Research Article

Combustion Synthesis of Large Bulk Nanostructured Ni_{65}Al_{21}Cr_{14} Alloy

Jiqiang Ma, 1, 2 Jun Yang, 1 Qinling Bi, 1Licai Fu, 1 Yonghai Kang, 1, 2 and Weimin Liu 1

1 State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
2 Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Correspondence should be addressed to Jun Yang, jyang@lzb.ac.cn

Received 11 January 2011; Accepted 17 February 2011

1. Introduction

Nanostructured materials exhibited enhanced strength, hardness, ductility at low temperature, wear-resistance, and other unusual properties in comparison with corresponding coarse counterparts [1–5]. Nanostructured materials can be produced by several methods, including consolidation of nanopowder by pressing and sintering, electrodeposition, devitrification of amorphous, and severe plastic deformation [6, 7]. However, bulk nanostructured materials obtained by the above methods often suffer from porosity, contamination, weak bonding, and small dimensions. Furthermore, extortionate equipment and enormous energy have to be used in the above methods usually. Specially, the size of the prepared nanostructured materials is very limited. Consequently, it is of great interest to develop new processes that are convenient, low in cost, and capable of being scaled up for tailoring the nanostructured materials. Because the process is inexpensive and can obtain large bulk materials with good mechanical properties [8–13], combustion synthesis (CS) could become a promising method to produce bulk nanostructured materials.

Nickel-aluminium-based intermetallic compounds have been extensively studied because of their high melting points, relatively low densities, high strength, as well as good corrosion and oxidation resistances [14–21]. The chromium alloying not only plays a solid solution strengthening role for the γ-Ni matrix and γ′ precipitates but also improves corrosion and oxidation resistances by creating a native, adherent oxide film [21, 22]. Moreover, the chromium alloying can also reduce brittleness at temperatures of 600–800 °C in oxidizing atmosphere [23].

In this study, a bulk nanostructured Ni_{65}Al_{21}Cr_{14} alloy has been synthesized successfully by CS technique associated with rapid solidification by designing an aluminothermic reaction route. The obtained bulk nanostructured Ni_{65}Al_{21}Cr_{14} alloy exhibits simultaneously high strength and large ductility.

2. Experimental

Nickel, aluminum, chromium sesquioxide, and chromium trioxide powders were weighed according to the stoichiometry of the aluminothermic reaction (1) which is characterized by releasing a large amount of exothermic heat. The powders were dry-pressed for 8 hours with Al_{2}O_{3} spheres in a stainless steel jar, and then 800 g of the mixed powders were cold-pressed on a copper substrate which was 170 mm in the diameter and fixed in a copper tube as a mold under
a uniaxial pressure of 30 MPa. The substrate and tube were cleaned by ethanol before use. Characteristics of the reactant powders are given in Table 1.

\[
10\mathrm{CrO}_3 + 2\mathrm{Cr}_2\mathrm{O}_3 + 45\mathrm{Al} + 65\mathrm{Ni} \\
= \mathrm{Ni}_{65}\mathrm{Al}_{21}\mathrm{Cr}_{14} + 12\mathrm{Al}_2\mathrm{O}_3
\]  

Table 1: Properties of the raw material powders.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Size (mesh)</th>
<th>Purity (wt.%)</th>
<th>Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>200</td>
<td>&gt;99.5</td>
<td>Zn, Pb, Mn, Si</td>
</tr>
<tr>
<td>Al</td>
<td>100–200</td>
<td>&gt;99</td>
<td>Fe, Si, Cu, H₂O</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>—</td>
<td>&gt;99</td>
<td>Cl¹⁻, SO₄²⁻, Na, Al, Fe</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>—</td>
<td>&gt;99</td>
<td>Cl¹⁻, SO₄²⁻, Fe</td>
</tr>
</tbody>
</table>

Five grams of Al, S, and MnO₂ powder mixture in mass ratio of 1:1:1 was pressed into a pellet. The pellet was then put on top of the pressed reactant powders as an igniter. The chemical reaction of the igniter can be initiated at about 260°C, which results in an instantaneous release of a large amount of heat that ignites the aluminothermic reaction.

The copper mold with the reactants was placed into a cylindrical bar with dimensions of 0.03 mm × 5 mm, and the surfaces were polished with 1000-grit emery paper. Quasi-static compression tests at a strain rate of 3 × 10⁴ s⁻¹ were conducted at room temperature on a universal tester (Adamel, French). To minimize friction effect, the specimen interfaces were lubricated with graphite. Vickers micro-hardness of the Ni₆₅Al₂₁Cr₁₄ sample was measured using an MH-5 microhardness tester under a load of 300 g and a dwell time of 10 s. The sample density was measured by Archimedes method using a balance with a sensitivity of 0.1 mg.

3. Results and Discussion

The chemical reaction of the igniter is initiated at about 260°C and instantaneously releases large heat, which ignites the reaction of the reactants. Then combustion wave of the reaction propagates from top to bottom of the reactant compact and the reactants transform to Ni-Al-Cr alloy and Al₂O₃ melt where the combustion wave has passed. The adiabatic temperature (Tₐd) of the combustion reaction at 260°C is approximately calculated to be about 2700°C by the method as described in the literature [8, 24]. The products of the Ni₆₅Al₂₁Cr₁₄ and Al₂O₃ are in superheat liquid state but nearly do not vaporize during the processing because their boiling point rises to above 4500°C under the 4 MPa gas pressure by calculation based on the Clausius-Clapeyron equation and Trouton rule as described in supporting information of the literature [8]. Since liquid Al₂O₃ is immiscible with liquid Ni₆₅Al₂₁Cr₁₄, it separates automatically and lifts to the top owing to its low density [8]. The liquid Ni₆₅Al₂₁Cr₁₄ is deposited on the copper substrate surface.

Figure 2(a) shows a typical X-ray diffraction pattern of the Ni₆₅Al₂₁Cr₁₄ alloy, which indicates that the alloy consists of γ'-Ni₃Al and γ-Ni(Al, Cr) solid solution phases and the crystallographic structures of the alloy have a highly preferred orientation of (200) face. The XRD peaks are significantly broadened, indicating that the alloy has small grain/domain sizes. Scherrer formulation was used to quantitatively analyze the XRD broadenings; the averaged grain size is calculated to be 24.97 nm, and the lattice parameter is calculated to be 0.3550 nm. The contamination phases from igniter (Al₂O₃, MnS) are mainly dissolved in the reaction of the igniter (Al₂O₃, MnS) are very small quantity, so they are not detected by XRD test. Although not shown here, the outgrowth black Al₂O₃ on top of the Ni₆₅Al₂₁Cr₁₄ alloy is mainly composed of α-Al₂O₃ phase by the XRD analysis.

The SEM secondary electronic image of the Ni₆₅Al₂₁Cr₁₄ alloy is shown in Figure 2(b). It can be seen that the Ni₆₅Al₂₁Cr₁₄ alloy is a composite structure of micrometer...
scaled dendrites dispersed in a matrix. The dendrite occupies about 50% in volume according to the statistic of the SEM observations. Figures 2(c) and 2(d) show the fine microstructures of the matrix and dendrite by the FESEM secondary electronic images, respectively. It can be seen that the matrix is composed of 80–150 nm cubic γ’ precipitated phase and 2–5 nm boundary γ phase (Figure 2(c)). The dendrites consist mainly of 50–100 nm lamellar or fiber γ phase and a minor cubic γ’ phase (Figure 2(d)). The bright field TEM images of the matrix and dendrites and corresponding selected area diffraction patterns (SAED) are presented in Figure 3. Figure 3(a) indicates that the matrix is composed of

**Figure 2**: XRD pattern of the Ni₆₅Al₂₁Cr₁₄ alloy (a); SEM secondary electron image of the Ni₆₅Al₂₁Cr₁₄ alloy (b) and FSEM secondary electron images of the matrix (c) and the dendrite (d).

**Figure 3**: Bright field TEM images of the matrix (a) and dendrite (b) and corresponding SAED patterns.
roughly 80–150 nm cubic crystallites and 2–5 nm boundary γ phase, which are in good agreement with the result of FESEM. The corresponding SAED pattern shows discontinuous rings, indicating that many different orientations among the grains. By TEM images and corresponding SAED patterns, it can be further found that the nanolamellar and fiber in the dendrites consist of about 3–20 nm high dense twins (see Figure 3(b)). It has been proved that both nano/ultrafine eutectic structure [9, 25–27] and nanotwinned structure [28, 29] could enhance strength and ductility of metallic materials.

The formation of the special composite nanostructure is attributed to three factors [30]. First, the contaminants (Al₂O₃, MnS₅, etc.) introduced from reactants and igniter dissolve in the metallic melt under the very high degree of superheating \( T_{\text{ad}} = 2700 \degree C \), and hence there are no heterogeneous nucleation sites available for liquid to crystallize on. Metallic liquid without nucleation sites for crystallization has a high undercooling degree and low crystallization onset temperature, the nuclei growth determined by diffusion of Ni, Al, and Cr atoms is slow. Third, the time of nuclei growth is short because of the high cooling rate resulting from the copper substrate quenching.

Figure 4(a) shows a typical compressive engineering stress–strain curve of the nanostructured Ni₆₅Al₂₁Cr₁₄ alloy. The yield strength is about 750 MPa, which is comparable to a nickel-based superalloy [31]. Impressive fracture strength of 2200 MPa and plastic strain of 26% was reached in compression test, respectively. The nanostructured Ni₆₅Al₂₁Cr₁₄ alloy exhibits a continuous stress increase with increasing strain, indicating continuous strain hardening until failure. Figure 4(b) shows lots of dimples with a diameter of 10–20 μm in the fracture surface from the compression test. Although large numbers of slip bands were observed in the fractured profile surface (Figure 4(c)), the local deformation may be impeded by the dendrites which means local stress concentration in compressive deformation [32], which can explain the high strain hardening ability of the nanostructured Ni₆₅Al₂₁Cr₁₄ alloy. On the other hand, nanotwin boundaries are much more stable against migration than conventional grain boundaries [28, 29]. Twin strengthening has been obtained in the nanostructured Ni₆₅Al₂₁Cr₁₄ alloy.
So, in our experiment the nanostructure with dendrites composite and high density nanotwins is responsible for high fracture stress and good ductility in the compression test.

4. Conclusion

The large bulk nanostructured Ni<sub>65</sub>Al<sub>21</sub>Cr<sub>14</sub> alloy is obtained by using combustion synthesis technique associated with rapid solidification. The nanostructured Ni<sub>65</sub>Al<sub>21</sub>Cr<sub>14</sub> alloy samples are characterized by SEM, XRD, and TEM. The as-produced large bulk nanostructured Ni<sub>65</sub>Al<sub>21</sub>Cr<sub>14</sub> alloy exhibits simultaneously high compressive fracture strength (2200 MPa) and good ductility (∼26%).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (50801064) and the National 973 Project of China (2007CB607601).

References


