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Research Article

Fabrication and Characterization of Al/NiO Energetic Nanomultilayers

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The redox reaction between Al and metallic oxide has its advantage compared with intermetallic reaction and Al/NiO nanomutlilayers are a promising candidate for enhancing the performance of energetic igniter. Al/NiO nanomutlilayers with different modulation periods are prepared on alumina substrate by direct current (DC) magnetron sputtering. The thicknesses of each period are 250 nm, 500 nm, 750 nm, 1000 nm, and 1500 nm, respectively, and the total thickness is 3 μm. The X-ray diffraction (XRD) and scanning electron microscope (SEM) results of the as-deposited Al/NiO nanomutlilayers show that the NiO films are amorphous and the layered structures are clearly distinguished. The X-ray photoelectron spectroscopy (XPS) demonstrates that the thickness of Al_2O_3 increases on the side of Al monolayer after annealing at 450°C. The thermal diffusion time becomes greater significantly as the amount of thermal boundary conductance across the interfaces increases with relatively smaller modulation period. Differential scanning calorimeter (DSC) curve suggests that the energy release per unit mass is below the theoretical heat of the reaction due to the nonstoichiometric ratio between Al and NiO and the presence of impurities.

1. Introduction

In recent years, film ignition bridge devices have been widely reported, such as doped polycrystalline silicon [1–4], platinum [5], titanium [6], and chromium bridge [7], which can function in a few tens of microseconds and operate at one-tenth the input energy with over 30 times smaller in volume compared with the hot-wire devices. Thermal plasma is generated to ignite explosive powder by passing current through film bridge. A variety of energetic nanomultilayers, which can provide large negative reaction heats, consist of alternating nanoscale layers of metal or metal oxide such as Al/Ni [8–11], B/Ti [12], Al/CuO [13–15], and Al/MoO_x [16]. In order to improve the transient ignition temperature and output energy, the nanomultilayers integrated on the semiconductor or metal film bridges have been investigated in many research groups. In the discharge mechanism of integrated ignition bridge, thermal plasma generated by the semiconductor or metal film bridges transfers along the nanomultilayers to make atoms diffuse normal to the layers and result in a rapid self-propagating exothermic reactions. Hence, the integrated structure combines the advantages of film ignition bridge devices and reactive multilayer films, which may improve the ignition performance and reliability in the case of low electrical energy consumption, fast energy release rate, and large amount of reaction heat.

According to the literature [17], the amount of reaction heat released in redox reaction such as Al/CuO, Al/MoO_x, and Al/NiO is almost two times than that of intermetallic reaction. In addition, Al/NiO nanomultilayer redox reaction shows its advantage among the vast range of Al/metallic oxide reactions, which have been confirmed by the investigation of Al/metallic oxide nanocomposites such as nanowire [18, 19] and nanohoneycomb [20]. The various oxidation state of nickel in nickel oxides is an important parameter for released reaction heat. A number of nickel oxides with various oxidation states of nickel such as NiO, NiO_2, Ni_2O_3, Ni_3O_4, and NiO_4 have been reported, showing that the presence of nickel cation vacancy or interstitial oxygen in NiO crystalline lattice results in nonstoichiometric NiO_x.

It is well known that the coefficient of heat conduction, elements diffusivity, and grain boundary in nanomultilayers

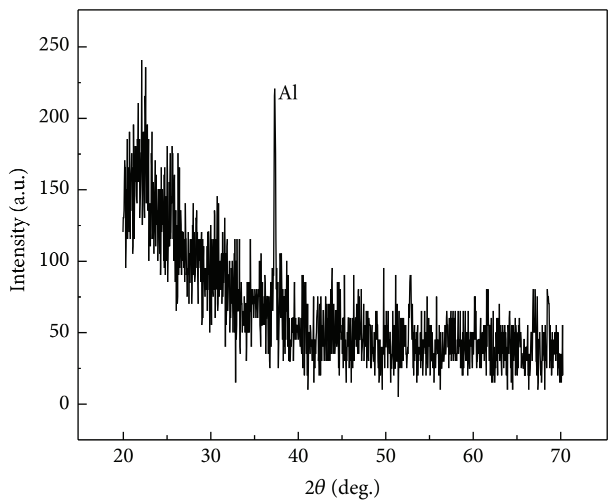


Figure 1: XRD spectrum of Al/NiO nanomultilayers with modulation period thickness of 1500 nm where the thickness ratio of Al to NiO per period is maintained at 1 : 1.5.

are mainly influenced by the film interfaces existing in nanomultilayers and deposition conditions, which can enhance the interfacial contact area. In this study, we focus on the preparation and characterization of the Al/NiO nanomultilayers with different modulation periods. The fabricated Al/NiO nanomultilayers are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), ultrafast measurement system of thermal properties of thin film materials, and differential scanning calorimetry (DSC).

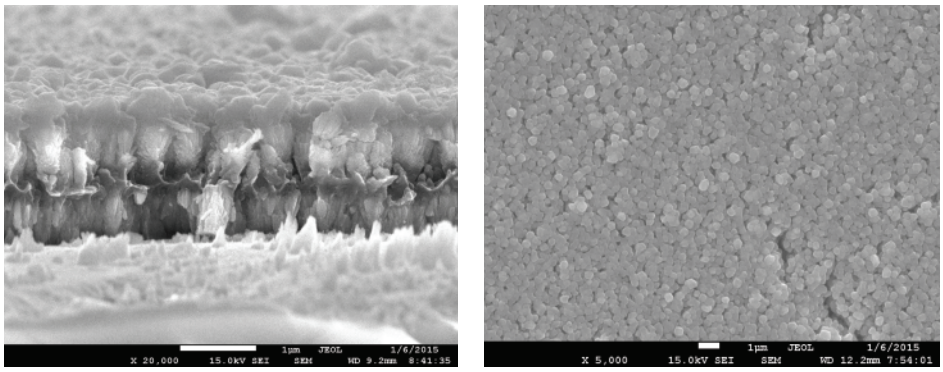
2. Experimental

Al and NiO films are sputter-deposited from Al (purity > 99.99%) and Ni (purity > 99.95%) targets of diameter 50 mm on alumina substrate (10 mm × 5 mm × 0.5 mm) in a multilayer form by direct current (DC) magnetron sputtering and DC reactive magnetron sputtering, respectively. Before deposition, the substrates are cleaned using acetone, alcohol, and deionized water in an ultrasonic bath for 10 min, respectively, which subsequently are dried by nitrogen gas and placed in the oven at 200°C for 20 min for further drying. The substrates move alternately under the afterglow from sputtered Al and Ni targets through a shield with optimized shape to allow for homogeneous film, where the distance between target and substrate is 60 mm. The sputtering power is fixed at 100 W for Al and Ni targets. In addition, the Al target is sputtered under argon ambient and the Ni target is sputtered under argon and oxygen ambient with argon partial pressure at 1.5 Pa and oxygen partial pressure at 0.25 Pa in order to obtain amorphous NiO film. After NiO monolayer is deposited at a time, the work gas argon and reactive gas oxygen in the chamber are pumped out completely to remove oxygen for preventing alumina. The base pressure is 4×10^{-4} Pa and the substrate temperature remains at room temperature in order to prevent the interdiffusion and reaction during deposition. The growth rates of Al monolayer and NiO monolayer are a calculation of monolayer thickness divided by deposition time. The thickness ratio of Al to NiO per period is maintained at 1 : 1.5 to obtain final products with alumina and metal nickel. The total thickness of Al/NiO nanomultilayers is 3 μm with NiO monolayer on the bottom and Al monolayer on the top and the thicknesses of each period keep at 250 nm, 500 nm, 750 nm, 1000 nm, and 1500 nm, respectively.

The crystallographic structure of Al/NiO nanomultilayers is determined by Bede D1 XRD using Cu Ka radiation. The cross-sectional and top-view morphologies are performed using a JEOL-7500F SEM. The diffusion process is confirmed after postdeposition annealing at 450°C in flow argon gas using XPS (Axis Ultra DLD, Kratos Analytical Ltd.). The scanning pass energy is 40 eV and the step size is 0.1 eV. Ultrafast measurement system of thermal properties of thin film materials (NanoTR, PicoTherm) is performed to qualify the influence of the interfaces on the characteristic of heat conduction at room temperature with laser pulse width 1 ns and laser wavelength 1550 nm. The sample surface is coated with a thin molybdenum monolayer with thickness 100 nm so that the change in reflectivity of the sample surface is an indication of the change in temperature of the Al/NiO nanomultilayers. The onset temperatures and energy release values are investigated by DSC, the samples for DSC analysis are scraped from the substrates with a sharp blade, and the DSC experiment is carried out at a temperature range from 20 to 850°C at a heating rate of 5°C/min under a N_2 flow with a sample mass of 12 mg.

3. Results and Discussion

The XRD spectrum of the as-deposited Al/NiO nanomultilayers with modulation period thickness of 1500 nm is shown in Figure 1; metal Al diffraction peak can be clearly seen from the XRD spectrum. There are no peaks for metal Ni or NiO, indicating that the metal Ni is completely oxidized into



(a) (b)

Figure 2: The cross-sectional (a) and top-view (b) SEM morphologies of Al/NiO nanomultilayer with modulation period thickness of 1500 nm.

amorphous NiO. Although there are no peaks for the Al_2O_3 in the XRD spectrum, part of the metal Al on the top surface of Al/NiO nanomultilayers is oxidized as the amorphous Al_2O_3, which is confirmed by SEM and XPS analysis in Figures 2 and 3. This means that the redox reaction between metal Al and NiO has not happened for as-deposited Al/NiO nanomultilayers, ascribing to the deposition condition of room temperature.

Figure 2 shows cross-sectional and top-view SEM morphologies of Al/NiO nanomultilayer with modulation thickness of 1500 nm. All the monolayers exhibit a columnar structure with the growth direction perpendicular to the interfaces alternately. As can be seen in the figure, the layered structures of Al/NiO nanomultilayers are clearly distinguished and the interfaces are sharp. As described previously, there is an obvious Al_2O_3 oxide layer on the top of Al monolayer. It can be identified that the diameters of the grain on multilayer surface are relatively not uniform because of oxidized metal Al surface.

The XPS spectra in Figure 3 indicate the presence of Al, Ni, O, and some organic contamination on the top of nanomultilayers. It can be observed that there is an obvious Al_2O_3 layer at the surface in the range of 1-2 nm in Figure 3(a). The Ni atoms are also detected in the as-deposited nanomultilayers; this means that only a small number of Ni atoms are not oxidized and diffuse into Al monolayer on the top; this is because the melting point of Ni is higher than that of Al, making it much easier for Ni atoms to diffuse into Al lattice due to the weaker bonds between Al atoms. After annealing at 450°C, when more oxygen atoms diffuse into Al monolayer significantly, the thickness of Al_2O_3 layer increases and much larger amount of Ni atoms accumulates at the surface as can be seen in Figure 3(b), indicating that redox reaction has happened and more metal Al is oxidized.

The change in thermoreflectivity of the sample surface in Figure 4 is an indication of the change in temperature of the Al/NiO nanomultilayers as described previously. The characteristic of heat conduction is determined by thermal diffusion time in monolayer film model where the heat diffuses from the surface to the substrate. Thermal diffusion time with different modulation thicknesses at 1500 nm, 1000 nm, 750 nm, 500 nm, and 250 nm is 5×10^{-9} s, 8×10^{-8} s, 9.6×10^{-8} s, 1.1×10^{-7} s, and 1.4×10^{-7} s, respectively. The amount of the interfaces between Al monolayer and NiO monolayer increases as the modulation period decreases, which indicates that the amount of the thermal boundary conductance across the interfaces increases and the thermal diffusion time becomes greater significantly. In addition, there is much smaller change in the rate of reduction of thermal diffusion time with increased interfaces.

Figure 5 shows the DSC data measured from Al/NiO nanomultilayers with modulation period thickness of 250 nm. The first exotherm is not easily distinguished starting at around 460°C and the second one is with an onset temperature of about 566°C, where the energy generation from the redox reaction is clearly visible and it reacts before the metal Al melts, suggesting the solid-solid diffusion reaction mechanism. There is a sharply rising endothermic peak at 635°C as the metal Al begins to melt; the remaining Al reacts with NiO by the liquid-solid diffusion mechanism with an onset temperature of about 812°C. The area integration of exotherm with an onset temperature of about 566°C based on the heat flow curve provides the energy release per unit mass of 2440 J/g, which is below the theoretical heat of the reaction (3440 J/g); this could be because the masses between Al and NiO are at nonstoichiometric ratio and the deposition process results in the presence of impurities and the oxidized Al on the surface. In addition, the smaller modulation period nanomultilayers can enhance the interfacial contact area and surface area, which will reduce the onset temperature and increase energy output of nanomultilayers. From this point of view, the nanomultilayers with much smaller modulation period are more suitable for energetic igniter.

4. Conclusions

The technique of integrating nanomultilayers on the semiconductor or metal film ignition bridge has been proven to be an effective approach for increasing the output energy in a short time. Al/NiO nanomultilayers with different modulation thicknesses of 250 nm, 500 nm, 750 nm, 1000 nm,

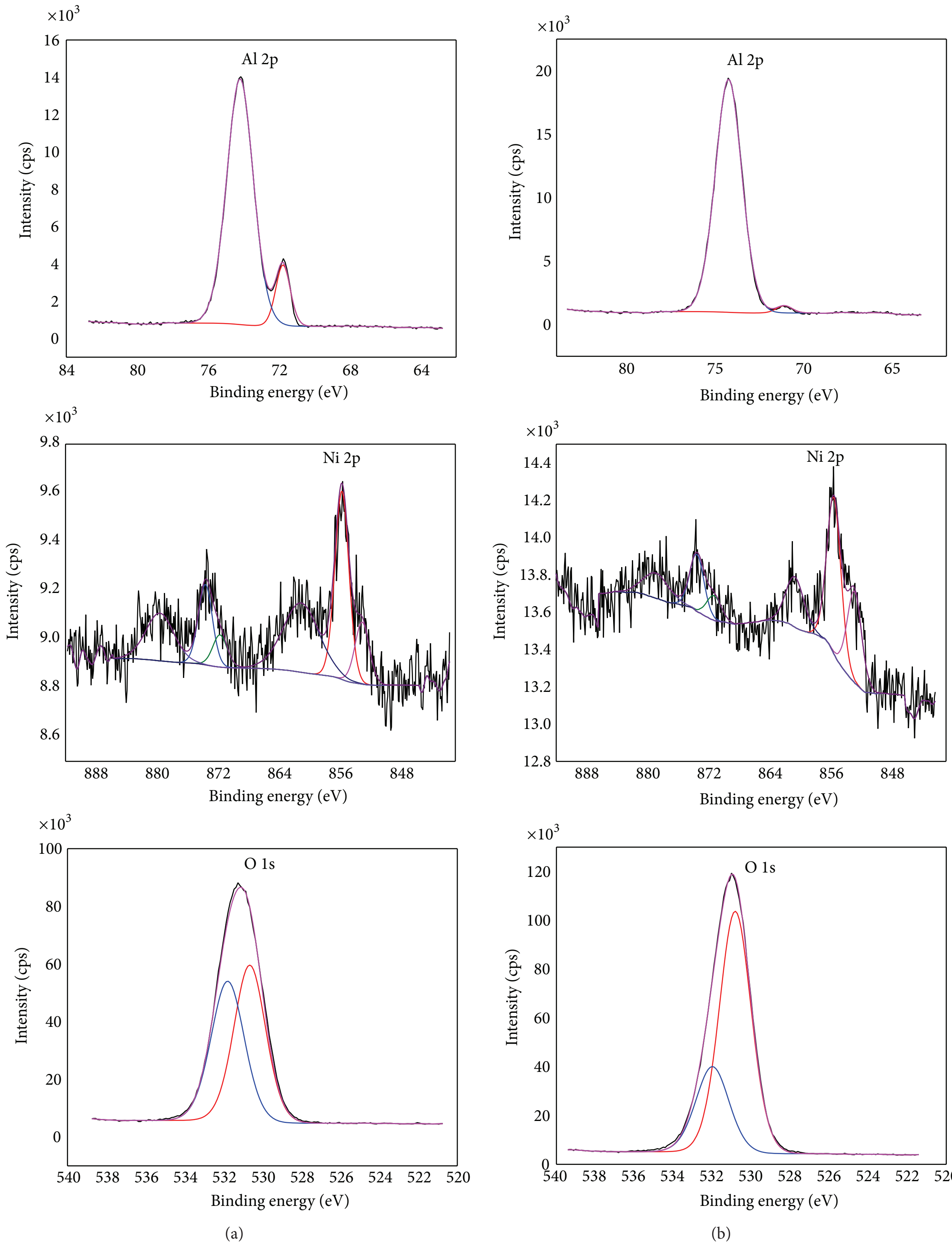


Figure 3: XPS spectra of Al/NiO nanomultilayers with modulation period thickness of 250 nm: (a) the up, middle, and down spectra show Al 2p, Ni 2p, and O 1s peaks of as-deposited nanomultilayers, respectively; (b) the up, middle, and down spectra show Al 2p, Ni 2p, and O 1s peaks of annealed nanomultilayers at 450°C, respectively.

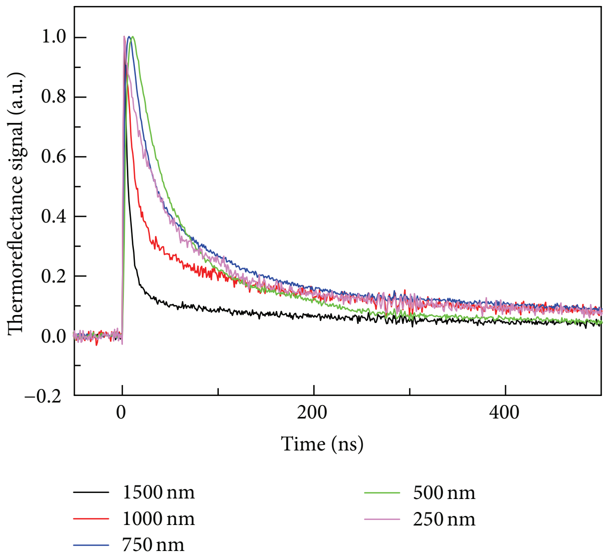


Figure 4: The characteristic of heat conduction of Al/NiO nanomultilayers with different modulation periods.

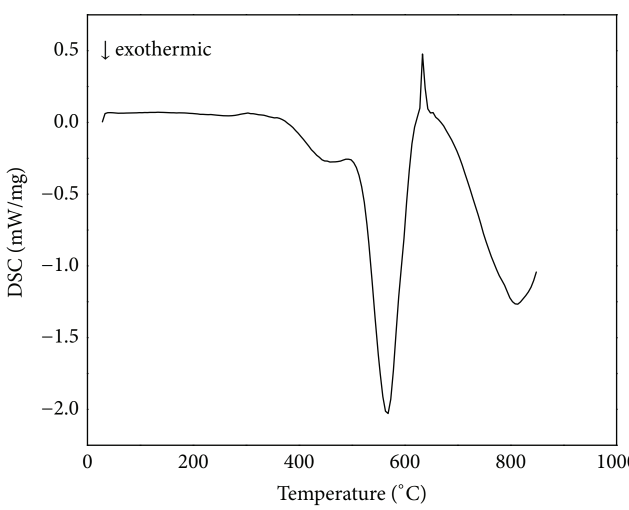


Figure 5: DSC curve of Al/NiO nanomultilayers with modulation period thickness of 250 nm.

and 1500 nm are successfully prepared, showing the clearly layered. The XPS result indicates that the thickness of Al_2O_3 increases at the monolayer of Al after annealing at 450°C. The thermal diffusion time becomes greater significantly as the amount of thermal boundary conductance across the interfaces increases with relatively smaller modulation period. DSC curve suggests that the reaction is based on the solid-solid diffusion mechanism at the early stage and the energy release per unit mass is below the theoretical heat of the reaction due to the nonstoichiometric ratio between Al and NiO and the presence of impurities. In general, the parameters including thermal diffusion time, onset temperature, and energy release need an overall consideration and a continuously optimized fabrication process. It should be noted that Al/NiO nanomultilayers could be realized by standard microfabrication techniques that allow batch fabrication and high level of integration.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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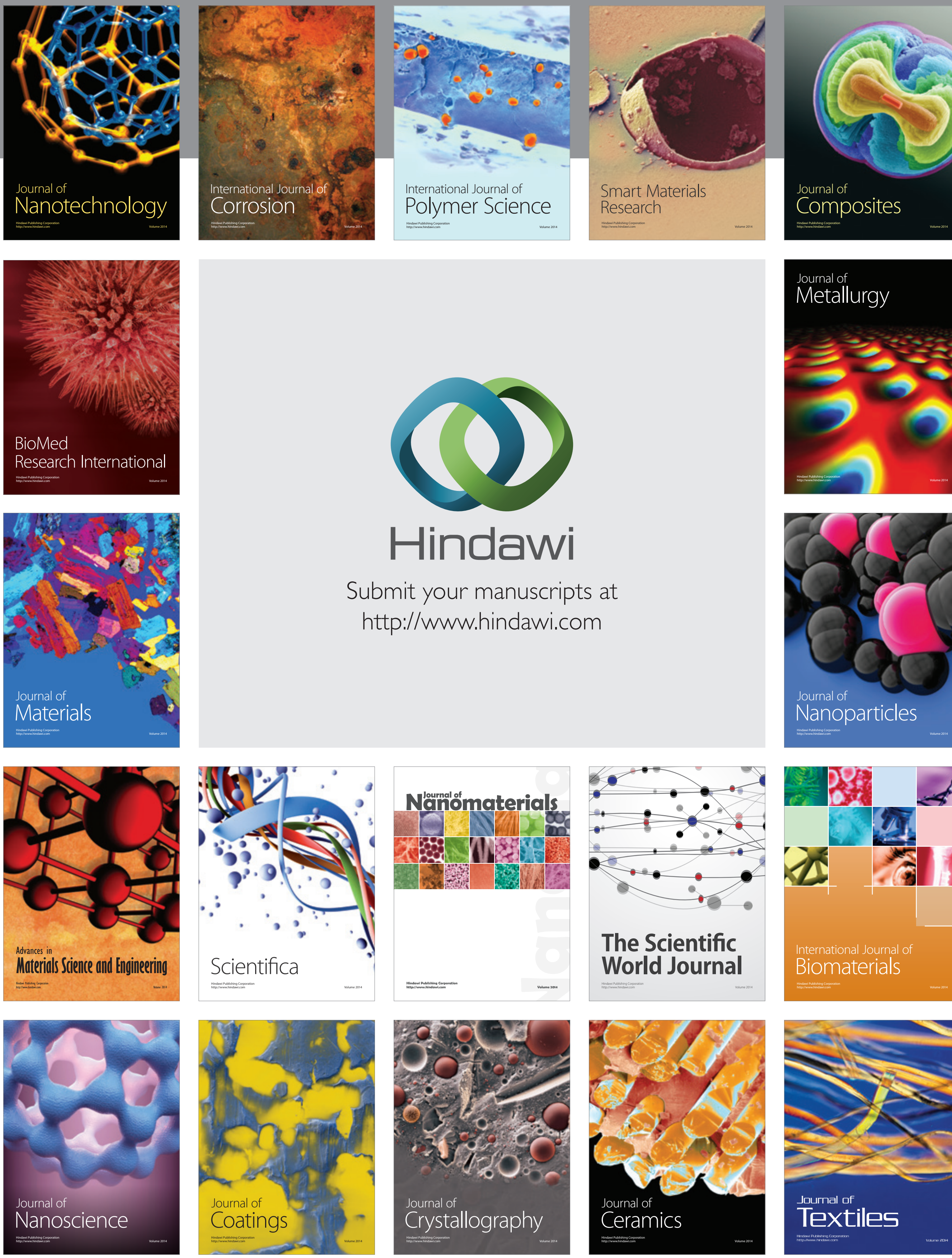
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