Journal of Materials Processing Technology 222 (2015) 142–147

Contents lists available at ScienceDirect

Journal of Materials Processing Technology

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

Refining of metallurgical grade Si by solidification of Al–Si melt under electromagnetic stirring

Boyuan Ban[a], Yanlei Li[a], Qiuxia Zuo[b], Taotao Zhang[a], Jian Chen[a,*], Songyuan Dai[a,c]

[a] Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, China
[b] Shandong Aluminum Vocational College, Zibo 255065, China
[c] State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

ARTICLE INFO

Article history:
Received 14 September 2014
Received in revised form 29 January 2015
Accepted 5 March 2015
Available online 14 March 2015

Keywords:
Electromagnetic stirring
Refining
Solidification
Al–Si alloy

ABSTRACT

Aiming at developing a Si solidification purification process in the Al–Si alloy system, series of experiments on the effect of electromagnetic stirring on refining of metallurgical grade Si(MG–Si) were carried out. By the use of electromagnetic stirring, an increase of size and average mass of primary Si flakes with the increasing voltage of the electromagnet were obtained. Impurity elements formed intermetallic compounds with Al and Si, such as Al_7Fe_2Si(α phase) and Al_5FeSi(β phase). An intermetallic compound type transformation with electromagnetic stirring was observed. The refined Si under the alternative electromagnetic field contains much lower B and P than those without the electromagnetic stirring. An apparent segregation coefficient was introduced to describe the segregation between solid Si and Al–Si melt. The apparent segregation coefficients of B and P are determined to be 0.37 and 0.17, respectively, when the voltage of the electromagnet is 210 V and cooling rate is 0.5 K min^{-1}.

1. Introduction

Lynch (2009) suggested that using Si produced by the Siemens process to make solar-grade Si(SoG–Si) is both costly and far purer (9 Nines) than needed for the PV industry (6 Nines). So it is necessary to have a more efficient and economical method to purify MG–Si to SoG–Si. Recently, various techniques such as directional solidification, slag treatment, plasma refining have been proposed to meet this requirement.

Directional solidification is a well-known process for removing metallic impurities such as Fe and Ti from Si due to their small segregation coefficients between solid and liquid Si. Martorano et al. (2010) used this method successfully removing Fe, Al, Cu, Ti, V, Mn, Cr, Ni, Zr from MG–Si. But the removal of B and P, which are important dopants in Si, is practically impossible by the directional solidification method due to their relatively large segregation coefficients ($k_B = 0.8$, $k_P = 0.35$). A slag treatment was used to refine the MG–Si, however it is not efficient to remove B because the distribution coefficient between the Si and the slag is not small. Ma et al. (2014) used slag treatment combined with Sn–Si solvent refining to make impurities enrich in the slag and separate with the refined Si. The plasma refining uses heat of the plasma torch to activate gases such as O_2 and H_2. When these activated elements meet atomic B on the surface of Si melt, they produce volatile H–B–O species that are evaporated. Recently, Wang et al. (2013) reported a new microwave-assisted plasma refining, which indicates a ultra-high removal rate of P. But the high cost of the device and large energy consumption limit this technique from industrial application.

Solvent refining with Al–Si alloy is a promising process to produce SoG–Si at large scale and with low cost. Lee et al. (2013) used fractional melting process to remove 99% of B by 2%Al–Si alloy. Gu et al. (2011) used powder metallurgy technique alloying Al–Si powder to purify Si and increase the yield of Si products. Li et al. (2012) used super gravity to separate the Si flakes from Al during the refining. Yoshikawa and Morita (2012) summarized that the purification can be achieved by redistributing the impurities in the solid/liquid interface. Compared with the directional solidification of Si, solvent refining is carried out at much lower temperature, and the removal of B and P is more efficient. This process is conducted by (1) alloying MG–Si with Al to obtain Al–Si solvent, (2) cooling and solidification of the Al–Si solvent and (3) acid leaching to collect the primary Si flakes. Li et al. (2014) recent proved that kinetic is a very important factor controlling the removal efficiency of the impurity elements. Considering the kinetics of the impurities removal (diffusion of the impurities nearby the growing Si surface), solidification may take several weeks or even months in order to remove impurities effectively. The very slow solidification process will definitely limit this technique from future application.

* Corresponding author. Tel.: +86 0551 65592171.
E-mail address: jchen@ipp.ac.cn (J. Chen).

http://dx.doi.org/10.1016/j.jmatprotec.2015.03.012
0924-0136/

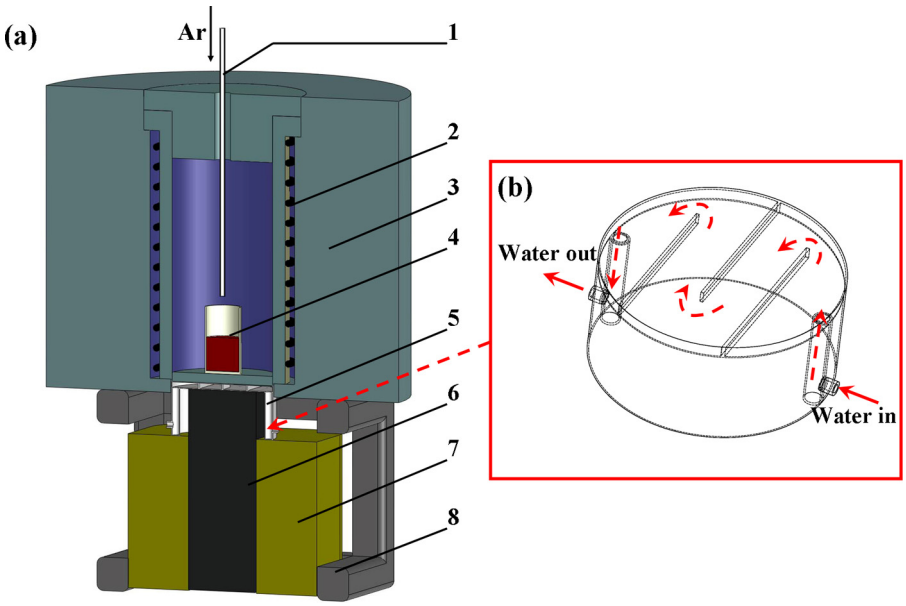

Fig. 1. (a) Schematic drawing of the experimental apparatus. 1—Ar injecting tube; 2—resistance heater wire; 3—furnace body; 4—alumina crucible and melt; 5—water-cooled jacket; 6—electromagnet core; 7—electromagnet coil; 8—supporting frame. (b) Water flow in the water-cooled jacket.

In this work, a voltage controlled alternative electromagnetic field was applied during solidification of the Al–Si solvent to improve liquid convection. From these results, the removal efficiencies of the impurities by the electromagnetic stirring are studied. Furthermore the effect of the electromagnetic stirring on the alloy microstructures, the size distribution and the average mass of the primary Si flakes are comparatively studied.

2. Experimental procedure

Fig. 1(a) shows the experimental apparatus. An electric resistance furnace with a bottom electromagnet was used for all the experiments. The electromagnet was connected to AC power controlled by a voltage transformer (0–220 V, 50 Hz), and the strongest top surface electromagnetic field strength of the electromagnet is 0.41 T. A water-cooled jacket was placed between the furnace and electromagnet to insulate the heat from the furnace bottom, Fig. 1(b) shows the detail of the water flow in the cooled jacket. Two different cooling rate series (series I and II) were used in this work, which are summarized in Table 1.

MG–Si lumps were crushed, and then blended with commercial Al to form a mixture of Al–30Si (wt%). The composition of the MG–Si and the Al determined by inductively coupled plasma optical emission spectrometry (ICP-OES) are shown in Table 2. A total of about 75 g Si and 175 g Al were put into an alumina crucible (ID = 56 mm, OD = 60 mm, height = 100 mm). The crucible was placed in an electric resistance furnace, heated to 1373 K at a rate of 5 K min^{-1} in Ar atmosphere, and then held for 3 h, within which the melt was agitated twice by a quartz rod for homogenization of the molten alloy. After that, it was cooled down quickly to 10 K above the liquidus temperature (1127 K for Al–30Si melt) and then cooled to 833 K with the pre-determined cooling rates (1.5 K min^{-1}, 0.5 K min^{-1}) under the voltage controlled alternative electromagnetic field (0, 60 V, 150 V, 220 V, respectively). Then the refined Si flakes from the Al–Si alloy ingot were extracted by acid leaching. After the acid leaching, the Si flakes and powder were rinsed with deionized water, dried and separated.

The size distribution and the average mass of the refined primary Si flakes of each sample were measured by sieve analysis. Microstructure of the Si samples and composition of intermetallic compounds in the sample after the solvent refining processes were examined by scanning electron microscope-energy dispersive spectroscopy (SEM-EDS). In addition, the concentrations of impurities from the refined Si flake samples were analyzed by ICP-OES.

Table 1
List of experiments.

Series	Exp. no.	Voltage of electromagnet (V)	Cooling rate (K min^{-1})
Series I	I-1	0	1.5
	I-2	60	1.5
	I-3	150	1.5
	I-4	210	1.5
Series II	II-1	0	0.5
	II-2	60	0.5
	II-3	150	0.5
	II-4	210	0.5

3. Results and discussion

3.1. Induced melt flow

In the sample shown in Fig. 2, Lorentz force from the alternative electromagnetic field is generated through the center of the melt, and the upward and downward circulations are induced. In addition, the temperature gradient is driven from the periphery to the center. Therefore the Si phase is expected to start solidifying from the edge of the sample with lower temperature, and some of the Si grains are carried to the center part of the melt. During the growth of the Si grains, solute atoms are rejected from the solid phase into the liquid. These atoms build up in the liquid just in front

Table 2
Composition of MG–Si and commercial Al (ppmw).

	B	P	Al	Fe	Ti	Cr	Ni
MG–Si	28	46	2434	2818	437	7	154
Al	1	26	Bal	14,152	33	18	49
	Ca	Cu	Mg	Mn	Sn	V	Zn
MG–Si	37	35	8	105	0	351	1
Al	111	28	60	41	4	171	47