Study of Electrical and Structural Properties of WC-Co Composites

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Abstract

A study was conducted on the electrical properties of WC-Co composites with increasing volume percentages of Co (6.0, 7.0, 10.0, 14.0) over temperatures ranging from 0 to 200 °C. The measurement was performed using two-probe method to examine how the volume fraction and the morphology of Co particles affect the electrical behavior of WC-Co composite. It was observed that above 10 volume percentage of Co the composite showed higher conductivity which might be due to the percolation effect. Below 10 volume %, the electrical conductivity behavior is still similar to that of pure WC. X-ray characterization was performed to provide a structural view of the WC-Co composites.

I. Introduction

Cemented tungsten carbides are commercially one of the oldest and most successful powder metallurgy products. These composites are essentially aggregates of particles of tungsten carbide bonded with cobalt metal via liquid-phase sintering. The properties of these materials are derived from those of constituents- namely, the hard and brittle carbide and the softer, more ductile binder. The wide applications of cemented carbides for cutting tools and wear parts arise because of their unique combination of mechanical, physical and chemical properties¹. The performance of cemented carbide as a cutting tools lies between that of tool steel and cermets. Compared to tool steels, cemented carbides are harder and more wear resistance, but also exhibit lower fracture resistance and thermal conductivities than tool steel.

The electrical measurement can have a variety of technological applications such as heater, ignites, heat exchangers, resistors, electrical stress relief in high voltage devices, electrodes for fuel cells and potentially also as crucibles for vacuum induction furnaces. Moreover if the electrical conductivity of these composites is high enough it is feasible to use electrical discharge method (EDM), an economical way to prepare complex shapes of very hard materials. Recently, composites with controlled electrical conductivity have been used for replacing metal parts in electrical and electronic devices, improving not only the performance of the components but also the temperature of their applications^{2,3}.

As regards composites the main interest is the improvement of both electrical and mechanical properties. In this respect the design of composites and especially metal matrix composites is usually a compromise between the desire to raise the conductivity as much as possible and retain refractoriness, hardness and stiffness that will be depleted by the embedded metal particles. Metal particles are also used in ceramic matrices to increase their toughness. However, often the amount of metal inclusion in these cermets, in order to have enough electrical conductivity for technological applications, is above 20-30 vol%. Therefore, in order to design composites for specific applications it is useful to be able to model the properties theoretically based on knowledge of the constituent phases and their relative distribution.

Usually at a certain threshold value of volume fraction of metal particles, they are sufficiently close-packed to form an unbroken conducting pathway through the composites and the conductivity of the material increases sharply. This threshold is known as the percolation limit. A way of maximizing composite conductivity while retaining the good properties typical of ceramic materials would be to control not only the amount but also the shape and size of the embedded particle in order to reach the percolation limit at relatively low volume fractions⁴. For these reasons, WC-Co composites can be ideal for applications where two distinct properties, toughness and electrical conductivity, need to be combined in the same material.

In our work, WC-Co composites with different volume percentages of Co have been prepared to observe the electrical properties using two-probe method as well as structural properties by X-ray diffraction (XRD) method. In our study, WC-Co has been chosen as a convenient model to begin a systematic investigation of electrical properties as well as structural properties.

II. Experimental Details

Cobalt is a hard transition metal. Because of its unique set of physical and electrical properties, it was chosen as the dispersoid in the WC matrix. Increasing amounts (6 to 14 vol %) of Co powder (Japan New Metals Co., Japan) were mixed with high purity tungsten carbide (WC) powder (AKP53, Sumitomo Chemicals Ltd., Japan).

The ceramic-metal powder mixtures were attrition milled in isopropyl alcohol for 5 h. After drying, samples of each composite were hot-pressed in a graphite die with its inner walls coated with BN slurry to avoid any interaction between specimens and graphite die. The hot press atmosphere was argon. For all the composites, the maximum

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hot pressing pressure was 30 Mpa. The selected sintering temperature and time were 1640 °C and 1 h, respectively. The samples were then cooled down (200 °C/h) to room temperature. The hot -pressed samples were in the form of rectangular solid bars with length, width and thickness of 100 mm, 12 mm and 3 mm, respectively. The samples were then cut into convenient sizes for the experimental purpose.

III. Results and Discussion

Structural measurement by the Powder Diffraction Technique

A Shimadzu LAB-X, SRD-6000, X-ray diffractometer was used to get x-ray data for the WC-Co samples using powder diffraction technique with a primary beam power of 40 kV and 30 mA. All X-ray data of the samples were analyzed using computer to get 'd' value of the fundamental peaks and their integral intensity. The interplanar spacing was calculated using the formula $2d \sin \theta = \lambda$, where A is the wavelength of the incident radiation.

The XRD pattern revealed that the samples are polycrystalline in nature and homogeneous as can be observed from the sharp diffraction peaks shown in Fig. 1. The major peaks correspond to phase of hexagonal structure of WC as identified in Fig. 1. From the X-ray curve it is also observed that WC and Co atoms are positioned themselves in such a way so as to make separate phases, which is one of the important characteristics of composites. The different weight percentages of cobalt in WC matrix were also determined by this measurement. The concentration of WC and Co for each sample was estimated from their strongest peak of 100% I, where I is the intensity of the peak.



Fig. 1. XRD pattern of WC-Co composite.

Both WC and Co peaks were identified precisely and their concentration estimated within the error of maximum ± 2 % using XRD method. The background of the system has been determined and subtracted from the total intensity data. The total amount of WC and Co in a sample was considered as 100 percent. Then only one peak for a single material was selected, which has the maximum peak intensity (100% of I) among all the peaks of that particular material (i.e. WC or Co). Then the total integrated intensity for a particular peak was calculated by using the formula

$$I_A = I_P \times FWHM$$

Where I_A is the integrated intensity of a particular peak, I_P is the peak intensity of that particular peak and FWHM is the full width at half maximum of the peak.

Again,

$$I_{T} = (I_{1} + I_{2} + \dots I_{n}) = \sum I_{n}$$

where I_T is the total integrated intensity of the detected materials and A = 1, 2,n. The concentration of a particular material is calculated by

$$C_A = \frac{I_A}{I_T} \times 100$$

where C_A is the concentration of a particular material in the sample in weight percent. Using the above formula the concentration of WC and Co in different sample is listed in Table 1.

 Table. 1. Concentration of WC and Co in different sample.

| Sample | Sample | Constituent | Volume % | Weight % |
|--------|--------|-------------|----------|----------|
| no. | | material | | |
| 1 | WC-Co | WC | 86 | 81.5 |
| | | Со | 14 | 18.5 |
| 2 | WC-Co | WC | 90 | 90.1 |
| | | Со | 10 | 9.9 |
| 3 | WC-Co | WC | 93 | 95.05 |
| | | Со | 7 | 4.95 |
| 4 | WC-Co | WC | 94 | 97.3 |
| | | Со | 6 | 2.7 |

The lattice parameters (a, b, c) of the sample were determined by plotting the lattice parameter values versus Nelson-Riley (N.R.) function (Fig. 2 and Fig. 3). Table 2 shows the comparison between the calculated lattice parameters and cell volume of WC with the reference value. It is observed from Table 2 that the calculated values are in good agreement with the reported values. But there is little difference between the calculated values and reference values; this is due to the defect in crystal structure when it is grown.

Comparison of Positive Solutions for two Boundary Value Problems Arising



Fig. 2. Lattice parameter value '*a*' versus N.R function of WC-Co composite.



Fig. 3. Lattice parameter value 'c' versus N.R function WC-Co composite.

 Table. 2. Table for Lattice parameter and Cell volume of WC crystal.

| Lattice parameter | | | | Cell volume | |
|-------------------------|--------|------------|------|--------------------|------------|
| Ref. value ⁵ | | Calculated | | Ref. | Calculated |
| | | value | | value ⁵ | value |
| a = b | С | a = b | С | | |
| 2.9062 | 2.8378 | 2.9047 | 2.82 | 20 | 23.86956 |
| | | | 75 | | |

Electrical Measurement by Two-Point Probe Method

For the electrical conductivity measurement of the WC-Co samples, voltage drop across the sample in note allowed currents starting from the mA range. A set of current voltage data was noted down. From the current voltage data, I-V graph is plotted from where the value of the resistivity ρ is used

$$\rho = \frac{R}{L}A = \frac{V}{IL} \times B \times t$$

where L is the length of the specimen, B is the width, and t is the thickness of the sample. Figure 4 shows the conductivity vs temperature characteristic curves for WC-Co composites for different volume percentages of Cobalt (Co). The temperature range has been selected from 0°C to 200°C. It has been observed that (i) from 0° to room temperature the conductivity of the samples rises sharply marked as Region 1, and (ii) the conductivity decreases above room temperature showing the metallic behavior marked as Region 2.



Fig. 4. The temperature dependence of conductivity of WC-Co composite for different volume percentages of Co: (a) 6 vol%, (b) 8 vol%, (c) 10 vol% and (d) 14 vol%.

Figure 5 shows the typical electrical behavior of WC-Co composites. The electrical conductivity is plotted as a function of Co concentration in a WC matrix. It has been observed that below 10 volume % the electrical conductivity did not show any significant change. Above 10 volume % of Co, the conductivity rises sharply. The critical volumetric fraction is 10 ± 2 volume %.

As described in Landauer's percolation model, composite materials built by components with different thermal expansion coefficients, the percolation phenomenon can be induced by the temperature variation^{6,7}. A volumetric fraction change caused by different expansion coefficients can lead to the percolation region, mainly if there are some spaces available among metal particles to allow their expansion. As the temperature is raised the filler fraction

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volume reaches the critical fraction and the filler particles touch themselves forming conducting paths.



Fig. 5. The electrical conductivity as a function Co concentration.

In Fig. 5, the curve shows that below 10 volume % of Co the conductivity, no appreciable change has been change has been observed. Above 10 volume % of Co, the conductivity rises sharply. The critical volume fraction after which conductivity rises sharply is known as the percolation limit. From the figure it is evident that the electrical conductivity of composites depends on the Co volume fraction. Below 10 volume % of Co, the conductivity did not show any appreciable change implies that the composite conductivity is basically dominated by the matrix phase. At a critical volume fraction, the particles or fibres sufficiently close-packed to from an unbroken conductivity of the material rises sharply⁸.

It should however be noted that although the conductivity rises when Co particles are in contact, it does not necessarily follow that a fully connected network of Co is formed. McLachlan showed that at volume fraction just below the percolation limit, conducting particles would be arranged in such a way to from a large, but finite interconnected clusters, which do not span the entire specimen⁹.

IV. Conclusions

A systematic study has been performed on the structural and electrical properties of WC composites with increasing volume percentages of Co. Structural properties were analyzed by the XRD method. The XRD patterns of all the samples show the separate phases of WC and Co atoms. Moreover major peaks correspond to phases of WC indicates that WC is the main matrix. From the electrical measurements it was found that the electrical conductivity of composites depends on the Co volume fraction. Up to a certain volume fraction the conductivity of the composite did not change much. The sharp change in the conductivity after a certain volume fraction is mainly due to percolation phenomena where the particles are sufficiently close-packed to form an unbroken conducting pathway through the composites.

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