

## DEVELOPMENT OF NANOCOMPOSITES FOR SOLID FREEFORM FABRICATION

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### ABSTRACT

Nanocomposites in which the constituents are mixed on a nanometer scale can provide important advantages in the Selective Laser Sintering (SLS) and Selective Laser Reactive Sintering (SLRS) processes. The larger surface area and grain boundaries in the nanocomposites compared to that in the conventional microcomposites are expected to enhance the solid state diffusion during laser irradiation as well as during any other subsequent processes. Our strategy is to design and develop nanocomposites in which one nanosize component has a lower melting point than the other nanosize component, either of which can serve as the matrix phase. The nanoscale dispersion of the low melting component can aid the sintering process during SLS or SLRS. Nanocomposite powders of  $\text{Al}_2\text{O}_3\text{-CoO}_x$ ,  $\text{Al}_2\text{O}_3\text{-NiO}$ ,  $\text{Al}_2\text{O}_3\text{-Co}$  and  $\text{Al}_2\text{O}_3\text{-Ni}$  have been synthesized by sol-gel processing and are evaluated by SLS.

### INTRODUCTION

Nanostructured materials are characterized by ultrasmall building blocks whose sizes are of the order of 1-100 nanometers. These materials offer potentially useful and unusual combinations of mechanical, electrical, magnetic and optical properties that are otherwise unachievable in conventional materials [1]. The properties are controlled by a complex interplay among the building blocks and the interfaces between them that are determined primarily by the synthesis and processing conditions. Nanostructured materials promise to advance a range of technologies and there is intensive worldwide activity on these materials both from scientific and technological points of view.

While the terms "nanocrystalline" and "nanophase" materials refer generally to single phase solids of nanometer size, the term "nanocomposite" refers to multiphase solids of nanometer size [2]. The solid phases in a nanocomposite could be of different nature. They could be metals, inorganic ceramics or polymers or combinations thereof but all mixed on a truly nanometer scale. The phases could be amorphous, semicrystalline or crystalline.

Nanocomposites exhibit ultraheterogeneity or nanoheterogeneity, which offer several processing advantages. Because the different phases are mixed on a nanoscale, the diffusion length for solid-solid reaction is much smaller than that in conventional materials. The larger surface and grain boundary energies associated with nanocomposites provide the driving force for enhanced reactions. These factors reduce the reaction temperature as well as time. Nanocomposites have been shown to sinter close to theoretical densities in several systems such as  $\text{Al}_2\text{O}_3\text{-SiO}_2$ ,  $\text{Al}_2\text{O}_3\text{-TiO}_2$ ,  $\text{SiO}_2\text{-MgO}$ , *etc.* [3]. Nanocomposite gels store much higher metastable energy than homogeneous gels, and this extra energy enhances

densification. In addition, nanocomposites seem to undergo crystallization and densification simultaneously unlike homogeneous gels. Homogeneous gels, due to their atomic scale mixing, often undergo crystallization before densification occurs which either leads to lower densities or necessitates higher temperatures for sintering. It is clear that nanocomposites have the potential to offer lower processing temperatures and flaw-free parts with higher densities.

Our objective is to design and develop nanocomposites that can optimize Selective Laser Sintering (SLS) and selective Laser Reactive sintering (SLRS). Nanocomposites can be synthesized by sol-gel processing or other "soft chemistry" techniques. Although both sol-gel processing and solid freeform fabrication are well known, the idea of utilizing sol-gel derived nanocomposite powders that are specifically designed and synthesized to optimize SLS or SLRS have not been exploited. Our strategy is to select ceramic-ceramic or ceramic-metal nanocomposite systems in such a way that one nanosize component has a lower melting temperature than the other nanophase component, either of which can serve as the matrix phase. The objective is to achieve sintering aid from the low melting phase during SFF processing. Because the low melting component is dispersed on a nanoscale in the matrix phase, it is expected to aid the sintering process, during SFF or any other secondary processing, in a much better way than the mechanically mixed microcomposite powders. By proper selection of composite systems and control of agglomeration during sol-gel processing, the ability to achieve full density SFF parts can be enhanced. We present in this paper our preliminary results with  $\text{Al}_2\text{O}_3\text{-CoO}_x$ ,  $\text{Al}_2\text{O}_3\text{-NiO}$ ,  $\text{Al}_2\text{O}_3\text{-Co}$  and  $\text{Al}_2\text{O}_3\text{-Ni}$  nanocomposites. CoO, NiO, Co and Ni have melting points of respectively, 1795, 1984, 1495 and 1455 °C, which are lower than that of  $\text{Al}_2\text{O}_3$  (2050 °C).

## EXPERIMENTAL

The ceramic-ceramic nanocomposite powders of  $\text{Al}_2\text{O}_3\text{-CoO}_x$ , and  $\text{Al}_2\text{O}_3\text{-NiO}$  were synthesized by a sol-gel method [4]. The steps involved in the synthesis of  $\text{Al}_2\text{O}_3\text{-CoO}_x$  are summarized in Fig. 1. To an aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  maintained at about 80 °C, required amount of a solution of aluminum tri-sec-butoxide in iso-propyl alcohol was added under constant stirring. Aluminum-tri-sec-butoxide hydrolyzes during this process to give large suspended particles of  $\text{Al}(\text{OH})_3$ , which was then dissolved by adding nitric acid to obtain a homogeneous sol of  $\text{Al}^{3+}$  and  $\text{Co}^{2+}$ . The sol was heated gently on a hot plate to form a gel, which was then dried rapidly on the hot plate. The dry gel was then heated in a muffle furnace to decompose the nitrate and hydroxide, which resulted in a mixture of  $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$ . A similar procedure was adopted to obtain  $\text{Al}_2\text{O}_3\text{-NiO}$  also. The  $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$ , and  $\text{Al}_2\text{O}_3\text{-NiO}$  powders were also fired at different temperatures ranging from 300-1250 °C to evaluate the reaction process. The ceramic-ceramic nanocomposites so obtained were reduced in a stream of hydrogen at 400-1100 °C to obtain the ceramic-metal nanocomposites  $\text{Al}_2\text{O}_3\text{-Co}$ , and  $\text{Al}_2\text{O}_3\text{-Ni}$ .

The composite powders were characterized by x-ray diffraction, electron microscopy and density measurements. Since the large surface area associated with the nanosize powders lead to an adsorption of water,  $\text{CO}_2$  etc. on the surface, the powders were baked at about 200 °C for about 24 h before scanning with the laser beam. Single layer tests were performed with various power levels and scan speeds. The specimens obtained were characterized by x-ray diffraction and microscopy.

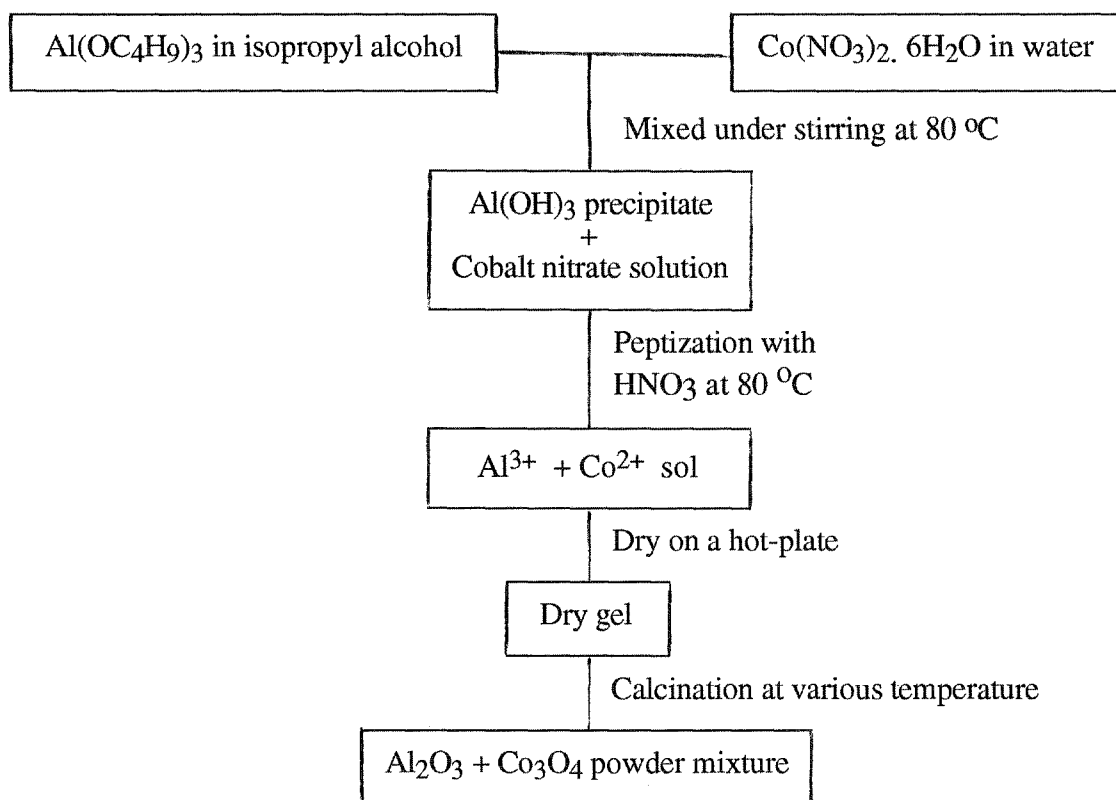


Fig.1 Synthesis scheme for Al<sub>2</sub>O<sub>3</sub>-Co<sub>3</sub>O<sub>4</sub> nanocomposite powder

## RESULTS AND DISCUSSION

### *Powder synthesis and characterization:*

The phase identification by x-ray of a nominal composition containing an atom ratio of Al:Co = 2:1 is summarized in Table 1. It can be seen that Co<sub>3</sub>O<sub>4</sub> is formed during the initial stages of drying on the hot plate. Although the exact temperature of hot-plate was not measured, it was presumed that Co<sub>3</sub>O<sub>4</sub> formation can occur at temperatures as low as 200 °C because firing of pure Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 200 °C for 20 h gives Co<sub>3</sub>O<sub>4</sub>. Up to about 450 °C, mostly the reflections of Co<sub>3</sub>O<sub>4</sub> are discernible in the x-ray pattern. Aluminum oxide or AlOOH present are very small in particle size and could not be detected by x-ray diffraction. In the region 580-900 °C, aluminum oxide was found to exist as γ-Al<sub>2</sub>O<sub>3</sub> having a cation-deficient spinel structure. The presence of γ-Al<sub>2</sub>O<sub>3</sub> is, for example, seen in the x-ray pattern (Fig. 2) of a powder mixture fired first at 580 °C in air and then at 700 °C in hydrogen atmosphere. A small reflection corresponding to γ-Al<sub>2</sub>O<sub>3</sub> is seen around 2θ = 67 ° among strong reflections of Co metal. Above 1000 °C, any aluminum oxide present is in the form of α-Al<sub>2</sub>O<sub>3</sub> having the corundum structure.

Table 1 Phase identification by x-ray diffraction of the  $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$  nanocomposites after heating at various temperatures for a constant time of 20 h

Temperature (°C)	Phase identification	Color
Dried on a hot-plate	$\text{Co}_3\text{O}_4$	Black
300	$\text{Co}_3\text{O}_4$	Black
450	$\text{Co}_3\text{O}_4$	Black
580	$\text{Co}_3\text{O}_4 + \gamma\text{-Al}_2\text{O}_3$	Black
650	$\text{Co}_3\text{O}_4 + \gamma\text{-Al}_2\text{O}_3$	Black
700	$\text{Co}_3\text{O}_4 + \gamma\text{-Al}_2\text{O}_3$	Black
800	$\text{Co}_3\text{O}_4 + \gamma\text{-Al}_2\text{O}_3 + \text{CoAl}_2\text{O}_4$	Dark blue
900	$\text{Co}_3\text{O}_4 + \gamma\text{-Al}_2\text{O}_3 + \text{CoAl}_2\text{O}_4$	Dark blue
1000	$\text{CoAl}_2\text{O}_4 + \alpha\text{-Al}_2\text{O}_3$	Dark blue
1250	$\text{CoAl}_2\text{O}_4$	Blue

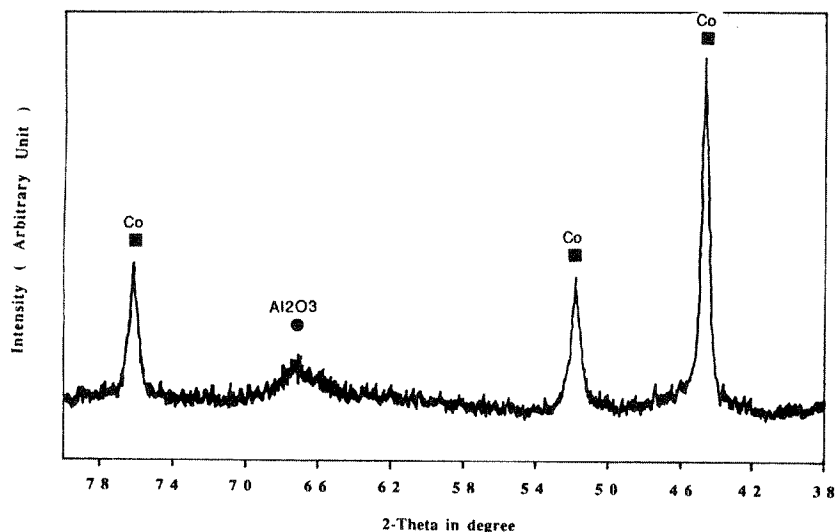


Fig. 2 X-ray diffraction pattern of 75 mole %  $\text{Al}_2\text{O}_3$  - 25 mole %  $\text{Co}_3\text{O}_4$  (Al : Co ratio = 2:1) nanocomposite after firing first at 580 °C in air and then at 700 °C in  $\text{H}_2$  for 20 h

The oxides of cobalt and aluminum can react to give the spinel oxide  $\text{CoAl}_2\text{O}_4$ , which is blue in color. The change in color from black to blue around 800 °C (Table 1) seems to suggest that the formation of  $\text{CoAl}_2\text{O}_4$  occurs around this temperature. However, the formation of  $\text{CoAl}_2\text{O}_4$  spinel can start much below 800 °C and we cannot rule out its presence below 800 °C from x-ray data since both  $\text{Co}_3\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  have spinel structure with close lattice parameters. The broad nature of the reflections at lower temperatures and their overlap make it extremely difficult to determine the exact temperature

at which  $\text{CoAl}_2\text{O}_4$  formation begins. Nevertheless, we could clearly see the formation of the spinel  $\text{NiAl}_2\text{O}_4$  in the analogous system  $\text{Al}_2\text{O}_3$ - $\text{NiO}$  at temperatures as low as 320 °C (Fig. 3). Formation of spinel phases around 300 °C has also been shown in several other systems such as  $\text{NiMn}_2\text{O}_4$  [5]. Furthermore, formation of  $\text{CoAl}_2\text{O}_4$  has been suggested to occur around 500 °C from an observation of a decline in the catalytic activity of  $\text{Co}_3\text{O}_4$  supported on  $\gamma\text{-Al}_2\text{O}_3$  [6]. The catalytic activity in this system is due to  $\text{Co}_3\text{O}_4$  and the degradation of catalytic activity corresponds to a conversion of  $\text{Co}_3\text{O}_4$  to  $\text{CoAl}_2\text{O}_4$ . So, it is likely that the formation of the  $\text{CoAl}_2\text{O}_4$  spinel occurs at temperatures below 500 °C.

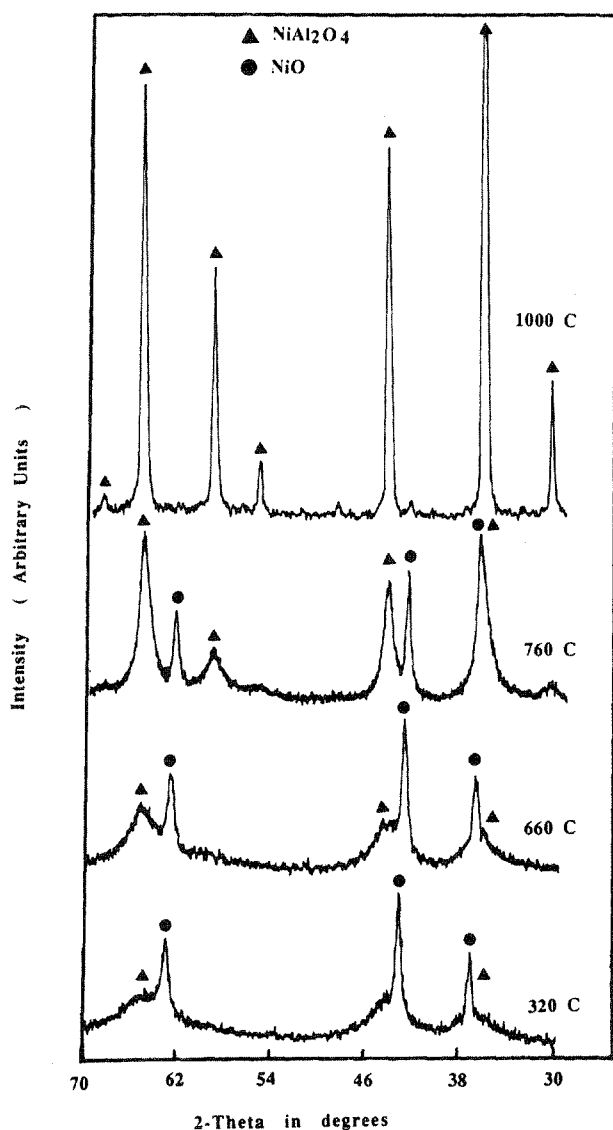


Fig. 3 X-ray diffraction pattern of 50 mole %  $\text{Al}_2\text{O}_3$  - 50 mole %  $\text{NiO}$  (Al : Ni ratio = 2:1) nanocomposite after firing at various temperatures for about 20 h

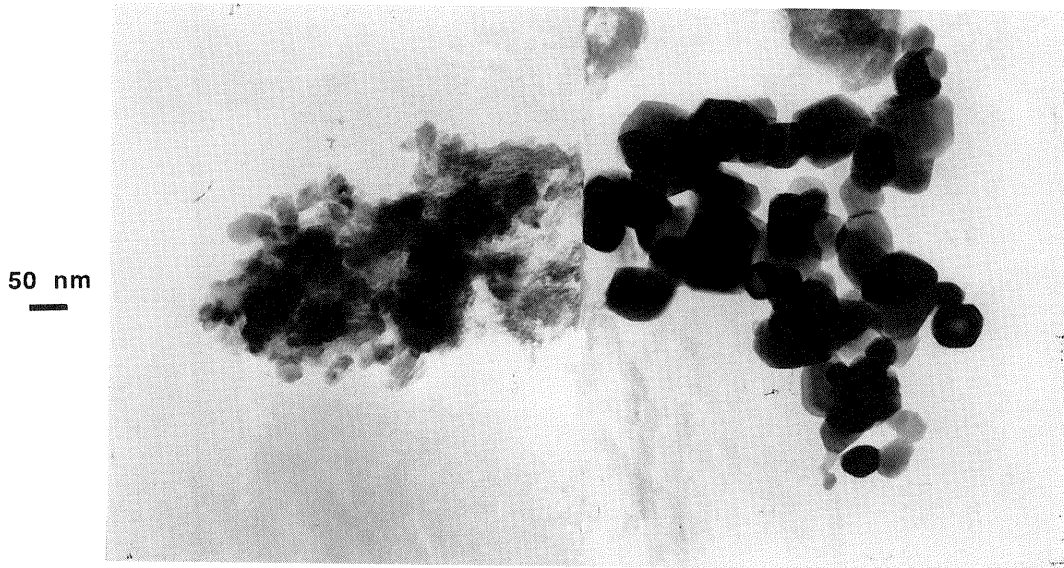


Fig. 4 TEM micrograph of 75 mole %  $\text{Al}_2\text{O}_3$  - 25 mol %  $\text{Co}_3\text{O}_4$  (Co : Al ratio = 1:2) nanocomposite after firing at 580 °C in air for 20 h

The TEM micrograph of the  $\text{Al}_2\text{O}_3$ - $\text{Co}_3\text{O}_4$  nanocomposite powder after heating at 580 °C in air for 20 h is shown in Fig. 4. The large particles are about 50 nm in size and were presumed to be  $\text{Co}_3\text{O}_4$  since they were shown to be rich in Co by EDS analysis. The small particles are less than 10 nm and were shown to be rich in Al by EDS analysis. These observations are consistent with the x-ray results. The TEM image of the nanocomposite powder after heating at 700 °C for 20 h is shown in Fig. 5. The particles have grown significantly to about 150 nm during this process. However, the rise in firing temperature did not have any significant influence on the size and distribution of the agglomerates. An SEM micrograph of the powder heated at 700 °C is shown in Fig. 6, which indicates an agglomerate size of about 100  $\mu\text{m}$ .

#### *Selective laser sintering:*

Preliminary SLS experiments with the  $\text{Al}_2\text{O}_3$ - $\text{Co}_3\text{O}_4$  nanocomposites indicated blowing up of the powder under the laser beam. A low powder density of about 20 % together with the adsorbed moisture seem to cause this problem. The powder was then ball-milled for about 30 min and subjected to SLS under an *in situ* baking around 200 °C. This modification allowed use of high enough laser power without the powder being blown. During this process, the color of the powder changed from black to blue indicating the reaction of  $\text{Al}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  under the laser beam to form the spinel oxide  $\text{CoAl}_2\text{O}_4$ . A top view after SLS of a 83.2 mole %  $\text{Al}_2\text{O}_3$  - 16.8 mol %  $\text{Co}_3\text{O}_4$  nanocomposite is shown in Fig. 7. The corresponding SEM micrograph of the cross section is shown in Fig. 8. Although the powder sinters locally during the SLS process to give relatively higher density, large cracks were found to occur. The low density of the initial powder with large porosity was suspected to cause this problem. Similar results were also obtained with  $\text{Al}_2\text{O}_3$ -NiO.

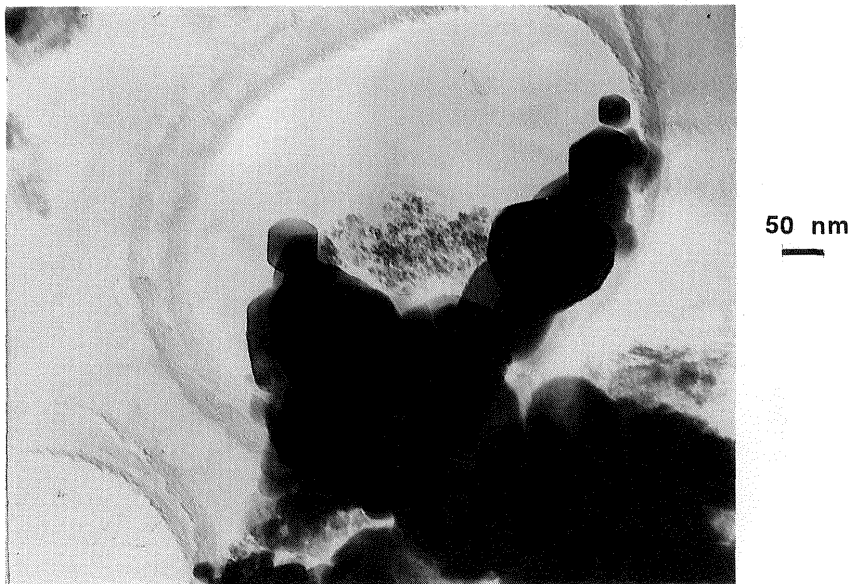


Fig. 5 TEM micrograph of 75 mole % Al<sub>2</sub>O<sub>3</sub> - 25 mole % Co<sub>3</sub>O<sub>4</sub> (Co : Al ratio = 1:2) nanocomposite after firing at 700 °C in air for 20 h

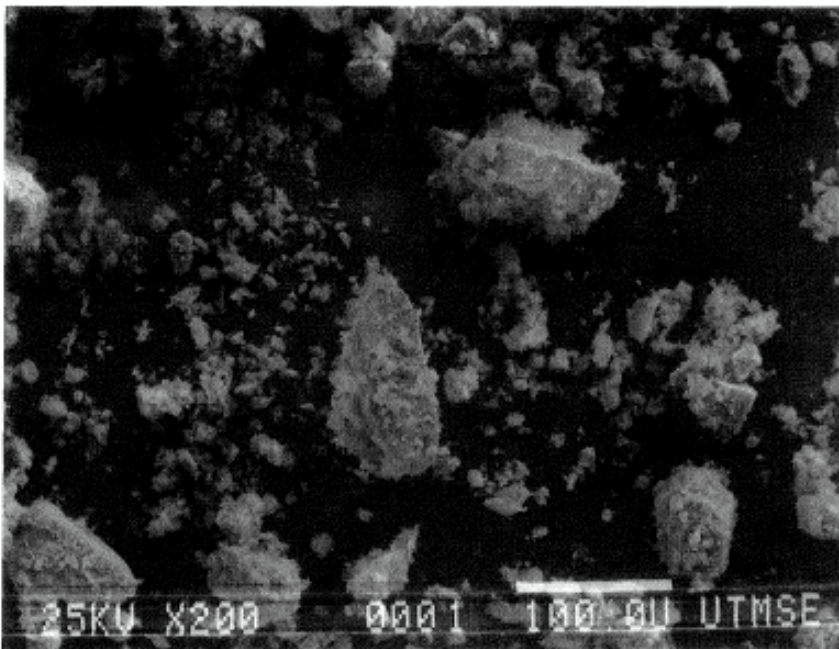


Fig. 6 SEM micrograph of 75 mole % Al<sub>2</sub>O<sub>3</sub> - 25 mole % Co<sub>3</sub>O<sub>4</sub> (Co : Al ratio = 1:2) nanocomposite after firing at 700 °C in air for 20 h

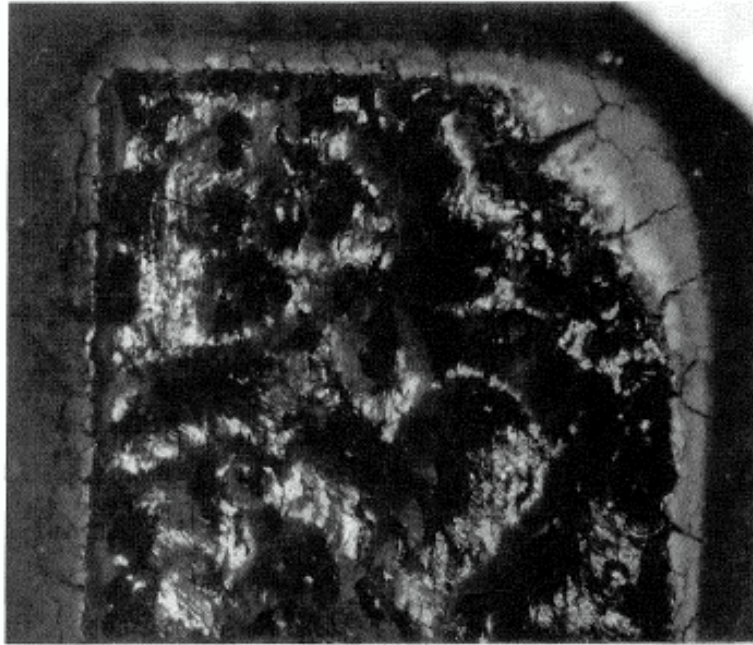


Fig. 7 Photograph of the top view of 83.2 mole %  $\text{Al}_2\text{O}_3$  - 16.8 mole %  $\text{Co}_3\text{O}_4$  nanocomposite after firing at 580 °C in air for 20 h and subjecting to SLS.

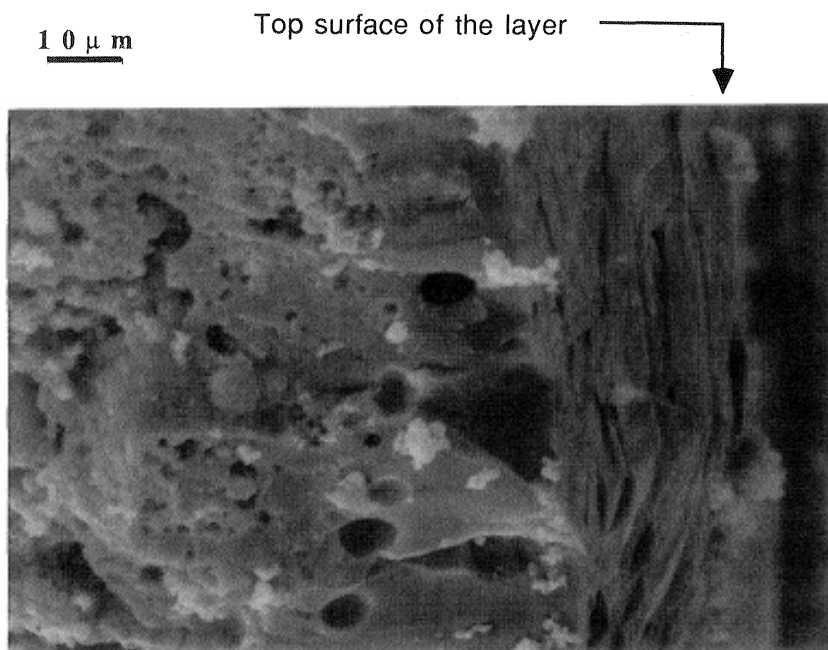


Fig. 8 SEM micrograph of 83.2 mole %  $\text{Al}_2\text{O}_3$  - 16.8 mole %  $\text{Co}_3\text{O}_4$  nanocomposite after firing at 580 °C in air for 20 h and subjecting to SLS.



In order to circumvent the above difficulties, strategies to increase the density of the initial powders without sacrificing much of the nanoscale mixing were pursued. One way to achieve higher densities in the powder is to anneal the nanocomposites at relatively higher temperatures (~ 1000 °C). However, such an annealing around 1000 °C of the  $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$  nanocomposite will result in the formation of the spinel oxide  $\text{CoAl}_2\text{O}_4$ , which will in essence consume the low melting component  $\text{Co}_3\text{O}_4$  and jeopardize our approach to SLS. Therefore, to demonstrate the feasibility of our objective, we decided to pursue the ceramic-metal nanocomposite  $\text{Al}_2\text{O}_3\text{-Co}$ , which will not undergo any chemical reaction during the preannealing of the powder at higher temperatures. Accordingly,  $\text{Al}_2\text{O}_3\text{-Co}$  nanocomposites were first obtained by reducing the  $\text{Al}_2\text{O}_3\text{-Co}_3\text{O}_4$  oxide nanocomposite in hydrogen around 1000 °C. The powder was then annealed in  $\text{N}_2$  atm at 1350 °C for 8 h to increase the density, and reduced again in hydrogen around 1000 °C to convert back any cobalt oxide that might have formed by reaction with the residual oxygen during  $\text{N}_2$  annealing. The resulting  $\text{Al}_2\text{O}_3\text{-Co}$  powder was found to have a density of about 42 % and sinter under the laser beam. The single layer test coupons appear to have better structural integrity with much reduced macrocrack formation. An SEM photograph of the powder after SLS is shown in Fig. 9.

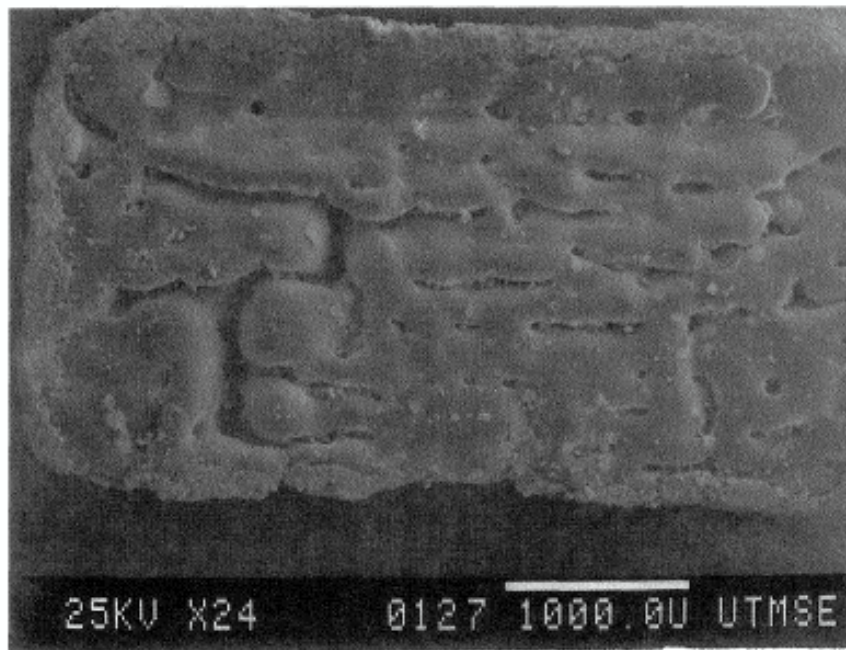


Fig. 9 SEM micrograph of 50 mole %  $\text{Al}_2\text{O}_3$  - 50 mole % Co nanocomposite after firing at 1350 °C in  $\text{N}_2$  for 8 h, 1000 °C in  $\text{H}_2$  for 8 h and subjecting to SLS

## CONCLUSIONS

Nanocomposite powders of  $\text{Al}_2\text{O}_3\text{-CoO}_x$ ,  $\text{Al}_2\text{O}_3\text{-NiO}$ ,  $\text{Al}_2\text{O}_3\text{-Co}$  and  $\text{Al}_2\text{O}_3\text{-Ni}$  have been successfully synthesized by sol-gel processing. The powders have been investigated by SLS. Low densities (about 20 %) of the initial powders not only lead to a formation of macrocracks during SLS, but also prevent use of high enough laser power that can cause sintering. Increasing the initial powder densities to about 40 % seems to avoid this difficulty significantly and give structurally sound specimens. Further increase in the densities of the initial powders promises to enhance the success of our strategy, and such experiments are currently being pursued.

## ACKNOWLEDGEMENT

Financial support by the DARPA-ONR grant No. N00014-92-J-1394 and ONR grant No. N00014-92-J-1514 is gratefully acknowledged.

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