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Synthesis and Characterization of Hypoeutectic Al-Si Alloys by Reduction of Sodium-Fluosilicate Using Powdered Aluminium

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Abstract- Al-Si alloys and sodium aluminum fluorides were obtained by reduction of Sodium-Fluosilicate (S.F) with Al powder and molten aluminum. Different factors affecting the composition of the produced Al-Si alloys are studied. These factors are sodium fluosilicate to aluminum weight ratio, Al powder to S.F weight ratio and reaction time. The produced Al-Si alloys are self-modified due to sodium fluoride existence in the reaction's bath, which changed the morphology of Si crystals. This modification process assists in improving the mechanical properties. Microstructure examination, chemical analysis, x-ray diffraction, and Differential Thermal Analysis (DTA) are performed to characterize the as received materials and the produced alloys. The results indicated that the mechanism of the reaction was taken place as follows; when S.F is added to Al, the S.F decomposes to produce SiF_4 gas which reduced in the presence of Al powder to silicon ion. The silicon ions combine with Al to form the Al-Si alloy and the fluorine ions react with Al and the residue of sodium fluoride to produce cryolite. The produced Al-Si alloy in this study is a high quality containing Si up to 12%, with less than 0.2 total impurities and the produced cryolite can be used in aluminium electrolysis.

Index Terms— Al–Si alloys; sodium-fluosilicate decomposition, modification, .

1 Introduction

ALUMINIUM- Silicon alloys are the mostly important of aluminium alloys. The prevalent use of these alloys compared with the other types of aluminium cast alloy refer to their good physical and mechanical properties, such as: high castability, low specific gravity, low shrinkage, good weldability and good resistance to wear and corrosion [1], [2]. The main uses of aluminium silicon alloys in wrought forms are: the welding rods, the low melting point cladding for brazing quality sheet, for forging such as cylinder barrels, for radial aircraft, internal combustion engines and on application in the automotive industry. It is also used in architectural applications, because the anodized Al-Si alloy sheets have good dark gray color [3]. Al-Si alloys are produced by several methods. Conventionally, Al-Si alloys were prepared by adding relatively pure silicon to molten aluminium at temperature about 900 oC in muffle furnaces [4], [5].

S.F is produced from super-phosphate fertilizers plants as a by-product. S.F has many uses in a small scale, such as: ceramic, enamels, glass [6], [7]. One of the very important applications of S.F is the production of aluminium silicon alloy (Al-Si) and cryolite [8[, [9]. These materials represent a great importance for aluminium plants. Some studies were carried out in preparation of Al-Si alloys using S.F as alloying materials. The quantity of S.F to be submerged in molten aluminum plays a significant role in increasing the content of dissolved silicon; this depends in turn on the decomposition efficiency of S.F and also on the dissolution process which occurs in the liquid bath [4], [10]. The produced Al-Si alloys are self-modified due to sodium presence in the reaction's bath; this modification will enhance the mechanical properties.

The present work aims to produce a modified Al-Si alloys and cryolite from reduction of sodium fluosilicate with aluminium powder within molten aluminium. Also an attempt to study the factors affecting on the preparation of Al-Si alloys from reduction of S.F by molten aluminium.

2 Experimental Work

2.1 Materials

The materials used in the experiments were commercial aluminum, commercial aluminum powder and sodium fluosilicate. Commercial aluminum (99.7% Al), was obtained from Egyptalum company, in the form of cylinders (25 x 30 mm). Commercial aluminum powder with average size of (-125+63μm) was obtained from El-Nasr pharmaceutical chemicals company. Sodium fluosilicate powder has average size (-150+106μm). Tables 1, 2 show the chemical analysis of the used aluminum and the sodium fluosilicate. The as-received materials are investigated by XRD, and Differential Thermal Analysis (DTA).

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TABLE 1
THE CHEMICAL ANALYSIS OF THE ALUMINUM CYLINDERS

Component	Al	Fe	Si	Cu	Mn	Mg	Ti	Zn	V	Na
Percentage,%	99.7	0.03-0.09	0.01	0.005	0.004	0.004	0.005	0.005	0.005	0.0001

TABLE 2
THE CHEMICAL ANALYSIS OF THE SODIUM FLUOSILICATE

Component	Na	Si	F	SO4	Fe	Ca
Percentage,%	23.72	14.02	57.54	0.05	0.02	0.30

2.2 Fabrication procedures

The powders (Al and S.F) are manually mixed to obtain a homogeneous mixture. The homogeneous powder is pressed in a hardened steel die with 250 k N pressure force. This compaction produces a green compacts with 38 mm diameter and 25 mm height. The purpose of compaction process is to obtain a green compact of Al-powder and S.F, which can withstand against the elevated temperatures to avoid the early decomposition of S.F (Na_2SiF_6).

For each experiment, 200 gr from aluminum cylinders is melted in the laboratory scale electrical furnace at temperature of 900℃. The green compact Al and S.F is added to the molten aluminum after it is completely melted, and then stirring process is accomplished, mechanically, using stirrer of 400 RPM speed, to ensure that the S.F is well distributed into the molten aluminum. In the last step, the molten alloy is poured into the metal mold and is kept at room temperature until they are completely solidified. The experiments were carried out to study the factors affecting on the dissolved silicon in the produced Al-Si alloys and fluorides.

2.3 Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) was performed to estimate the enthalpy output of the transformations from the integrated area of the peaks. In a cell of Platinum, and at Nitrogen atmosphere with a flow rate of 40 ml/min, two samples of Al- S.F (26, 19 mg) at 800 and 900^{o}C respectively, were analyzed with a temperature rate of 10 ^{o} C/min.

2.4 Microscopic examinations

The surface of the produced Al-Si alloy samples is prepared using standard metallographic techniques before the examination, by various methods of grinding, polishing, and etching. After preparation, microstructures of the alloy samples were observed under computerized optical microscope (Model: Olympus BX51).

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction of the received materials

The as-received materials were examined by X-ray diffraction technique to identify the crystal structure and the phases present. The experimental X-ray diffraction patterns of the as-received Al and S.F are shown in Figures 1 and 2 respectively. Figure 1 shows that in case of commercial aluminum five main peaks are registered in the 2θ range of 0o to 90°. Sharp peaks in the diffraction pattern of pure aluminum indicate the crystalline nature of the material. Also for S.F (Figure 2), the crystalline nature of the material is appeared from the sharp peaks in the diffraction pattern of it.

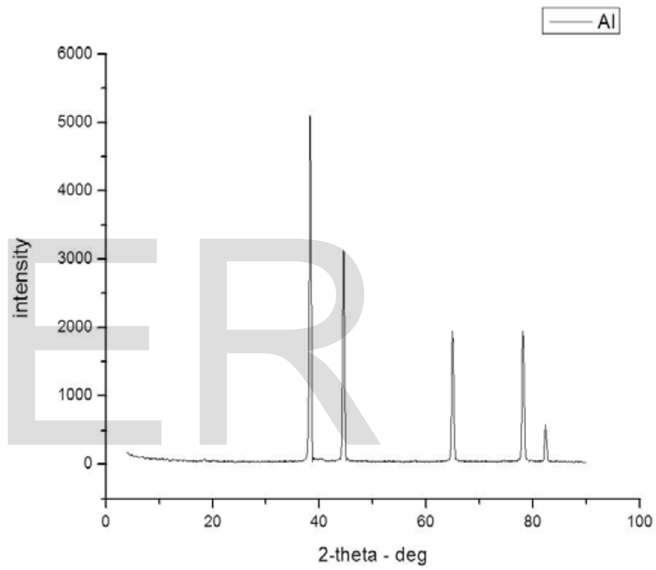

Fig. 1 Experimental XRD pattern of the as-received Aluminum

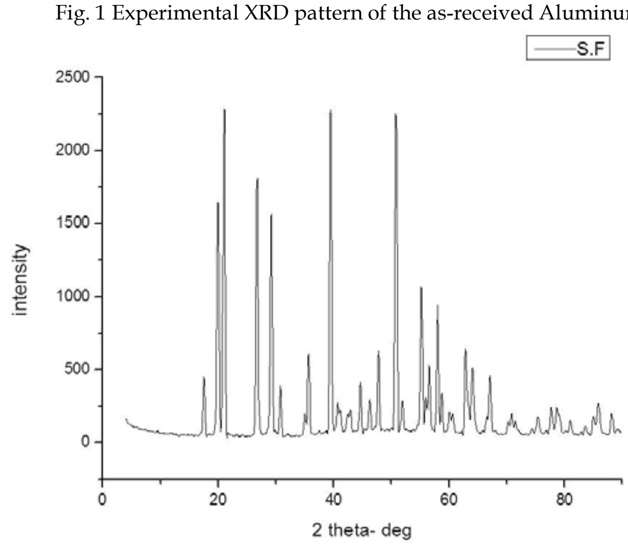

Fig. 2: XRD pattern of the as-received sodium fluosilicate

3.2 Thermal Analysis

Figure 3 shows differential thermal analysis (DTA) and thermogravimetry (TGA) for Al-S.F mixture. For DTA, two endothermic peaks (blue line) appear at 560 and 570 ^{o}C and the other shows peak at 658^{o}C. The first two peaks represent the decomposition of S.F according to reaction (equation 1):-

$$Na_2SiF_6 \longrightarrow 2NaF + SiF_4 \text{ (gas)} \quad (1)$$

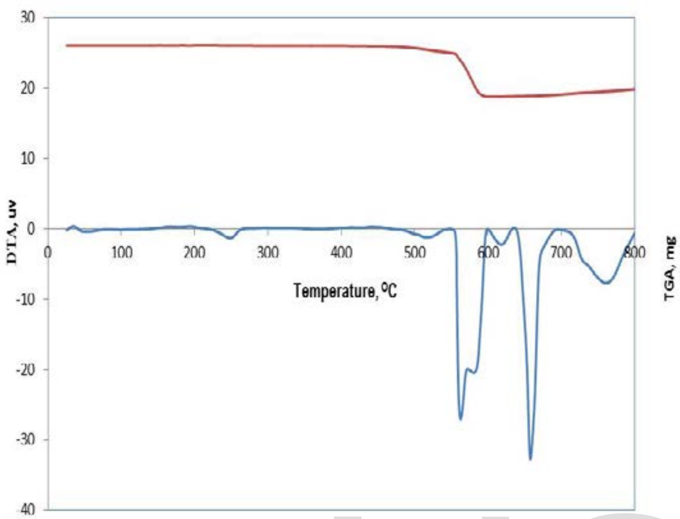

Fig.3 Differential thermal analysis (DTA) and thermos-gravimetry (TGA) for Al-F.S mixture

The second endothermic peak represents the transformation of Al from solid to liquid state (latent heat of Al fusion). TGA was applied for studying decomposition reactions; the mass of the tested sample was measured with the increasing temperature. From the shown figure, it can be noticed that the weight is decreased from 26 to 19 mg at temperature ranged from 556 to 596^{o}C. The loss of about 7 mg is come from the decomposition of S.F to SiF_4 and NaF according to reaction 1. The residue of the decomposed sample is Al about (13 mg) and NaF about (6mg)

4. Study the factors affecting on the production of the Al-Si alloy.

4-1 Effect of S.F / molten Al weight ratio on Si recovery.

The experimental tests were conducted to study the effect of S.F to Al ratio on the silicon dissolution in molten aluminum. These tests were carried out at various S.F / Al wt. ratios of ; 0.25, 0.5, 0.75, 1, and 1.25. The obtained results are shown in Figure 4. It can be seen that the silicon dissolution rate under the experimental conditions increases linearly with increasing the S.F to Al ratio, where the Si recovery reaches to 11.92 % at a ratio R= 1.25. The high rate of Si dissolution can be attributed to the increase of silicon quantity in input material. This leads to push the reaction in the direction of producing more Si which dissolves in liquid aluminum. This explanation is in good agreement with others [7], [8], [11].

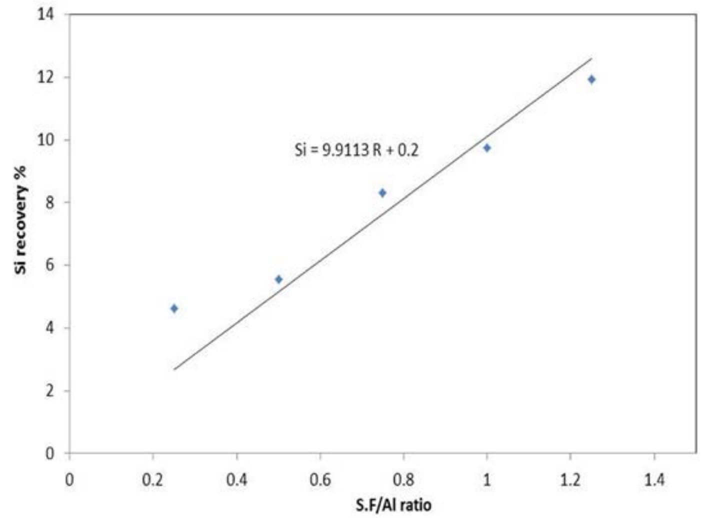

Fig. 4 Effect of S.F /Al wt. ratio on Si recovery of the produced Al-Si alloys .

4.2 Effect of Al powder / S.F weight ratio on Si recovery

These tests were carried out at various ratios of Al powder / S. F; 0.13, 0.17, 0.2, 0.23 and 0.27. The obtained results are shown in Figure 5. It can be seen that the silicon dissolution rate under this experimental conditions increases gradually with increasing the S.F to Al powder ratio until it reaches to 9 % Si at a ratio (R= 0.3). The increasing of silicon dissolution is related to the increase of the contact area between Al powdered and S.F which leads to push the reaction in the direction of producing more Si which dissolves in liquid aluminum [4], [11].

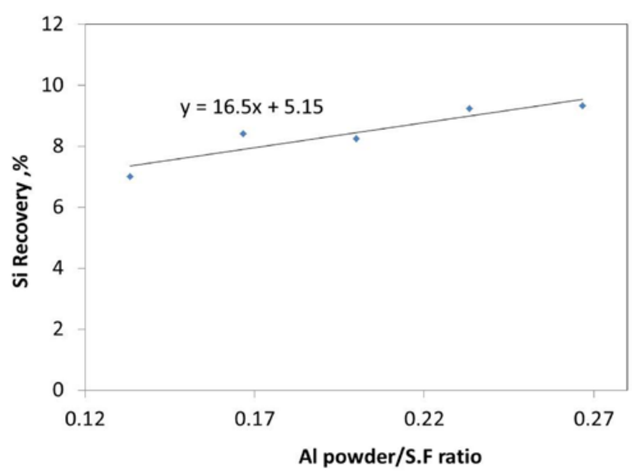

Fig. 5 Effect of Al powder/ Na2SiF6 wt. ratio on Si recovery %

4-3 The effect of reaction time on Si recovery.

Figure 6 shows the dependence of silicon dissolution rate on the reaction time, it has been observed that the silicon dissolution rate is accelerated in the molten aluminum with increas-

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ing the reaction time.

Silicon dissolution rate is increased at the beginning of the reaction at which the decomposition of S.F as well as the increase of Si solute in molten alloy can take place at the same period, and then silicon dissolution rate became nearly constant at the ending of the reaction. This is attributed to the decomposition of S.F at temperature above 600°C into sodium fluoride and silicon tetrafluoride gas as mentioned before. SiF4 gas reacts with molten Al to form Al-Si alloys. The concentration of silicon in molten Al increases with time which leads to some decreasing of reaction kinetic until the equilibrium occurred. This result was also observed by others [4], [7], [11].

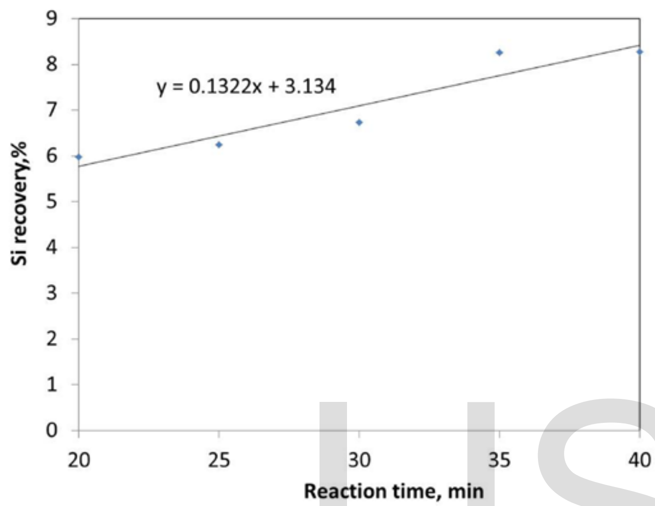

Fig. 6 Effect of reaction time on Si recovery% of the produced Al-Si alloys.

For the dissolution mechanism of S.F in molten aluminum, a kinetic study suggested that the dissolution of S.F in molten aluminum to produce Al-Si alloys could be occurred at temperature more than 600 °C according to the reactions appeared in equations 1 and 2:

$$3SiF_{4\,(gas)} + 4Al \longrightarrow 4AlF_3 + 3Si\ (alloy) \qquad (2)$$

It can be predicted that the mechanism of the reaction takes as follows; when added S.F to molten aluminum, the S.F firstly decomposes according to reaction (equation 1) to produce SiF4 gas which reduced to silicon ion in the presence of Al powder within the molten bath which in turn combined with molten Al to form the Al-Si alloy. The fluorine ions react with molten Al to produce AlF_3 which combined with the residue NaF to produce cryolite. This result is conformed to Omran [7], but the new in this work is presence of Al powder. The presence of Al powder plays an important role in the reduction of S.F by increasing the surface area between it and the S.F within molten Al. So, the rate of kinetic increases by increase of surface reaction.

5. Characterization of the Produced Al-Si Alloys

5.1 Chemical analysis

The chemical composition of the produced Al-Si Alloys for every specimen was studied in the previous factors. From the obtained results; it can be seen that the Si content is ranged from 4.63 to 11.92 % in the produced alloys. This result is obtained according to the composition of the samples and it is coming from the S.F. Sodium content in the produced alloys ranging from 0.0001 to 0.005 % and most of the sodium coming from the used S.F. Chemical analysis shows that total impurities in the Al-Si alloys less than 0.2% as shown in Table 3.

TABLE 3
THE CHEMICAL ANALYSIS OF THE PRODUCED AL-SI ALLOYS

Component	Al	Fe	Si	Cu	Mn	Mg	Ti	Zn	V	Na
Percentage,%	Rem.	0.18	11.92	0.006	0.003	0.001	0.004	0.003	0.004	0.005

5.2 Microstructural analysis

The results of optical microscopy as indicated in Figures (7a, 6d) show that the presence of α Al dendrites and eutectic silicon phase in the content of Al–5 Si and Al–12 Si samples. The blocky morphology appeared with the primary Si, while the eutectic silicon exhibited needle shape morphology. The microstructure of Al-Si alloys near to the eutectic exhibit lamellar eutectic silicon which is in the form of large plates with sharp edges. The obtained results show that with increasing of the silicon content, a transition from cellular to dendritic growth occurred, due to crystal growth and a coarser grain structure [14], [15]. So, alloys with a predominantly eutectic structure are modified to obtain adequate mechanical properties. In the present work, the produced alloys are self-modified due to sodium presence. Figure 4d shows micrograph of modified Al-Si alloys containing 12%Si, although this composition closed to eutectic composition, the microstructure indicated that there is aluminium within the eutectic mixture due to the presence of sodium in the reaction's bath. Sodium causes modification of the microstructure and effectively moves the eutectic point to a higher silicon concentration and lower temperature. This modifies the growth of the eutectic silicon to produce an irregular fibrous form rather than the usual flakes. The eutectic point has moved far enough to make the alloy, at this composition hypoeutectic, so new primary alpha forms, rather than primary Si. This result is also observed in other literatures [4], [7], [11], [13].

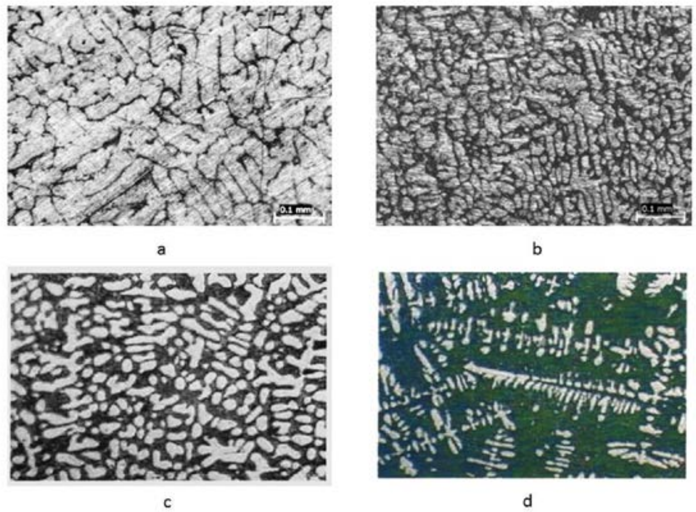

Fig. 7 Microstructure of the produced Al-Si casing alloys with different Si % content using light microscopy X= 100; a) 5 % Si, b) 7 % Si, c) 9 %Si and d) 12 %Si

6 Conclusion

The present study was carried out to fabricate the Al-Si alloys with silicon content between 4 to 12 %, and cryolite, according the reduction of S.F with Al powder and molten aluminum. Factors affecting the composition of the produced Al-Si alloys were studied. The silicon dissolution rate under the experimental conditions increases linearly with increasing the S.F content, due to the increase of silicon quantity in input material. The produced alloys were self-modified due to the presence of sodium. Sodium presence improves of silicon morphology and refines it, which lead to improve in the mechanical properties of the produced alloys. From DTA and TGA for Al and S.F reaction, the mechanism of this reaction can be explained and the existence of Al powder plays an important function in the reduction of S.F.

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