

## Electron Diffraction Specimen Holder for the Study of Gas-Metal Reaction at Elevated Temperatures

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A new specimen-treating adapter was devised for the electron diffraction study of successive structure changes of metal surfaces occurring in the reaction gas atmosphere at elevated temperatures. This attachment contains specimen holder with furnace, gas leakage system, additional evacuating system and gas preparation system, and is possible to observe the structure changes of the specimen surfaces up to 1000°C and in the pressure of  $\sim 0.1$  mmHg of gas under the irradiation of 50 kV electrons. Some applications on the oxidation of evaporated thin metallic films of iron, nickel, chromium and iron-chromium alloy are described. The results suggest that the technique is applicable to the study of mechanism of oxidation and reduction of metals and oxides.

### Introduction

Corrosion resistance of metals and alloys against various kinds of high temperature gas is one of important problems in chemical industry and in metallurgy. Electron diffraction method is a useful tool to investigate the structure of surface products resulting from the reaction between metals and gas. Many papers have been published in this field especially in the oxidation of metals, but the specimens used in most cases were heated in furnaces in the outside of the diffraction apparatus and exposed in air after cooling, so the specimens may be affected more or less by oxygen or by moisture in air. As regards the high temperature furnace for specimen-treating in the electron diffraction camera, several authors, e.g., Yearian and Howe<sup>1)</sup>, Jackson and Quarrell<sup>2)</sup>, Gulbransen<sup>3)</sup>, Trillat<sup>4)</sup> etc., have reported in the past. Particularly, Gulbransen and his coworkers have published many papers contributing to the field of oxidation of metals. But, for complete interpretation of the reaction mechanism between metal and gas, it is necessary to observe directly the successive changes of the surface occurring under the reaction gas atmosphere.

In the present paper, a new type of specimen-treating adapter which is possible to observe the structure changes of metal surfaces under a certain gas pressure at elevated temperatures, and its applications are described.

### Apparatus

Fig. 1 is the outside view of the apparatus used in this study, which is modified type of HU-10 electron microscope. This apparatus can be used not only for high magnification microscope but also for high resolution electron diffraction. The high voltage can be changed from 50 to 100 kV. The diffraction specimen chamber contains a specimen holder with furnace (A) and gas leakage system, and is connected to gas preparation system (B) through thin pipe (C), and evacuated by diffusion pump through thick pipe (D). Fig. 2 shows a schematic diagram of the gas preparation system. The reaction gas passes through silica gel, platinum asbestos, liquid air trap, several sections for dividing the volume of gas and is stocked in a gas reservoir, and

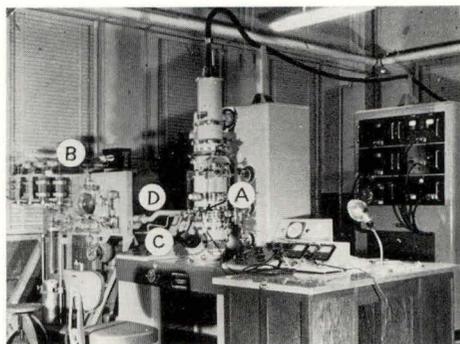


Fig. 1. Electron diffraction apparatus for study of reaction between metals and gas at elevated temperatures.

then is sent to the specimen surface. Details of the specimen holder is shown in Fig. 3. The specimen is mounted in a stainless steel pipe with thermocouple of Pt-Pt·Rh. The furnace consists of platinum

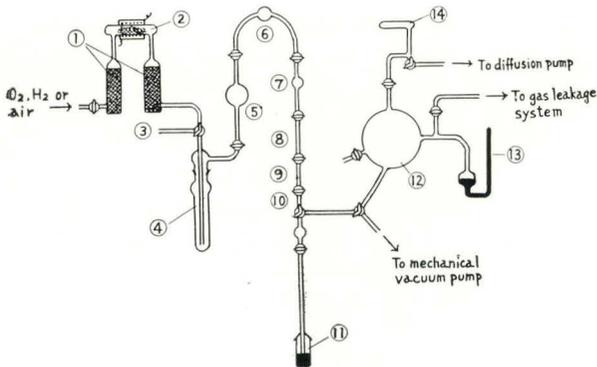


Fig. 2. Schematic diagram of gas preparation system. 1: silica gel, 2: platinum asbestos, 3: two of the same sets as 1 and 2 connected in parallel, 4: liquid air trap, 5-10: sections for dividing volume of gas, 11: mercury vessel, 12: gas reservoir 13: manometer, 14: ion gauge.

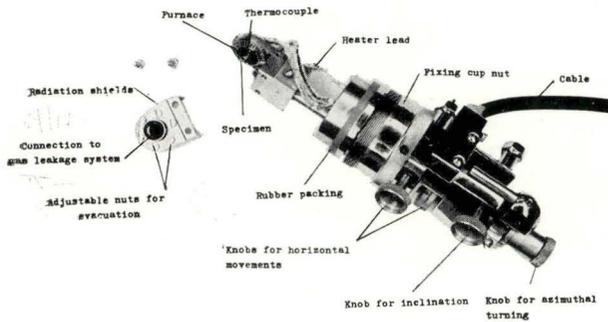


Fig. 3. Specimen manipulator with furnace.

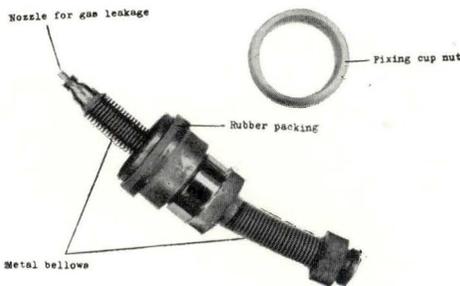


Fig. 4. Gas leakage system.

or tungsten wire and can heat the specimen up to  $1000^{\circ}\text{C}$ . Radiation shield of stainless steel is used for constancy of the temperature and of reaction gas pressure. This specimen holder can be used both for transmission and reflection experiments. Fig. 4 is details of the gas leakage system. The top of the tube can be connected to the radiation shield of the specimen holder and the other side to the gas introducing system. The reaction gas passes through two metal bellows and is sent through a nozzle to

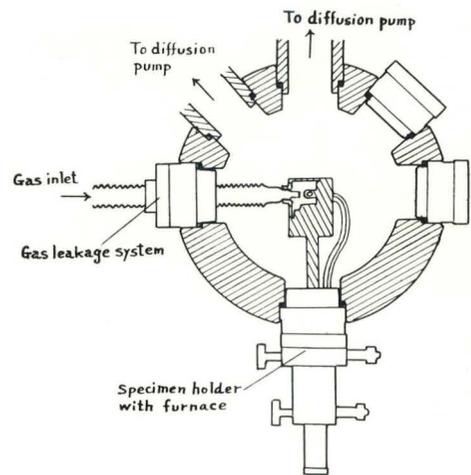


Fig. 5. Schematic view of diffraction chamber.

the specimen surface. The arrangement of the diffraction chamber is shown schematically in Fig. 5. This system was possible to introduce about  $0.1\text{ mmHg}$  of gas under the irradiation of  $50\text{ kV}$  electrons.

### Applications

Using this apparatus, evaporated polycrystalline metallic films of iron, nickel, chromium and iron-chromium (50:50) alloy were investigated by transmission method under the pressure of  $\sim 10^{-2}$  to  $\sim 10^{-4}$  mmHg of dry air at elevated temperatures.

Fig. 6 shows typical diffraction patterns obtained from heat-treatment of the nickel film. Before the heat-treatment, the specimen shows diffuse rings due to face-centered cubic nickel (a). When the specimen was heated in  $10^{-4}$  mmHg of air, new extra rings due to hexagonal closed packed nickel was observed

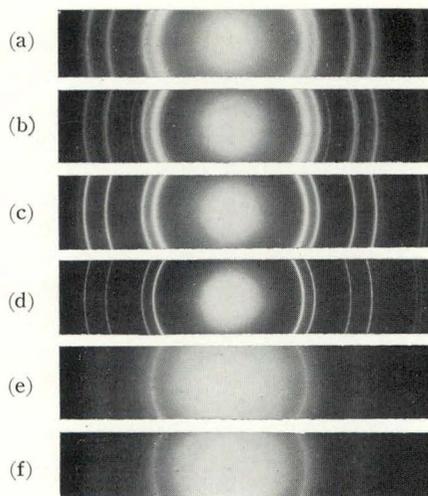


Fig. 6. Transmission patterns through evaporated nickel film heated in  $10^{-4}$ – $10^{-2}$  mm Hg of dry air. a, b, c and d were obtained at room temperature, at 235°, at 365° and 600°C in  $\sim 10^{-4}$  mm Hg, respectively. e and f were observed after 2 min and after 5 min in  $\sim 10^{-2}$  mm Hg, at 600°C, respectively.

at 235°C (b), but the hexagonal phase disappeared at 365°C (c). Grain growth of the cubic nickel was only observed above 365°C and no oxide was detected up to 600°C (d). But, the film heated in  $10^{-2}$  mmHg of air for 2 min. at the same temperature indicated the presence of NiO (e), and the rings due to NiO became predominate in the pattern by successive heating for three min. (f). The results obtained in the present study are tabulated in Table 1. Some interesting facts can be seen in the table. In case of iron film, the observation of FeO at 400°C is of interest. Similar observation has been reported by Gulbransen and Ruka<sup>5)</sup> for oxidation of iron block and also by Haase<sup>6)</sup> for single crystal films of iron heated in high vacuum. According to the phase diagram of iron-oxygen<sup>7)</sup>, FeO (wustite) is unstable as bulk below 570°C and decomposes into Fe<sub>3</sub>O<sub>4</sub> and Fe. In the present case, thin films were used, and the observation corresponds to the inter-

Table I. Results on oxidation of thin metallic films.

Metals and Alloy	Pressure of Air mmHg	Oxide Structure
Fe	$\sim 10^{-4}$	RT–350°C $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> or Fe <sub>3</sub> O <sub>4</sub>
		400°C FeO+tr Fe <sub>3</sub> O <sub>4</sub>
		450°–500°C FeO
		550°–600°C FeO+tr Fe <sub>3</sub> O <sub>4</sub> +tr Unknown Oxide
Fe	$\sim 10^{-2}$	RT–350°C $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> or Fe <sub>3</sub> O <sub>4</sub>
		400°–600°C Fe <sub>3</sub> O <sub>4</sub> +FeO
		650°C FeO+tr Fe <sub>3</sub> O <sub>4</sub> +tr $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> +tr Unknown Oxide
Ni	$\sim 10^{-4}$	RT–600°C No oxide detectable
		RT–200°C Distorted fcc Ni
		235°–350°C fcc Ni+cph Ni
		400°–600°C fcc Ni
Ni	$\sim 10^{-2}$	RT–550°C No oxide detectable
		600°C NiO
Cr	$\sim 10^{-4}$	RT–500°C Cubic Oxide ( $\gamma$ -Cr <sub>2</sub> O <sub>3</sub> or Cr <sub>3</sub> O <sub>4</sub> )
		550°–600°C $\alpha$ -Cr <sub>2</sub> O <sub>3</sub>
Cr	$\sim 10^{-2}$	RT–500°C Cubic Oxide ( $\gamma$ -Cr <sub>2</sub> O <sub>3</sub> or Cr <sub>3</sub> O <sub>4</sub> )
		550°–600°C Cubic Oxide+ $\alpha$ -Cr <sub>2</sub> O <sub>3</sub>
Fe–Cr (50 : 50)	$\sim 10^{-4}$	RT–650°C $\gamma$ -(Fe, Cr) <sub>2</sub> O <sub>3</sub>
		670°C $\alpha$ -(Fe, Cr) <sub>2</sub> O <sub>3</sub>
	$\sim 10^{-2}$	RT–600°C $\gamma$ -(Fe, Cr) <sub>2</sub> O <sub>3</sub>

RT: room temperature.

tr: traces.

mediate process of decomposition of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  resulting from diffusion of iron atoms in thin film. In case of nickel film, no oxide was observed in  $\sim 10^{-4}$  mmHg of air, but the results of the crystallization of hexagonal nickel at  $235^\circ\text{C}$  and the transformation to f.c.c. nickel at  $400^\circ\text{C}$  is of interest. The evaporated primary nickel film seems to have many imperfections due to stresses and stacking faults, and is stabilized at higher temperatures by absorption of some energy. Similar result was observed by Reimer<sup>8)</sup> in nickel films prepared by cathode sputtering. In case of chromium film, cubic oxide probably due to  $\gamma\text{-Cr}_2\text{O}_3$  or  $\text{Cr}_3\text{O}_4$  is observed at relatively low temperatures. This result is in agreement with the observation by Miyake<sup>9)</sup> and also by Mahla and Nielsen<sup>10)</sup>. This suggests that such an oxide exists at the interface between chromium and hexagonal  $\text{Cr}_2\text{O}_3$ . In case of Fe-Cr alloy system, it was difficult to determine the exact composition of the specimen, but the improvement of the oxidation resistance is clearly observed, and the interface structure between metal and oxide can be seen. The composition of

such a composite film will be determined by means of electron probe microanalyser. These results suggest that the techniques are applicable to studies of the mechanism of oxidation and reduction of metals and oxides.

In conclusion, the author wishes to thank Mr. Y. Ohnuma of Naka-works of Hitachi, Ltd. for his assistance in the designing of the apparatus used, and also thanks Dr. U. Hashimoto of NRIM for his constant encouragement in the course of this study.

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### DISCUSSION

E. MENZEL: The hexagonal Ni that you observed would be Ni-nitride formed by the residual gas, I think. Mr. H. Gärtner\* has shown that the apparent hexagonal Ni grown by sputtering in air of  $10^{-3}$  mmHg in a magnetic field is Ni-nitride. By sputtering in pure Ar, always f.c.c. Ni appears. (\*H. Gärtner: *Z. Naturforsch.* **16A** (1961) 840).

G. SHIMAOKA: The nickel specimens used in this experiment were prepared by evaporation in air of  $10^{-5}$  mmHg, but the effect of residual gas might not be excluded.

M. J. WHELAN: Is there no possibility that your hexagonal reflections came from double Bragg reflections between a f.c.c. crystal and its twin?

G. SHIMAOKA: As we used the polycrystalline films of nickel specimen and they showed complete Debye-Scherrer rings, the observed hexagonal reflections may be ascribed to the structure of nickel unit cell itself. But your suggestion is of interest, and further examination by using mono-crystal or by the method of selected area diffraction will be tried.

S. OGAWA: What value is the axial ratio of your hexagonal nickel?

G. SHIMAOKA:  $c/a=1.64$ . ( $a_0=2.62 \text{ \AA}$ ,  $c_0=4.31 \text{ \AA}$ )

S. OGAWA: I believe that hexagonal nickel prepared by sputtering is not reproducible with respect to the temperature change.

G. SHIMAOKA: We cannot find it when the specimen is cooled from the temperatures where they have disappeared in the pattern.

A. GOSWAMI: We have observed  $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  at lower temperature, but it decomposes to  $\text{FeO}$  at high temperature, say  $\sim 600^\circ\text{C}$ . What do you think about it?

G. SHIMAOKA: According to the phase diagram of iron-oxygen system, the transformation of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  may occur above  $570^\circ\text{C}$ . But, under the lower pressure of oxygen, we can observe the  $\text{FeO}$  phase below  $570^\circ\text{C}$ , say  $300\sim 400^\circ\text{C}$ .