detected by Craig, Diller, and Rowe (*12*) may be derived from it. Experimentally determined stoichiometric ratios are summarized in Table 1, for comparison with Eq. 7.

No attempt is made at present to specify the structure of the crosslinks formed, which may depend on temperature. The instability of olefinic disulfides at curing temperatures is well known (*13, 14*).

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18. Determined in the system squalene-TMTD-zinc oxide by direct titration of water with Karl Fischer reagent.
19. At 150°C. It should be noted that the maximum efficiency of crosslinking will be obtained only under mild conditions. At normal "curing" temperatures (130° to 160°C) in the absence of added fatty acid or zinc soap, TMTD may be wasted in side reactions. The concentration of so called "sulfide" sulfur in a rubber-TMTD-zinc oxide mixture after vulcanization is a direct measure of the side reactions, as is a low ratio of sulfur combined to TMTD taken.
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16 May 1958

Hydrothermal Recrystallization of Molybdenum Trioxide

Whisker-like crystal growth in metals has been the object of several investigations, especially within the past few years (*1*). Not until very recently has whisker growth in an oxide system been reported (*2*).

In this investigation, whisker-like crystals were grown in the system MoO_3–SiO_2 under hydrothermal conditions. Homogeneous MoO_3–SiO_2 solid mixtures were prepared by "flash-drying" a solution of ammonium heptamolybdate in ammonia-stabilized Ludox (*3*). This was accomplished by dropping the solution, a drop at a time, into a platinum crucible that was heated to a dull red.

It was found that whisker growth could be carried out by placing small ampules containing the MoO_3–SiO_2 solid, together with capillary tubes filled with water, directly into a controlled-temperature furnace. A temperature of 375°C, a steam pressure of 5 atm, and a hydrothermal treatment time of 72 hours produced abundant whisker growth from a 3 weight percent MoO_3–97 weight percent SiO_2 substrate.

A photomicrograph of a MoO_3–SiO_2 solid which was subjected to hydrothermal treatment is shown in Fig. 1*A*. An electron micrograph of a sample of these whiskers is shown in Fig. 1*B*. Their size was observed to vary widely: diameters of 5 to 50 μ and lengths up to about 5 mm were typical.

Physical property measurements were not undertaken as a part of this investigation. However, it was qualitatively observed that MoO_3 whiskers could be bent over a large radius of curvature with no apparent permanent deformation. If the bending were continued, whiskers tended to split longitudinally rather than break along the shorter dimension.

Samples of the whiskers were separated from the MoO_3–SiO_2 substrate and subjected to x-ray diffraction, infrared spectrometer, and arc-emission spectrographic analysis. As a result of these analyses, it was concluded that the whiskers consisted of high-purity MoO_3.

In one series of experiments, films of SiO_2 were prepared by grinding flash-dried Ludox silica sol with enough water to form a paste and spreading the resulting paste on platinum slides. Similar films of MoO_3 were prepared by spreading MoO_3–H_2O paste on the slides. In one of these experiments a film of SiO_2, about 1 mm thick and 2 cm long, was laid down in such a way as to cover one half of a slide. On the other half of the slide a MoO_3 film of similar dimensions was laid down. The two films were in contact. The films were rapidly dried in a furnace at 480°C, and the slide supporting the films was subjected to hydrothermal conditions (400°C and 4.85 atm steam pressure) for 96 hours. The slide was then examined with the aid of a microscope. Whiskers were observed over the entire length of the SiO_2 film. No whiskers were observed on the MoO_3 film.

In a similar experiment but with the SiO_2 and MoO_3 films separated by a 2-mm gap, no whiskers were observed on either the SiO_2 or MoO_3 films.

These data indicate that the migration of molybdena in the growth of MoO_3 whiskers occurs via the solid phase rather than by a vapor-phase process. The silica substrate is believed to play a unique part in the molybdena transport and crystal-growth process.

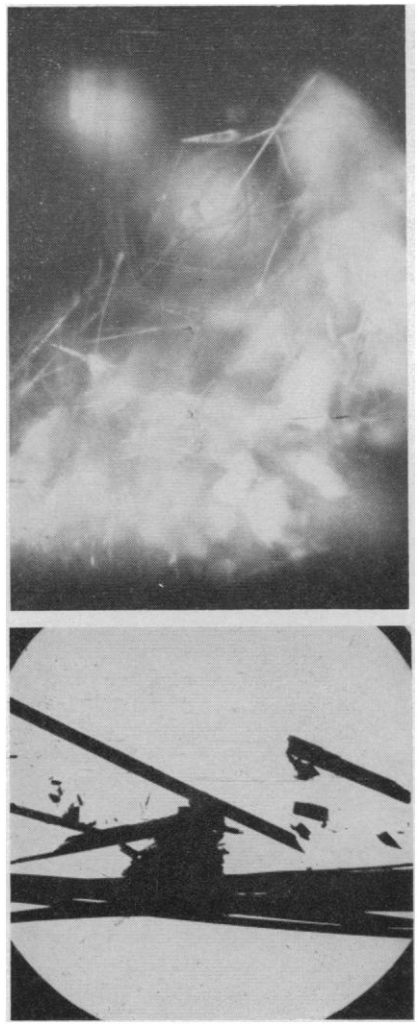

Fig. 1. (Top) Photomicrograph of MoO_3 whiskers grown from a MoO_3–SiO_2 substrate (about × 80). (Bottom) Electron micrograph (2800X) of MoO_3 whiskers (about × 2200).

This is suggested by the fact that whiskers were observed on the silica substrate but not on the molybdena substrate in the film migration study.

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7 May 1958