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Research Article

The Preparation and Characterization of β-SiAlON Nanostructure Whiskers

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Two kinds of β-SiAlON nanostructure whiskers, rod-like and wool-like whiskers, were synthesized by pressure-less sintering method at 1773 K for 5 hours. The whiskers synthesized were characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and high-resolution electron microscope (HREM) techniques. It was found that diameter distribution of rod-like whiskers was about 80–250 nm, while it was about 45–55 nm in diameter for the wool-like whiskers. The growth mechanisms of β-SiAlON nanostructure whiskers are discussed by the vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms, respectively.

1. INTRODUCTION

β-SiAlON is the solid solution of β-Si_3N_4, Al_2O_3, and AlN. The composition of β-SiAlON can be represented by the formula $Si_{6-Z}Al_ZO_ZN_{8-Z}$, and the Z value varies constantly from zero to 4.2 [1, 2]. Hexagonal β-SiAlON has a crystalline structure similar to β-Si_3N_4 and exhibits excellent properties such as good corrosion resistance, antioxidation, and high fracture toughness [3–6]. Therefore, β-SiAlON can be used as refractory, cutter material, and high performance ceramics. It can also be made into medical instruments, oxidation resistant, and corrosion resistant materials at high temperature in aerospace [7–12].

It is well known that nanowhiskers and fibers are significant in improving the strength and toughness of composite structural materials, owing to their small particle size and the high-aspect ratio [13–18]. β-SiAlON whiskers inserted into matrix are expected to increase the fracture toughness of β-SiAlON composite ceramics. To the knowledge of the authors, there are few works dealing with the synthesis of abundant of β-SiAlON whiskers with nanostructure and its growth mechanism. Jia et al. prepared a few β-SiAlON particles of about 30 nm in diameter using organic precursors [19]. The results show that a few novel rod-like β-SiAlON whiskers were found at the surface of α-SiAlON (5%) and β-SiAlON (95%) composites. They also did related analysis for α-SiAlON whiskers [20–22]. Fu et al. [23] synthesized β-SiAlON whiskers by a combustion method, using of silicon and aluminum powders as raw materials, with SiO_2 and Y_2O_3 as additives and α-Si_3N_4 or β-SiAlON powders as diluents. SEM results showed that the aspect ratio of whiskers was higher than 5. Dickon fabricated single crystalline β-SiAlON nanowires with 100–500 nm in diameter by sintering powder mixture of Al, Si, and SiO_2 at 1873 K [24]. Chen synthesized β-SiAlON whiskers from silica fume and α-alumina via carbothermal reduction and which formed by VLS growth mechanism involving SiO, $FeCl_3$, and other vapor species [25]. Other research works on α-SiAlON or β-SiAlON whiskers can be referred to from references [26, 27].

In the present paper, large quantity of β-SiAlON nanostructure whiskers were synthesized by the pressure-less sintering technique under the proper conditions. The phase composition and morphology of β-SiAlON nanostructure whiskers were investigated by the XRD, SEM, TEM, HREM techniques. The growth mechanisms of the rod-like and wool-like whiskers were discussed.

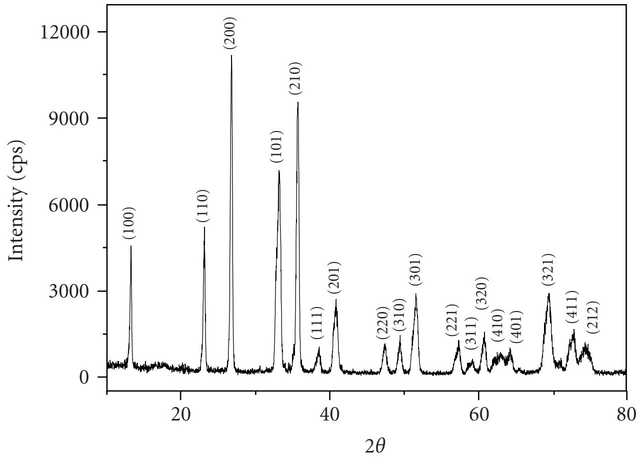


Figure 1: XRD pattern of β-SiAlON ($Z = 1.3$) nanostructure whiskers prepared by pressure-less sintering technique at 1773 K for 5 hours.

2. EXPERIMENT

2.1. Preparation

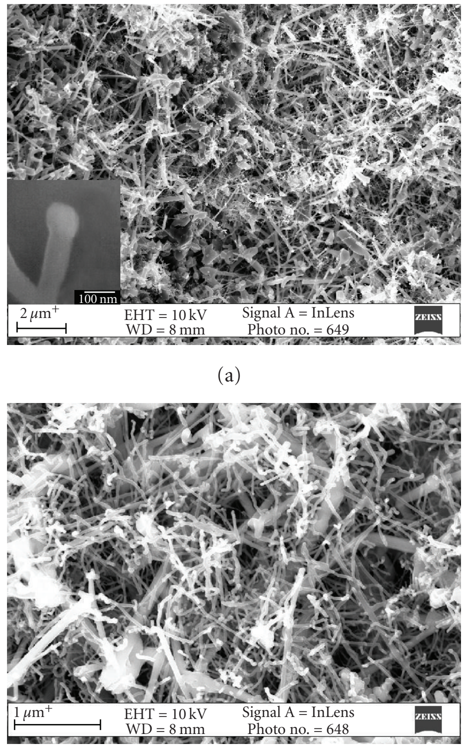
Silicon (≥99.9%, 3.256 μm, C.R., Beijing Chemical Co., Beijing, China), aluminum (≥99.5%, 3.360 μm, C.R., Shanghai, China), and alumina (≥99%, 3.873 μm, A.R., Guangdong, China) powders were used as raw materials to synthesize β-SiAlON (with the formula $Si_{6\text{-}Z}Al_ZO_ZN_{8\text{-}Z}$) nanostructure whiskers by pressure-less sintering technique. The starting materials with proper ratio of $Z = 1.3$ [mol (Al_2O_3 + AlN)/mol Si_3N_4 = 1.3:4.7] were milled for 24 hours by using absolute ethyl alcohol as the medium. The slurry was dried and pressed into pallets of 13 mm in diameter and 3.0 mm in thickness at the pressure of 100 MPa; the pallets were placed into an alumina crucible, covered with silicon nitride powders, sieved by 300-mesh, and then sintered at 1773 K for 5 hours. The nitrogen gas with high purity was introduced into alumina reaction tube, and the partial pressure was maintained at 0.1 MPa by keeping the flow rate of 1 mL/min.

2.2. Phase and microstructure characterization

The phase composition of the obtained products was identified by X-ray diffraction measurement on a M21X-SRA X-ray diffractometer (manufactured by MAC Science Co. Ltd, Yokohama, Japan) equipped with graphite crystal diffracted-beam monochromator. The accelerating voltage and current are 40 kV and 150 mA, respectively. Scanning speed is 8°/min, step wise is 0.02°, and scanning region is from 10° to 80°.

Scanning electron microscope (ZJIESS CSM 950, Carl Zeiss Co., Oberkochen, Germany) was used to observe the morphology and the particle size of the prepared samples by scanning on the cross-sections of fracture. Amorphous carbon was sputtered on the section before SEM measurement.

Both transmission electron microscope (HITACHI H-8100, Hitachi, Tokyo, Japan) and high resolution electron microscope (JEM2010, Joel Ltd., Tokyo, Japan) operating at 200 kV are used to certificate the phase and crystal morphology of the products.



(a)

(b)

Figure 2: SEM micrographs of β-SiAlON nanostructure whiskers prepared by using silicon, aluminum, and alumina powders as raw materials. ((a) Most of rod-like whiskers and (b) most of wool-like whiskers magnified image of rod-like whisker on the left bottom of Figure 2(a)).

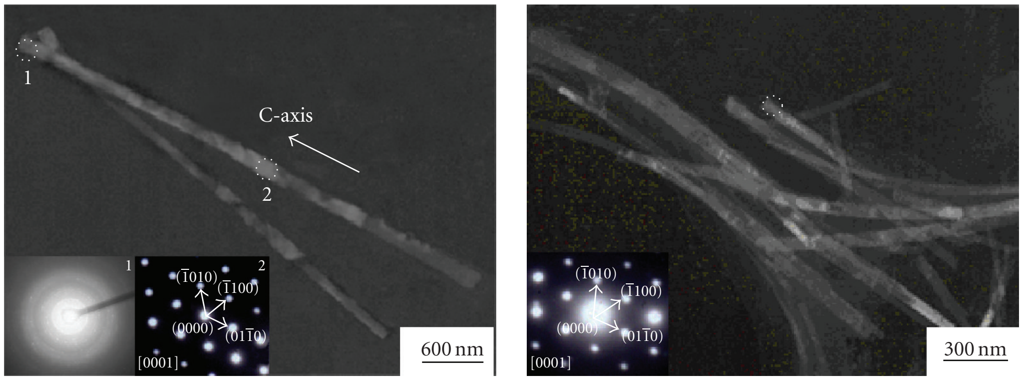
3. RESULTS AND DISCUSSIONS

3.1. Composition analysis

Figure 1 shows the XRD patterns of β-SiAlON prepared by pressure-less sinter technique at 1773 K for 5 hours. The diffraction pattern is in agreement with the data reported by the JCPDS (48–1615) card. The spectra identified that β-SiAlON is the main phase, and no impurities were found within the analysis uncertainty limits. The sharper peaks of diffraction illustrated that β-SiAlON presents a high degree of crystallization.

3.2. Morphology and microstructure observation

Two kinds of whiskers have been observed in the present products. It can be seen in Figure 2 that most whiskers illustrated in Figure 2(a) were straight and column-shaped crystals which were denoted as rod-like whiskers. This kind of whiskers has a wider distribution of diameter, and it is between 80 and 250 nm with high-aspect ratio. In the small photo on the left bottom in the Figure 2(a), a spheric node can be seen on the tip of rod-like whiskers, which might be



(a) (b)

Figure 3: TEM micrographs of β-SiAlON nanostructure whiskers with the corresponding SAEDs analysis. ((a) Rod-like whiskers, (1) SAEDs analysis for the top of rod-like whiskers and diffraction rings include Si, Al, and β-SiAlON amorphous, (2) SAEDs analysis for the top of rod-like whiskers corresponding to single β-SiAlON, (b) wool-like whiskers and diffraction spots for the top of wool-like whiskers corresponding to single β-SiAlON).

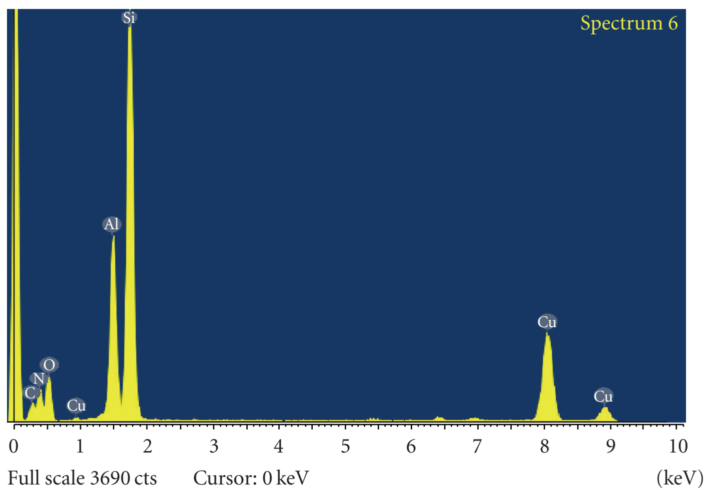


Figure 4: EDS analysis for one wool-like whisker corresponding to TEM analysis.

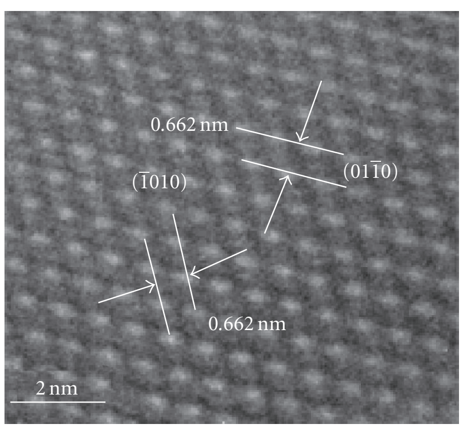


Figure 5: HREM results of wool-like β-SiAlON nanostructure whiskers and plane distance are about 0.662 nm corresponding to (1000) plane of β-SiAlON.

the evidence for the VLS mechanism of the rod-like whiskers. In Figure 2(b), a large quantity of whiskers with smaller diameter and flexible microstructure denoted as wool-like whiskers are also observed. The diameter of this kind of whiskers is quite homogeneous and it is about 45–55 nm. The two kinds of whiskers interlaced each other, which would improve the strength and toughness of the material.

TEM micrograph of β-SiAlON nanostructure whiskers together with results of the selected area election diffraction (SAED) investigation is shown in Figure 3. The straight column-shaped whiskers with 160 nm in diameter could be observed in Figure 3(a), their aspect ratio having reached more than 40. The diffraction pattern, marked dots on the body, indicated that the nanostructure whisker is a single crystal and it grew along the *c*-axis, corresponding to the single β-SiAlON structure. At the same time, the diffractions on the tip of β-SiAlON nanostructure whiskers

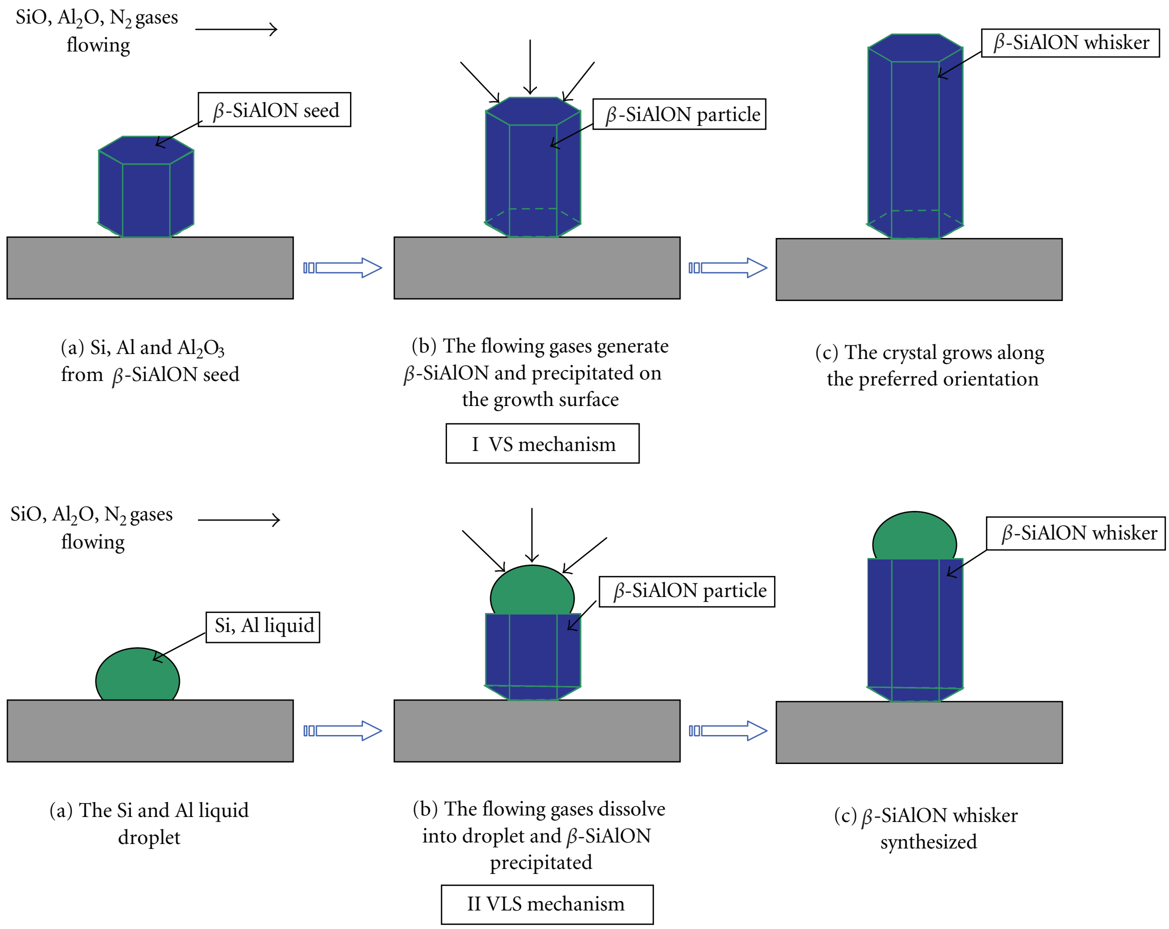


FIGURE 6: Simplified sketch of growth mechanism of β-SiAlON whiskers. (Process I is the vapor-solid (VS) mechanism for formation of rod-like β-SiAlON whiskers, process II is the vapor-liquid-solid (VLS) mechanism for formation of rod-like β-SiAlON whiskers).

show that they are multiphase crystal diffraction rings. This phenomenon might result from the VLS growth mechanism. Figure 3(b) exhibited a series of wool-like whiskers with high-aspect ratio intercross together. The diffraction spots for the tip and end of whisker were proved to have the same component corresponding to single-crystals of β-SiAlON, which is likely to explain that the growth mechanism of wool-like whiskers is based on VS mechanism. EDS analysis for one wool-like whisker carried out and it certificated that the whiskers are β-SiAlON phase, and it can be seen in Figure 4. The surface of two kinds of whiskers is very smooth during β-SiAlON whiskers growing process. HREM was also employed to analyze the structure of the single crystal wool-like β-SiAlON nanostructure whiskers. The results are shown in Figure 5. Lattice image indicated that the plane distance of single β-SiAlON material is about 0.662 nm, corresponding to (1000) plane of β-SiAlON.

3.3. *Mechanism of whisker growth*

In the present work, vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms [28–30] were used to explain the growth mechanism of wool-like and rod-like whiskers during sinter process, respectively.

The vapor-solid (VS) mechanism, for the wool like whiskers, was assumed as the main growth mechanism. The main reactions were listed from (1) to (3), and growth schematic diagram of whisker is illustrated in Figure 6 for part I. At the starting reaction step, silicon, aluminum, and alumina reacted and formed β-SiAlON seeds under the flowing nitrogen atmosphere as (1). These β-SiAlON seeds act as active centers and accelerate the growth of whiskers:

$$\mathrm{Si}_{(s)} + \mathrm{Al}_{(s)} + \mathrm{Al_2O}_{3(s)} + \mathrm{N}_{2(g)} \longrightarrow \beta\text{-SiAlON}_{(\text{seeds})}. \qquad (1)$$

The partial evaporation of silicon monoxide (SiO) and aluminum suboxide (Al_2O) is likely to be formed as (2), owing to the low oxygen partial pressure under the reactant condition:

$$\begin{aligned} 2\mathrm{Si}_{(l)} + \mathrm{Al_2O}_{3(s)} &= 2\mathrm{SiO}_{(g)} + \mathrm{Al_2O}_{(g)}, \\ 4\mathrm{Al}_{(l)} + \mathrm{Al_2O}_{3(s)} &= 3\mathrm{Al_2O}_{(g)}. \end{aligned} \qquad (2)$$

The above vapor phases, SiO and Al_2O, react with flowing nitrogen gas and deposited on the preferential growth plane of β-SiAlON seeds. With the continuous cycle, the

β-SiAlON nanostructure whiskers, with high-aspect ratio, finally formed. The reaction can be described as

$$SiO_{(g)} + Al_2O_{(g)} + N_{2(g)} \xrightarrow{\beta\text{-SiAlON.seeds}\rightarrow\beta\text{-SiAlON.particles}} \beta\text{-SiAlON}_{(\text{whiskers})}. \quad (3)$$

The rod-like whiskers may form through a vapor-liquid-solid (VLS) process. Mechanism analysis sketch diagram could be seen in Figure 6 for part II, and the procedure is described as follows. Based on reactions (2), the vapor phases may reacted with nitrogen and dissolve into the spherical liquid droplets of silicon and aluminum and some impurities, although the content of impurities is very small to form β-SiAlON containing liquid. When the content of β-SiAlON in droplet became supersaturated, a new complete β-SiAlON crystalline particle would precipitate from the droplet. With the procedure getting repeated, rod-like β-SiAlON whiskers would grow up as

$$SiO_{(g)} + Al_2O_{(g)} + N_2 \xrightarrow[\text{supersaturated}]{\text{dissolvedin[Al],[Si]}} \beta\text{-SiAlON}_{(s)}. \quad (4)$$

A lot of spheric nodes on the tip of rod-like whiskers also proved that VLS growth mechanism is interested for rod-like whiskers.

4. CONCLUSIONS

β-SiAlON nanostructure whiskers were synthesized by pressure-less sintering method at 1773 K for 5 hours under the nitrogen gas with pressure of 0.1 MPa. There were two kinds of whiskers, rod-like nanostructure whiskers and wool-like structure, produced during the process. It was found that the diameter distribution of rod-like whiskers was about 80–250 nm, and most of them are straight crystals. However, the diameter of wool-like whiskers is relatively narrow and homogeneous, about 45–55 nm. These two structures which interlaced each other might form a designing reinforced structural material. The growth mechanism of the rod-like and wool-like structure of β-SiAlON has been investigated through a series means of microstructure and phase analyses with XRD, SEM, TEM, and HREM.

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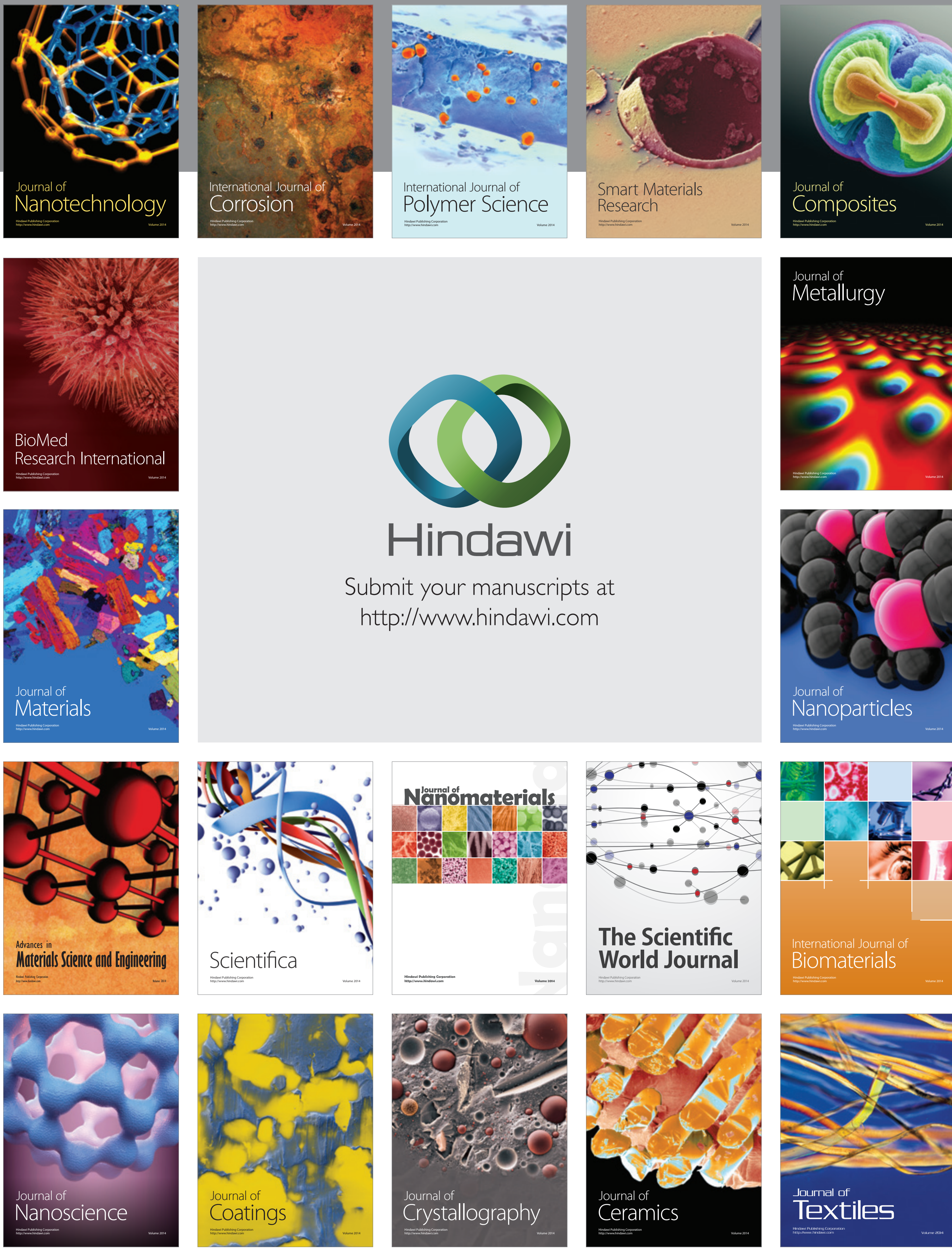

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