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Electron-Microscope Autoradiographs of Tritium on Nickel Plate

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The study of the adsorbed hydrogen on nickel plate was carried out by means of electron-microscope autoradiography using tritium as tracer. Tritium was impregnated by means of the nuclear reaction of $^{6}Li(n,\alpha)\,^{3}H$ using lithium, which had been deposited on the surface of nickel plate.

Most patterns of the autoradiographs are composed of the groups of parallel stripes which line up in various directions. The pattern and the interval between the slip bands observed in the surface of the metal by electron microscope were in accord approximately with those in the autoradiographs. These agreements lead to the conclusion that hydrogen accumulates preferentially at the edge-steps of the slip band of nickel.

INTRODUCTION

The behavior of hydrogen on metal catalysts in hydrogenation reactions has been studied by various methods. However, there are few reports on the application of the autoradiographical method in this field. The autoradiographical method seems very effective in the direct observation of the distribution of not only the adsorbed hydrogen but also other adsorbing species on the catalyst in the hydrogenation reaction. Recently, the authors attempted the study of adsorbed hydrogen on nickel and copper–nickel alloy using ordinary autoradiography (*1–3*), and obtained information on heterogeneity in the adsorbed hydrogen on these metals. However, it is desirable to increase the resolution of the autoradiograph to learn more about the adsorption of hydrogen. The resolution of the normal stripping film is ca. 0.5–1.0 μm, markedly worse than that of the emulsion of the electron-microscope autoradiography, whose resolution is ca. 500 Å. Electron-microscope autoradiography has mainly developed in the field of biology (*4*). To date, only a few studies (*5,6*) on metal surface have utilized electronmicroscope autoradiography.

This report deals with electron-microscope autoradiography of tritium adsorbed on nickel plate. In autoradiographical studies, it is desirable to clearly determine the surface structure of the metal before the adsorption of gas. Etching with chemical reagents is usually employed to disclose the surface structure. However, chemical reagents contaminate the active sites and thus disturb the adsorption of the gas. To avoid such problems, it is desirable to impregnate the surface layer of the metal with hydrogen before the etching. In this study, tritium was impregnated by means of the nuclear reaction of $^{6}Li(n,\alpha)^{3}H$ using lithium which had been deposited on the surface of nickel plate.

EXPERIMENTAL METHODS

The preparation of the nickel plate was practically the same as was described elsewhere (*3*). Nickel does not alloy with lithium. Therefore, nickel plate was covered with lithium by means of vacuum deposition before irradiation by neutrons.

The nickel plate used was 4–6 mm wide, 20 mm long, 0.3 mm thick, and 99.9% pure. Prior to the deposition of lithium, the plate was heated to 1000°C, gradually cooled, and then polished with fine emery paper and subjected to electrolytic polishing. The electrolytic polishing was conducted at 60°C with a current density of 2.5 A/cm^2, employing nickel as the anode and dipping it in a solution which had been prepared by mixing 50 cc of phosphoric acid, 1 g of agar-agar, and 0.5 g of sodium hydroxide. The surface structure of nickel was disclosed by this electrolytic polishing. The plate thus treated was washed with distilled water and dried sufficiently in air. The plate was then placed in the B portion of the quartz vessel shown in Fig. 1. One-half gram of lithium was placed in the tube A, which was heated from outside the vessel after the vessel had been evacuated under a pressure of 10^{-6} Torr. During the heating, the B portion was cooled with a dry ice bath to accelerate the deposition of lithium vapor on the surface of the nickel plate. Metallic lithium was placed inside the double quartz tube avoid breaking the tube by the formation of lithium silicate. After the deposition of lithium on the nickel plate, the plate was transferred by the aid of a magnet to the C portion, which was then sealed off by fusing the connecting tube.

The metallic lithium used was natural and contained 7.5% ^{6}Li. The irradiation with thermal neutrons was carried out by means of the JRR-2 of the Japan Atomic Energy Research Institute. The irradiation dose was ca. 4×10^{19} nvt. The irradiated nickel plate was kept standing for 2 mo; during this period, the induced radioactivity of the plate decayed to below the prescribed safe limit. The nickel plate was shaved again with emery paper and electrolytic polishing to remove the lithium remaining on the surface, and then subjected to autoradiographical study. The liquid emulsion used for the electron-microscope autoradiograph was prepared as a trial manufacture of Fuji Photo Film Co. Its particle size was ca. 300 Å. The emulsion was coated on ethyl cellulose film, which had been covered with carbon by evaporation, until the film became brown. The evaporation of carbon was accomplished by discharging the arc in a vacuum. The sample was in contact with the emulsion film shown in Fig. 2 for about 40 hr in a lighttight box. The development of the emulsion film was carried out according to Kodak Formula D-19. After development, the sample was washed well with water and the ethyl cellulose was dissolved with trichloroethylene; then the carbon film which remained in the solvent was scooped out with a mesh and observed under an electron microscope.

In order to study the penetration range of tritium produced by the nuclear reaction, an autoradiograph of the nickel plate section was taken by means of the ordinary autoradiographical technique. The stripping film used in this case was Fuji ET-2F. The contact time of the film was 20 hr.

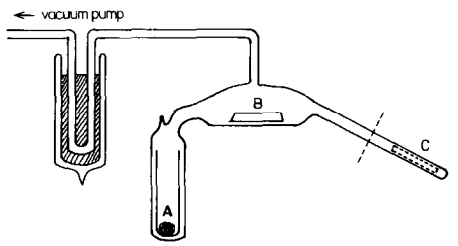

FIG. 1. The vessel used for the deposition of lithium on nickel plate.

RESULTS

The appearance of silver grains produced by the development depends upon

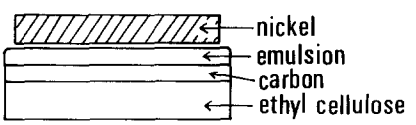

FIG. 2. Electron-microscope autoradiographical method.

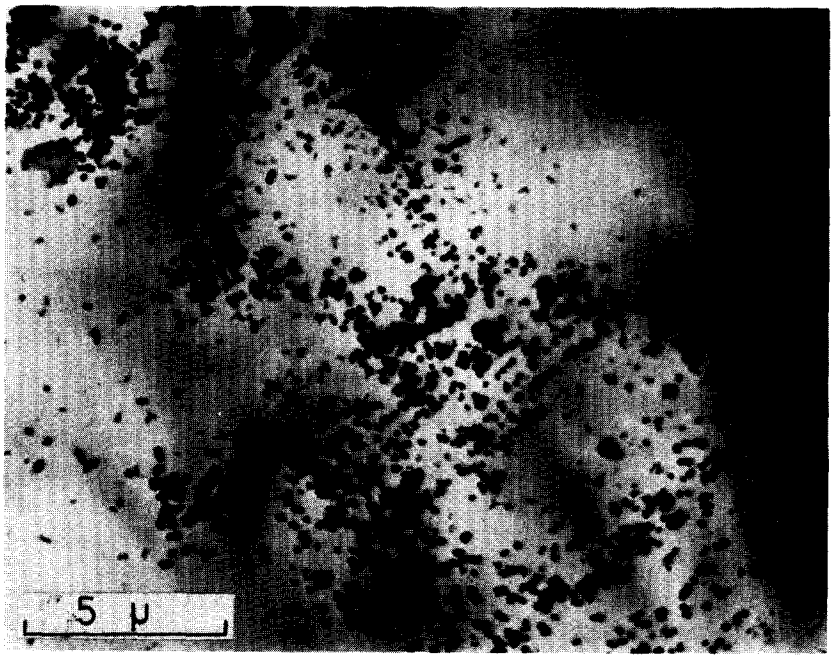

FIG. 3. Electron-microscope autoradiograph of tritium on nickel plate.

the length of exposure and the condition of the development procedure. It looks sometimes like ribbon which coils to form a tangled mass. The density of these silver grains is related to the concentration of tritium which exists under the emulsion.

The typical electron-microscope autoradiographs obtained are shown in Figs.

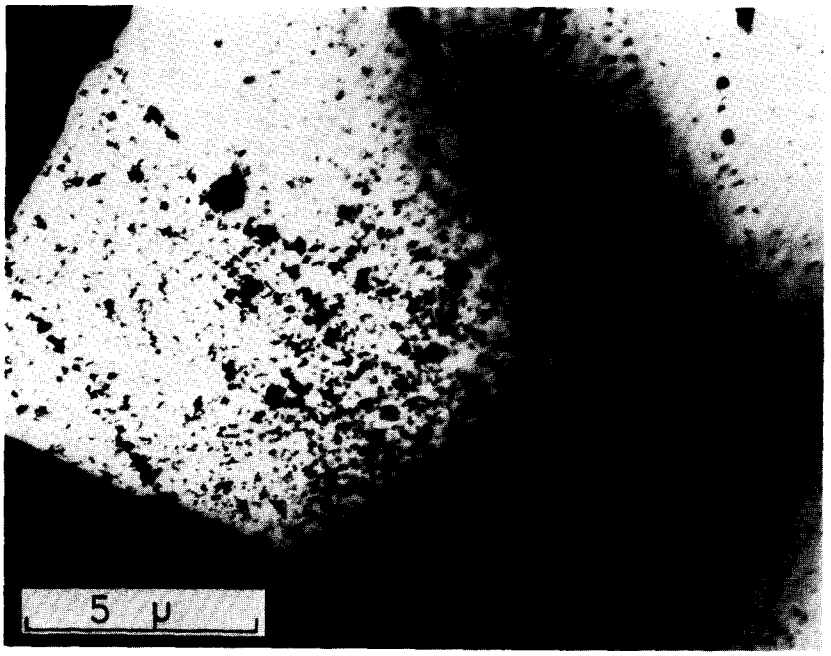

FIG. 4. Electron-microscope autoradiograph of tritium on nickel plate.

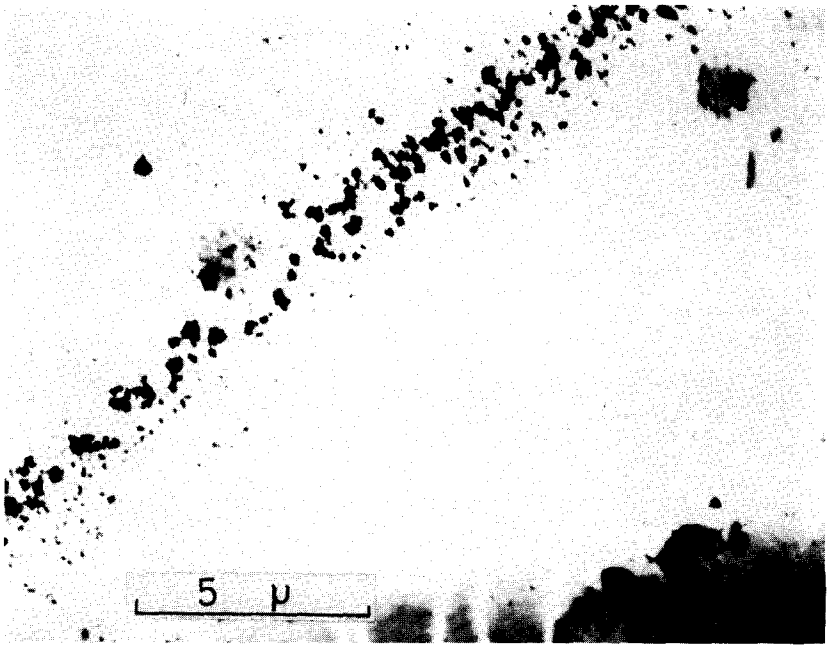

FIG. 5. Electron-microscope autoradiograph of tritium on nickel plate.

3–5. Most patterns of the deposited silver are parallel stripes. The distance between these lines is approximately less than 0.3 μm. Figure 4 is composed of several groups of parallel stripes which line up in different direction. It is noticeable in this picture that weak images of the stripes overlap with strong stripes going in a different direction. Figure 5 shows a part of long narrow lines in the autoradiographical patterns. The concentration of silver grains at the both sides of the line is conspicuously small.

Figure 6 shows an autoradiograph taken

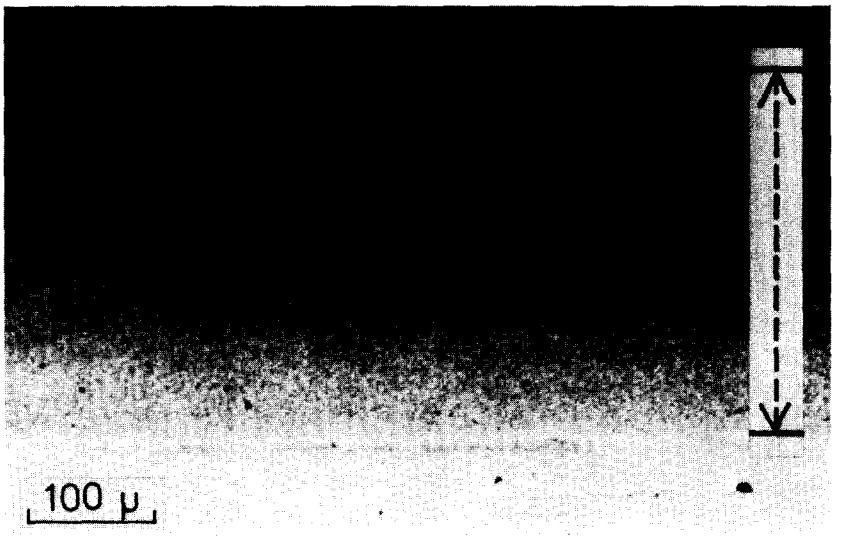

FIG. 6. Autoradiograph of the section of nickel plate (stripping-film method). Vertical broken arrow: width of nickel plate.

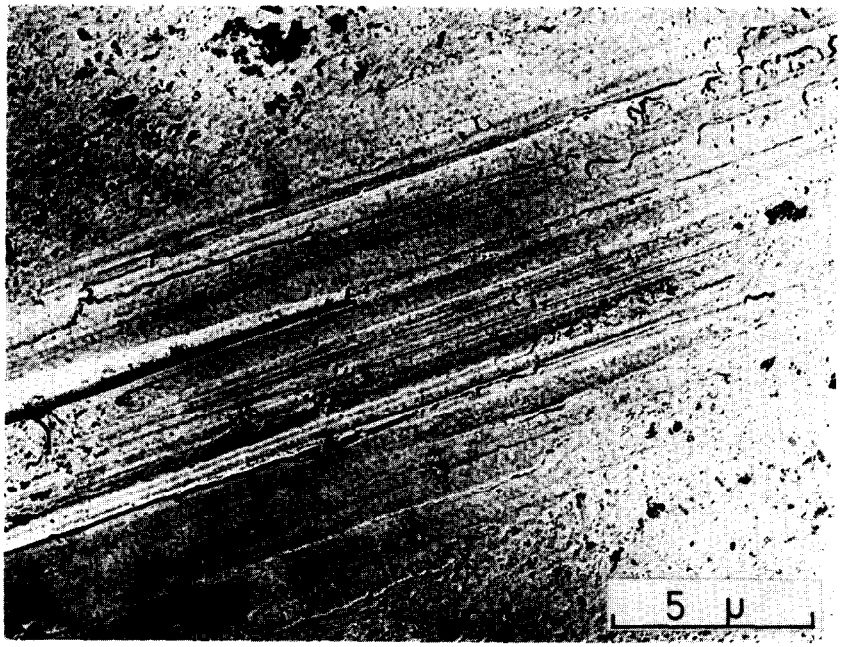

FIG. 7. Electron micrograph of the surface of nickel plate.

by means of ordinary stripping film for a section of nickel plate. This figure indicates that tritium exists even at the depth of more than 200 μm. Figure 7 shows an example of electron-micrograph obtained by means of replica on the surface of the nickel plate used in this study. The parallel lines in this picture shows the slip band on the surface.

DISCUSSION

The β-particle of tritium has a maximum energy of 18 keV, which is particularly small in the β-radiation elements. The maximum penetration range of the β-particle in metal is theoretically given as 300 Å (*7*), ca. 1000 layers of nickel atoms. The energy spectrum of tritium shows that the most probable energy is ca. 1/10 of the maximum energy. It is assumed, therefore, that the sensitization of silver bromide in the photographic emulsion is caused by the tritium which exists within only the top several hundred layers of nickel atom.

The nuclear reaction of ^{6}Li is assumed to occur on the surface of the nickel plate, because the penetration power given lithium by the collision with thermal neutrons, 0.025 eV, is negligibly small. The theoretical penetration range of tritium in transition metals is ca. 20 μm (*8*). However, the autoradiograph of the section of nickel plate (cf. Fig. 6) indicated that the tritium existed at a depth of more than 200 μm, which is 10 times greater than that obtained theoretically. The temperature of nickel plate under irradiation was not measured in this study. It can be assumed, however, that the temperature would be ca. 600°C from the decrease in the BET area of powdered nickel catalyst under the same condition of irradiation. Because the rate of diffusion as well as the solubility of hydrogen on nickel increase conspicuously at above 200°C (*9*), the penetration range of tritium is assumed to increase during irradiation in the atomic pile.

The interval between the layers in the slip band observed by electron microscope accords approximately with that of the

parallel lines in the autoradiographs. This agreement in the pattern reveals that tritium accumulates preferentially at the slip band of nickel. We may conclude that hydrogen adsorbs preferentially on edge-steps of the slip band, because edge-steps of metal include lattice imperfections such as defects and dislocations (*10*). Such lattice imperfections would be the strained sites which are active for the adsorption of gas.

The autoradiograph in Fig. 5 seems to show a narrow slip band or grain boundary on the surface. The slip band or grain boundary of this photograph would exist between two crystal planes, which are inactive for the adsorption of tritium. Grain boundaries are readily etched by the electrolytic polishing and would became broad as shown in this photograph.

The adsorbed tritium on the surface of nickel would oxidize to OH or H_2O in the process of the autoradiography. However, the possibility of a change in their adsorbing positions, that is, surface migration, seems to be negligibly small, because the naked active sites of nickel would be occupied by oxygen soon after the nickel was exposed to air, and the vacant sites would disappear.

Many types of fresh lattice imperfections are produced by fission spikes in the nuclear reaction (*11,12*). Tritium produced by a nuclear reaction on the surface layer of the nickel would diffuse into the metal along such lattice imperfections, and would be distributed to the inner step-edges as well as grain boundaries (cf. Fig. 4). However, it moves again to the surface when the tritium on the surface is consumed by the hydrogenation reaction, as was confirmed by the authors in a previous study (*3*).

There is much evidence (*13–15*) which indicates that special face on the metal is active for catalytic reactions as well as adsorption of gas. The recent application of low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) to stepped surface of a single crystal of platinum by Long and co-workers (*16*) and Joyner *et al.* (*17*) showed very important result that the terraces of the special face are particularly active in the adsorption and the catalytic reaction. The autoradiographs obtained in our study visualize the fine distribution of the adsorbing hydrogen on the surface of nickel plate. The conclusion obtained from these autoradiographs coincides with that obtained by LEED and AES on platinum.

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