Synthesis of Stoichiometric Phase Pure NiAl₂O₄ Using Molten Salt Method

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Abstract
Stoichiometric NiAl₂O₄ powder, with spinel structure, has been synthesized at moderate temperature by molten salt method. NaCl-LiCl salt system was used as a reaction medium and equimolar of Ni(NO₃)₂·6H₂O and α/γ-Al₂O₃ were used as precursors. The process parameters including the reaction temperature, salt type, and salt to precursor weight ratio were investigated. Rietveld refinement calculations were used to calculate the percent of each phase present in the resulting powders. The results of these calculations were followed in order to choose the salt system that requires the least reaction temperature to produce the highest Nickel aluminates percent. The as-prepared NiAl₂O₄ was characterized by various techniques such as X-Ray diffraction (XRD), energy dispersive X-Ray spectrometry (EDX), Fourier transform infrared spectrometry (FTIR) and field emission scanning electron microscope (FE-SEM). The results showed that the reaction obeys the dissolution-precipitation mechanism and phase pure Nickel aluminates, with equiaxed particles of blunt edges and smooth surfaces, could be prepared at 1400°C with wide particle distribution range from 200 to 700 nm without any other detectable impurities.

Keywords: Powders-chemical preparation; Nickel aluminates; NiAl₂O₄; Molten salt method; Rietveld Refinement.

Table 1: The process parameters used to preparation stoichiometric NiAl₂O₄

<table>
<thead>
<tr>
<th>Parameter</th>
<th>State</th>
<th>Value(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni: Al molar ratio</td>
<td>Fixed</td>
<td>(1:2)</td>
</tr>
<tr>
<td>Ni precursor type</td>
<td>Fixed</td>
<td>Ni(NO₃)₂·6H₂O</td>
</tr>
<tr>
<td>Salt system</td>
<td>Fixed</td>
<td>(NaCl-LiCl)</td>
</tr>
<tr>
<td>Salt: precursor weight</td>
<td>Fixed</td>
<td>(3:1)</td>
</tr>
<tr>
<td>Heating rate</td>
<td>Fixed</td>
<td>7°C/min</td>
</tr>
<tr>
<td>Holding time</td>
<td>Fixed</td>
<td>3hours</td>
</tr>
<tr>
<td>calcination temperature</td>
<td>Variable</td>
<td>800-1400 °C</td>
</tr>
<tr>
<td>(Al) Precursor type</td>
<td>Variable</td>
<td>Nano α and γ-Al₂O₃</td>
</tr>
</tbody>
</table>

INTRODUCTION
Spinel are an important group of compounds with a structure similar to that of the mineral spinel MgAl₂O₄. At the first, the thought was that ions with a particular valence occupy only one type of the tetrahedral and octahedral sites in the spinel structure. However, it had been proved that divalent and trivalent cations can occupy both tetrahedral and octahedral sites (Barth and Posnjak, 1932). Nickel aluminates spinel, as a transition metal spinel, has the general formula [Alₓ,ₓ Bₓ₋ₓ]([Aₓ,ₓ Bₓ₋ₓ]O₄) where A and B are cations occupying tetrahedral (Ni²⁺) and octahedral (Al³⁺) sites, respectively and (X) represent the degree of inversion. The degree of inversion, which increases with increase the temperature, determines the spinel type. It takes values in the range from 0 to 1 for the perfectly normal and the inverse spinel, respectively. On the other hand, when the X is between (0-1), the spinel is partially inversed (Roelofsen et al. 1992)(Jastrzębska et al. 2017).

NiAl₂O₄ possesses many attractive properties; these include its high mechanical resistance (Hasan et al., 2015), high thermal and chemical stabilities in acidic or basic environments (Ribeiro et al., 2010)(Leal et al., 2011)(Hasan et al., 2015), and possible environmental friendly treatments for recycling of the spent catalysts (Nazemi et al., 2012). It was extensively employed in many important applications for example, it was employed as catalyst support (Ribeiro et al., 2010) in various chemical reactions, such as hydrodechlorination (Cesteros et al., 2000), partial oxidation of methane to syngas (López-FONSECA et al., 2012), CO₂ reforming of methane (Zhou et al., 2008), chemical-looping combustion (Jin et al., 1999)(Hai-bo et al., 2008), acetylene hydrogenation (J.A. Peña, J.C. Rodriguez, J. Heruguido, 1994), steam reforming of methane (Zhou et al., 2008), combustion of methane (Yazdanpanah et al., 2014) and steam reforming of glycerol to hydrogen production (Dou et al., 2013) for his high mechanical resistance, as well as its high thermal and chemical stabilities (JAVANMARDI et al., 2016). Moreover, it is a good photocatalyst for the degradation of methyl orange (Védrine et al., 2015). Also it has been used as magnetic material, pigment, catalyst and refractory material (Kim et al., 2006). It is also a candidate material in high-temperature fuel cells (Kou and Selman, 2000).
Various methods have been employed to prepare NiAl$_2$O$_4$ such as solid state reaction (Han et al., 2004b) (Han et al., 2004a) which requires multi steps of high calcination temperature up to ~1600°C (Zygmuntowicz et al., 2015) and additional milling processes for long period of time up to ~168 hours, co-precipitation (Ribeiro et al., 2010), combustion reaction method (Leal et al., 2011). In many of these methods, the resulting powder contains other minor phases beside NiAl$_2$O$_4$ such as NiO and Al$_2$O$_3$. This complains that it is still difficult to prepare pure Nickel aluminate from stoichiometric reactants of NiO: Al$_2$O$_3$ (COOLEY and REED, 1972)(Otero and Fernandez J.M., 2011)(Han et al., 2011). This was used using X’Pert HighScore Plus apparatus. Fourier transformed infrared (FTIR) spectra of the samples were recorded using (Shimadzu 6000 diffractometer) equipped with Cu-Kα radiation (λ=0.15406nm) operated at 40 kV and 30 mA. Rietveld refinements on X-ray powder diffraction patterns were performed using XPert HighScore Plus software. Powder morphology including the size and shape of the prepared particles was observed by field emission scanning electron microscopy (FE-SEM) with a MIRA3 instrument and Transmission electron microscopy (TEM) using (Philips CM120) instrument. The phase purity was confirmed using energy dispersive X-ray spectrometry (EDS) using TESCAN instrument. Fourier transformed infrared (FTIR) spectra of the samples were recorded using (Shimadzu 1800, Japan) to evaluate molecular structure of the functional group in inorganic materials. Specific surface area measurements by Nitrogen adsorption/desorption isotherms were obtained with an (QSURF surface area analyzer) apparatus.

RESULTS AND DISCUSSION

Selecting The Salt System

Figure (1) shows the results of the XRD analysis for selecting the salt system for the preparation of NiAl$_2$O$_4$. It has been found that (LiCl) has undesirable peak at 2θ of (25.6°) which is related neither to the precursors nor to the desired NiAl$_2$O$_4$, thus, LiCl salt was disqualified. Table (2) illustrates the results of the Rietveld refinement calculations for the other five salt systems. These results clearly show that NaCl-LiCl is the best salt system as it produces the highest NiAl$_2$O$_4$ content and the lowest NiO content at the same reaction temperature. This result indicates that the nucleation and/or the growth of NiAl$_2$O$_4$ in the NaCl-LiCl salt system requires lower activation energy. This could be attributed to the solubility of NiO in the NaCl-LiCl which might be much higher than that in other systems. Moreover, the lower viscosity of the NaCl-LiCl system may enhance the formation of NiAl$_2$O$_4$ as the viscosity of KCl-LiCl at 640°C is 1.69(c,poise) while for NaCl-LiCl is 1.63(c,poise) at the same temperature (Matsumura and Nishihara, 1967).

MATERIAL AND METHOD

All the materials and chemicals used in the current work were XRD tested and used as received without further treatment. Ni(NO$_3$)$_2$.6H$_2$O hexahydrate (HIMEDIA, India, 97% purity), α-Al$_2$O$_3$ (Hongwu, China, 99.9% purity) and γ-Al$_2$O$_3$ (EVNANO, China, 99% purity) were used for preparing NiAl$_2$O$_4$ powder. In the first step, equimolar amounts of Ni(NO$_3$)$_2$.6H$_2$O and (α or γ) Al$_2$O$_3$ were mixed with the salt system for five minutes using agate mortar with salt to precursors weight ratio (S:P) of (3:1). Then, the mixture was transferred into alumina crucible with alumina lid and heat treated at different temperature (850-1400)°C for 3 hours. The product was washed thoroughly with hot distilled water for 5 times in order to remove any chloride residual salt.

Six types of salt systems were used including (NaCl, KCl, LiCl, NaCl-KCl, NaCl-LiCl, KCl-LiCl). To select the appropriate salt system, the criterion of needing the minimum synthesis temperature to produce the highest quantity of Nickel aluminate was followed. Rietveld refinement calculations were used to calculate each phase present in the resulting powders. After choosing the appropriate salt system, many experiments were carried out to find out the appropriate Al precursor and the reaction temperature.

Phase identification and the calculations of the amount of each phase present were carried out using XRD analysis and Rietveld refinement. The patterns were recorded at room temperature using (Shimadzu 6000 diffractometer) equipped with Cu-Kα radiation (λ=0.15406nm) operated at 40 kV and 30 mA. Rietveld refinements on X-ray powder diffraction patterns were performed using XPert HighScore Plus software. Powder morphology including the size and shape of the prepared particles was observed by field emission scanning electron microscopy (FE-SEM) with a MIRA3 instrument and Transmission electron microscopy (TEM) using (Philips CM120) instrument. The phase purity was confirmed using energy dispersive X-ray spectrometry (EDS) using TESCAN instrument. Fourier transformed infrared (FTIR) spectra of the samples were recorded using (Shimadzu 1800, Japan) to evaluate molecular structure of the functional group in inorganic materials. Specific surface area measurements by Nitrogen adsorption/desorption isotherms were obtained with an (QSURF surface area analyzer) apparatus.

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Figure 1: XRD patterns of NiAl₂O₄ prepared by different salt systems (all unmarked peaks corresponding with NA)

Figure 2: XRD Patterns of NiAl₂O₄ prepared from (a) Al(NO₃)₃.9H₂O and (b) α-Al₂O₃

Selecting The Al Precursor

Figures (2-a) and (2-b) show the XRD patterns of the Nickel aluminate prepared from Al(NO₃)₃.9H₂O and Al₂O₃, respectively. The diffraction data in Figure (2-a) are found to be identical with (JCPDS 01-073-1523) of NiO while that in Figure (2-b) represent a combination of (JCPDS 01-073-1523) of NiO and (ICSD 98-000-2662) of NiAl₂O₄. Based on that, Al₂O₃ was chosen as Al precursor for the preparation of NiAl₂O₄. In the case of using the nitrite, the absence of NiAl₂O₄ can be explained by the decomposition of aluminum nitrates upon heating where NO and NO₂ gases evolve during the reaction and cause distortion in the contact between the reactant particles and hinder the interaction between them (Han et al., 2004b). The absence of the peaks of Al₂O₃ in the XRD indicates that the NiO is the component that has the

Table 2: Rietveld quantitative phase analysis of NiAl₂O₄ samples prepared from different salt systems

<table>
<thead>
<tr>
<th>Salt System</th>
<th>Phase amount (Wt.%)</th>
<th>NiO</th>
<th>NiAl₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-LiCl</td>
<td>21.3</td>
<td>78.7</td>
<td></td>
</tr>
<tr>
<td>KCl-LiCl</td>
<td>30.4</td>
<td>69.6</td>
<td></td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>33.5</td>
<td>66.5</td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td>Disqualified</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>37.5</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>42</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>
higher solubility between reactants which dissolve first in the molten salt and diffused onto and into the surface of Al₂O₃. Thus, Al₂O₃ is not exposed to the X-ray during the test as it covered by NiO.

**Effect of Temperature and Precursor Phase**

Figure (3) shows the XRD patterns of NiAl₂O₄ prepared with stoichiometric ratio of Ni(NO₃)₂·6H₂O and Nano γ-Al₂O₃ (1:1) processed at different temperature ranged from 800°C to 1400°C for 3 hours. At all temperatures, diffraction data corresponding to NiAl₂O₄ were observed; however, for the temperature up to 1300°C, NiO was present in different ratio. At temperature of 1400°C phase pure stoichiometric NiAl₂O₄ was obtained.

Figure (4) shows the XRD results of NiAl₂O₄ prepared from stoichiometric ratio of Ni(NO₃)₂·6H₂O and α-Al₂O₃ processed at different temperatures of (1000-1400°C) for 3 hours. As shown in Figures (3) and (4), with increasing the temperature, the peaks width of NiAl₂O₄ decreased along with increasing in the peaks intensity. This indicates that the crystallinity and crystallite size of NiAl₂O₄ were increased. At the temperature of 800°C, the formation of NiAl₂O₄ is already become evident in the sample but a significant amount of the unreacted NiO was still remained. Upon increasing the temperature to 1000°C, NiAl₂O₄ peaks increased considerably, while NiO peaks decreased suggesting the enhancement of the reaction. On further increasing the temperature to 1400°C, NiAl₂O₄ peaks become noticeably higher than that at 1000°C and NiO peaks disappeared revealing the formation of phase pure of NiAl₂O₄.

**Figure 3:** XRD patterns of stoichiometric Na from γ-Al₂O₃ processed at different temperatures (NiAl₂O₄, NiO)

**Figure 4:** XRD patterns of stoichiometric Na from α-Al₂O₃ processed at different temperatures (NiAl₂O₄, NiO)
The formation of phase pure NiAl$_2$O$_4$ at 1400°C regardless the Al sources, which have different activity and particle size, indicates that the presence of NiO phase, below this temperature, is related to another common parameter in both cases. It may be related to the separation of the reactants due to the floating of NiO on the surface of the molten salt. The high temperature of 1400°C seems to be sufficient to thoroughly mix the reactant.

**Effect of Salt Content**

Figure (5) shows the FE-SEM images of the γ-Al$_2$O$_3$ along with that of the stoichiometrical phase pure NiAl$_2$O$_4$ prepared from γ-Al$_2$O$_3$ at 1400°C for 3 hours with different salt to precursor weight ratio. The NiAl$_2$O$_4$ particles, shown in Figure (5-b), prepared with salt to precursor ratio of (3:1) are equiaxed with blunt edges and smooth surfaces with wide particle distribution range from (200 to 700) nm. It has been noticed that there are small particles attached to the surface of the larger particles, this may be attributed to the formation mechanism (dissolution$\gg$precipitation$\gg$re-dissolution$\gg$re-precipitation). Figure (5-c) illustrates the FE-SEM images of the NiAl$_2$O$_4$ prepared with higher salt to precursor ratio of (6:1). The absence of the small particles attached to the surface of the large particles, indicates that the presence of larger amount of molten salt leads to the increase of critical size of particle that can be formed in the molten salt. It is believed that the smaller particles dissolved in the molten salt and re-precipitate onto larger particles due to Ostwald ripening effect.

**The Formation Mechanism**

In many previous works specially in the preparation of MgAl$_2$O$_4$ in molten salt method, it was reported that the formation mechanism followed the template formation, where the γ-Al$_2$O$_3$ did not dissolve in the molten salt and act as template with which the dissolved MgO reacts γ-Al$_2$O$_3$(Jayaseelan et al., 2007)(Zhang et al., 2015). However, the FE-SEM results, shown in Figure (5), clearly shows that NiAl$_2$O$_4$ didn’t retain the size and morphology of the precursor indicating that the formation of NiAl$_2$O$_4$ in molten NaCl-LiCl did not follow the template formation mechanism which is reported for many spinels (Jayaseelan et al., 2007). This could be attributed to the high dissolution of Al$_2$O$_3$ in the NaCl-LiCl salt system unlike what was reported in the other molten salts for preparation of aluminates (Jayaseelan et al., 2007).

![Figure 5: FE-SEM of (a) γ-Al$_2$O$_3$(b) NiAl$_2$O$_4$ with S:P=3:1(c) NiAl$_2$O$_4$ with S:P=6:1](image1)

![Figure 6: TEM of (a) γ-Al$_2$O$_3$(b) NiAl$_2$O$_4$ with S:P=3:1](image2)
Figures (6-a) and (6-b) show the TEM images of the γ-Al₂O₃ and the stoichiometric phase pure NiAl₂O₄ prepared from γ-Al₂O₃ at 1400°C for 3 hours with salt to precursor ratio of (3:1), respectively. The TEM results confirm the findings of the SEM results; the prepared NiAl₂O₄ particles with the wide size distribution and polyhedral morphology didn’t retain the shape and the size of γ-Al₂O₃ particles which have mostly needle like shapes.

Table (3) lists the values of the surface area of the pure NiAl₂O₄ prepared with different salt to precursor ratio and different Al precursors (α and γ-Al₂O₃). It can be seen that the use of α-Al₂O₃ produces NiAl₂O₄ with higher surface area as compared with that prepared using γ-Al₂O₃. This is another evidence to exclude the template formation mechanism as γ-Al₂O₃ has higher surface area as compared with α-Al₂O₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α- alumina (starting material)</td>
<td>8.9126</td>
</tr>
<tr>
<td>γ- alumina (starting material)</td>
<td>148.505</td>
</tr>
<tr>
<td>NA prepared with α- alumina at 1400°C S:P 3:1</td>
<td>2.1978</td>
</tr>
<tr>
<td>NA prepared with γ- alumina at 1400°C S:P 3:1</td>
<td>1.5187</td>
</tr>
<tr>
<td>NA prepared with γ- alumina at 1400°C S:P 6:1</td>
<td>1.7858</td>
</tr>
</tbody>
</table>

Based on that, it is strongly confirmed that the mechanism of formation of NiAl₂O₄ in the molten NaCl-LiCl salt is not a template mechanism. This can be attributed to many reasons including (i) the use of binary salt system NaCl-LiCl instead of the single salt (NaCl, KCl or LiCl) as mentioned in the previous works, (ii) the unknown role of Ni(NO₃)₂·6H₂O that was used as NiO precursors which may has the ability to dissolve γ-Al₂O₃, and (iii) the ability of the molten NaCl-LiCl containing the dissolved NiO to dissolve either γ-Al₂O₃ or NiAl₂O₄.

The Stoichiometry of NiAl₂O₄

Figures (7) and (8) show the EDS results for NiAl₂O₄ prepared at 1400°C for 3 hours with α-Al₂O₃ and γ-Al₂O₃ precursors, respectively. EDS analyses showed that the molar ratio of Nickel to aluminum was about 1:2, which is in accordance with the stoichiometric proportions of NiAl₂O₄. Furthermore, none of the possible contaminants from Na, Li and Cl ions were detected in the EDS spectrums, suggesting a high purity of the obtained NiAl₂O₄.

Figure 7: EDX analysis of stoichiometric phase pure NA prepared with (α-Al₂O₃)
**Figure 8:** EDS analysis of stoichiometric phase pure NA prepared with (with $\gamma$-$\text{Al}_2\text{O}_3$)

<table>
<thead>
<tr>
<th>Elt</th>
<th>Standard Name</th>
<th>W%</th>
<th>A%</th>
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<tr>
<td>O</td>
<td>oxygen</td>
<td>41.01</td>
<td>62.37</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
<td>27.07</td>
<td>24.41</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
<td>31.92</td>
<td>13.23</td>
</tr>
</tbody>
</table>

**Figure 9:** FTIR spectra of stoichiometric phase pure NA prepared from ($\alpha$-$\text{Al}_2\text{O}_3$)

**Figure 10:** FTIR spectra of stoichiometric phase pure NA prepared from ($\gamma$-$\text{Al}_2\text{O}_3$)
Figures (9) and (10) show the infrared spectra of pure stoichiometric NiAl₂O₄ powder prepared at 1400°C for 3 hours with α-Al₂O₃ and γ-Al₂O₃ precursors, respectively. The two samples contain a common band at 3452 and 3437 cm⁻¹ which accounts for the hydroxyl stretching frequency (OH) due to surface adsorbed water (physi sorbed water). The width and intensity of this peak is very small, this peak likely originates from moisture adsorbed from the atmosphere during sample preparation (Bengal, 1997). The peaks at 501 and 507 cm⁻¹ represent the characteristic Ni-O stretching frequency in NiAl₂O₄. The peaks at 727 and 729 cm⁻¹ are attributed to tetrahedral coordinated Al-O. The bands at about 607 and 613 cm⁻¹ can be assigned to the stretching vibration mode of Al-O for the octahedral coordinated aluminum ions (Kurien, 2005).

CONCLUSION

The molten salt synthesis method was used to synthesis NiAl₂O₄. The appropriate salt system and the Aluminum precursor were selected based on Rietveld refinement calculation. The effect of the Al₂O₃ phase, reaction temperature, and the salt to precursor ratio were investigated. It has been found that the Al₂O₃ and NaCl-LiCl salt system were found to be the suitable to synthesis phase pure stoichiometric NiAl₂O₄ at moderate temperature of 1400°C and short time of 3 hours. These conditions are much lower than that used by most of the conventional techniques. It has been confirmed that the reaction doesn’t follow the template formation mechanism.

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REFERENCES


