*Formation and Aging of Precipitates. VII. Habit of Crystals in Vanadium Pentoxide Sols by Electron Microdiffraction Method**

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Morphological studies on the crystals in three kinds of vanadium pentoxide sol, such as Biltz-, Müller-, and ion-exchange sols, were reported in a previous paper[1]. Watson, Heller and Wojtowicz[2] indicated the electron diffraction patterns of the crystals in Biltz sol and showed that the patterns verified the crystal growth. This paper describes the identification of crystals in three kinds of sol and the crystal habit of the Biltz sol crystals.

Experiments and Results

Identification of Crystals in Various Sols by Electron Diffraction Method.— Electron diffraction patterns obtained from the crystals in Biltz-, Müller- and ion-exchange sols, reported in the previous paper[1], are shown in Fig. 1. From these patterns the interplanar spacings of each crystal were calculated and the diagrams

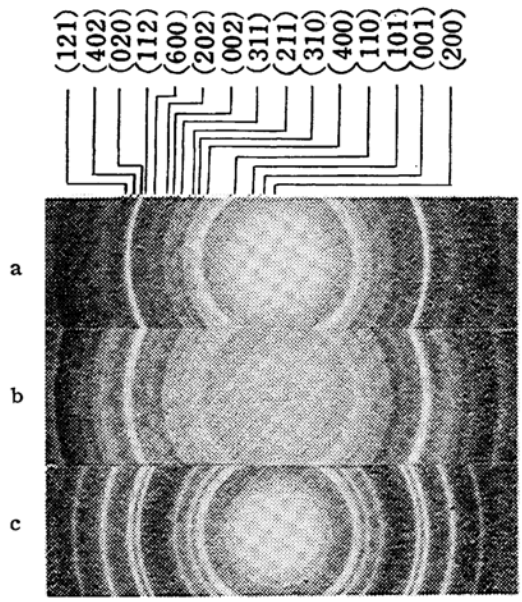


Fig. 1. Electron diffraction patterns of crystals in various sols.
a. Biltz sol
b. Müller sol
c. Ion-exchange sol

* Some parts of this experiment were published in *Proc. Japan Acad.*, **30**, 752 (1954) and were read in advance at the First Regional Conference on Electron Microscopy in Asia and Oceania on October 27, 1956.

1) K. Takiyama, This Bulletin, **31**, 329 (1958).

2) J. H. L. Watson, W. Heller and W. Wojtowicz, *Science*, **109**, 274 (1949).

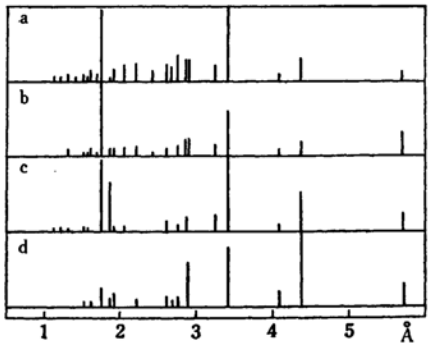


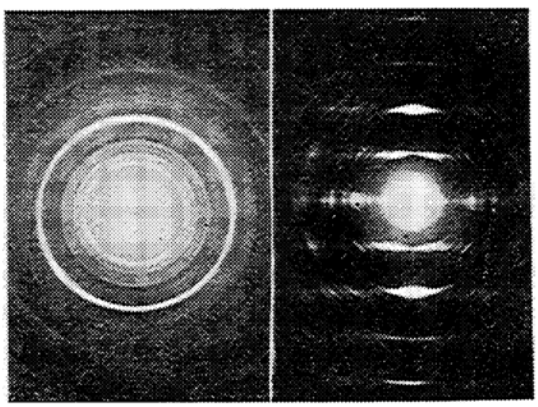
Fig. 2. Diagrams of electron diffraction patterns obtained from crystals in various sols.
a. Biltz sol
b. Müller sol
c. Ion-exchange sol
d. Vanadium pentoxide crystal by means of X-ray diffraction method

of the patterns are shown in Fig. 2. The interplanar spacings of the crystals in every sol agree with those of vanadium pentoxide crystal determined by X-ray diffraction method[3], so that all of the crystals in the sols were identified with vanadium pentoxide.

The Habit of Crystals in Biltz Sol.— The crystals in Biltz sol grew like long fibers upon aging as described in the previous paper[1]. When an aged sol was mounted onto a specimen holder for electron microscopy by the usual method, the photograph was obtained which showed the network of fiber-like crystals as shown in Fig. 3a in the previous paper[1] and its electron diffraction pattern obtained by means of the selected area electron diffraction technique (electron microdiffraction method) was that of Debye-Scherrer rings as shown in Fig. 3a, in which interplanar spacings agreed with those of vanadium pentoxide. The tiny film formed on the surface of the aged sol contained tactoid as shown in Fig. 3b in the previous paper[1], in which the fibrous crystals were oriented parallel to one another. As the direction of the specimen, accordingly that of the fiber axis, was perpendicular to the electron beam, the electron diffraction pattern obtained from the tactoid was a typical fiber pattern as shown in Fig. 3b. Space indices of each reflection point are indicated in Fig. 4. As indicated in Fig. 4, the layer lines are $k=0, \pm1, \pm2, \cdots\cdots$, and the reflection points of (020) and (040) appear on the meridian. By measuring the distance of each layer line from the equatorial line, the fiber period can be calculated by the following equation

$$c = nL\lambda/r_n,$$

where c is the fiber period, L camera



(a) (b)

Fig. 3. Electron diffraction patterns obtained from the two types of crystals in one year old Biltz sol by the selected area electron diffraction technique.
a. Electron diffraction pattern obtained from the part of the network structure.
b. Electron diffraction pattern obtained from the part of the tactoid.

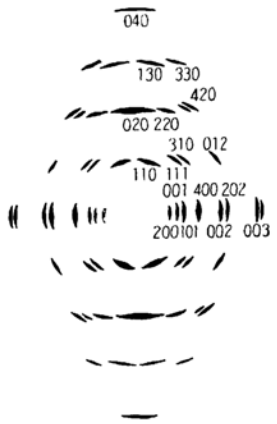


Fig. 4. Space indices of fiber pattern shown in Fig. 3b.

3) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 510 (1938).

length, λ wave length of the electron beam and r_n distance of the n-th layer line from the equatorial line. The value of $L\lambda$ was calculated from the Debye-Scherrer ring pattern obtained from an evaporated aluminum film used as a standard. The fiber period was calculated from 17 electron diffraction patterns as 3.56±0.011 Å which was in accord with the lattice constant of b-axis of vanadium pentoxide, that is b_0= 3.564Å[4]. So the fiber axis, the direction of the crystal growth, was also clearly confirmed as b-axis.

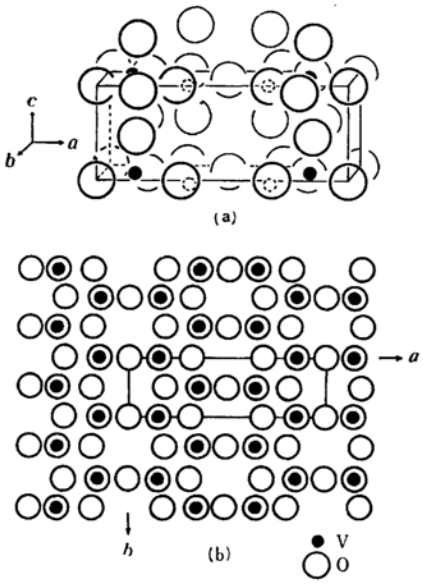


Fig. 5. a: Configuration of vanadium pentoxide crystal.
b: Projection of the structure of vanadium pentoxide crystal on (001).

The fibrous crystals in Biltz sol grew along the b-axis and no growth along the a- and c-axis occurred. The configuration of vanadium pentoxide crystal[4] and the structure projection on (001) of it are given in Fig. 5 a and b. The distribution of vanadium and oxygen atoms along the b-axis is denser than that along other axes. The direction of the growth of the fibrous crystals in Biltz sol agrees with the direction of the dense distribution of atoms.

Summary

The crystals in Biltz-, Müller-, and ion-exchange sols were all identified with vanadium pentoxide by the electron diffraction method.

The crystals in aged Biltz sol were fiber-like. The specimen prepared ordinarily gave rise to the Debye-Scherrer pattern and that of the tactoid corresponded to the fiber pattern. The fiber axis of the fibrous crystal was decided to be the b-axis.

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4) A. J. C. Wilson, "Structure Report", International Union of Crystallography, N.V.A. Oosthoek's Uitgevers, MIJ, Utrecht (1950), p. 232.