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Copper Oxide Precipitates in NBS Standard Reference Material 482

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Copper oxide has been detected in the copper containing alloys of NBS Standard Reference Material (SRM) 482. This occurrence is significant because it represents heterogeneity within a standard reference material that was certified to be homogeneous on a micrometer scale. Oxide occurs as elliptically to spherically shaped precipitates whose size differs with alloy composition. The largest precipitates occur in the Au20-Cu80 alloy and range in size from submicrometer up to 2 µm in diameter. Precipitates are observed using light microscopy, electron microscopy, and secondary ion mass spectrometry (SIMS). SIMS has demonstrated that the precipitates are present within all the SRM 482 wires that contain copper. Only the pure gold wire is precipitate free. Initial results from the analysis of the Au20-Cu80 alloy indicate that the percentage of precipitates is less than 1 % by area. Electron probe microanalysis (EPMA) of large (2 µm) precipitates in this same alloy indicates that precipitates are detectable by EPMA and that their composition differs significantly from the certified alloy composition. The small size and low percentage of these oxide precipitates minimizes the impact that they have upon the intended use of this standard for electron probe microanalysis. Heterogeneity caused by these oxide precipitates may however preclude the use of this standard for automated EPMA analyses and other microanalysis techniques.

Key words: copper-gold alloy; electron probe microanalysis; metallography; NBS Standard Reference Material 482; oxide inclusions; sample preparation; secondary ion mass spectrometry.

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1. Introduction

Standard Reference Material (SRM) 482 was issued in 1969 by the National Bureau of Standards (NBS)[1]. It has been continuously available to the public for 33 years. The standard consists of a set of six wires (Fig. 1). Each wire is of a different composition within the copper-gold binary alloy system. Two uncoated wires represent the pure end member compositions of pure copper (Cu) and pure gold (Au). The remaining four wires are alloys with nominal compositions varying in steps of 0.2 mass fraction. For identification purposes, each alloy wire was coated with a different colored paint. Their composition and color is as follows: Au20-Cu80 (red), Au40-Cu60 (blue), Au60-Cu40 (yellow), and Au80-Cu20 (gray). Each wire is approximately 5 cm long and 0.5 mm in diameter. SRM 482 was issued specifically as a standard for microanalysis. Therefore, each wire was certified for both chemical composition and homogeneity on a micrometer scale (Appendix A).

At the time that SRM 482 was issued, Heinrich [1] reported that there was concern about the usefulness of

[1] NBS was renamed The National Institute of Standards and Technology (NIST) in 1987.

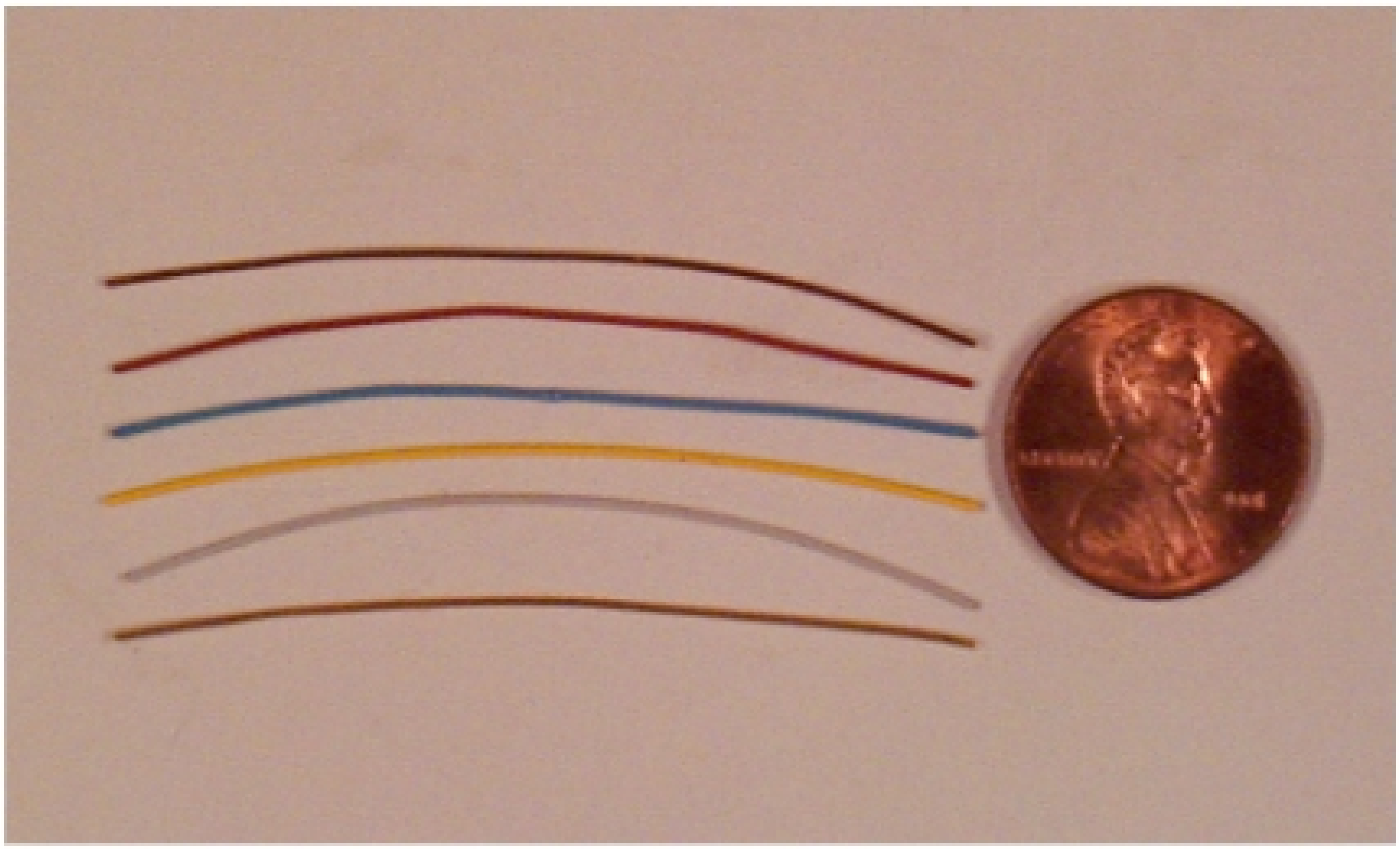


Fig. 1. SRM 482. Copper-Gold binary alloys for microanalysis. The SRM is a set of six wires. Wires are approximately 5 cm long and 0.5 mm in diameter. Each wire has a different composition within the copper-gold binary system.

the electron probe microanalyzer (EPMA) as a quantitative tool for chemical analysis. Often, analyses performed on the same material by different experienced investigators varied in excess of 10 % relative. Factors contributing to these high relative errors included systematic errors in addition to errors resulting from the application of different matrix correction procedures. Additionally, Heinrich determined that a major contributing factor to these errors was the lack of standard materials of accurately known chemical composition and microscopic homogeneity [2]. SRM 482 was then issued in response to this need for chemically characterized homogeneous standards.

Since the time it was issued, SRM 482 has been well accepted and widely used throughout the microanalysis community. Uses include the evaluation and modification of matrix correction procedures [3-7], evaluation of EPMA instrument performance [8], and investigation of systematic errors associated with electron probe microanalysis [9]. To this day, SRM 482 remains one of a very limited number of standard reference materials available from NIST that is certified to be homogeneous on a microscopic scale [10].

Recently, homogeneity of SRM 482 has been questioned. Carlton reported the occurrence of spots on metallographically prepared surfaces of the Au20-Cu80 and the Au60-Cu40 wires [11]. The presence of these spots was then verified by independent preparations performed at NIST [12].

The occurrence of these spots raises the following questions:

(1) Do the spots represent heterogeneity within the wires or are they artifacts that were created during metallographic sample preparation?

(2) What is the chemical composition of these spots?

(3) Does the occurrence of these spots affect the use of SRM 482 as a standard for electron probe microanalysis?

(4) If these spots represent heterogeneity within the wires, then why were they not detected prior to certification and why have they not been reported in 33 years since SRM 482 was issued?

The purpose of this manuscript is to report results from work that is in progress to answer these questions and investigate the possibility of heterogeneity within SRM 482. Our investigation centers on the Au20-Cu80 wire because the spots are largest and appear most abundant in this composition. Therefore, if the spots do significantly affect the microanalysis of SRM 482, we would expect this effect to be most noticeable in the Au20-Cu80 wire.

2. Samples, Preparation, and Initial Observations

When the wires of SRM 482 were manufactured, they were drawn as one continuous wire [1]. Wire length was approximately 150 m. Extensive homogeneity testing was performed prior to the issuance of SRM 482 as a standard for microanalysis [1]. This original homogeneity testing is summarized in Appendix B and Fig. 12. Historically, there has been only one issue of SRM 482. Therefore, wire sets (SRM 482) obtained today should be equivalent to those purchased 30 years ago.

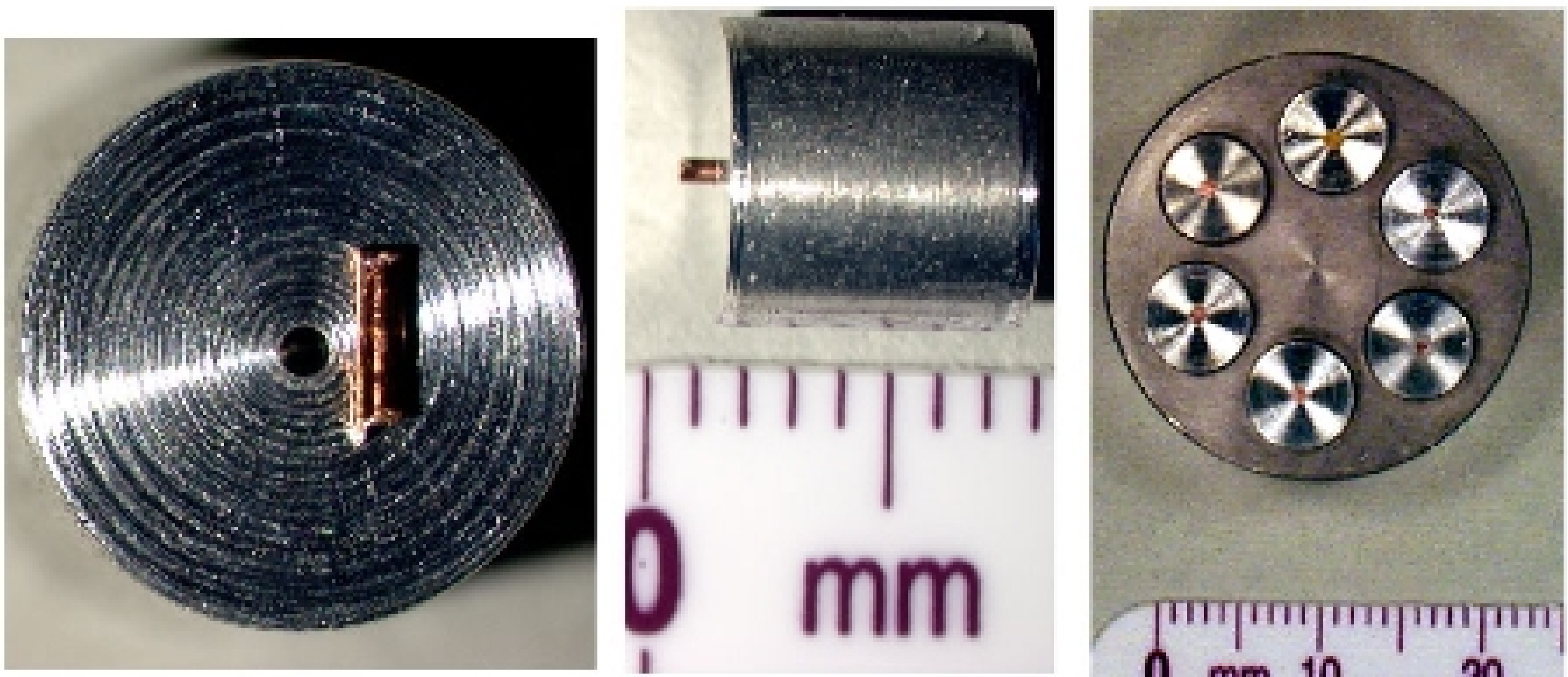
2.1 Samples

At NIST, three different sets of SRM 482 were used to investigate the reported occurrence of spots on metallographically prepared surfaces of these wires. Two sets were new boxes of SRM 482 obtained from the office of The Standard Reference Materials Program (SRMP). The third set was donated by Carlton and consisted of pieces of wire from the set that was originally reported to contain these spots [11]. The wire sets obtained from SRMP represent random samples of SRM 482 that are currently available for sale to the general public. For the remainder of this manuscript, wire sets purchased from SRMP will be referred to as set A and set B. Carlton's wires will be referred to as set C.

2.2 Sample Preparation

At NIST, initial preparations consisted of one metallographically polished mount from each set (A, B, and C). The wires were mounted in aluminum so that the samples would be completely conductive in the electron beam without the need to add a conductive surface coating such as carbon. Each wire was mounted into a 6.3 mm (1/4 in) diameter aluminum rod that had been previously cut into pieces referred to as "bullets." Bullets are approximately 6 mm to 7 mm long. In order to mount the wires into the bullets, a single hole was drilled into one end of each bullet (Fig. 2). A #76 drill bit produced a hole just slightly larger than the diameter of the wire itself. Holes were drilled to a depth of 1.5 mm and wires were cut into pieces approximately 2 mm long. The wire pieces were then inserted into the holes and press fit down into the aluminum bullets using a mounting press. All six wires from each set were prepared in this manner. These six bullets were then inserted into a single bullet holder 25.4 mm (1 in) in diameter (Fig. 2). At this point the wires were ready for grinding and polishing.

Samples were ground and polished using a Buehler Ecomet 3 Variable Speed Grinder/Polisher interfaced with an Automet 2 Power Head[2]. As a guide, we followed the grinding and polishing procedure recommended for the preparation of copper and copper alloys by ASM International [13]. Our initial preparation procedure is listed as preparation procedure #1 in Appendix C.



(A) (B) (C)

Fig. 2. SRM 482 wires are mounted into aluminum bullets prior to grinding and polishing. (A) Using a #76 drill bit, a hole slightly larger than the diameter of the wire is drilled into each bullet. Holes are drilled 1.5 mm deep. Wire pieces are cut to a length of 2 mm. (B) Wire pieces are inserted into drilled holes. The wire is then impressed down into the holes using a mounting press. (C) Six bullets, (one for each wire composition in SRM 482) with wires impressed, are mounted into a 25.4 mm (1 in) diameter bullet holder for grinding and polishing.

[2] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.