A comparative study between the addition of NH₄Cl and KCl in NaNO₃ and NaF-based degassers in aluminum casting

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Abstract. The quality of Al-Si casting product is important for its applications, however the molten aluminum has high solubility of H₂ at melting temperature in the casting process, so the formation of gas porosity during aluminum solidification is inevitable. This can cause a major drawback to the mechanical properties. The most common method to remove hydrogen gases in the molten metal is degassing. In this experiment, a conventional degassing method using Sodium Nitrate-Sodium Fluoride based degasser is conducted. Al-Si12 was melted at 720 °C then the degasser was plunged into the furnace bottom and held for three minutes. The results show better mechanical properties by the addition of degasser. This is because the degasser binds H₂ gases which is formed in the melting process. The mechanical properties between casting products that use NaF-NaNO₃ degasser and NaF-NaNO₃ with addition of NH₄Cl or KCl were measured and compared. The lowest mechanical properties were obtained when using degasser without NH₄Cl or KCl. This is because NH₄Cl or KCl is reactive and helps with the efficiency of degasser.

1. Introduction

Aluminum is the most widely used non-ferrous metal in the world being present in sectors as diverse as transportation, packaging, construction, electricity, and medicine [1]. The use of cast aluminum alloys are increasing in the automotive industry due to their significant advantages of lightweight, attractive appearance, excellent processability and corrosion resistance [2,3]. However, in the industry, aluminum is often used as an alloy because aluminum itself is not particularly strong. One of the alloying element often used is silicon, and the silicon content normally varies from 5 to 12 wt%. Al-Si cast alloys have been used widely to produce automotive components because of the excellent characteristics, one of those is excellent castability. The higher content of silicon in aluminum, the lower is its thermal expansion coefficient. Silicon is also a very hard phase, so its presence in the aluminum alloy will improve the alloy’s wear resistance significantly [4].

However, numerous studies shown that cast aluminum alloys are very sensitive to casting defects and the presence of large pore near the specimen’s surface will be the dominant cause of fatigue crack initiation [5,12]. Molten aluminum is prone to hydrogen adsorption and oxidation, so gas porosity and oxide inclusions are inevitably found in aluminum castings [2]. Porosity is one of the major defects on aluminum alloy casting and its presence causes a major drawback to the mechanical properties of the casting products. Porosity can either formed by hydrogen precipitation in the liquid solution during solidification, or the inability of the liquid metal to feed through the interdendritic regions [6,7], or other factors like mold-metal reaction, high temperature oxidation, blowholes, or the combinations of
these effects [10,11]. Hydrogen is the only significant gas soluble in molten aluminum [6,7,8], so it is important to control the dissolved hydrogen. Once solidification of the alloy progresses, any excess hydrogen, not soluble in the solid and not able to escape the solidified section, will form porosity within the casting, and reducing its properties [4].

Some effective ways to reduce hydrogen porosity is through degassing and fluxing [6]. These methods include the application of nitrogen, argon, or even a mixture of both with chlorine and hexachloroethane (C₂Cl₆) tablets [6,9]. In a smaller industry, degassing is usually conducted by using tablet degasser, and the common tablet degasser is from hexachloroethane (C₂Cl₆) [13] which generates Cl₂ and gaseous AlCl₃ [14]. But the use of C₂Cl₆ was prohibited in EU in 1998 because it is also moderately irritating to the skin, and classified as possible human carcinogen [14]. Thus, C₂Cl₆ tablet degassing has been replaced by degassing with dry nitrogen or argon using a lance.

In this experiment, degassing is conducted using tablet degasser, but this degasser is sodium nitrate-sodium fluoride based. In this paper, the tablet degasser was added with ammonium chloride (NH₄Cl) or potassium chloride (KCl). From there, we can determine which one is better at yielding higher mechanical properties from the casting products. The expected result is that by adding NH₄Cl or KCl into the degasser, the mechanical properties of casting products will be improved. This is because the degassing and fluxing can improve the cleanliness of the molten alloy [14].

2. Experimental

2.1 Materials
The degasser used here is mainly a combination of NaNO₃ in powder form and NaF with the concentration of 18 wt% and 40 wt% respectively. The other 42 wt% consists of NaCl, NH₄Cl or KCl, Na₂SO₄, and food colorants. In this study some of the tablet degassers contain NH₄Cl or KCl, as shown on Table 1.

Table 1. Chemical composition of NaNO₃-NaF based degasser.

| Composition | Degasser 1 Weight (kg) | Degasser 2 Weight (kg) | Degasser 3 Weight (kg) |
|-------------|------------------------|------------------------|------------------------|
| NaNO₃       | 0.8                    | 0.8                    | 0.8                    |
| NaF         | 1.25                   | 1.25                   | 1.25                   |
| NaCl        | 1.6                    | 1.6                    | 1.6                    |
| Na₂SO₄      | 1.2                    | 1.2                    | 1.2                    |
| NH₄Cl       | 0.175                  | 0                      | 0                      |
| KCl         | 0                      | 0                      | 0.175                  |

2.2 Methods

2.2.1 Making of NaNO₃ and NaF based degasser. The materials for degasser were then mixed using mixer with the addition of water, and the stirring time is about 30 to 60 minutes so the mixture is well homogenized. Furthermore, the mixed material then processed and formed into a cylindrical tablet shape using a printing machine. Then this degasser tablet was put into the oven at temperature 100 °C for about 60 minutes to evaporate the moisture content so we achieve the tablet degasser with minimum moisture content. The last step if the finishing process of the tablet degasser where it was cut, or polished, and eventually packed.

2.2.2 Casting process of Al-Si12. The chemical composition of Al-Si12 was obtained from conducting Optical Emission Spectrometry (OES) testing and the result was shown in Table 2. The main component is aluminum with majority alloying element is silicon.
Table 2. Chemical composition of the experimental Al-Si12 (wt%).

|   | Al  | Si  | Fe  | Cu  | Mn  | Mg  | Zn  | Cr  |
|---|-----|-----|-----|-----|-----|-----|-----|-----|
|   | 87.3| 12.4| 0.0938| 0.0015| 0.0045| 0.0003| 0.0024| 0.0048|

The casting procedure started with melting the Al-Si12 in an electric furnace at 720 °C until the material was melted completely. While the materials were melted, the mold was coated with a mixture of zircon and thinner then preheated at 350 °C for 15 minutes. The tablet degasser was also preheated using a muffle furnace at 100 °C for 1 hour to make sure there was no moisture content left in the degasser. After the aluminum alloy melted completely, the preheated degasser then plunged into the bottom of the furnace using a coated plunger, and held until the tablet degasser totally dissolved and mixed with the molten metal which takes about 3 - 5 minutes. This degassing process was effective in removing the gas inside the molten aluminum which then bring the undesired hydrogen gas up to the surface of the molten metal. Next, this degassed molten metal was poured into a metal mold at pouring temperature 690 °C and also into a porosity testing cup. While the molten metal inside the mold underwent solidification, the one in the porosity testing cup was put into a vacuum condition at a constant pressure of 100mmHg for 315 seconds using Ostek Motorized Porosity Tester. The schematic casting design can be seen in figure 1.

Figure 1. Schematic of casting design. (a) Top View; (b) Front View; (c) Bottom View; (1) Down Sprue; (2) Runner; (3) Gas Tunnel; (t1, t2, t3, t4) Tensile Specimens; (i1, i2, i3) Impact Specimens.
From this mold, we can obtain two types of testing specimens, including the tensile test specimens obtained from t1, t2, and t3, and also impact test specimens obtained from i1, i2, and i3. On the far left side is the down sprue with a diameter of 12 mm, which is where the molten metal was poured. Show as number 2 is the runner, which is where the molten metal flows and will fill in all of the specimen’s casting. The other component of the mold is a gas tunnel, which placed in the top right side of the mold as the place for removing gas from within the mold, here shown as number 3. After the casting process was completed, the specimen then prepared and observed to investigate the mechanical properties of the casting products.

3. Results and Discussion

3.1 Mechanical properties of casting Al-Si12 with degasser
The mechanical properties of the Al-Si12 casting products were characterized by tensile test, impact test, hardness test and microstructure observation. The tensile test was conducted using GOTECH AI-7000 LA 10 machine with JIS Z2241 standard. In order to obtain the impact value, the impact test was conducted using Frank impact testing machine with the charpy method. The hardness test was conducted by using LCB3100 LECO Brinell hardness tester with 10 mm diameter of steel ball indenter and the force parameter of 1000 kgf. For the porosity testing sample, they were solidified in a vacuum condition using Ostek Motorized Porosity Tester, then quenched in water to fasten the solidification of the remaining liquid metal. This sample was cut, prepared and then observed to investigate the microstructure, so the amount of gas porosity in the sample can be determined.

After conducting the tensile test on each specimen, we obtained the results, as shown in figure 2. The addition of NH4Cl and KCl surely plays a significant role in improving the tensile strength of Al-Si12 casting products. From figure 2, we can see that the highest tensile strength was obtained when adding NH4Cl to the tablet degasser. Meanwhile, the lowest tensile strength value was obtained with the basic tablet degasser, without the addition of NH4Cl or KCl. Reasonably, reducing the hydrogen content will certainly improve the mechanical properties of the resultant aluminum alloys. The effect of degassing on the quality of aluminum alloys include not only controlling the hydrogen content but also the resultant quality of the melt and its cleanliness [14]. Therefore, with the addition of NH4Cl or

![Figure 2. Effect of the addition of NH4Cl and KCl in NaNO3 and NaF based degasser on tensile strength of Al-Si12.](image-url)
KCl in this degasser helps to achieve a better aluminum casting products quality, and from this tensile result, the addition of NH₄Cl resulted in the best tensile strength, means it works the best on removing the porosities of the Al-Si12 casting products.

**Figure 3.** Effect of the addition of NH₄Cl and KCl in NaNO₃ and NaF based degasser on impact strength of Al-Si12.

Figure 3 above shows the effect of addition of NH₄Cl or KCl in the degasser on the impact strength. From this result we can also see that by the addition of NH₄Cl the impact value is increased and the lowest value is from the degasser without any addition of NH₄Cl or KCl. The highest value is indeed obtained when using the addition of NH₄Cl because it helps to eliminate gas porosities and other oxide inclusions, resulted in clean molten metal, thus able to withstand any sudden load, and has higher impact value.

**Figure 4.** Effect of the addition of NH₄Cl and KCl in NaNO₃ and NaF based degasser on hardness of Al-Si12.
The result of hardness test was shown in Figure 4 above. It shows that the highest hardness value was obtained from the degasser without the addition of NH₄Cl or KCl, but still the hardness values are relatively the same, around 73 BHN, and there are no significant changes. The sample produce relatively high hardness values because all of them use degasser. Effect addition of degasser is to reduce the porosities and increasing the hardness [15], and from this result it is also proved.

3.2 Microstructural Observation of Al-Si12

![Microstructure of Al-Si12 casting product with variation of degasser](image)

Figure 5. Microstructure of Al-Si12 casting product with variation of degasser (a) with the addition of NH₄Cl; (b) without the addition of NH₄Cl or KCl; (c) with the addition of KCl.

Figure 5 shows the optical micrograph results for all the tablet degasser variations. This microstructure affects the mechanical properties of the alloy. Al-Si solidify by a primary precipitation of dendrites. Dendrites are often drawn having about four secondary arms growing around the primary stem at each junction [4,16]. The illustration of primary aluminum dendrite (α-Al) is shown in figure 5 pointed by the black arrow, and the black dots that are pointed by the red arrows are the porosities that occurred in the casting products. From the microstructure we can see that the number of porosities formed in the casting product is relatively low. It is possible because the tablet degassers are effective to remove gas. By comparing all the microstructures from figure 5, we can see the lowest amount of porosity was obtained by the addition of NH₄Cl to the tablet degasser.
Figure 6. Macrostructure of Al-Si12 casting product with variation of degasser (a) with the addition of NH$_4$Cl; (b) without the addition of NH$_4$Cl or KCl; (c) with the addition of KCl

Figure 6 shows the macrostructure appearance of Al-Si12 with all the tablet degasser variations. From the macrostructure, it could be seen that every cast result has low amount of gas porosities, but on figure 6b it shows much more gas porosities than the others, which is true because it resulted from the basic degasser without the addition of NH$_4$Cl or KCl. Meanwhile the macrostructure on figure 6a shows a very low even almost nonexistent content of porosities, due to the addition of NH$_4$Cl to the tablet degasser. It could be concluded that the addition of NH$_4$Cl in the tablet degasser works more effective in removing gas because of the micro and macrostructure, which also correlates to the mechanical properties results.

3.3 Effect of NaNO$_3$ and NaF tablet degassing with addition of NH$_4$Cl or KCl
Gas porosities and oxides are two common defects in Al-Si which are initiated through poor melt treatment or non-optimized casting route. When the molten aluminum meets with oxygen, it will immediately oxidize forming a skin of oxide. If the oxide skin is removed or cracked, a new oxide layer will immediately form. This oxide film has an amorphous structure and low permeability, therefore creates a protective layer at the surface of the liquid aluminum. As long as the oxides are at the surface of the molten metal, they do not present any significant threat to the quality of casting product.

However, melting, pouring and transferring liquid metal will most certainly entrain newly formed thin oxides into the melt making them possibly harmful [4,17]. The most effective way to solve this is by degassing and fluxing, and the simplest degassing method is by using tablet degasser. In this study,
we use NaNO$_3$ and NaF based degassers, and the chemical reaction with hydrogen gas can be inferred in equation (1) and (2).

\[ 2 \text{NaNO}_3 + \text{H}_2 \rightarrow 2 \text{Na} + 2 \text{HNO}_3 \]  \hspace{1cm} (1)

\[ 2 \text{NaF} + \text{H}_2 \rightarrow 2 \text{Na} + 2 \text{HF} \]  \hspace{1cm} (2)

The tablet degasser when plunged under the metal surface will produce nitrogen gas. The presence of nitrogen gas and bubbles will bind hydrogen gas and carry it to the surface of molten aluminum. The degasser can also remove impurities within the molten aluminum and carry it to the surface as a dross.

The addition of NH$_4$Cl or KCl in the degassing tablet is also used as a fluxing agent. Solid fluxes are mainly blends of chloride and fluoride salts, which forms a low-temperature (665 °C) eutectic. A low melting point is important since it will improve the fluidity of the flux [14]. These salt fluxes are often used to eliminate or reduce the formation of oxides, so we can obtain a clean molten metal which also gives high mechanical properties. The mechanism for cleaning the metal is to wet the oxides with flux so that they will either float or sink, but will not stay suspended in the melt.

4. Conclusion

From this experiment, the use of NaNO$_3$ and NaF based degasser in Al-Si12 casting process produces a relatively low amount of gas porosity. From the mechanical properties test, this low amount of porosity also improves the mechanical properties such as tensile strength, impact strength, and hardness. The addition of NH$_4$Cl or KCl in the tablet degasser also has better results than the basic NaNO$_3$-NaF degasser. By comparing all the results, we obtain the best mechanical properties from using NaNO$_3$-NaF degasser with the addition of NH$_4$Cl, due to the least amount of gas porosity based on the microstructure result. It is possible because the addition of NH$_4$Cl not only remove the hydrogen gas, but also reduce oxidation and other impurities.

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