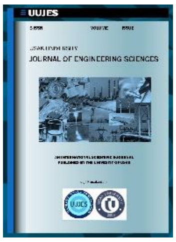

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Research article

THE USE OF ELECTROLESS COATING IN THE PRODUCTION OF HIGH CERAMIC-TO-METAL RATIO COMPOSITES USING WC POWDER

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Abstract

In this study, the production of high ceramic-to-metal ratio composite using tungsten carbide (WC) powders plated with Nickel (Ni) by electroless method was attempted by means of transient liquid phase sintering. Microstructural characterization in specimens before and after sintering process have been carried out using Scanning Electron Microscope (SEM) and DTA-TG and XRD techniques and microhardness measurements for various processing conditions. Results showed that WC powders can be successfully Ni plated by electroless plating method and optimal condition for the production of high ceramic-to-metal ratio composite is found to be 1150°C in both air and Ar protected furnace conditions.

Keywords: *Electroless nickel plating; composite materials; sintering.*

1. Introduction

Metal matrix composites are widely utilized in various industrial areas and also have potential applications in aerospace industry. The advantages of metal matrix composites over the conventional metals and their alloys are the superior mechanical, corrosion resistance, high strength-to-weight ratio and wear properties at higher operational temperatures [1-4]. Nickel and cobalt were used as binder materials for hard materials for mechanical and functional properties of ceramics are developed with metal-reinforced ceramic matrix composites [5-9]. Generally, metal-coated ceramic powders can be prepared by precipitation, sol–gel, reduction, mechanical mixing, ball milling, and

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electroless plating [10]. Electroless plating has been recognized as one of the most effective techniques [7]. Electroless plating plays an important role as a metal-coated technique on ceramic substrates [11]. Electroless nickel plating have found wide application in many fields and high hardness, high-performance products, wear resistance and corrosion resistance are produced [12]. Electroless plating on ceramic powders have been practically applied to produce long lasting wear resistant surfaces and intricate shapes from powder mixtures, allowing the use of high ceramic-to-metal ratio within the composite [13-14].

In this study, ceramic reinforced composites were produced by which ceramic powders, WC, plated with a metal, Ni, were sintered to make final product. Ni plating has been applied to WC powders by means of electroless method and results from various characterization techniques are presented.

2. Experimental Procedures

Composites of Co, Cr, Al and Ni base metals reinforced with WC find commercial applications. For this reason, Ni coating of WC powders by electroless method was attempted to produce high ceramic-to-metal ratio composites. The Ni plating method was easy to use as well as less costly. Water soluble Nickel Chloride ($NiCI_2.6H_2O$) was mixed with Hydrazine Hydrate ($N_2H_4.H_2O$) heated to a temperature at which the reaction is maintainable. Following the electroless plating process various materials characterization techniques, such as Scanning Electron Microscopy (SEM), DTA-TG and Xray Diffraction (XRD) were used to define microstructure and phases formed during the process if exist.

In this study, electroless plating of WC powders with Ni is accomplished in a bath of which its control is dependent on two main factors: bath temperature and pH. WC to Ni ratio is arranged from 7 to 3, therefore it is high in ceramics than metal components. The acidity of bath was kept at pH 9 which was of slightly acidic nature and operational temperature was kept at 95°C throughout specimen preparation. The adjustment of pH is done through ammonia addition at 95°C. Process parameters are given in Table 1.

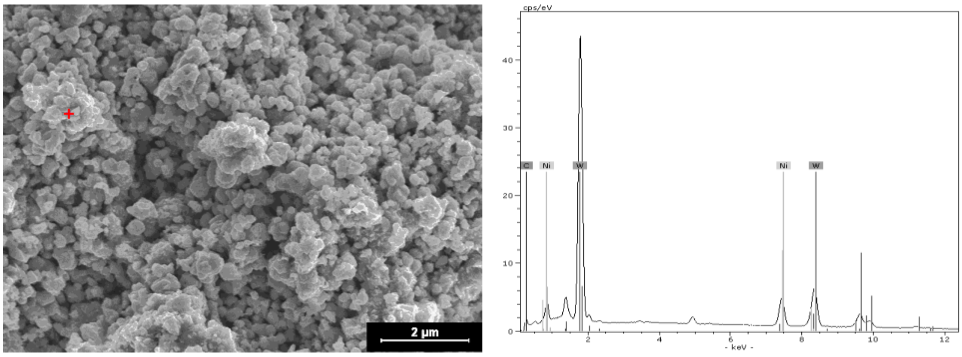
Table 1 Chemical bath components for electroless coating of WC with Ni

Components	Additions
Tungsten Carbide (WC)	14 (by weight)
$NiCI_2.6H_2O$ (Nickel chloride)	24 (by weight)
Hydrazine Hydrate ($N_2H_4.H_2O$)	30 vol.
Distilled water	70 vol.

Powders plated with Ni were compacted using a hydraulic press at a pressure of 140 Bar and sintered at temperatures of 1050°C, 1150°C and 1250°C with or without Ar gas shroud. Hardness measurements were made using Shimadzu HMV 2L micro tester. DTA data from specimens were obtained in air up to 1150°C maximum temperature with 59 grs of Ni plated WC powders using LINSEIS DTA-TGL-81 equipment. For XRD measurements Shimadzu 6000 model was used for the analysis of sintered specimens, using Cu target and at a wavelength of 1.544°A (Cu-Kα X rays).

3. Results and Discussion

SEM image of Ni plated WC particles are given in Figure 1a and Figure 1b also shows EDX analysis of Ni plated WC powders, indicating a shell of Ni existing around WC powders.



(a) (b)

Fig. 1 (a) SEM image of Ni plated WC powders (b) EDS analysis of Ni plated WC powders.

Average particle size of WC powders was measured to be 1.1 µm, however, average particle size of plated powders were 1.33 µm after electroless plating process. It can be concluded that 0.115 µm of Ni was deposited onto WC powders by electroless plating process. Such thickness of Ni may help form bonding during the sintering process. It is conclusive that plating is successful however DTA data (air, 1150°C max) of Ni plated WC powders show a weight increase at around 500°C due probably to fact that oxidation of Ni takes place. A complete reaction up to 1150°C is given in Figure 2 below.

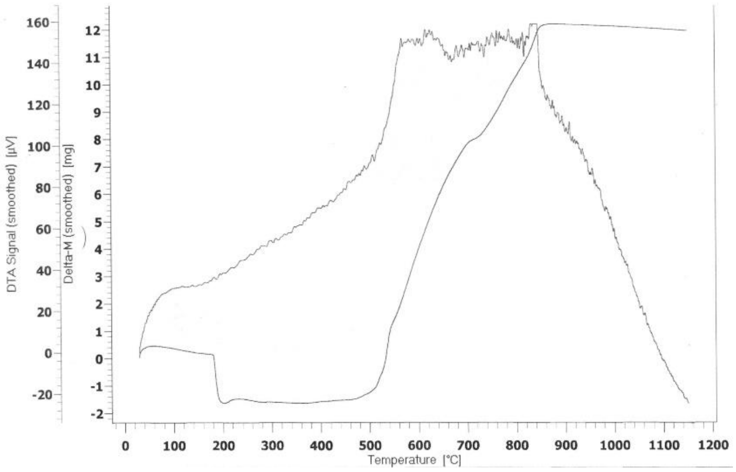
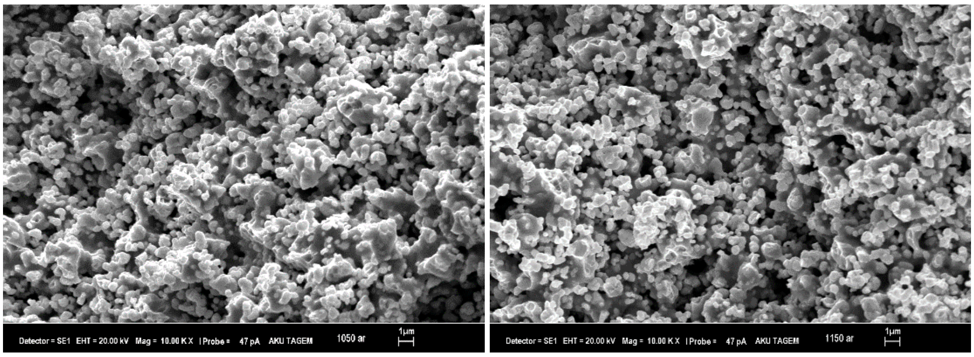


Fig. 2 DTA analysis results obtained from Ni plated WC powders (up to 1150°C in air)

According to these results an increase in weight on TG line at 500°C is due to oxidation of powders in the air, which was expected on the course of heating. It is also possible to see exothermic reactions occurring in the temperature range 540°C and 860°C and some unexpected endothermic reactions were also detected. Between these two points it is possible to say that reactions lead to the formation of an intermediate phase of WC-Ni system, WC_xNi_y, which can be proposed from W-Ni phase diagram. It is, however, possible that some oxides of Ni may also be formed.

Using the data obtained from literature [14] and DTA results above two sets of experiments were arranged and in addition three sintering experiments were carried out. The First set of experiments were carried out in air with three different temperatures of 1050°C, 1150°C and 1250°C and at a heating rate of 10°C per minute and for 1 hour holding time. The Second set of experiments were carried out under Ar gases atmosphere at temperatures of 1050°C and 1150°C (Figure 3a-Figure 3b) at a heating rate of 10°C per minute and for 1 hour holding time.



(a) (b)

Fig. 3 SEM images of the specimens sintered at (a)1050°C (b)1150 ˚C under Ar atmosphere (10.000X)

Results showed that, specimens sintered in air at temperatures of 1050°C and 1250°C did not produce good results, however, specimen treated at 1150°C was successfully sintered. Specimens treated under Ar gases atmosphere were also successfully sintered. Temperature 1250°C was not attempted because this temperature is not feasible since one of the purposes of this work was to reduce the cost of applications.

From SEM images in Figure 3a and Figure 3b, it can be seen that in specimen sintered at 1150°C under Ar gases atmosphere WC powders are in close contact with each other and formed a continuous agglomerated structure. It was envisaged that bonding between the plated particles occurred with a mechanism by which a liquid phase formed and advanced by capillary force. Particle size was found to increase from 1.33 µm to 3.97 µm because of agglomeration.

Electroless plating of WC powders were used by many scientific researchers however the bath composition for plating was different. For example, Sharma and co-workers [13] attempted to electroless Ni plating in a bath containing P which resulted in the formation of Ni_3P phase. Considering the adverse effect of P compounds, the presence of Ni_3P may be undesired. However, the use of $NiCI_2.6H_2O$ and Hydrazine Hydrate ($N_2H_4.H_2O$) prevented undesired effects of newly formed compounds during the process of sintering by effectively forming Ni layer around WC particles. Such a layer is supposedly helped the formation of liquid phase which advanced by a diffusion driven capillary forces and sintered WC particles as a result of such action. Products of reactions are thought to be Ni derivatives with a substantial amount of solute C; Gidikova and co-workers [15] proposed a W rich compound of Ni_2W_4C, which is probably the compound of interest in this study. EDX analysis indicates that the presence of such elements is confirmed.

However, in order to ensure that the compound Ni_2W_4C exists an XRD analysis was run on specimen air-sintered at 1150°C (Figure 4a) and specimen Ar-sintered at 1050°C (Figure 4b). Results indicate that the presence of Ni_2W_4C compound in both specimens was shown and other phases, such as NiO and W_2C are also present. The effect of air and Ar shroud differs from the presence of oxides of Ni and the amount of carbides of W in both specimens. Specimens sintered at 1150°C under air atmosphere produced peaks of NiO due probably to contact with O from air (Figure 4b). Carbides of W, such as WC and W_2C, is shown to exist in both specimens but specimen sintered under air contains less due probably to dissociation of WC from which CO is possibly formed when in contact with air, releasing W and hence the formation of Ni_2W_4C compound is justified. The intensity figures imply that WC powder had been coated with Ni but, when in contact with air Ni formed an oxide, NiO. For Figure 4b, however, the effects are clearly seen, such that, intensity of Ni_2W_4C and WC are higher and the formation of W_2C was made possible. From Figure 4, it can be concluded that Ar shroud has produced target compounds in this study, namely Ni_2W_4C and W_2C.

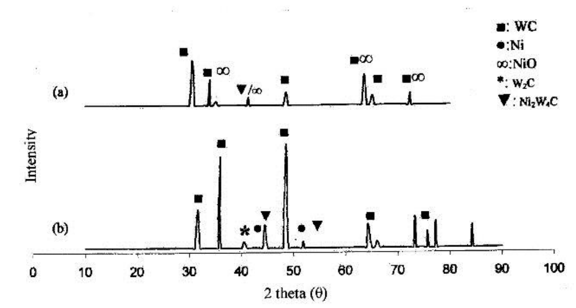
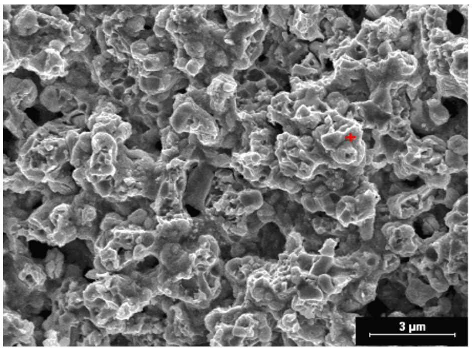


Fig. 4 XRD results of specimens sintered at (a)1050°C air atmosphere, (b)1050°C Ar atmosphere

However, the degraded appearance of sintered Ni plates WC powders sintered in air given in Figure 5 is also a subject of discussion. At such a high temperature the formation of Ni oxides is highly possible according to Ellingham diagram [16]. The activity of C is also higher and therefore the formation of CO may not be eliminated despite the higher stability of WC. Sintering in air did not result in extensive oxidation degradation, the formation of Ni oxide probably prevented further diffusion of oxygen through the oxide layer formed on the WC plating. With air sintering experiments the thickening of Ni oxides may be difficult since the dissociation of oxides of Ni is easily attainable and the formation of CO is thermo-dynamically favoured. Therefore, the O freed from the dissociation of Ni oxides may be taken by C and lead to the formation of CO and hence corroded WC and freed some Ni for sintering. It is evidential that there is NiO peaks observed in XRD analysis as a result of air sintered specimens (Figure 5).



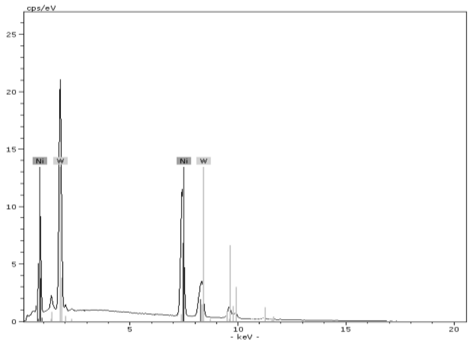


Fig.5 SEM image and EDS analysis of specimens sintered at 1150°C in air

Hardness measurement on sintered specimens were carried out following a metallurgical preparation of specimens mounted on Bakalite and Vickers scale was used for hardness measurements. The average of five measurements was taken for more accurate readings which are given in Table 2.

Table 2 Average micro hardness values of specimens sintered at various temperatures

Sintering Conditions	1050°C (Ar)	1150°C (Ar)	1150°C (Air)
Hardness (HV)	113,6	159,8	239,8

Using the recipe described in experimental procedures section and data obtained from literature and DTA experiments temperatures of 1050°C, 1150°C and 1250°C were chosen for sintering for both air and Ar atmosphere. As a general view, the formation of strong and uniform bonds between the particles plated with Ni occurred at 1150°C for both atmospheres. However, sintering at 1050°C under Ar atmosphere is also sufficient to produce high ceramic-to-metal ratio ceramics with desired intermetallic phase. An increase in hardness value when specimens treated in air is probably because of O forming hard phases of oxides with Ni, leaving the matrix exposed to WC powders as a result of thinned or diminished Ni layer. For Ar atmosphere sintered specimens, the hardness is relatively low and did not produce hard phases that may cause premature failure of composite as a result of the presence of hard phases.

4. Conclusions

Results suggest that electroless plating of WC powders are useful for plating Ni onto particles, producing high purity Ni layer. The production of high ceramic-to-metal ratio composites is optimized and therefore results below can be given:

i. WC powders are successfully Ni plated by electroless method.
ii. Optimal temperature for sintering is proposed to be 1150°C for both Ar atmosphere and air sintering. However, 1050°C sintering temperature is also sufficient to produce high ceramic-to-metal ratio ceramics under Ar atmosphere.
iii. As a result of sintering, the formation of an intermediate phase of Ni_2W_4C is proposed from DTA and EDS results and XRD results showed the presence of the compound Ni_2W_4C.
iv. A decrease in hardness with respect to sintering temperature is due probably to the effect of Ni forming agglomeration. This is also affected by the porous

structure of composite since the deformation is easily attained through weakly connected WC particles.

v. The presence of Ni coating on WC powders enhanced the bonding strength between particles by forming intermetallics and uniformly distributing Ni layer between the particles of WC.

Acknowledgement

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