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FINAL REPORT

AN AUTORADIOGRAPHIC STUDY OF SINTERED TUNGSTEN CARBIDE-NICKEL COMPACTS

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ABSTRACT

Preliminary studies on the use of autoradiography for observing the distribution of radioactive nickel in Ni-WC sintered carbide compacts have been completed. The particle size of the compacts used is very close to the resolution limit of this technique but some conclusions can be drawn as to the distribution of nickel in the compacts. Future work should be carried out with a larger grain size of WC and with a smaller quantity of radioactive nickel.

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INTRODUCTION

This research was initiated by the Carboloy Department of the General Electric Company and performed at the University of Michigan for the purpose of determining the capabilities of high-resolution autoradiography in detecting and locating the binder phase in cemented carbides.

The system selected for study was tungsten carbide-nickel; it was chosen because of the desirable radioactive properties of nickel-63 in high-resolution autoradiography.

EXPERIMENTAL PROCEDURES

Several preliminary studies had to be carried out prior to using the radioactive nickel isotope in order to determine the compositions and procedures that should be used. In general, the normal procedures of cemented carbide production were followed as closely as possible in order to insure that the distribution of the binder phase in the experimental compacts would be similar to its distribution in conventional compacts.

The first study was concerned with the selection of a compact composition which would result in relatively large grains of tungsten carbide in the sintered product. This was necessary since the normal grain size of sintered carbides is generally smaller than the resolution limit of the autoradiographic technique that was to be used. This phase of the work was performed by Carboloy under their Project Number X-3567.

The results showed that a binder content of 4 to 6 percent nickel with a mixed carbide powder of 30 percent 03 microns maximum and 70 percent 40 microns maximum would be the most suitable.

Since the radioactive nickel would have to be processed to nickel powder at the University, a study was initiated to duplicate the powder produced by Carboloy using nonactive nickel. Reagent-grade metallic nickel was dissolved in concentrated nitric acid and the excess was evaporated to obtain $Ni(NO_3)_2$. The nitrate was then slowly heated to 800°C to convert the nitrate to the oxide. On cooling the NiO was crushed and reduced to metallic nickel powder in a purified hydrogen atmosphere at 500°C. Examination of this product by Carboloy showed it to be similar to their normal product.

Because of the high unit cost of the nickel isotope and the hazards involved in handling large quantities, a series of tests were made to determine if a small amount of nickel and tungsten carbide could be ball milled and compacted to obtain a final microstructure that is similar to the conventional compacts made on milling samples of 50 grams total weight. For this purpose several batches of 25-gram and 50-gram samples of the compositions given in Table I were milled.

TABLE I

CHARGE AND MILLING DATA FOR TUNGSTEN CARBIDE-NICKEL COMPACTS

Batch No.	Total Weight, gm	Nickel Weight, gm	WC 03 Weight, gm	WC 40 Weight, gm	Volume Acetone, cc	Ball Weight, gm	rpm	Time, hr
TC-3	50	2	14.4	33.6	60	300	220	12
TC-3	25	1	7.2	16.8	40	200	220	12
TC-6	50	3	14.1	32.9	60	300	220	12
TC-6	25	1.5	7.05	16.45	40	200	220	12

The milling was done in a steel tube 5 inches in length and 1-3/4 inches in diameter with carbide balls of mixed sizes supplied by Carboloy.

After milling, the acetone-powder mixture was screened to retain the balls and these were washed in acetone to remove adhering powder. The acetone was allowed to evaporate from the powder and the process was

completed by drying at 200 to 300°C in a hydrogen atmosphere. The milled powder was then screened through a 100-mesh screen and pressed into compacts 5/8 inch in diameter and 1/8 inch thick with a pressure of 10 tons per square inch. Each compact weighed approximately 8 grams. They were vacuum sintered at 1600°F and 1700°C for 1/2 hour. Examination of the resulting microstructures showed no essential differences between the 25-gram and the 50-gram batches.

Additional studies at Carboloy on determining the optimum sintering conditions resulted in the information that large grains of tungsten carbide could be produced with a minimum of porosity if a vacuum sinter at 1350°C was followed by a hydrogen sinter up to and at 1700°C for 1 hour.

Radioactive Compacts

As a result of the above studies it was agreed that the composition of batch No. TC-3 (4% nickel binder) would be used for the autoradiographic studies. The radioactive nickel used for preparing these samples was obtained from the Atomic Energy Commission and has the following specifications:

Shipment Date:	1-22-54
Specific Activity:	13.45 mcs/gram
Chemical Form:	$NiCl_2$ in HCl solution
Solution Volume:	2.3 ml

This nickel solution was converted to nickel powder by the following chemical procedures:

(a) Several drops of concentrated H_2SO_4 were added to the as-received solution and the solution carefully evaporated to dryness to convert the $NiCl_2$ to $NiSO_4$.

(b) Distilled water was added to the residue to dissolve the $NiSO_4$ and to increase the volume to 250 ml.

(c) Concentrated NH_4OH was added to complex the nickel. A precipitate will form at first but this dissolves when an excess of NH_4OH is added.

(d) The nickel is electroplated onto a clean platinum-gauze cathode at a potential of 2.2 volts until the blue color of the solution disappears indicating the complete deposition of nickel. The weight of nickel is determined gravimetrically by weighing the gauze before and after deposition.

(e) The electroplated nickel is dissolved from the platinum in concentrated HNO_3 and a weighed amount of stable nickel is added to dilute the radioactive nickel solution to the desired dilution factor.

(f) The solution is transferred to an evaporating dish and evaporated to dryness.

(g) The $Ni(NO_3)_2$ is converted to NiO by heating at 800°C.

(h) The NiO is crushed and reduced to metallic nickel powder by heating in a purified hydrogen atmosphere at 500°C.

Once the radioactive powder has been obtained, the procedures used to make the pressed and sintered compacts were identical to those described earlier with the exception that all the operations of charging into the ball mill, removing, screening, filling dies, etc., were done in a "dry box" designed for working with radioactive materials. Whenever possible the powder was kept wet with acetone to minimize dusting.

In the work being reported some 0.3346 grams of radioactive nickel were blended with stable nickel to give a total of 1 gram of nickel. The specific activity of the nickel after dilution was 4.5 mcs per gram.

In preparing the compacts for metallography and autoradiography the sintered compacts were fractured and the surfaces were rough-ground by hand on silicon carbide papers and with diamond powders for health-physics reasons. The final polishing and etching were performed by Carboloy using their metallographic technique.

Autoradiographs of etched and unetched surfaces were made by the stripping-film technique of autoradiography. An exposure time of two days was used for all autoradiographs.

Autoradiographic Technique

Since one of the primary purposes of this work was to determine the suitability of autoradiography for studies on sintered carbides and since the results are encouraging enough to warrant further investigation, the details of the autoradiographic technique will be given to assist the personnel of Carboloy if they wish to continue this type of work.

Kodak Experimental Permeable Base Autoradiographic Stripping Film was used exclusively in the work reported. It is a fairly stable emulsion if kept under refrigeration. The same roll has been used in work at the University for over a period of 5 to 6 months.

The surface preparation used is exactly the same as would be used for an ordinary metallurgical examination. In polishing the specimen care must be taken to avoid smearing any radioactive material across the surface. If an etchant is used careful washing is necessary to remove any etchant entrapped in cracks, structural porosities, etc. Autoradiographs can be made on either etched or unetched surfaces.

Since the emulsion is processed intact with the specimen in stripping-film autoradiography, it is necessary to protect the specimen surface from corrosion by the developing and fixing solutions. Several kinds of coating have been tried but the most satisfactory results have been obtained with a 2% solution of vinylite (Bakelite designation VYNS) in methyl-ethyl ketone. This solution tends to dissolve some of the bakelite mounting if the mount-curing temperature is too low; curing the mounts at 135°C eliminated this problem. The mounted and polished specimen is immersed in the plastic solution for about 15 seconds. The specimen is then removed from the plastic solution and held vertically so that the excess solution drains down across the surface of the specimen. After air drying for 2 minutes, the specimen is placed face-up under a heat lamp to harden the plastic coating. With the lamp placed 18 inches from the specimen a heating time of from 1/2 to 1 hour is sufficient. On cooling, the specimen is ready for the application of the stripping film.

There are several possible ways that the stripping film may be applied but the procedure described below has been found to be the most satisfactory. Since the whole operation must be done in a darkroom with a red safelight, only practice can develop proficiency. The following is a general step-by-step outline of the operation.

1. Place specimen mount face-up and put a pool of water on the surface of the specimen. The water should have about 1 percent of sodium lauryl sulfate (Dupanol "C") added to act as a wetting agent.

2. Cut a piece of stripping film that is one-half the final size desired, since the emulsion swells during application.

3. With tweezers strip the emulsion away from the backing material and float it on the pool of water for a period of about 1 minute.

4. Remove excess water by blotting it with filter paper. The emulsion can be positioned over the sample by the proper choice of the direction of removing the water.

5. Water trapped under the emulsion can be removed by tilting the mount so that the water collects to one side where it can be removed.

Figure 1 illustrates some of these steps. By this procedure the emulsion is slowly settled onto the specimen surface and good contact is obtained. The specimen is then stored in a light-tight box for the desired exposure time. This time is best determined by making a series of autoradiographs similar to the techniques used in light photomicrography.

After exposure the emulsion is processed without removal from the specimen by immersing the whole specimen mount in the developer, fixer, and wash water. The solutions and times used for the various processing steps are as follows:

Developer: Kodak D-19 diluted 1 part stock, 2 parts distilled water; time, 90 seconds

Stop Bath: Distilled water; time, 3 to 4 seconds

Fixer: Kodak F-5; time, 2 minutes

Wash: Distilled water; time, 10 minutes.

After removal from the wash water and air drying, the autoradiograph is ready for examination.

A great deal of care and caution should be exercised in interpreting and evaluating the autoradiographs, since many factors introduced in processing can produce results which can mistakenly be attributed to radioactivity. For reference purposes it is essential that a control sample of a nonradioactive material always be autoradiographed with the active materials to distinguish background fogging and extraneous radiation effects.

DISCUSSION AND CONCLUSIONS

Stripping-film autoradiography has a potential for yielding additional information on the structure and distribution of the various binder elements in sintered carbides. Several tentative conclusions can be made on the basis of the preliminary study that has been completed.

1. Radioactive nickel is present in some of the carbide boundaries and generally tends to be associated more with the smaller carbide particles than with the massive carbide aggregates.

2. The areas which we presumed to be the binder or nickel-rich areas do not show any autoradiographic response, indicating the absence of nickel in this phase.

3. Areas of porosity show reduced autoradiographic response and the porosity does not interfere with the stripping-film techniques.

The results are still somewhat inconclusive in that the particle size of the carbides is smaller than the usual limits of resolution of the autoradiographic technique that has been used. Another difficulty stems from the fact that too much radioactive nickel was used in the compact. It is believed that an activity one-tenth of that used would have been more satisfactory.

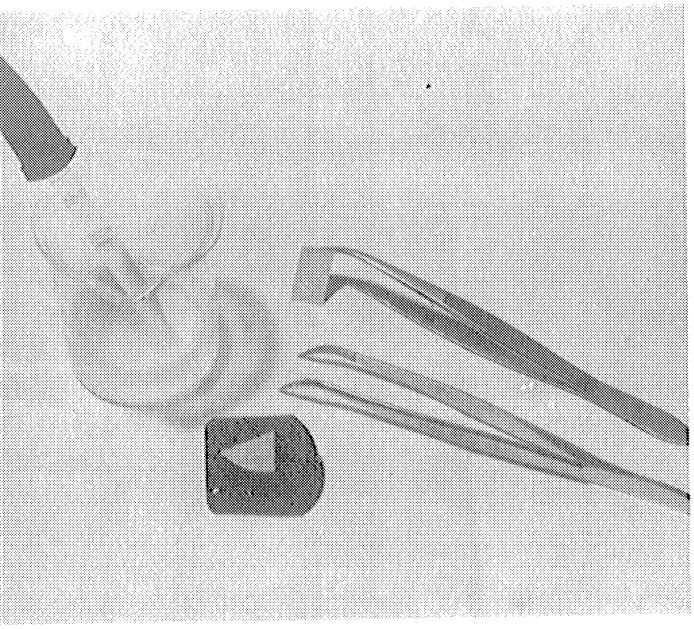
The autoradiographs and photomicrographs supporting the above conclusions are included in this report. Figures 2 and 3 are an autoradiograph and photomicrograph of identical areas on a transverse-etched section of the radioactive compact. It will be noted that what has been termed the binder phase shows no activity. The radioactivity appears to be clustered more at the interstices of the smaller carbide particles than in the boundaries of the larger carbide grains. Figures 4 and 5 are also identical areas and show the same characteristics as Figs. 2 and 3.

Figures 6 and 7 are identical areas and show the low activity over the porous regions of the compact and the fact that the areas of maximum activity correspond to those of minimum WC grain size.

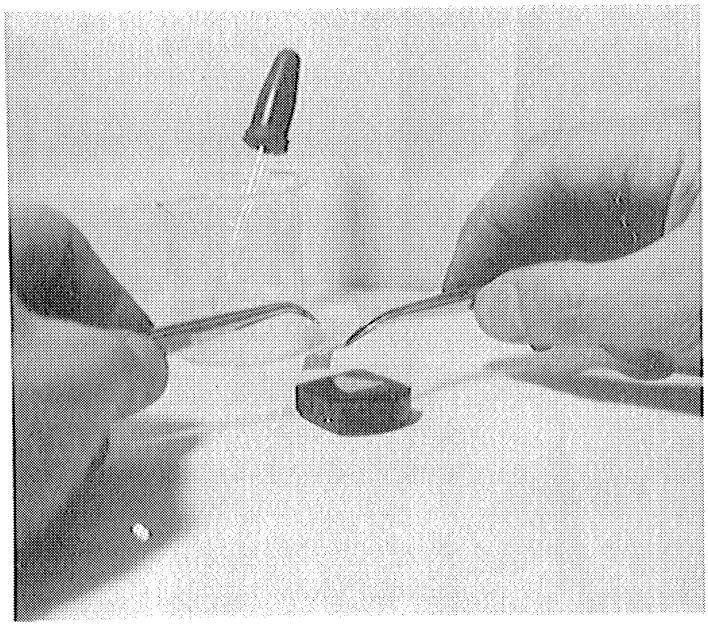
Figures 8 and 9 are unetched autoradiographs and show the distribution of the radionickel in the compacts. Figure 8 is a section

of area which showed low activity although in general the compact on the whole was quite uniform. Both Figs. 8 and 9 have been deliberately printed very dark to show the presence of the binder phase and its lack of activity.

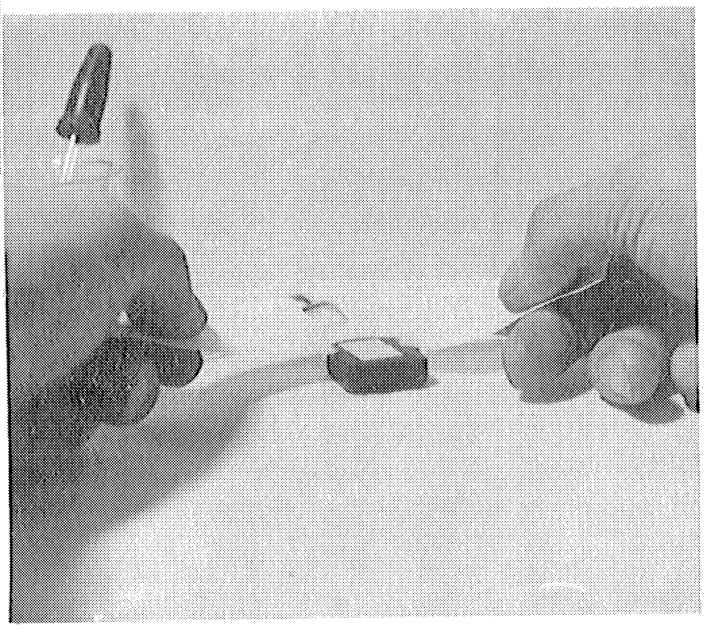
Figures 10 and 11 are autoradiographs of etched and unetched structures which were obtained by repolishing the original sections and making new autoradiographs. The film used in making these autoradiographs was from a new shipment and was a little thicker than the film previously used on the earlier autoradiographs; this resulted in lowered resolution. The results are essentially the same as those obtained from the first autoradiographs.



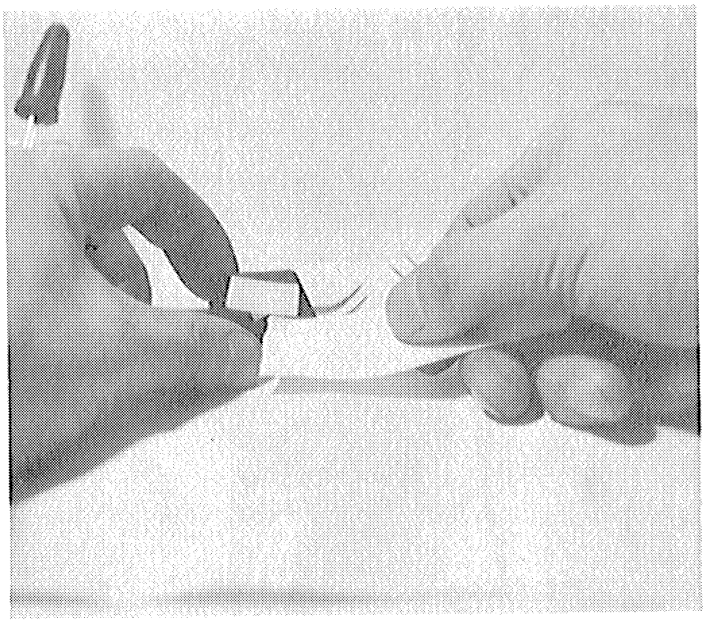
Mounted specimen ready for application of stripping film. Beaker contains water with wetting-agent addition. The film cut to proper size is shown resting against tweezer.



Stripping the film from the backing material with tweezers. As the film is stripped, it is laid on pool of water on the specimen surface.



Removing the water from under the stripping film with pieces of filter paper.



Removing last drops of water by tilting the specimen mount.

Fig. 1

Techniques of Stripping-Film Autoradiography

Note: For Figures 2 to 11, refer to file copy.