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BDX-613-1744 (Rev.)

DEVELOPMENT OF A METALLOGRAPHIC
METHOD FOR TUNGSTEN-RHENIUM

Final Report

A. H. Rahe, Project Leader

Project Team:
G. E. Crabtree
E. H. Stahl

Published March 1978

Prepared for the United States Department of Energy
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Prepared by A. H. Rahe, D/812

A metallographic method was developed for chemical vapor deposited tungsten-rhenium alloys consisting of a two-phase structure of β solid solution and a finely dispersed A-15 or federite phase. This method provides fast and reliable information on the structure and composition of the CVD deposit.

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SUMMARY

Work has been conducted to establish a simple and reliable metallographic procedure to prepare chemical vapor deposited tungsten-rhenium alloys for optical metallography and electron microprobe analysis. Quality metallography and reliable microprobe analyses of the as-plated deposit are required to select optimum plating conditions to deposit tungsten-25 w/o rhenium alloy with a finely dispersed federite phase.

The procedure established consists of mounting and rough grinding tungsten-rhenium specimens, followed by vibratory polishing first with diamond abrasive on nylon and then with alumina abrasive on microcloth. The polished specimens are chemically etched with 30-percent hydrogen peroxide to reveal the microstructure. Flat surfaces and excellent structural detail of the federite phase are obtained with this metallographic method. In addition, this method is applicable to preparing small 0.38-mm diameter core samples obtained by core drilling. A TZM holder was designed to hold the cores in their mounts through the grinding, vibratory polishing, and metallurgical analyzing processes. Microprobe analysis of the mounted sample is made prior to chemical etching.

DISCUSSION

SCOPE AND PURPOSE

The purpose of this project was to establish a fast and reliable procedure for obtaining electron microprobe and optical metallography data from chemical vapor deposited (CVD) tungsten-rhenium alloy deposits. This data is required to determine plating parameters for producing tungsten-25 w/o rhenium deposits with the desired microstructure. This work was done during the period January to July, 1976.

PRIOR WORK

Initial CVD tungsten-rhenium development activity has concentrated on selecting operating conditions for depositing a 25 w/o rhenium alloy containing a finely dispersed federite phase (metastable A-15 phase) in the tungsten-rhenium solid solution. The tungsten-rhenium deposits have been sectioned, metallographically prepared, and then analyzed with electron microprobe and optical metallography to determine the alloy composition and microstructure. A procedure was used which had previously proved to be a satisfactory method for tungsten.¹ It consisted of mounting and grinding a sectioned deposit with 600 grit silicon carbide, followed by electropolishing in a 2-percent sodium hydroxide solution and etching with a Murakami potassium ferric cyanide reagent. However, this method proved to be unsatisfactory for CVD tungsten-rhenium deposits. The polished surfaces were not flat and the Murakami etchant preferentially etched the federite phase resulting in an overetched appearance.

At Lawrence Livermore Laboratories, CVD tungsten-rhenium specimens are prepared by following the 600 grit grinding step mentioned above with vibratory polishing of the specimens with 1- μ m diamond for 24 hours and then with 0.05- μ m alumina for an additional hour. The etchant used at LLL is a mixture of 2 parts saturated copper sulfate and 1 part concentrated ammonium hydroxide.

ACTIVITY

Polishing Development

Both electropolishing and vibratory polishing were investigated for polishing CVD tungsten-rhenium metallographic specimens. Specimens were mounted in clear epoxy. In each case, polishing followed grinding of the specimens with 320 and then 600 grit

silicon carbide paper. Excellent polished surfaces could be obtained with either method; however, vibratory polishing was simpler and less operator dependent than electropolishing. In addition, electropolishing tended to round the edges of the mounted specimens. This edge rounding was primarily due to the mounting media having a faster wear rate than the tungsten-rhenium, causing the specimen to extend slightly above the mount surface after rough grinding. When polished, the sharp edges of the specimen had a higher current density than the specimen surface, resulting in higher metal removal rates. A harder mounting material or the use of an intermediate diamond polishing step to shorten the electropolishing time might have eliminated or reduced the edge rounding, but because of the vibratory polishing success these approaches were not investigated.

The electropolishing study was made with an aqueous electrolyte composed of 5 percent sulfuric acid (H_2SO_4) and 1.25 percent hydrofluoric acid (HF) in methanol.² None of the conventional alkaline electrolytes for tungsten and its alloys¹ were evaluated since the previous electropolishing of CVD tungsten-rhenium in 2-percent sodium hydroxide had not been satisfactory. Polishing on each specimen was restricted to a 24-mm² area by covering the previously ground surface with a strip of chemical resistant tape which had a 5.5-mm-diameter hole punched in it. The mounted specimen was placed with the exposed area up in a 250-ml beaker of the H_2SO_4 - HF -methanol mixture at room temperature and agitated with a magnetic stirrer. A stainless steel bracket used to hold the mount served as the cathode while the anode connection with the specimen was made by touching the exposed specimen area with a probe.

Polishing was achieved with a dc voltage around 20 volts for 60 to 90 minutes. The appearance of the surfaces was dependent upon operator control as long polishing times resulted in uneven polishing and a low voltage resulted in overetching.

The vibratory polishing method consisted of polishing the previously ground specimen in a vibratory polishing machine for 16 to 24 hours on nylon cloth using 1- μm diamond abrasive and John Crane lapping oil (Crane Packing Company, Morton Grove, Illinois). This step was followed with a vibratory polish for one hour using microcloth (A. B. Buehler Limited, Evanston, Illinois) and 0.05 μm Al_2O_3 (Linde B) (Union Carbide, East Chicago, Indiana) abrasive with distilled water. During both steps, a 350-g weight was placed on the specimen to help its motion on the polishing cloth and provide good polishing action. The polished specimens showed excellent edge retention and structure relief between the federite and solid solution phases (Figure 1). Microstructural details can then be revealed by lightly etching the polished surface.

Figure 1. Photomicrograph of a Vibratory Polished Specimen of a CVD Tungsten-25 w/o Rhenium Showing Edge Retention on Vibratory Polished Surface (Polishing conditions were 1 μm diamond on nylon for 16 hours, followed with 0.05 μm alumina on microcloth for 30 minutes.) (125X)

Several variations to the vibratory polishing process were evaluated. A low viscosity lapping lubricant was tried in place of the John Crane oil. This lubricant resulted in the cloth becoming gummy, causing poor polishing action. Dur cloth (Struers Scientific Instruments; Olsen Scientific Instruments, Long Island, New York), a synthetic material also recommended for diamond polishing, was tried instead of nylon. However, no significant difference in polishing between the two types of cloth was observed. Both provided about the same removal rate of 0.25 μm per hour, which was determined by measuring the reduction in the dimensions of hardness impressions.³ The only problem which was encountered with the vibratory polishing method was a tendency of a mount containing a thin tungsten-rhenium specimen to polish along only one edge of the cross-section. This was primarily due to relief polishing of the softer mounting material around the specimen, causing the mount to pivot on one edge. The problem was eliminated by mounting a 15-mm-diameter circle of 0.25-mm tungsten wire around the specimen. During polishing, the wire ring prevents the mount from rocking, keeping the surface flat across the specimen.

In general, the only operator requirements with vibratory polishing are keeping the polishing cloths clean, lubricated, and charged with abrasives. The nylon cloth should be charged with diamond every 6 to 8 hours to insure continuous polishing. The diamond polishing may also be run overnight provided the cloth is charged prior to leaving the setup unattended. When used daily, the nylon cloth should be replaced about every 2 weeks. The polishing times are not critical, but the alumina polish should not last more than 2 hours. Polishing too long in this last step causes the federite phase to be pulled out of the polished surface.

Etching CVD Tungsten-Rhenium

Various chemical etchants and electrolytic etching with a H_2SO_4 -HF-methanol mixture were evaluated for revealing the microstructure in the CVD tungsten-rhenium polished specimens. Of particular interest was the federite phase discussed previously. The chemical etchants included the Murakami potassium ferric cyanide ($\text{K}_3\text{Fe}[\text{CN}]_6$) reagent,¹ a 2-part saturated copper sulfate (CuSO_4) and 1-part concentrated ammonium hydroxide (NH_4OH) mixture,⁴ and a 30-percent hydrogen peroxide (H_2O_2) solution.⁵ Both the Murakami and the CuSO_4 - NH_4OH mixture appeared to preferentially etch the federite phase and often resulted in overetched microstructures. Etching with H_2O_2 , however, was simpler to control and was effective in bringing out the federite phase. This etching method consisted of submerging the mounted specimen in a beaker of the H_2O_2 solution for 15 to 20 seconds. Figure 2 shows the federite structure in a W-25 w/o Re deposit etched for 20 seconds with 30 percent hydrogen peroxide.

The composition of the electrolyte used for electrolytic etching was the same as that used in the electropolishing study. The operating procedures and the electrolytic cell were also the same. Etching at a voltage of less than 1 volt for 5 to 10 seconds brought out the microstructure in the CVD tungsten-rhenium alloy (Figure 3). A major disadvantage of this electroetching method, however, is that an electrical contact must be made with the specimen. On the small core specimens removed from W-Re device hardware, an electrical connection is difficult to achieve and chemical etching is much easier.

Interference Contrast Microscopy

Differential-interference-contrast (DIC) microscopy was evaluated as a technique for enhancing the details of the etched microstructure. This capability is available on both Bausch & Lomb Research II and Zeiss Ultraphot metallographs which are used at Bendix for optical metallography. No significant improvement was obtained with this technique.

Figure 2. Federite Structure Revealed in CVD Tungsten-25 w/o Rhenium Alloy by Etching With 30 Percent Hydrogen Peroxide (Etching time was 20 Minutes.) (1000X)

Figure 3. Federite Structure Revealed in CVD Tungsten-25 w/o Rhenium Alloy by Electroetching in H_2SO_4 -HF-Methanol Reagent (Electrolytic etching conditions were 1 volt potential for 10 seconds.) (1000X)

Core Metallography

A process was developed for mounting and polishing 0.43-mm-diameter by 0.64-mm-long core samples of CVD tungsten-rhenium. These core samples are removed from deposits during the processing of device hardware and can be used for microprobe and microstructural analysis. Mounting of a core is achieved by supporting and orienting it in a mount with a TZM holder. The holder consists of a 6.2-mm-long by 6.2-mm-diameter TZM rod with a 3.8-mm flat machined along its length. A 0.5-mm-diameter by 1.1-mm-long hole is drilled into one end of the holder parallel to its axis and 0.5 mm from the center line of the flat. The core is then potted in the drilled hole with the core axis (plating direction) parallel with the axis of the hole. Trapped air bubbles are removed from the epoxy by vacuum evacuation. The holder is then mounted in a 25-mm-diameter clear epoxy mount and so oriented that the machined flat on the holder is contained in one of the mount faces. This surface is then mechanically ground with 600 grit silicon carbide until a longitudinal section has been ground several micrometers deep into the core.

By grinding parallel to the flat on the holder, the core section remains parallel to the plating direction. The grinding operation is followed by vibratory polishing with 1- μ m diamond and then 0.05- μ m alumina as previously described.

The TZM holder provides a larger metal surface area to be polished than is available with the core alone. This reduces the chance of accidentally grinding completely through the core or grinding away too much material and allowing the core to fall out of the mount. The surface and edges of the core section are also maintained flat during polishing due to the holder surface around the core. Figure 4 shows a photograph of a TZM holder containing an etched tungsten-rhenium core.

A 10- to 20-nm carbon layer is deposited on each polished mount to provide a conductive surface during electron microprobe analysis. Without the layer, an electrical charge builds up on the nonconductive epoxy, causing the microprobe beam to drift near the core edges and give incorrect readings. Effects of the carbon deposit on the results were evaluated with a tungsten-25 w/o rhenium wire specimen mounted in epoxy. No beam drifting near the edges or any negative effects due to the carbon layer were indicated. Following the microprobe analysis, each core mount is repolished to remove the carbon layer. Diamond pyramid hardness measurements are taken across the core section and it is then etched for optical metallography.

Structure and Composition Analysis

In order to optimize CVD plating processes, almost every deposit must be analyzed for alloy composition and structure. It is

Figure 4. TZM Holder Containing a Tungsten-Rhenium Core (125X)

important that the samples be prepared by a reliable and repeatable method to insure reliable results. It is also important that quick turnaround on the analyses is achieved because many times the next plating run cannot begin until results from the previous run have been analyzed. The metallographic procedure developed on this project does both. It permits reliable results to be obtained within two days after a plating run. Figure 5 is an example of the type of data obtained using this procedure. This figure shows the microstructure of a CVD deposit superimposed on a microprobe trace of the rhenium composition across the deposit.

ACCOMPLISHMENTS

A simple and reliable metallographic procedure to prepare CVD tungsten-rhenium alloy specimens for optical metallography and

Figure 5. Electron Microprobe Analysis of Rhenium Content and Photomicrograph of As-Deposited Tungsten-Rhenium Microstructure (Deposit specimen was vibratory polished and then etched with Murakami ferric cyanide reagent.¹)

electron microprobe analysis has been established. This procedure is also applicable for preparing 0.38 mm diameter core samples using a specially developed method for holding the core in the mount. This procedure provides us with a capability to sample and metallographically analyze CVD W-Re deposits within two days from the time the part was plated.

FUTURE WORK

No additional work is planned.

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SPECIAL PROJECTS: Analysis of CVD Deposits

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