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The Oxidation of Molybdenum Ditelluride Studied by ESR Spectroscopy

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The oxidation of $MoTe_2$ to Te_2MoO_7 in air at different temperatures is investigated by using ESR spectroscopy. Mild oxidation conditions give rise to an ESR signal characteristic of oxomolybdenum(V) ions with a heterogeneous distribution in the solid. Higher temperatures promote first the formation of a broad signal typical of $TeMo_5O_{16}$, and then the formation of Te_2MoO_7 which is ESR inactive.

Introduction

Knowledge of the stabilization of molybdenum ions in different valence states and geometric environments in oxides is of considerable interest in relation to a better understanding of the catalytic activity of these systems. Thermal treatment of (Te, Mo)O compositions in the solid state may induce complex redox processes and formation of $TeMo_5O_{16}$ in the bulk [1]. We have recently used ESR spectroscopy to study the hydrogen reduction of the one binary phase in the TeO_2–MoO_3 system, Te_2MoO_7, both in the crystalline α- and glassy β-form; also in these conditions $TeMo_5O_{16}$ is indicated as one of the reduced phases [2]. During the reduction process various isolated paramagnetic oxomolybdenum(V) species are generated at first, which subsequently (at higher density) form phase concentrations characterized by strong antiferromagnetic exchange interactions. The solid state equilibria relations in the reverse process, namely oxidation of $MoTe_2$ to Te_2MoO_7, have also been described [3]. This process involves the following sequence of bulk binary product formation:

$$MoTe_2 \rightarrow TeMo_5O_{16} \rightarrow \alpha\text{-}Te_2MoO_7 \xrightarrow{>550\,^{\circ}C} \beta\text{-}Te_2MoO_7$$

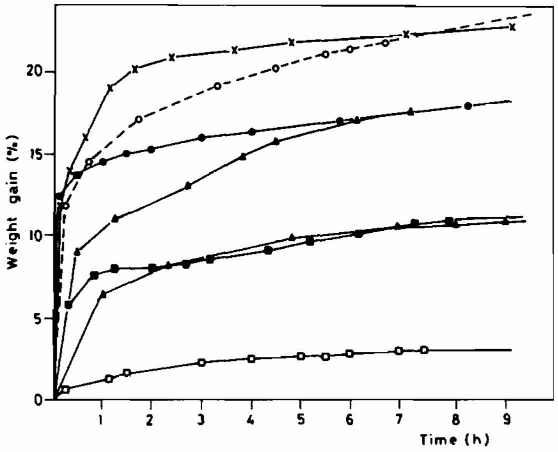

Fig. 1. Oxidation isotherms of molybdenum ditelluride in a static air atmosphere at various reaction temperatures: (□) 300 °C; (△) 350 °C; (■) 400 °C; (▲) 450 °C; (×) 500 °C; (●) 550 °C; (○) 600 °C.

However, the detailed, complex mechanisms involved in these transformations have not been reported. It therefore appeared to us that an ESR study of the oxidation of $MoTe_2$ in air would contribute to an understanding of the effects produced by variation in crystal field associated with phase formation. At the same time, it is of interest to verify whether the mechanisms involved in the generation of Mo(V) ions are similar to those occurring in the reduction process of Te_2MoO_7.

Experimental Part

Materials

Small charges of $MoTe_2$ (0.5 g of Alfa product, 99.9%) were heated in quartz crucibles in air within the range 300 to 600 °C for different times (up to 8 h). Figure 1 shows the variations in weight during the isothermal oxidation process in air, whereas Fig.

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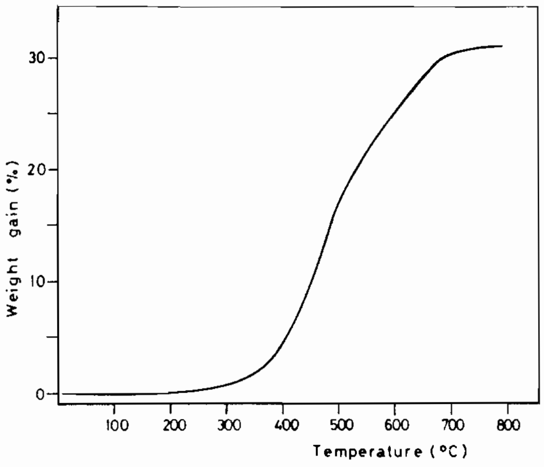

Fig. 2. Oxidation of $MoTe_2$ to Te_2MoO_7 in a static air atmosphere at 5 °C min^{-1}.

2 indicates that total oxidation of $MoTe_2$ to Te_2MoO_7 ($\Delta W_{theor.}$ = 31.9 wt.%, $\Delta W_{exp.}$ = 30.9 wt.%) is readily achieved by heating in static air (Δt = 5 °C min^{-1}) up to 780 °C. In isothermal conditions at 500 °C the latter process requires 15–20 h [4]. For characterization of the bulk, X-ray powder diffraction patterns were obtained as stated in ref. [3].

ESR Measurements

Electron spin resonance experiments were made on equal amounts of powdered samples (100 mg) using a Varian E 9 spectrometer working at X-band frequency. DPPH was the standard field marker. Constant values of modulation amplitude and power level were employed, and neither broadening nor saturation were observed. Other instrument settings were maintained at pre-set values with the exception of the receiver gain which was varied to give comparable signals.

Results and Discussion

Oxidation of $MoTe_2$ to Te_2MoO_7 consists of steps involving not only variations in the valence state of molybdenum atoms but also phase modifications. The bulk reaction products obtained conform to previous results [(Table I of ref. [3]). $MoTe_2$ is readily oxidized in air above about 250 °C (Fig. 2). Small amounts of Te, MoO_2 and $TeMo_5O_{16}$ are obtained at low temperatures (300 °C); at 350–400 °C TeO_2 is formed, whereas MoO_2 disappears. Bulk formation of Te_2MoO_7 occurs above about 500 °C, while Te, TeO_2 and $TeMo_5O_{16}$ are the other components in these systems.

It is obvious that the different molecular and intermolecular arrangements around the paramagnetic

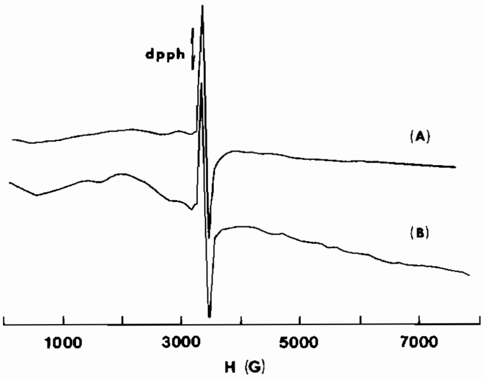

Fig. 3. Room temperature ESR spectra of $MoTe_2$ oxidized in air for 2 h at 300 °C (A) and for 6 h at 350 °C (B).

Mo-species in these reaction mixtures determine the observable magnetic properties. Mild oxidation of $MoTe_2$ in air at 300 °C gives rise to an ESR signal characteristic of oxomolybdenum(V) ions (Fig. 3) absent in the starting material. The intensity of the signal does not vary appreciably with reaction times up to 8 h. The almost symmetrical shape ($g \sim 1.9$) and lack of hyperfine structure, due to the odd molybdenum isotopes, together suggest a heterogeneous distribution of paramagnetic species in the solid [5]. As already observed for Mo(V) species in α- and β-Te_2MoO_7 matrices [2], the paramagnetic centers are not located on the surface, as shown by the lack of line broadening in the spectra of samples exposed to a high partial oxygen pressure at room temperature. The signals of the isolated Mo(V) ions have the features of resonances attributable to oxomolybdenum(V) species with distorted octahedral structure distributed in the matrix as species without short-range interactions ([2] and references therein).

After heating $MoTe_2$ in air at 350 °C for 2 h, neither the structure of the paramagnetic signals nor their intensity (*i.e.* the number of isolated Mo(V) ions) were modified. However, a weak and broad signal is evidenced at higher and lower magnetic field values with respect to that of the sharp signal described above (Fig. 3). Again, reaction times up to 8 h do not significantly affect the ESR spectrum. At these low temperatures (up to 350 °C) the number of Mo(V) ions is apparently not greatly dependent on the reaction time, as the oxidation process is controlled by the slow oxygen diffusion through the lattice. At higher temperatures (400 °C), when the oxygen transport is favoured, the number of Mo(V) oxo-ions is expected to increase. At the same time, however, the number of the isolated paramagnetic Mo(V) ions decreases considerably. From the estimated intensity of the ESR signal it appears that only about one fourth of the centers

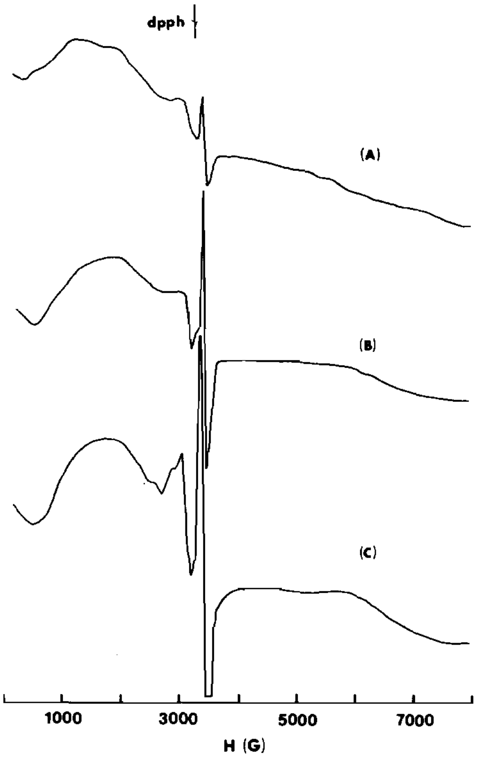

Fig. 4. ESR spectra of $MoTe_2$ oxidized at 400 °C for 2 h. Recording temperatures are: (A) 293 K; (B) 173 K and (C) 133 K.

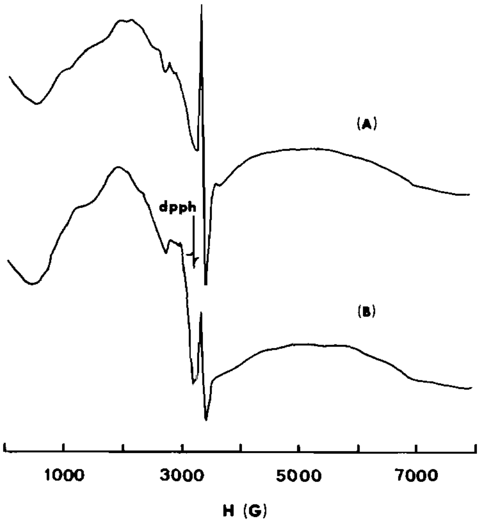

Fig. 5. ESR spectra of $MoTe_2$ oxidized at 500 °C for 6 h (A) and at 550 °C for 4 h (B). Recording temperature: 153 K.

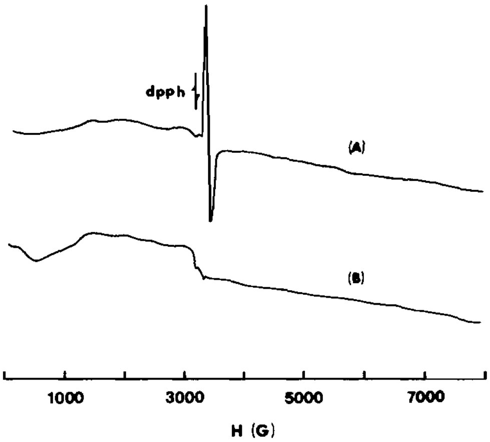

Fig. 6. Room temperature ESR spectra of $MoTe_2$ after oxidation at 600 °C for 2 h (A) and 8 h (B).

found in samples oxidized at 300–350 °C are observable in those heated at 400 °C, in spite of reasonable expectance for the Mo(V) ion concentration. This behaviour can be attributed to the occurrence of exchange interactions between Mo(V) ions, giving rise to signals characteristic of direct coupling mechanisms. The observed broad band typical of $TeMo_5O_{16}$, which quickly increases in intensity after oxidation at higher temperatures until becoming the main absorption observable in the spectra (Fig. 4), is not remarkably dependent upon the recording temperature T_R, at difference to the sharp signal, which increases in intensity at lower T_R (Fig. 4). This different spectral behaviour confirms that, contrary to the $g \sim 1.9$ signal, the broad resonance canot be accounted for by usual paramagnetic species but by exchange phenomena in antiferromagnetic or ferromagnetic systems [6].

Essentially similar spectra with predominant broad resonances and weak absorptions due to isolated ions are found for samples heated at 450, 500 and 550 °C (Fig. 5). Prolonged reaction times (up to 8 h) at these temperatures do not introduce any substantially new spectral features. The similarity of these spectra suggests that, in spite of the different phase compositions in this temperature range (*cf.* Table I of ref. [3]), the ions responsible for the ESR signals are distributed in the matrix in a similar fashion.

In contrast to this behaviour, oxidation of $MoTe_2$ at 600 °C for at least 1 h leads only to a sharp signal in the ESR spectrum (Fig. 6), which is characteristic of Mo(V) ions in a partially reduced β-Te_2MoO_7 matrix. The anisotropic features ($g_\perp = 1.93, g_\parallel = 1.87$) of this signal are due to the presence of an axial symmetry in the oxygen coordination around the ion [5]. Either prolonged reaction at 600 °C or an increase in temperature (630–650 °C) leads to complete oxidation of $MoTe_2$ to Te_2MoO_7 and disappearance of the Mo(V) signal in the ESR spectrum (Fig. 6).

At variance with the case of reduction of α- and β-Te_2MoO_7 [2], formation of $TeMo_5O_{16}$ by oxidation of $MoTe_2$ does not proceed through the formation of a variety of different isolated Mo(V) species. This suggests a stabilizing effect on such oxomolybdenum-(V) environments in oxygen-rich samples. The simultaneous presence of several oxidation products in the samples is not only evident from X-ray data but also from the ESR spectra. Moreover, the observed isolated Mo(V) ions are only compatible with bulk phases without structural Mo(V), such as $MoTe_2$ and Te_2MoO_7.

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