



The modification of electroless deposited Ni–P master alloy for hypereutectic Al–Si alloy

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ABSTRACT

Ni–P alloy with overall composition of 7.0 wt.% phosphorus was fabricated via electroless plating on substrate of aluminum foil. The effects of this Ni–P master alloy on the modification and the processing for hypereutectic Al–20 wt.%Si alloy have been investigated. Primary silicon of hypereutectic alloy can be refined sufficiently by adding this Ni–P master alloy with total amount of 0.008 wt.% phosphorus above 800 °C. There is no phosphorus burning loss during fabrication of hypereutectic Al–Si alloy modifier by electroless deposition, and environment pollution is reduced. Refinement of primary silicon can be achieved with less addition and a shorter time of processing by use of this electroless deposited Ni–P master alloy as modifier.

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1. Introduction

Hypereutectic Al–Si alloys are attractive materials for many commercial applications due to their low density, low thermal expansion coefficient and high wear resistance. They are ideal piston materials [1–3]. However conventional ingot metallurgy leads to a coarse primary silicon phase, which causes low mechanical properties of the alloys. It is necessary to refine primary silicon for improving the properties. In conventional casting phosphorus-based master alloys such as Cu–P alloys and Al–P alloys are currently used as modifier to refine primary silicon of hypereutectic Al–Si alloys [4–6]. When the master alloys containing phosphorus are fabricated by metallurgy method, large burned loss of phosphorus happens due to its volatility at heating, which could cause environment pollution. Moreover, Cu–P alloys are prone to segregate and need a long time to uniformly refine primary silicon in molten Al–Si alloy [5,6]. This prolongs the processing time of modification.

Phosphorus is the effective component in modifier for hypereutectic Al–Si alloys. Therefore, in principle all kinds of alloys containing phosphorus can modify hypereutectic Al–Si alloys when they are melted into these alloys. Electroless deposited Ni–P master alloy is one of such alloys and can be prepared by electroless plating. This master alloy should be available for modified primary silicon in hypereutectic Al–Si alloys. By means of electroless plating, there is no phosphorus burning loss. In this work, the preparation of

this Ni–P master alloy, its modification effect and the modification processing are investigated.

2. Experimental procedures

2.1. Preparation of Ni–P master alloy and hypereutectic Al–Si alloy

Ni–P master alloy was prepared by electroless plating. The plating substrate was 50 μm aluminum foil. Nickel sulfate (NiSO₄·6H₂O) was main salt in plating bath. The pH scale of plating bath was 5 and plating temperature was 88 °C. Plating for 2 h, about 20 μm coating was obtained. The mass of the electroless plating alloy was measured by following procedures, weighting aluminum foil before electroless plating, and then weighting the foil again after plating. The difference between these two weights is the mass of Ni–P alloy. The P content of Ni–P master alloy was estimated using energy dispersive spectroscopy (EDS) in JSM-6360LV scanning electron microscopy (SEM). The Ni–P plating was peeled from substrate of aluminum foil and then analyzed with X-ray diffractometry (XRD) and differential scanning calorimetry (DSC) in order to determine the characteristic of the master alloy.

Al–20%Si alloy was prepared in a clay-bonded graphite crucible within an electric resistance furnace using 99.70% industrial purity aluminum and 99.0% crystalline silicon (all compositions quoted in this work are in wt.%).

2.2. Modification process of hypereutectic Al–Si alloy

The modification process was as following, 1 kg Al–20%Si alloy was melted in the graphite crucible and heated to a set temperature, and then electroless deposited Ni–P master alloy was added into the melt while stirring slightly with a zirconia-coating steel rod. The melt was then held for 3–5 min and cooled to 780 °C before casting into a steel mold which was preheated to 250 °C to form sample rods.

Al–20%Si alloy was molten and heated to 780, 800, and 820 °C, respectively, and different content of Ni–P master alloy was added. Thus the proper modification temperatures and amount of Ni–P additions will be determined according to the sufficient modification effect. In those experiments, the selected addition level of Ni–P master alloy was 0.06%, 0.12%, and 0.24%, respectively, for the Al–20%Si alloy.

For each modification processing test, the samples for metallographic analyses were taken out from the sample rods. After the samples had been carefully pol-

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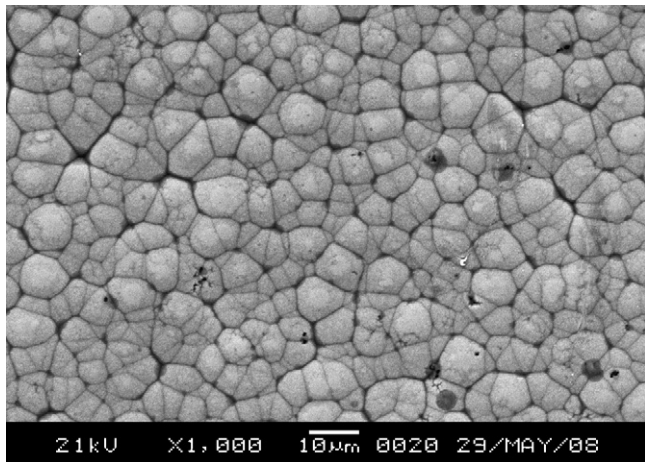


Fig. 1. Surface micrograph of electroless deposited Ni–P master alloy.

ished, the micrographs were taken using a common digital camera on a Leica optical microscope to determine the modification effect.

3. Results and discussion

SEM examination shows that the surface of Ni–P plating presents a nodular aspect and is relatively homogeneous as shown in Fig. 1. The diameter of the nodules is about 10 μm . In the Ni–P alloy, an average 7.0% phosphorus content was determined by using EDS. This alloy was plated at pH 5 plating bath. The P content of Ni–P plating increases with decreasing pH value, but the plating rate decreases with increasing pH value.

Fig. 2 shows the XRD pattern for the Ni–P plating sample. The XRD pattern exhibits only a single broad peak at around 2θ of 45° , corresponding to an amorphous structure. Theoretically, a disorder in the atomic arrangement manifests itself as a broad peak in XRD patterns. The plating Ni–P alloy is obtained below 100°C , and only exists mechanical bonding between the plating alloy and the plating substrate. The XRD of the plating alloy also shows that other phases do not formed in the interface between the plating alloy and the Al foil.

DSC curve of the Ni–P plating is showed in Fig. 3. The DSC trace indicates that the obtained Ni–P alloy is an amorphous structure and its crystallization temperature (T_x) is 329°C at a heating rate of $10^\circ\text{C}/\text{min}$.

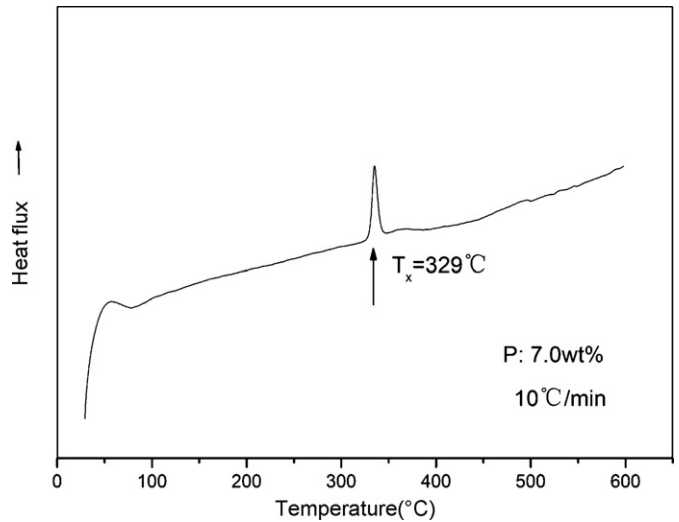


Fig. 3. DSC curve of electroless deposited Ni–P master alloy.

Fig. 4 shows the unmodified typical micro morphology of primary silicon in as-cast Al–20%Si alloy. Crystallites of primary silicon exhibit coarse irregular and star-shaped morphologies in the as-cast alloy. It has been known that the star-shaped primary Si crystals grow from a twinned decahedral nucleus at conventional cooling rate which is an assembly of five silicon crystals in twinned orientation [7].

Fig. 5 shows that after modification the primary silicon is refined drastically at each processing temperature and different adding levels of the Ni–P alloy. Nevertheless some of primary silicon form coarse platelet or block type and the refinement is not completeness with different adding levels of the modifier at 780°C , as shown in Fig. 5a–c. For adding 0.12% and 0.24% Ni–P alloy, i.e. 0.008%, 0.016% phosphorus, at both 800°C and 820°C , satisfactory modifications are achieved, and the crystallites of primary silicon are small in size and uniformly distributed in Al–20%Si alloy, as shown in Fig. 5e, f, h and i. For adding the 0.06% Ni–P alloy, i.e. 0.004% phosphorus, at both 800°C and 820°C , the refinement is also insufficient, as shown in Fig. 5d and g.

The modification mechanism of primary silicon is regarded generally as a heterogeneous nucleation with addition of the master alloys containing phosphorus. Small AlP particles within the modified primary silicon had been ascertained in hypereutectic Al–Si

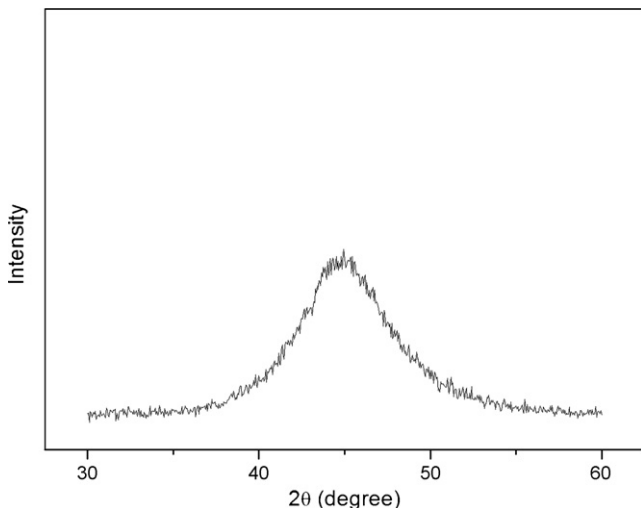


Fig. 2. XRD pattern of electroless deposited Ni–P master alloy.

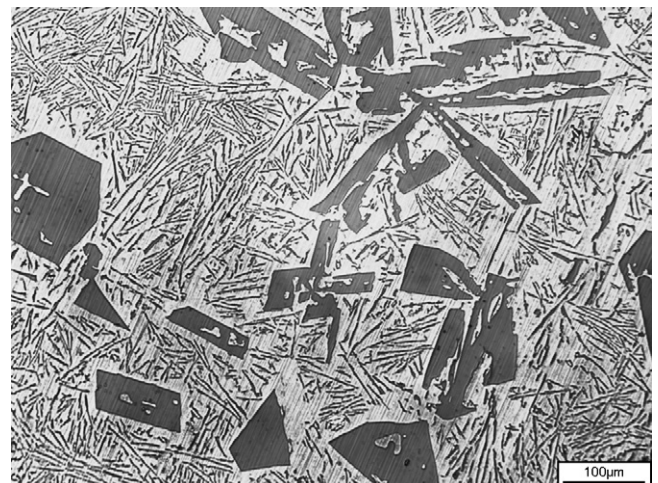


Fig. 4. Micrograph of unmodified Al–20 wt.%Si alloy.

alloys [8–11]. The crystal silicon is a cubic structure with $a = 5.431 \text{ \AA}$ crystal constant, and AlP phase is also the cubic structure with $a = 5.451 \text{ \AA}$ crystal constant. AlP and Si are both diamond cubic with very similar lattice parameters. Primary Si nucleates heterogeneously on the solid AlP particles with a cube–cube orientation relationship and solidifies, which promotes the modification and

refinement of primary silicon. According to the heterogeneous nucleation theory of crystal, in order to refine primary silicon completely AlP particles must form a sufficient number and distribute uniformly in the molten hypereutectic Al–Si alloy. It can be presumed that adding 0.06% Ni–P master alloy, i.e. 0.004% phosphorus is not enough for formation of an adequate number of AlP parti-

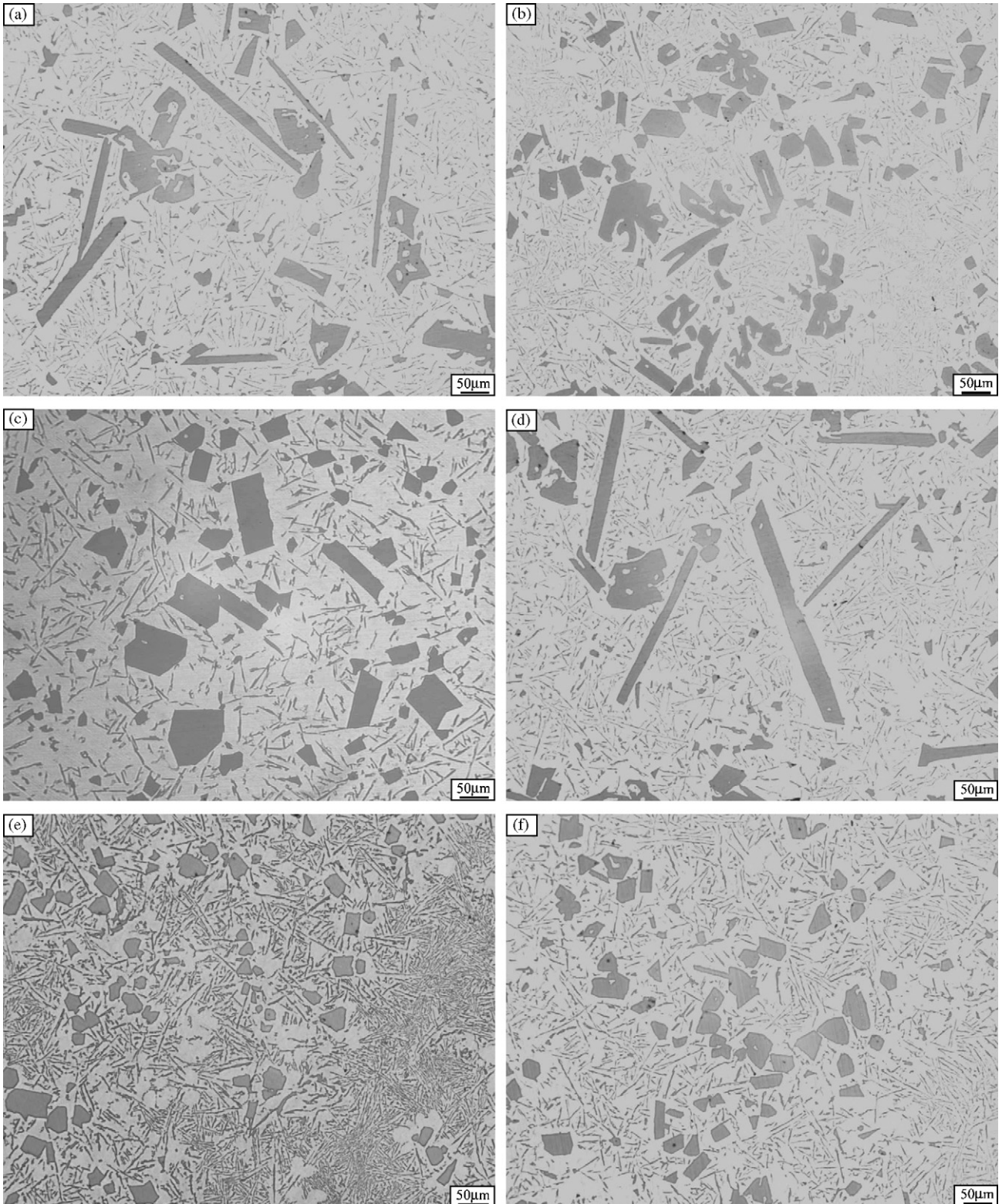


Fig. 5. Optical morphologies of modified Al–20 wt.%Si alloy by electroless deposited Ni–P master alloy (a) 0.06% Ni–P, 780 °C; (b) 0.12% Ni–P, 780 °C; (c) 0.24% Ni–P, 780 °C; (d) 0.06% Ni–P, 800 °C; (e) 0.12% Ni–P, 800 °C; (f) 0.24% Ni–P, 800 °C; (g) 0.06% Ni–P, 820 °C; (h) 0.12% Ni–P, 820 °C; (i) 0.24% Ni–P, 820 °C.

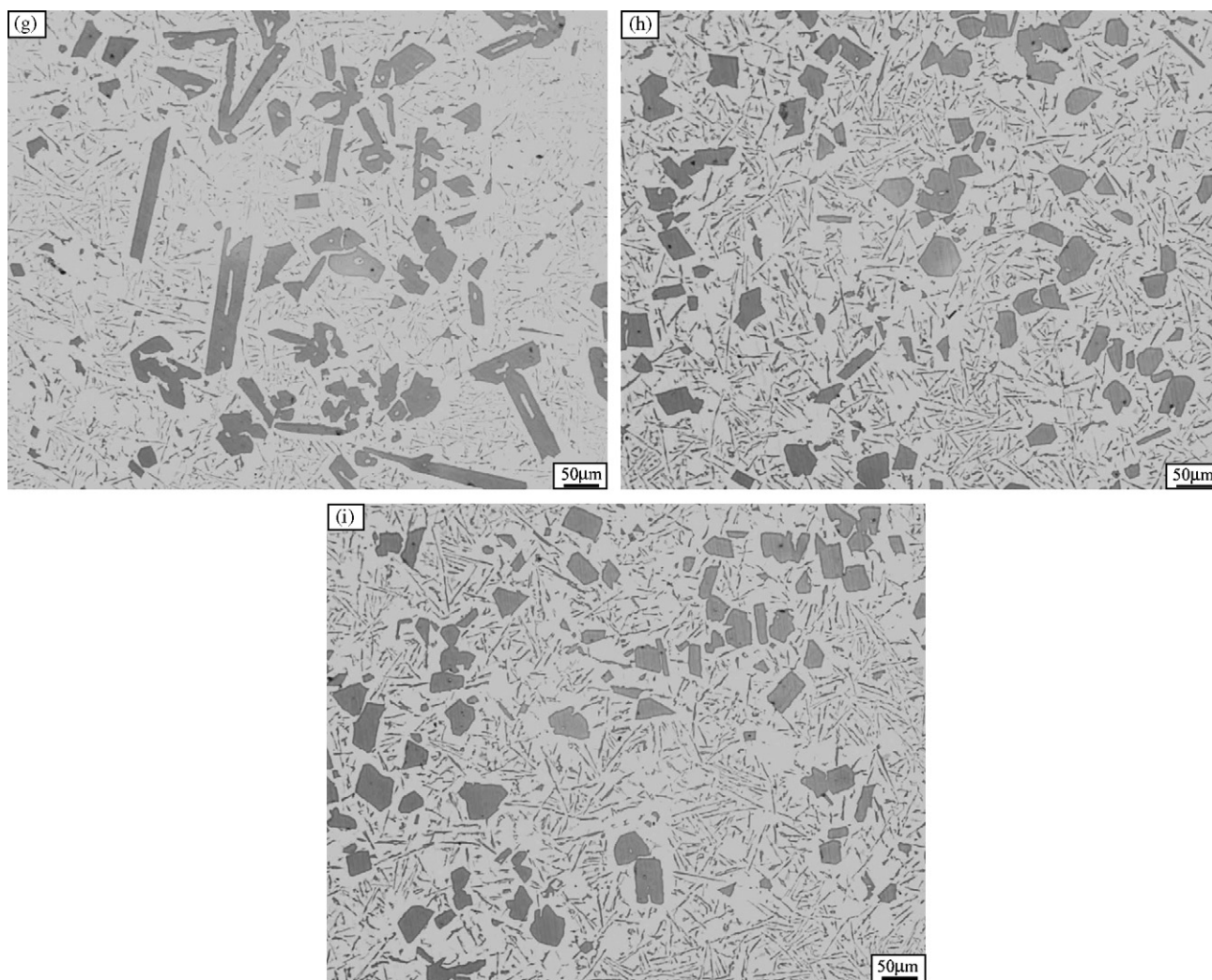


Fig. 5. (Continued).

cles and the refinement of primary silicon is insufficient. Adding 0.12% or 0.24% Ni–P modifier i.e. 0.008% or 0.016% phosphorus for the Al–20%Si alloy at 780 °C, AlP phase could not form fine particles and distribute uniformly in the molten alloy, which results in insufficient modification at short holding time.

Those master alloys containing P, which are fabricated by smelting methods, are in a bulk form when they are added into the melt of hypereutectic Al–Si alloys for modification. Longer time is required for those master alloys to dissolve into the molten alloy in order to obtain a satisfactory modification effect [2]. The needed addition levels of those bulk master alloys are generally 0.02–0.08% phosphorus for hypereutectic Al–Si alloys [4,6,8,9]. Adding the electroless plating Ni–P master alloy with a total amount of 0.008 wt.% phosphorus, sufficient modification can be achieved. Chemical composition test shows that the contents of P in the modified alloy are 0.0039, 0.004, and 0.0034 wt.%, respectively, at the modification temperatures of 780, 800 and 820 °C adding 0.12 wt.% of Ni–P master alloy (0.008 wt.% P). It is shown that the high recovery rate of phosphorus can be obtained by adding the Ni–P alloy. The electroless deposited Ni–P alloy is a metal thin foil on the aluminum foil substrate. The kind of master alloy possesses a large surface and is an amorphous alloy in which the element of phosphorus distributes uniformly. After the amorphous Ni–P master alloy is added into the molten alloy it will crystallize, but owing to rapid heating phosphorus will disperse and form AlP quickly in the molten hypereutectic Al–Si alloy. Therefore

adding the Ni–P master alloy for a satisfactory modification effect the holding time of modification is very shorter and the adding level is lower than those of conventional modification processing with the bulk master alloys.

As a result of the addition of 0.12% or 0.24% Ni–P modifier the nickel contents should be less than 0.11% or 0.22%, respectively, in Al–20%Si alloy while satisfactory modification is obtained. Element of nickel should form NiAl_3 mainly in the modified Al–20%Si alloy. Nickel can improve mechanical properties for aluminum alloys at elevated temperatures, for example the aluminum alloy, A332 used for engine pistons contains 2.5% nickel. However, lower content of nickel will not affect the properties obviously.

4. Conclusions

Primary silicon in hypereutectic Al–Si alloys can be modified by amorphous Ni–P master alloy fabricated via electroless plating. Adding 0.12% such Ni–P master alloy (i.e. 0.008% phosphorus) above 800 °C, the primary silicon in hypereutectic Al–20%Si alloy is modified satisfactorily.

A lower addition level and a shorter time are required for a satisfactory modification on hypereutectic Al–Si alloy with the electroless plating Ni–P master alloy. The modification processing is simple.

There is no phosphorus burning loss for modifier's fabrication of hypereutectic Al–Si alloys by electroless deposition, and environment pollution is reduced.

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