Research Article

Bulk Synthesis and Characterization of Ti$_3$Al Nanoparticles by Flow-Levitation Method

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A novel bulk synthesis method for preparing high pure Ti$_3$Al nanoparticles was developed by flow-levitation method (FL). The Ti and Al vapours ascending from the high temperature levitated droplet were condensed by cryogenic Ar gas under atmospheric pressure. The morphology, crystalline structure, and chemical composition of Ti$_3$Al nanoparticles were, respectively, investigated by transmission electron microscopy, X-ray diffraction, and inductively coupled plasma atomic emission spectrometry. The results indicated that the Ti$_3$Al powders are nearly spherical-shaped, and the particle size ranges from several nanometers to 100 nm in diameter. Measurements of the d-spacing from X-ray (XRD) and electron diffraction studies confirmed that the Ti$_3$Al nanoparticles have a hexagonal structure. A thin oxidation coating of 2-3 nm in thickness was formed around the particles after exposure to air. Based on the XPS measurements, the surface coating of the Ti$_3$Al nanoparticles is a mixture of Al$_2$O$_3$ and TiO$_2$. The production rate of Ti$_3$Al nanoparticles was estimated to be about 3 g/h. This method has a great potential in mass production of Ti$_3$Al nanoparticles.

1. Introduction

Intermetallic compounds, especially titanium aluminides, having a positive temperature dependence of yield strength are becoming one of the most promising candidates for a high-temperature material to realize an aerospace plane [1]. This is due to their outstanding engineering performances such as low density, good corrosion resistance, high specific Young's modulus, strength, and their good oxidation and burn resistances [2]. However, their intrinsic low tensile ductility at room temperature and poor high temperature strength have limited their potential applications, particularly in the aerospace field [3]. During recent years, many attempts have been made to improve the ductility. Attempts adapted include techniques such as grain refinement to nanoscale structure [4–6] and microstructure modification [7, 8]. Thus research aiming to produce nanocrystalline materials by improved experimental techniques is relevant. Now, ball mill method is one of the methods used for preparation of titanium aluminium nanoparticles. Calderon et al. have prepared nanocrystalline powders of titanium aluminum by ball milling [9–11]. But ball milling is associated with long periods of milling times in order to obtain crystallite size below 100 nm. The phase composition of titanium aluminum nanoparticles is very difficult to be controlled, and the particles size distribution of them is also very wide. Liu Tong prepared nanocrystalline powders of Ti-Al nanoparticles by hydrogen plasma-metal reaction [12]. Nevertheless, nanoparticles prepared by this method are not pure, and the phase composition is also very difficult to be controlled by this method.

Flow-levitation (FL) method is based on the levitation melting technology [13] and has been used as a successful method for the preparation of some metals [14–16] and zinc oxide nanoparticles [17]. Also, the method has been used for the preparation of alloy nanoparticles. Sivaprasam et al. used this method for the synthesis of FeCu nanopowders [18]. Recently, we developed this method for the synthesis of intermetallic Ag$_2$Al, FeAl, and FeNi$_3$ nanoparticles [19–21]. In comparison to the conventional evaporation-condensation
methods, the main advantages of the FL method are high purity of the product (due to the containerless nature of the process) and high production rate (due to the rapid heating and continuous manner of the method). FL method is a novel method capable of producing high purity intermetallic nanoparticles with a relatively high production rate.

Until now, little work has yet been reported on the synthesis of high pure Ti3Al nanoparticles [12]. In the present work, we have developed a novel method for the synthesis of high pure Ti3Al nanoparticles with the production rate of about 3 g/h in a continuous manner, by using flow-levitation (FL) method. The morphology and structure of the Ti3Al nanoparticles were investigated. The surface compositions of the samples were also studied.

2. Experiments

Ti3Al nanoparticles were synthesized by the FL method (see Figure 1). In principle, the solid metal wires (Ti and Al) are first heated by a high-frequency electromagnetic induction coil, and a metal liquid droplet is formed. The droplet is levitated and heated continuously under its interaction with the magnetic field generated by another reverse electromagnetic coil, and a metal liquid droplet is formed. The droplet is levitated and heated continuously under its interaction with the magnetic field generated by another reverse electromagnetic induction coil. Atoms at the surface of the droplet are evaporated when a high temperature (about 2050 °C) is reached. These evaporated atoms are quickly cooled through their collision with the inert gas and form nanoparticles. When the inert gas with a special gradient pressure is imposed in the vapour environment, metal atoms and resultant nanoparticles can flow in a definite direction in no contact with the reactor wall and finally enter the collector. Consequently, both high yield and high purity of nanoparticles are expected. In synthesizing nanoparticles by the FL method, the aerosol is rapidly cooled and diluted to prevent extensive sintering and coalescence to improve their dispersion. For synthesizing Ti3Al nanoparticles, the temperature was about 2400 °C, resource materials Al and Ti were supplied at a rate of 23.04 Hz and 67.75 Hz, and Ar flow rates ν₁ and ν₂ are equal to 0.2 and 0.8 m³·h⁻¹, respectively.

Structures of the nanoparticles were investigated by X-ray diffraction (XRD) method using Cu Kα (λ = 0.15405 nm) radiation. The morphology and the particle size of the prepared nanoparticles were directly observed by transmission electron microscopy. The chemical composition of the particles was examined by inductively-coupled plasma spectroscopy (ICP). X-ray photoelectron spectroscopy with Mg Kα radiation as exciting source was used to examine the chemical composition of the surface samples.

3. Results and Discussion

The chemical compositions of Ti3Al nanoparticles were determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements. There are 74.42% (molar fraction) Ti and 25.28% Al in the nanoparticles as determined by the ICP analyses. And the Ti/Al atomic ratio of the nanoparticles is about 3 : 1.

Figure 2 shows the XRD pattern of nanoparticles obtained by the FL method. All of the diffraction peaks can be indexed according to the JCPDF card no. 14-0451I, indicating the hexagonal Ti₃Al (space group: P63/mmc (194), cell parameters: a = 0.577 nm, b = 0.577 nm, and c = 0.462 nm) [22]. The prominent diffraction peaks at the scattering angles of 26.4°, 36.1°, 39.0°, 41.2°, 53.9°, 64.6°, 71.5°, and 79.4° are assigned to scattering from the 101, 200, 002, 201, 202, 220, 203, and 401 planes, respectively, of the Ti₃Al crystal lattice [22]. The XRD results indicate that the products we obtained were Ti₃Al nanoparticles. The purity of titanium aluminide nanoparticles produced by FL method is higher than that by HPMR [12], in which some quantities of TiAl and Al were still present in the Ti₃Al samples from XRD patterns. According to the XRD patterns of Ti₃Al
nanoparticles, the average crystalline size can be calculated based on the Scherrer equation $D = \frac{0.89\lambda}{\beta\cos\theta}$ [23], where $\lambda$ is the X-ray wavelength, $D$ is the average diameter of the crystals in Angstroms, $\beta$ is the full width at half maximum (FWHM) in radians, and $\theta$ is the Bragg angle in degrees. According to Scherrer’s relation, the average crystalline size of Ti$_3$Al nanoparticles is about 25 nm. Also, we have estimated the crystallite size using the Williamson-Hall equation [24]. Result of W-H calculation shows that the crystallite size of Ti$_3$Al samples is 23 nm, which is similar and consistent with Debye-Scherrer’s calculations.

Figures 3(a) and 3(b) show the typical TEM image along with the particle size distribution of the Ti$_3$Al nanoparticles. Statistically, Ti$_3$Al nanoparticles are spherical in shape, and the particle size ranges from several nanometers to 100 nm in diameter, with a lognormal particle size distribution typical of other vapor phase synthesized nanopowders [25]. It is worth to note that these primary spherical particles often occur as chain aggregates of several individual nanoparticles. The selected area electron diffraction (SAED) patterns of samples which were conducted in the whole areas of Figure 3(a) are shown in Figure 3(c). The observation of multiple rings indicates no preferential orientation within the nanoparticles sample. The SAED pattern exhibits the diffraction peaks from (200), (002), (201), (202), (210), and (222) planes of Ti$_3$Al, which further confirms the results of XRD pattern.

Structural information from a single Ti$_3$Al nanoparticle was obtained using high resolution TEM (HRTEM). Figure 4 shows the high resolution TEM images of samples. In Figure 4, well-developed lattice fringes are resolved in Ti$_3$Al nanocrystals, which indicate that Ti$_3$Al particles are well crystallized. Lattice fringes are measured to be 0.2365 nm, which are very close to the (002) lattice spacing of the hexagonal Ti$_3$Al phase. The existence of lattice planes on the HRTEM image further confirmed the crystallinity of Ti$_3$Al nanoparticles.

We also attempted to characterize the amorphous coating using X-ray photoelectron spectroscopy (XPS) measurements. Figure 5 displays XPS of the Ti$_3$Al nanoparticles. We can see that the main elements contained in the sample surface are Ti, Al and O, and C. To compensate for sample charging, binding energies were referenced to that of the adventitious carbon 1s peak at 285.0 eV. The Ti 2p spectrum is treated as two doublet peaks, which are assigned to Ti$^{4+}$ and metallic Ti, respectively [26, 27]. The Al 2p spectrum (Figure 5(c)) exhibits a doublet peak with binding energy of 71.5 eV and 74.1 eV, corresponding to metallic Al in metallic Ti$_3$Al, and the oxide state of Al in Al$_2$O$_3$ [28, 29]. In the O 1s spectrum (Figure 5(d)), only two peaks could be resolved. The first peak at 530.4 eV has a relatively large intensity and is probably due to O$^{2-}$ ions in TiO$_2$, and the other smaller peak at 532.2 eV could be due to O$^{2-}$ ions in Al$_2$O$_3$ [26]. Thus, the results from XPS measurement confirm that the chemical composition of the Ti$_3$Al nanoparticle surface could most likely be a mixture of Al$_2$O$_3$ and TiO$_2$.

4. Conclusion

In summary, stoichiometric Ti$_3$Al nanopowder has been successfully synthesized by the flow-levitation (FL) method.
TEM images indicate that the nanoparticles are nearly spherical and the particle size ranges from several nanometers to 100 nm in diameter. The as-synthesized nanoparticles have a hexagonal structure. The ICP results show that the Ti/Al atomic ratio of the nanoparticles is about 3:1. The Ti₃Al nanoparticles contain an amorphous layer of 2-3 nm in thickness surrounding the crystalline core after exposure to air. Results from XPS measurement show that the amorphous layer of the Ti₃Al nanoparticles could most likely be a mixture of Al₂O₃ and TiO₂. This work showed a simple and effective method to synthesize Ti₃Al nanoparticles, and this method has a great potential to be used in mass production of Ti₃Al ultrafine particles.

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References


Figure 5: XPS spectra of the nanoporous surface of Ti₃Al nanoparticles. (a) Full spectrum; (b) Ti 2p; (c) Al 2p, and (d) O 1s.


