys containing Fe might optimize the microstructure. However, the effects of Cr or (Mn + Cr) addition on the microstructures and properties of HEAS alloys containing Fe have not been investigated and reported to the present, therefore, the composite effects of (Mn + Cr) addition and SF process have been investigated presently aiming to obtain excellent microstructures.

2. Experimental procedure

2.1. Materials

The HEAS alloys with/without (2Mn + 1Cr, wt.%) addition had been prepared by TC and SF processes with basal composition: Al–25Si–5Fe–3Cu (wt.%) (Signed as 3C, also the alloy with (2Mn + 1Cr) addition was signed as MC21). The raw materials included pure Al (99.7% purity), Al–40Si and Al–50Cu master alloys and commercial Fe- (75 wt.% Fe), Mn- (75 wt.% Mn), Cr-additives (60 wt.% Cr). The others were refiners for Al alloys except for pure Fe, Mn and Cr elements in the three additives.

2.2. Traditional cast process

Both 3C and MC21 alloys were prepared by TC process. Firstly, after completely melting of the pure Al, Al–40Si and Al–50Cu master alloys in an intermediate frequency induction furnace, some commercial Fe-additives were added into the Al–Si–Cu alloy melts and held for 20–30 min among 1073–1123 K for the fully melting of Fe-additives. For alloy with (2Mn + 1Cr) addition, Fe-, Mn- and Cr-additives were orderly added into the melts and same heat preservation treatment as done to 3C alloy was used. And the temperature of alloy melts should be reduced to ∼1073 K and the alloy melts were subsequently poured into graphite mould with dimensions Ø30 mm × 100 mm for the ingots.

For the liquidus temperature of Al–Si binary alloy with 25 wt.% Si was about 1053 K [14], the temperature of heat preservation treatment should be 50–70 K high than liquidus temperature for the entire melting of all the alloying elements.

Table 1
The parameters of SF process.

Atomization gas	N_2
Atomization pressure/MPa	0.6–0.8
Deposition distance/mm	390–420
Melting temperature/K	1123–1203
Diameter of Tube/mm	3
Spray angle/°	22
Eccentricity/mm	16–20

2.3. Spray Forming process

The melting process was same with Section 2.2, but the degree of superheat during melting should be 100–150 K. And the melts should be held for 10–15 min among 1153–1203 K to eliminate any un-melted alloying elements or high temperature compounds, which could reduce the fluidity of alloy melts and affect the atomization process.

The atomization and deposition processes were finished in self-made SF facility and the parameters of SF process were shown in Table 1. An annular convergent–divergent nozzle had been utilized to get a spray of micro-sized droplets through a melt delivery tube from the alloy melts. The melts were atomized into droplets by Nitrogen gas and the droplets were deposited onto a rotating and withdrawing collector copper substrate below the atomizer to form a rapid solidified cylinder preform with dimensions Ø130 mm × 180 mm. In order to reduce oxidation of the spray, the atomization chamber had been filled with inert gas.

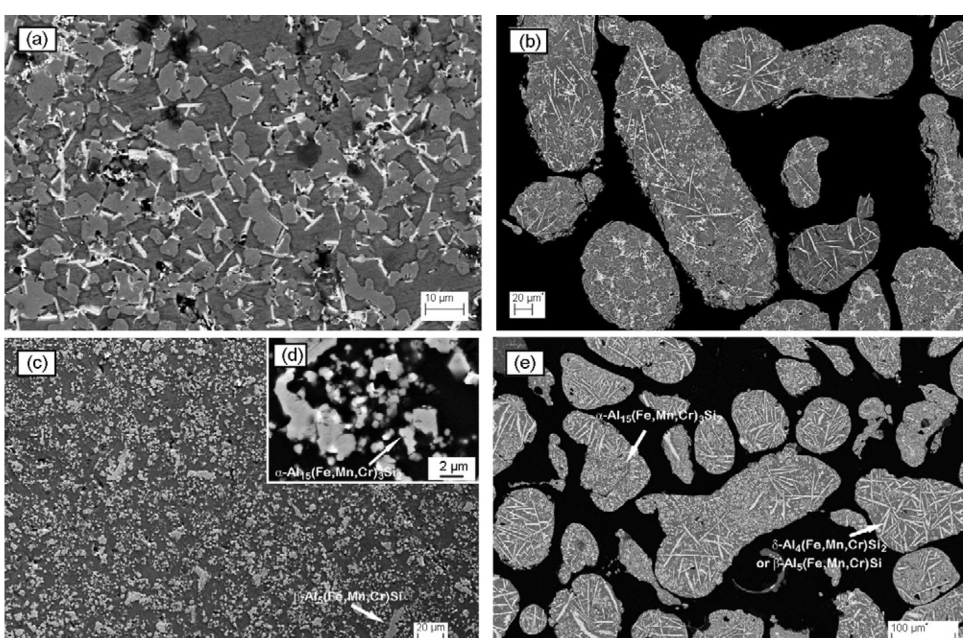

Fig. 1. Microstructures of spray-formed alloys (a and c) and their over-sprayed powders (b and e). (a and b) 3C, (c and e) MC21, (d) high magnification of (c).