Nanoparticles of Ni on Al$_2$O$_3$ Ceramic Powder Coated by Chemical Reactions

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Ceramic–metal composites are usually prepared by sintering ceramic with metal or metal oxide powders. An alternative technique is sintering ceramic powders coated by metal film. In the present study, the Ni coated Al$_2$O$_3$ powder was obtained by chemical reduction reaction. We used the phosphate bath for deposition of nickel–phosphorus on the surface of Al$_2$O$_3$ powder. The thickness and chemistry of Ni–P coating depend on the time and the parameters of the reaction process. Particles of Ni–P precipitate from a solution in two different forms: (a) spherical nanoparticles of Ni–P (50 nm) which grow on the surface of Al$_2$O$_3$ powder and can form tight, one diameter thick film; (b) large agglomerates of loosely connected spherical nanoparticles with a $50 \div 150$ nm diameter. The method proposed in this study allows obtaining Al$_2$O$_3$ powder covered with Ni–P nanoparticles in the forms of thin film or single nanoparticles, mixed with loose Ni–P agglomerates.

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1. Introduction

Applications of ceramic materials are limited by their brittleness. To overcome this problem Niihara and his group implemented a new concept of structural ceramic nanocomposites, which are characterized by significant improvement of mechanical properties, due to interaction of nanometric phase with matrix grains [1]. The concept has been developed for ceramic–metal nanocomposites, such as Al$_2$O$_3$/W [2], Al$_2$O$_3$/Mo [3], Al$_2$O$_3$/Ni [4, 5], and Al$_2$O$_3$/Cu [6]. It was found that the relationship between specific mechanical properties of the composite depends on the amount of the starting material, temperature of sintering, and dispersion of the component phases. In particular it has been suggested that

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improvement of fracture toughness is a result of fracture deflection, tip blunting, and bridging effect.

The melting temperature of the metallic phase is usually lower than the sintering temperature of the ceramic matrix. Thus, while sintering, the metal comes to a liquid phase. The diffusion processes in liquid phase are much more intense than in solid phase, and result in a large growth of metallic nanoinclusions and their unfavorable segregation. This phenomenon is more pronounced in the system with poor wetting by the liquid metal. To suppress the grain growth the application of a high pressure technique, like hot isostatic pressure (HIP), is an alternative. Under pressure, the sintering temperature could be lowered and it additionally reduced the growth of grains of the component phases.

In most of the literature reports, the ceramic metal nanocomposites were produced by grinding ceramic powders with metal oxides or pure metals. The present work concludes the preliminary results of production of nanocomposite Al_2O_3/Ni by sintering the alumina powder covered with nanoparticles of Ni–P by autocatalytic chemical reduction process. The method proposed here offers a possibility to obtain uniformly dispersed nanoparticles of Ni–P (a size range of 10–100 nm) on the surface of ceramic powders. Thus, we have reasons to believe that, with the application of proper sintering techniques, it will be possible to produce Al_2O_3/Ni nanocomposite with a very uniform distribution of Ni inclusions in the ceramic matrix. This shall improve greatly the mechanical properties of such material. It is also possible to select such process parameters so that the Ni particles deposited on the surface of Al_2O_3 grains form uniform nanolayers, so this process can be used to produce a composite with metallic phase percolation.

2. Experiments and results

An amorphous Ni–P was deposited on the surface of Al_2O_3 powder from a solution by autocatalytic chemical reduction process. The composition of the solutions which we used is given in Table I. Two Al_2O_3 powders were used: coarse-grained (G) and fine-grained (F). The starting powders were characterized as to their grain size distribution by laser diffraction, electron microscopy (Fig. 1a,b) and helium density. The coarse-grained powder was used to simplify

TABLE I

Composition of baths used for Ni deposition.

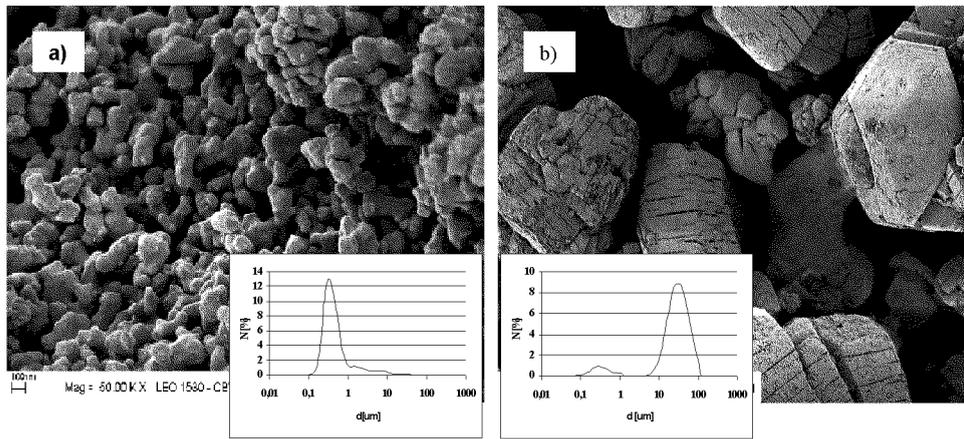| Solution components	Concentration [mol/dm^3]
[NaH$_2$PO$_2 \cdot$ H$_2$O]	0.28
[NiCl$_2 \cdot$ 6H$_2$O]	0.09
[C$_6$H$_5$O$_7$Na$_3 \cdot$ 2H$_2$O]	0.06

Fig. 1. Morphology (SEM) and grain size distribution of initial Al$_2$O$_3$ powders: (a) powder (F), (b) powder (G).
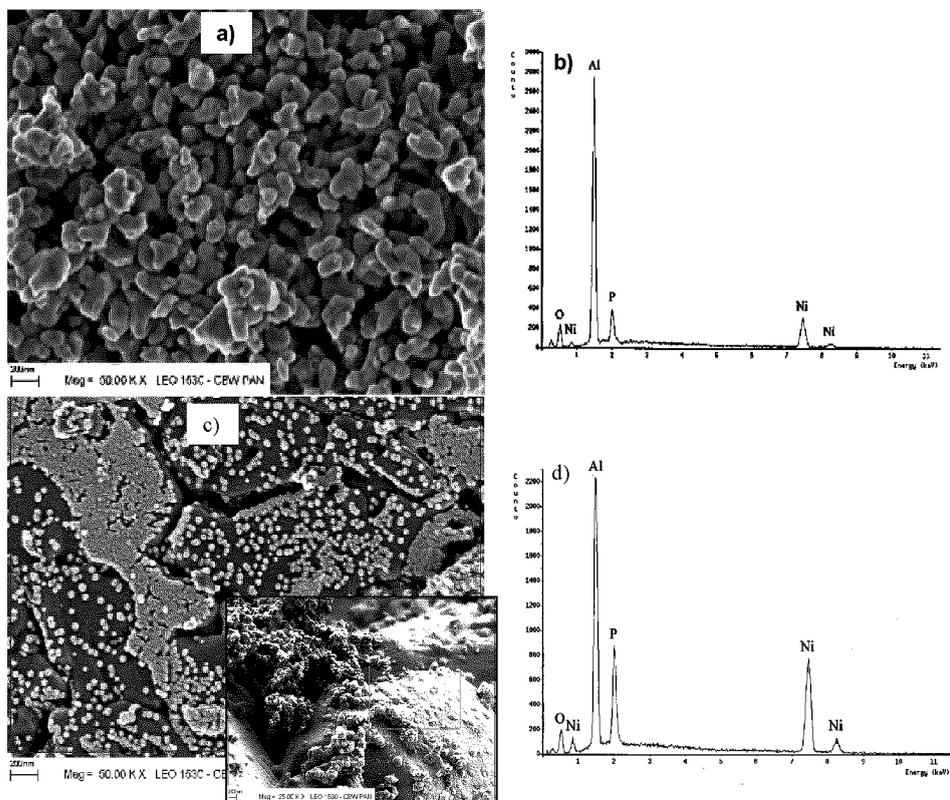

Fig. 2. SEM image and XRD pattern: (a, b) powder (F) after 1 h nickel plating; (c, d) powder (G) after 1 h nickel plating and after 2 h nickel plating (small picture).

the observations of deposited Ni–P particles. The Al_2O_3 powder surface was activated by Pd, a small amount of which is needed to start the process of Ni ions reduction. After this, the chemical reduction reaction is autocatalytic, catalyzed by deposited Ni.

The solution for deposition was heated in a glass container, equipped with a mechanic mixer, to a temperature of $80-90°C$. After reaching this temperature, Al_2O_3 powder was added into the solution. To test the influence of time on the amount of the deposited Ni–P phase on the ceramic powder grains, the samples were prepared for different times of the process: 10, 30, 60, and 120 min. Coated powders were then rinsed in distilled water and dried in air. Powder (F), due to a small size, was centrifuged after each rinse.

TABLE II

Helium density measured for powders (G) and (F) before and after nickel plating.

Sample symbol	Helium density	Ni–P percentage (%wt)
G	3.2318	–
G1/6+(d)	3.9111	27.26
G1/2+	3.7422	21.391
G1+(d)	3.8951	26.7303
G1+	3.8111	23.838
G2+N(d)	3.9053	27.073
F	3.6395	–
F1+	4.005	15.4307
F1+(d)	4.107	19.235
F1+	4.0256	16.2187
F2+	4.0286	16.3381

The coated powders were analyzed by electron microscopy (Fig. 2a,c), helium density measurement, and qualitative XRD analysis (Fig. 2b,d). The helium density analysis made it possible to estimate the mass fraction of Ni–P in the final material. The results are shown in Table II.

3. Discussion

The powders, which were white at the beginning of the process, turned dark gray. This is a clear proof of depositing of Ni layer on the surface of the powder particles.

The Al_2O_3 powders selected for further investigations differed distinctly as to their grain size, which can be observed in Fig. 1. When comparing the pictures of powder (F), given the same magnification, at the beginning of the nickel plating

(Fig. 1a) and after 1 h of the process (Fig. 2a), no differences are noticeable. However, as it was discussed earlier, the fact of obtaining a microscopic picture without additional conductive material, as well as easily observed Ni and P peaks in the diffraction pattern (Fig. 2b) are a clear proof of Ni–P plating on the surface of ceramic powder (F). The Ni–P particles are shown in Fig. 2c.

During the analysis of the images of the powder (G) grain surface obtained after different times of nickel plating (Fig. 2c) it is easy to detect the Ni–P particles due to their high contrast with a much darker base. All the observed Ni–P precipitations have typically sizes of 10–150 nm and a very homogeneous spherical shape. It is also clearly seen that their distribution on the powder surface is very uniform.

The resulting Ni–P particles are deposited from the bath solution in two different ways:

(a) as nanospherical particles, having a size of 10–50 nm, forming a thin film on the surface of powder particles, where further layers form on top of the already formed deposits (Fig. 2c);

(b) as loose agglomerates of spherical particles having sizes of 50−150 nm, which occasionally form clusters (Fig. 2c).

The amount of Ni–P obtained through chemical nickel plating was significantly higher when the solution bath has decomposed, as shown in Table II. We conclude that the reaction rate is the highest right after adding Al$_2$O$_3$ powder to the solution, with the process dynamics decreasing very fast. When comparing the results for powder (G) after 30 and 60 min and the results for powder (F) after 60 and 120 min, no significant differences in the amount of deposited Ni–P are noticed. The increase in amount of Ni–P is much slower between the plating time of 60 and 120 min than for times of 30 and 60 min.

When the solution bath has decomposed, a high increase in Ni–P content in the resulting material was observed. This is probably due to the formation of loose clusters of Ni–P. Particles of this kind are found after the decomposition of the solution when they form a sediment on the walls of the container. Mixing of the solution causes the deposited material to fall back into the solution and form agglomerates after the process is finished, and in consequence to an increase in content of Ni–P in the material. It is important to acknowledge that forming agglomerates by decomposition of the solution does not influence the plating of Ni–P particles in the two, described above, manners. Therefore, it might be possible to fix the amount of Ni–P by stimulation of the solution bath decomposition. The amount of Ni–P coating on the ceramic powder depends on the complexity of the powder Al$_2$O$_3$ surface. The more complex is the surface the bigger the amount of the coated material. This amount depends also on the number of active centers produced in the activating process. However, further investigations are needed to precisely define these relations.

4. Conclusions

We have shown that it is possible to deposit chemically Ni on the surface of Al_2O_3 powder. The plated Ni–P particles are characterized by a small size of 50–150 nm and uniform distribution on the surface ceramic. Ni–P particles may form thin layers as well as agglomerates. The amount of deposited Ni may be influenced by extension of the chemical process as well as, to a much higher degree, by stimulation of the decomposition of the bath solution.

Acknowledgment

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