Production of Ni-Al Foams with Hierarchical Porosity

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Open-cell nickel aluminide (Ni-Al) intermetallics foams have attracted much attention in industries at which high temperature and severe environment are concerned, due to their good physical and chemical properties. A combination of different pore structures and morphologies in a single monolithic matrix can extend the properties of a material from which a wide range of applications can be applied. In the present study, open-cell Ni-Al intermetallic foams with hierarchical porosities have been developed through a sintering and dissolution process (SDP) and reactive synthesis techniques. The carbamide particles of various contents were used as a space holder material to create macropores in the foams. Micropores were formed as the result of the formation of initial fine pores between the powders in the compacts, the volatilization of gases evolved during reactive sintering and different diffusion coefficients between Ni and Al. After sintering, only Ni,Al is present in the matrix.

Key words: Ni–Al intermetallics, metallic foam, powder metallurgy, porosity

1. INTRODUCTION

Open-cell metallic foams are attractive engineering materials which are effectively used in many functional applications such as heat exchanger, catalyst support, filter, sound insulator and bone-replacement implant, due to a combination of their appealing properties, including large surface area, interpenetrating porosity and high specific strength [1-4]. Among all types of open-cell metallic foams, nickel (Ni) foams have attracted much attention [5-11]. Application of Ni-based foams is commonly found in electronic and automotive industries as high power batteries, owing to their high capacity and safety characteristics. A recent development in hybrid electric vehicles has driven the use of Ni-based battery, such as nickel-metal-hydride (Ni-MH) as a hydrogen-storing alloy [11]. Another group of potential Ni-based foam is porous Ni-Al alloys. They have excellent oxidation and corrosion resistances due to the formation of protective α-Al2O3 on the surface at high temperatures [12, 13]. Due to their good physical and chemical properties, they can then be used in applications at which high temperature and severe environment are concerned.

There are many processing methods to fabricate open-cell metallic foams, ranging from the utilization of base metal that started out as a liquid [14] and the employment of base metal as metallic powder [15, 16]. The powder-based method has many advantages since high melting point metal and large alloying variation can be processed. Material handling also gives the ability to control size, structure, quantity, and inner cavity structure.

The sintering and dissolution process (SDP) method is a simple, convenient and effective technique [15]. It is considered as one of the most widely used replication processes. It enables manufacturers to control pore architecture, morphology and dimension. The process is carried out by blending base metal powder with suitable space holder, typically NaCl, and then pressed at a high compaction pressure, followed by sintering to strengthen the green compact and dissolution to eliminate the space holder. Several researchers have applied the SDP method to produce metallic foams with different space holders, such as carbamide (CO(NH2)2) and disaccharide [17, 18]. However, using a low-melting point space holder or organic material, it is necessary to modify the SDP process by removing the space holder with the dissolution prior to sintering, preventing possible contamination, such as soot, that could occur during sintering. In this case, higher compaction pressure of between 300 and 400 MPa is recommended, in order to hold porous structure without distortion of pore morphology [19].

A porous material with multi-level pore structure is commonly referred to as a material with hierarchical porosity. A combination of different pore sizes and morphologies in a single monolithic matrix can extend the properties of a material from which a wide range of applications can be applied. With multi-scale porosities, it is possible for foam materials to perform multiple functions. For example, micropores in foam are required for adsorption and purification of a gaseous stream, while macropores are needed for biomedical applications as bone scaffolds. In order to extend the potential applications of Ni-based foams, it is then necessary to fabricate Ni-based foams with multi-level porosities.

To our knowledge, although many types of Ni-Al foams have been developed through powder metallurgy processes, the foams only showed monolithic porous structure. The Ni-Al foams with hierarchical porosity have never been produced. To obtain the hierarchical structure, a novel technique, which combines SDP method and application of reactive synthesis of Ni and
Al elemental powders, could be employed with careful selection of suitable powder characteristics.

The present study aims to develop open-cell Ni-Al foams with hierarchical porosity through powder-based replication method. Specifically, the study will investigate the fabrication process of different foam structures and examine the influence of processing parameters on the structure and mechanical properties of the foam materials.

2. EXPERIMENTAL PROCEDURE

To manufacture open-cell Ni-Al intermetallic foams with multi-level porosity, a combination of two processing techniques as SDP and the step sintering reactive synthesis are employed together. The process began with a homogeneous mixing of Ni and Al powders in the ratios of Ni-14 wt.% Al. In the present study, carbamide particles were used as a space holder material. The Ni-Al powder mixture was then thoroughly blended with the carbamide particles of various contents between 50 and 80 vol.%, in a total amount of 15 g, using a rocking mill, for 60 min, followed by a uni-axial cold compaction to a pressure of approximately 330 MPa in a 22-mm cylindrical tool steel die to produce a green compact. Prior to sintering, the carbamide space holders were removed by dissolution in hot water at 80°C for 12 h. The compacts were then placed in a tube furnace and heated from a room temperature to 570°C with holding time of 3 h, under Ar atmosphere, followed by final sintering at 1000°C for 3 h, to produce highly porous Ni-Al samples. The heating rate was controlled at 3°C/min throughout the sintering process to preserve the original shape of the compacts.

The dimension and relative density of compacts and foam samples were comparatively determined using Archimedes method. The foam samples were half-sectioned in vertical direction using a high precision cutting machine. The morphology of particulate materials, cell morphology and cell wall microstructure of Ni-Al foams, were examined by optical microscope (OM) and JSM-6400 JEOL scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) to identify the phases present. The foam samples were also analyzed by X-ray diffraction (XRD) method using D8-Discover Bruker. Characterization of Ni and Al particle size and distribution was carried out using Mastersizers particle size laser analyzer. The average particle size of carbamide space holders and the pore size of the foams were measured from the SEM photographs. The microhardness of foam samples was measured using a HM-100 Mitutoyo microhardness tester. Each data reported is an average of ten measurements.

3. RESULTS AND DISCUSSION

Fig. 1 shows the particulate morphologies of Ni and Al powders, and carbamide space holder. The Ni and Al powders have angular and dendritic shapes, respectively, while the shape of carbamide particle is spherical. In all cases, no agglomeration of particular materials is observed. The distribution of particle size is summarized in Table I.

<table>
<thead>
<tr>
<th>Particle</th>
<th>D&lt;sub&gt;10&lt;/sub&gt; (µm)</th>
<th>D&lt;sub&gt;50&lt;/sub&gt; (µm)</th>
<th>D&lt;sub&gt;90&lt;/sub&gt; (µm)</th>
<th>Mean diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>4.50</td>
<td>10.95</td>
<td>29.77</td>
<td>14.45</td>
</tr>
<tr>
<td>Al</td>
<td>62.42</td>
<td>108.88</td>
<td>180.25</td>
<td>115.26</td>
</tr>
<tr>
<td>Carbamide</td>
<td>-</td>
<td>-</td>
<td>1120</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2 presents the cellular macrostructure of Ni-Al intermetallic foams made using various contents of carbamide space holders. It can be seen that the dimension and shape of foam samples are changed. Small shape distortion and some material loss were found more or less in all samples. The distortion is likely to be caused by foam expansion and contraction during heating and cooling, as a result of reaction between Ni and Al powders. The loss of materials was mostly found in the compacts, after dissolution of carbamide particles, leading to dimension alteration of foam samples. The foams appear to have both closed- and open-cell structure. It is observed that there are visually more interconnected macropores when more carbamide particles are employed. A larger content of carbamide space holders created more surface contact between them in the compacts, which left penetrable macrochannels after the dissolution. The macropore
morphology and size are virtually replicated to those of the carbamide particles.

The measured porosity of foam samples made with 50, 60, 70 and 80 vol.% carbamide particles are 58.14, 67.76, 75.23 and 83.58 %, respectively. The difference in these porosity is due to the formation of initial fine pores between the powders in the compacts and the volatilization of gases evolved during reactive sintering. It should be noted that the difference in the foam porosities decreases when more carbamide content increases. This is because the carbamide particles are much softer than the metal powders, leading to denser compacts when a higher volume fraction of carbamide is employed.

Fig. 2 Macrostructure of Ni-Al intermetallic foams made using various carbamide contents after sintering: (a) 50 vol.%, (b) 60 vol.%, (c) 70 vol.% and (d) 80 vol. %.

Fig. 3 shows SEM micrographs of Ni-Al intermetallic foams made using various carbamide contents. It is clear that all foam samples have homogeneous cellular structure with pore morphologies inheriting the shape and size of carbamide particles. The pores are uniformly distributed throughout the foam structure. It should be noted that homogeneity of cellular structure in this sense is defined through the distribution of foam porosity (density gradient) which is qualitatively based on the SEM micrographs. Moreover, a large number of penetrable microchannels are also observed in cell walls and struts, representing microporosity in foam structure. The hierarchical porosity of Ni-Al foams is observed as macropore and micropore. The macropores were created from the dissolution of carbamide space holder. As a result, the morphology of macropore is clearly replicated from the carbamide particles. For micropores, the initial pores in powder compact, gas volatilization during reaction synthesis and diffusion effect between Ni and Al are responsible for their formation. From SEM micrographs, the macropore and micropore sizes are approximately 600-1200 and 10-70 µm, respectively.

The XRD pattern of Ni-Al foams after sintering at 1000°C for 3 h was exhibited in Fig. 4. It can be seen that the final product of Ni3Al is present in the samples, suggesting that the reactions were completed.

Fig. 3 SEM micrographs showing cellular morphology of Ni-Al intermetallic foams made using various carbamide contents with different magnification.

Fig. 4 XRD pattern of Ni-Al foams after sintering at 1000°C for 3 h

The OM and SEM micrographs in back-scattered mode (BSM) showing cross-sectional structures of Ni-Al intermetallic foams are presented in Fig. 5. Different contrasts in the SEM images indicate different phases. The EDS analysis, performed on the microstructure for ten times, also shows that all foam samples have similar atomic percentages of Ni and Al which are averaged at 76.49 and 23.51 at.%, with standard deviation value of 1.98, respectively, suggesting that the final phase is Ni3Al.
Production of Ni-Al Foams with Hierarchical Porosity

It is known that the phase transformation of Ni-Al powder compacts during sintering can be varied with different sintering temperature [6, 7]. The formation of intermediate phases, such as Ni$_2$Al$_3$, NiAl and Ni$_3$Al phases, was found in the compacts at the sintering temperature of 600°C with sufficient holding time, owing to the interdiffusion and reaction of Al and Ni powders. In addition, other factors, such as the Al content, particle size, morphology and distribution, partial pressure and atmosphere, also affect the formation of intermediate phases. However, at high temperature sintering of 1000°C, complete reaction was detected and the final phase of Ni$_3$Al is present, as shown in Fig. 5. In the present study, the small amount of 14 wt.% Al is not likely to be sufficient to form a continuous Al network surrounding the Ni powders after the compaction. Therefore, a small amount of liquid phase appeared in the samples. Different intrinsic diffusion coefficients between Ni and Al also create micro pores, contributing to increasing microporosity in cell walls and struts. The sequence of phase formation in the Ni-Al intermetallic foams is thought to be as follows [7].

\[
\begin{align*}
\text{At 540-640°C:} & \quad \text{Ni } + \text{Al} = \text{Ni}_2\text{Al}_3 \quad (1) \\
\text{At 540-640°C:} & \quad \text{Ni } + \text{Ni}_2\text{Al}_3 = \text{NiAl} \quad (2) \\
\text{At 540-670°C:} & \quad \text{Ni } + \text{Al} = \text{Ni}_2\text{Al}_3 \quad (3) \\
\text{At 640-700°C:} & \quad \text{Ni}_2\text{Al}_3 + \text{Ni} = \text{Ni}_3\text{Al} \quad (4) \\
\text{At 700-800°C:} & \quad \text{Ni}_3\text{Al} = \text{Ni}_3\text{Al} \quad (5) \\
\text{At 950-1000°C:} & \quad \text{Ni}_3\text{Al} = \text{Ni}_3\text{Al} \quad (6)
\end{align*}
\]

Fig. 6 shows the microhardness values of Ni-Al intermetallic foams produced using various carbamide contents. Similar microhardness values in the range of between 400 and 430 HV were found in all foam samples. These values are slightly lower than the typical microhardness measurement of 450.6 HV for non-heat treated Ni$_3$Al [20]. It is likely that the indentation load was partly absorbed during testing by the epoxy resin in which the foam samples were mounted, resulting in a small lower value of HV measurement.

![Microhardness values of Ni-Al intermetallic foams using various carbamide contents.](image)

4. SUMMARY

The open-cell Ni-Al intermetallic foams with hierarchical porosities have been developed through a sintering and dissolution process (SDP) and reactive synthesis techniques. Different levels of porosity as macro- and micropores were created with different morphologies. Macropores were formed as a result of removal of carbamide particles. Micropores were formed as the result of the formation of initial fine pores between the powders in the compacts, the volatilization of gases evolved during reactive sintering and different diffusion coefficients between Ni and Al. After sintering, only Ni$_3$Al is present in the matrix.

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3.9 REFERENCES


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