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Low-temperature pressureless sintering of Al_2O_3-SiC-Ni nanocermets in air environment

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ABSTRACT

This paper introduces a simplified method for low-temperature pressureless sintering of Al_2O_3-Ni-SiC nanocermets in air environment. In this method, a thin and continuous Ni shell was coated on the surface of Al_2O_3 particles using electroless deposition method. The composite powders were subsequently compressed to prepare bulk specimens. By preventing the ceramic particles from direct contact during the densification of green specimens, sintering temperature of cermet materials was reduced from that of Al_2O_3 (> 1400 °C) to the range of Ni solid-phase sintering temperature. Furthermore, dissolution of a low amount of phosphorus in the composition of Ni coatings caused the further decrease of the sintering temperature to 800 °C. At such low temperatures, pressureless sintering of the cermets in the air environment was successfully performed instead of the common hot pressing process in a reducing atmosphere. Optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD) characterizations indicated that the microstructure of such sintered samples consists of a continuous Ni network surrounding Al_2O_3 grains, without any structural defects or Ni oxidation. Furthermore, mechanical properties of the cermet materials were improved through reinforcement of the continuous Ni network by different amounts of SiC nanoparticles. The results showed that Al_2O_3-Ni-5 wt% SiC nanocermets sintered at 800 °C obtain the highest compressive strength of 242.5 MPa, hardness of 56.8 RA, and the lowest wear weight loss of 0.04 mg/m.

1. Introduction

Aluminum oxide (Al_2O_3) is one of the most widely used ceramics in the advanced industries due to its high hardness, high strength and good chemical-corrosion resistance. However, the potential of Al_2O_3 has been limited by its poor fracture toughness. Incorporation of a ductile metallic phase, like nickel, into the ceramic matrix has been proved to be an effective method to improve fracture toughness of the ceramic materials. This kind of ceramic-metal composites (cermets) has been widely used in automotive, aerospace and military industries because of their high hardness and strength, excellent wear resistance and good toughness [1–9].

Powder metallurgy method has a high potential for manufacturing of cermet materials with complex shapes and adjusted amounts of metal and ceramic components [4,6,7,10,11]. However, work on cermet materials is scarce primarily due to the bellow difficulties associated with this method:

i) Due to the non-wetting characteristics of ceramics and metals, the metal phase usually segregates at some intergranular regions of cermet materials,
ii) The non-wettability and segregation of metal phase prevent uniform distribution of metallic phase, as a layer along the boundaries of ceramic particles, so a large fraction of ceramic particles remains in direct contact after sintering. Regarding to the direct contacts of ceramic particles, high temperatures are required for sintering of cermet materials.
iii) Due to the large differences between the melting temperatures of metal and ceramic components and also the air oxidation of metals at high temperatures, high advanced equipment and reducing environments are commonly required for consolidation of cermet materials.
iv) Sintering process at high temperatures intensifies the segregation and coarsening of the metallic component and leads to the significant loss of mechanical properties [4–7,10–14].

Metal coating the ceramic particles is an interesting idea for resolving of the above-mentioned limitations of powder metallurgy method.

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As the result of this process, a continuous Ni network is formed along the boundaries of ceramic particles, which prevents from segregation of metallic phase and leads to the uniform distribution of the metals within the ceramic matrix [15–19]. Furthermore, by preventing the ceramic particles from direct contact during the densification of green specimens, sintering temperature of the cermet material is expected to reduce from that of ceramic phase to the range of metallic solid-phase sintering temperature. The possibility of low-temperature sintering of cermet materials by metal coating of ceramic particles has been studied in some papers. Vélez et al. [20] investigated the electroless Ni-B deposition on VC and WC powders and subsequent liquid-phase sintering of the samples at 1035–1200 °C. Kim et al. [21] reported hot pressing of Al_2O_3-Ni cermets at 1350 °C in an argon atmosphere. Same sintering conditions were also successfully evaluated in temperature range of 1200–1400 °C [22,23]. Furthermore, Fiori et al. [24] investigated the hot pressing of Ni-Al_2O_3 composites at very high pressures and low sintering temperature of 600 °C.

While metal coating of ceramic particles and low-temperature sintering of cermet materials were mainly evaluated through hot pressing of composite powders in reducing environments, low temperature and pressureless sintering of cermet materials in air environment is introduced in the current paper. By dissolution of low amount of phosphorous in the composition of Ni shelling, the sintering temperature of cermet materials was lowered to the Ni-P eutectic alloys of 800 °C. Such low temperature sintering processes capacitated us to successfully densify the cermet materials by the simplified process of pressureless sintering in the air environment. Furthermore, we evaluated the idea of reinforcing of the metallic network by the addition of hard ceramic nanoparticles for further improving the mechanical properties of the cermet materials.

2. Experimental procedure

α-Al_2O_3 powder (average particle size of 15 μm, Merck, Germany) and β-SiC powder (average particle size of 20 nm, HeFei Kaier Nano Group, China) were used as the starting ceramic materials. As well, nickel sulfate ($NiSO_4{\cdot}2H_2O$), sodium hypophosphite ($NaH_2PO_2{\cdot}H_2O$), sodium citrate ($Na_3C_6H_5O_7{\cdot}5.5H_2O$), sodium hydroxide (NaOH), ammonia (NH_3), nitric acid (HNO_3, 65%), hydrogen chloride (HCl, 37%), tin chloride ($SnCl_2{\cdot}2H_2O$) and palladium chloride ($PdCl_2$) were supplied by Merck, for electroless Ni deposition on the surface of Al_2O_3 particles.

Before electroless deposition, the powders were pre-treated through the successive stages of washing, coarsening, sensitization and activation (Table 1), to obtain the suitable catalytic activity for Ni deposition. After the activation stage, the powders were washed several times in deionized water, separated by centrifugation, and then dried in an oven at 110 °C for one hour. The electroless method was used for deposition of Ni layers on 4 g of activated Al_2O_3 particles, in an aqueous bath with the specifications of Table 1. The bath was stirred for a half-hour at 80 °C, while its pH was set at 9.5. Finally, the powders were washed in distilled water for several times and dried in an oven at 80 °C for three hours.

Fig. 1 shows a schematic of the proposed method for fabrication of Al_2O_3-Ni-SiC nanocermets. In this method, the Ni-coated Al_2O_3 particles (Al_2O_3–20 wt% Ni) were mixed with different amounts of SiC nanoparticles (0, 2.5, 5, 7.5 and 10 wt%), then compressed in a stainless steel mold of 8 mm diameter under 15 bar pressure. The green bulk samples were subsequently sintered for two hours at temperatures varied from 650 to 1250 °C in an air atmosphere.

Microstructures of the sintered cermets and morphology of ceramic powders were investigated by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Particle size distribution of the uncoated and Ni-coated particles was measured by a Fritsch A22 particle size analyzer (PSA). Moreover, compositions of coated particles and sintered cermets were characterized by energy dispersive X-ray spectrometry (EDS) and Unisantis XMD300 X-ray diffraction (XRD) analysis using Cu Kα ($\lambda = 0.15406$ nm) irradiation.

Density of the samples was estimated by Archimedes method. Rockwell A hardness of the sintered cermets was measured using UV.1 universal device, and the average of three measurements was reported as the mean hardness of each sample. Compression tests were performed according to ASTM E9 standard by Zwick Z250 machine, at a strain rate of 0.5 mm/min, and at the ambient temperature. As well, abrasion wear tests were carried out using a pin-on-disk machine with pin geometry of 8 mm diameter and 4 mm long. SiC abrasive paper with grit size of 1000 was used as the disk and experiments were performed under dry sliding conditions at room temperature with a uniaxial load of 5 N and 150 m traveling distance.

3. Results and discussion

3.1. Electroless Ni deposition on Al_2O_3 particles

The mechanisms for catalytic activation of Al_2O_3 particles through the coarsening, sensitization and activation processes, as well as description of electroless Ni deposition on the activated particles are presented by the schematics of Fig. 2.

SEM micrographs and EDS spectra of the as-received, Pd-activated, and Ni-coated Al_2O_3 particles are shown in Fig. 3. As-received Al_2O_3 particles have a polygonal shape, and a particle size distribution between 5 and 30 μm (Fig. 3a). The EDS spectrum of activated particles confirms that the surfaces of the particles are decorated with the nano-sized palladium clusters (Fig. 3b). As a result of the electroless process, a thin, porous and multilayer Ni shell has been deposited on the surfaces of Al_2O_3 particles (Fig. 3c). The EDS spectrum also suggests that the shell layer has a low amount of phosphorus. The Au and C peaks in such spectra are related to the coats used for SEM sample preparations. According to the particle size analyzing (PSA) results, the average particle size before and after the electroless deposition process was about 15 and 25 μm, respectively. Accordingly, it can be concluded that the Al_2O_3 particles are coated with a porous shell of approximately 5 μm thickness. Furthermore, the weighting of powders before and after the Ni deposition suggests the preparation of Al_2O_3–20 wt% Ni composite powder.

Table 1
Description of pre-treatment stages and electroless Ni deposition on Al_2O_3 particles.

Stage	Chemical	Composition	Temperature (°C)	Time (min)
Washing	Cleaner	200 ml Acetone	25	15
Coarsening	Hydrophilic etcher	100 ml/l HNO_3	25	15
Sensitization	Sensitization hydrochloric acid solution	15 g/l $SnCl_2$ and 60 ml/l HCl	25	15
Activation	Activation hydrochloric acid solution	0. 5 g/l $PdCl_2$ and 10 ml/l HCl	25	30
Electroless deposition	Main salt	3.43 g $NiSO_4{\cdot}2H_2O$	80	30
	Reducing agent	7.42 g $NaH_2PO_2{\cdot}H_2O$		
	Buffering agent	0.5 g NaOH + 2 ml NH_3		
	Complexing agent	4.7 g $Na_3C_6H_5O_7{\cdot}H_2O$		