The Use of Silver Decoration Technique in the Study of Hydrogen Transport in Metallic Materials

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The silver decoration technique proposed by Schöber and Dieker for revealing local hydrogen flux in terms of microstructural characteristics is reinterpreted. The results of decoration tests in polycrystalline nickel and palladium with and without hydrogen charging show that hydrogen flux is not solely responsible, nor even a prerequisite, for the deposition of silver crystals on metal surfaces. There is, consequently, no one-to-one correspondence between escaped hydrogen atoms and deposited silver atoms during the decoration process as reported previously. It is the oxidation film formed during electropolishing that prevents silver deposition. Any damage to the film and any factor which reduces its stability may result in spontaneous silver deposition in the absence of hydrogen. With this new interpretation, one can use the silver decoration technique to obtain qualitative information regarding hydrogen transport along grain boundaries in metallic materials.

I. INTRODUCTION

Degradation of mechanical properties of many metals and alloys by hydrogen is a severe engineering problem on which much work has been expended. However, due to its complexity, many aspects of the problem require further investigation. Recently, Oriani stated in his Whitney Award Lecture, ten years after his first similar statement, that the history of hydrogen embrittlement (HE) research is an example of the fable of the blind men and the elephant. In fact, the situation is even worse if some aspects are considered. In the fable, each blind man correctly described the part he touched, while in HE research, conflicts between different research groups investigating similar aspects often exist because of experimental difficulties and other uncertainties. In recent years, great effort has been made in developing new techniques that will provide more direct and informative results and thus lead to a better understanding of the mechanism of HE.

In the early 1960's, Devanathan and Stachurski developed the electrochemical double-cell permeation technique. This technique enabled researchers to investigate diffusion behavior of hydrogen, trapping phenomena, surface effects, and other effects in metals and alloys and was modified to enable study of dislocation transport of hydrogen during deformation. A thermal analysis technique developed by Lee and his co-workers is useful in the study of various traps for hydrogen in metallic materials. However, these two techniques, although useful, do not provide direct evidence of the distribution of hydrogen in the material. A few techniques exist that are capable of providing such evidence; e.g., tritium autoradiography reveals the distribution of trapped hydrogen in a surface layer. However, since long exposure periods are required, it cannot be used in a dynamic way. Recently, Schöber and Dieker proposed a variation of the Ag-crystal decoration technique which is based on the assumption that adsorbed atomic hydrogen is active and able to reduce silver irons in a specific solution into metal crystals through the decoration reaction

\[ \text{Ag}^+ + \text{H}_2 \rightarrow \text{Ag} + \text{H}_2^+ \]  

The Ag crystals then deposit on the spot where hydrogen atoms escape from the metal. The microstructural distribution of hydrogen fluxes can be revealed by observing the deposited crystals under an optical microscope or a scanning electron microscope (SEM). This technique has been used in various metals and alloys in our laboratory in an attempt to identify the role of grain boundaries in mass transport of hydrogen. However, inconsistent results were obtained, and the reproducibility was poor. Therefore, an investigation of the technique itself was performed, which has led to a new interpretation of the decoration process. The decoration behavior of grain boundaries will be addressed in the present study.

II. EXPERIMENTAL

Ni270 (99.98 pct) and Pd (99.9 pct) were used in the present investigation. As-received Ni270 and Pd plates were cold rolled from 1.0-mm to 0.12-mm thickness. Nickel specimens were annealed at 1323 K for 30 minutes followed by water quenching, whereas Pd specimens were annealed at 1273 K for 30 minutes followed by air cooling. Palladium specimens were mechanically polished using 0.05 μm aluminum oxide powder for the final step since there is no convenient electropolishing method, and Ni270 specimens were initially mechanically polished to 6 μm and then electropolished in 60 pct H₂SO₄ at 5.5 V for about 8 minutes.

The current density for cathodic hydrogen charging was 100 A/m², which was applied only on half of the specimen surface. Re-electropolishing was done at 5.5 V for 1 minute on the whole surface in order to eliminate any contamination due to hydrogen charging. When necessary, outgassing was performed in vacuum at 0.00053 Pa.
(4 \times 10^{-6} \text{ torr}) for a given period of time. During decoration, the whole specimen surface was immersed in the decoration solution. Therefore, two distinguished areas were obtained on the specimen surface; one had undergone hydrogen charging, while the other was free from hydrogen. The hydrogen-free area was used as a reference.

Silver deposits were observed both under an optical microscope and the SEM (JXA-840). An X-ray diffractometer was used to determine the chemical composition and the structure of silver compounds that deposited on the specimen surfaces. Three stock solutions were used for the silver decoration tests and were prepared by adding (A) 20, (B) 28, or (C) 40 ml of a 4 pct KCN aqueous solution to 10 ml of 12 pct AgNO₃ solution. According to Schöber and Dieker, the following reactions take place:

\[
\begin{align*}
\text{AgNO}_3 + \text{KCN} & \rightarrow \text{AgCN} \downarrow + \text{KNO}_3 \quad [2] \\
\text{AgCN} + \text{KCN} & \rightarrow \text{K}[\text{Ag(CN)}_2] \quad [3]
\end{align*}
\]

Simple calculation shows that 25 ml of 4 pct KCN solution will consume about 10 ml of 12 pct AgNO₃ solution without any residual precipitates of AgCN from Reaction [2]. Since the dissociation reaction

\[
[\text{Ag(CN)}_2]^- \rightarrow \text{Ag}^+ + 2\text{CN}^- \quad [4]
\]

is the first step of the decoration process, an increase in the concentration of CN⁻ in the solution will shift Reaction [4] to the left, and therefore, solutions A, B, and C will all have different decoration capabilities. These stock solutions were used for decoration tests in dilutions of 1:50, as suggested by Schöber and Dieker.

### III. RESULTS AND DISCUSSION

#### A. In the Absence of Hydrogen

Results of the decoration tests on Ni and Pd specimens without hydrogen charging are summarized in Table I. It can be seen that Ni is active either in solution A, which can be considered as a saturated AgCN solution, or in solution C, which has surplus CN⁻ ions. Deposits on an electropolished and uncharged Ni270 specimen decorated in solution A for 12 hours are shown in Figure 1. Two kinds of deposits are evident, small white particles in the background and long needles randomly distributed in groups. Both these deposits were high in silver, as determined by energy dispersive spectrum (EDS) analysis on the SEM. X-ray diffractometer analysis showed the presence of both pure silver and AgCN crystals. Therefore, the long needles are most likely AgCN crystals.

Deposits formed during decoration in solution C for

\[
\begin{array}{c|c|c}
\text{Table I. Results of Decoration Tests without Hydrogen Charging} \\
\hline
\text{Solution A} & \text{Solution B} & \text{Solution C} \\
\hline
\text{Ni} & \text{white deposits formed in 10 min} & \text{no deposits up to 24 h} & \text{white deposits formed in 10 min} \\
\text{Pd} & \text{white deposits formed in 10 min} & \text{no deposits up to 24 h} & \text{no deposits up to 24 h}
\end{array}
\]

5 hours are shown in Figure 2. These deposits were identified as pure silver crystals by EDS and X-ray diffractometer analyses. They are of the same size and equiaxial in shape. Since Ni is chemically more active than silver, the following direct displacement reaction might take place:

\[
\text{Ni} + 2\text{Ag}^+ \rightarrow \text{Ni}^{++} + 2\text{Ag} \quad [5]
\]

This reaction may play an important role in the early stages of growth of the particles, which is supported by the fact that no deposits were observed on Pd decorated in this particular solution, since Pd is chemically more stable than Ag. In the later stages, the following reactions may also take place:

\[
\begin{align*}
\text{anodic reaction: } \text{Ni} & \rightarrow \text{Ni}^{++} + 2e \quad [6] \\
\text{cathodic reaction: } 2\text{Ag}^+ + 2e & \rightarrow 2\text{Ag} \quad [7]
\end{align*}
\]

which will result in the deposition of silver particles of various shapes not related to the microstructural distribution of hydrogen flux.

Deposits on a mechanically polished and uncharged