JOURNAL OF MATERIALS SCIENCE 33 (1998) 3079–3083

Thermogravimetric–differential thermal analysis of the solid-state decomposition of ammonium tetrathiomolybdate during heating in argon

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The formation of MoS_2 by thermal decomposition of ammonium tetrathiomolybdate (ATT) solids under an argon atmosphere has been studied by simultaneous thermogravimetric and differential thermal analysis. The sequential products for the decomposition upon heating to 700 °C is ATT (hydrated) $\rightarrow (NH_4)_2MoS_4 \rightarrow (NH_4)HMoS_4 \rightarrow H_2MoS_4 \rightarrow MoS_3 \rightarrow Mo_2S_5 \rightarrow MoS_2$. MoS_2 forms between 230 and 260 °C and remains stable up to about 360 °C when it tends to be oxidized by residual oxygen, if present in the atmosphere. These findings suggest that the synthesis of MoS_2 from $(NH_4)_2MoS_4$ via formation of MoS_3 is not a direct process, as previously reported, but rather a complex process involving a number of intermediate products $(NH_4)HMoS_4$, H_2MoS_4 and Mo_2S_5 which have not been reported before. That these products are only specific to the very narrow temperature regimes as revealed suggests that they are very unstable and short lived, that their presence is transient in nature and thus that *ex-situ* characterization of them is normally difficult. The presence of these intermediate products, as justified experimentally, is further interpreted in terms of their mutual structural similarities which improve understanding as to why MoS_2 can usually be prepared from ATT by thermal decomposition, as in this case, or by other techniques, such as anodizing. Laminar morphology of MoS_2 is revealed by transmission electron microscopy and its crystal structure examined by selected-area diffraction. Further *ex-situ* examination by X-ray photoelectron spectroscopy of this end product supports the feasibility of preparing MoS_2 from aqueous solutions by anodizing. © *1998 Kluwer Academic Publishers*

1. Introduction

Ammonium tetrathiomolybdate (ATT), $(NH_4)_2MoS_4$, belonging to a group of inorganic ammonium or alkaline salts of thiomolybdate or thiotungstate, including potassium tetrathiomolybdate (K_2MoS_4), and ammonium tetrathiotungstate $(NH_4)_2WS_4$), has been the focus of considerable research interest for its potential applications as a starting material for synthesis of molybdenum disulphide (MoS_2), an excellent solid lubricant or lubricant additive, and molybdenum trisulphide (MoS_3), which is, in turn, also an important starting reagent to prepare MoS_2 by solid-state decomposition [1, 2]. Attempts have also been made to form the solid lubricant electrochemically from ATT electrolytes [3, 4]. Generally, the dark-red ATT solids are prepared by passing hydrogen sulphide gas into ammonium molybdate solutions [5].

Previous X-ray diffraction studies of the thermal decomposition of $(NH_4)_2MoS_4$ showed that the ATT decomposed at about 150 °C to yield MoS_3 which subsequently lost sulphur when heated above 250 °C, but the product remained amorphous up to around 350 °C. Crystallinity set in at 400 °C when the first vague line appeared on the diffractograph [6]. Similar observations were reported in the study of decomposition of ATT by thermogravimetric analysis, which yielded crystalline MoS_2 above 400 °C [2]. In a different investigation, the solid decomposition products of MoS_3, obtained by a dry decomposition reaction of $(NH_4)_2MoS_4$, were amorphous MoS_2 formed above 250 °C, rhombohedral MoS_2 at increased temperatures and, finally, hexagonal MoS_2 at 900–1000 °C [7]. The following reactions were further proposed for the decomposition of ATT (and tetrathiotungstate)

$$(NH_4)_2MS_4 \xrightarrow{250\,^{\circ}C} MS_3 + 2NH_3\uparrow + H_2S\uparrow \quad (1)$$

$$MS_3 \xrightarrow{350-400\,^{\circ}C} MS_2 + S\uparrow, \quad M = Mo \text{ or } W \quad (2)$$

Although a measure of agreement is evident in the previous studies, there is ambiguity in the transition temperatures, and the considered reactions (1) and (2) are possibly oversimplifications to reveal detailed sequential stages of the decomposition. The present investigation concerns mainly these issues to assist our understanding of the inherent process of the decomposition, and to address relevant issues, concerning preparation of self-lubricating anodic films, for instance, by a novel anodizing technique [8, 9].

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2. Experimental procedure

ATT, of purity of 99.97% (Aldrich Chemicals), was thermally decomposed in a glass spring thermal balance, with a temperature ramp of 10 °C min^{-1} and an alumina reference, accompained by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) using a standard scanning thermogravimetric system, Stanton–Redcroft TG-750. Heating in high-purity argon atmosphere (100 ml min^{-1}) was started at room temperature and usually stopped at 600–700 °C. Further slowed heating, at temperature ramps of 2 °C min^{-1}, was attempted to reveal more details after a number of minor blips were found on the thermograms. Temperature regimes were defined and mass losses for each transitional stage determined, both of which allow determination of the identity of the compounds produced. The final product was *ex situ* studied by transmission electron microscopy (TEM) (Jeol FX 2000II) and its identity confirmed by selected-area diffraction. Comparison of this product, by X-ray photoelectron spectroscopy (XPS) (VG Scientific ESCA LAB 1), with that obtained through anodizing was also made.

3. Results, discussion and conclusions

Fig. 1 shows the TG, DTA and differential thermogravimetry (DTG) (or d*m*/d*t*) diagrams for a heating rate of 10 °C min^{-1}. Following initial removal of contamination (2.2% loss of total mass), by baking below 150 °C, four main distinct reactions (3), (4), (5) and (6) (as shown below) are resolved with cumulative mass losses of 35.4%, 40.5%, 51.2% and 56.7%, respectively, at the end of each reaction. The losses are in good agreement with the calculated values for production of Mo_2S_5 (34.4%), MoS_2 (40.3%), MoO_2 (52.3%) and Mo_2O_3 (55.3%), respectively, formed by the following reactions

$$\text{Stage I: } 2(NH_4)_2MoS_4 \xrightarrow{T_1=160\text{–}230\,^\circ C} Mo_2S_5 + 4NH_3\uparrow + 2H_2S\uparrow + S\uparrow \quad (3)$$

$$\text{Stage II: } 2Mo_2S_5 \xrightarrow{T_2=230\text{–}360\,^\circ C} 2MoS_2 + S\uparrow \quad (4)$$

$$\text{Stage III: } MoS_2 + O_2 \xrightarrow{T_3=360\text{–}430\,^\circ C} MoO_2 + 2S\uparrow \quad (5)$$

$$\text{Stage IV: } 4MoO_2 \xrightarrow{T_4=430\text{–}560\,^\circ C} 2Mo_2O_3 + O_2\uparrow \quad (6)$$

The indicated reaction temperature regimes are also suggested on the DTA and DTG diagrams. The DTA diagram reveals that the decomposition of ATT to Mo_2S_5 is typically endothermic, the oxidation of MoS_2 by occasional residual oxygen in the atmosphere to form MoO_2 typically exothermic, and the subsequent decomposition of MoO_2 at higher temperatures to Mo_2O_3, believed to be associated with an unusual reaction due to local oxygen deficiency, again endothermic. Of specific interest here is the formation of MoS_2 at 230–360 °C which is mostly consistent with previous investigations. Its subsequent oxidation could be avoided if argon had been sufficiently dried, or if an appropriate vacuum was used. This suggests that it is safe for MoS_2, as a solid lubricant, to be used under an atmosphere below this temperature regime to avoid oxidation, although minor addition of molybdenum oxides to MoS_2 could sometimes be an advantage [10]. Further examination of this reaction shows that the DTA thermogram in the range 230–360 °C has an exothermic peak, superimposed on a smaller endothermic peak, suggesting that the decomposition of Mo_2S_5 to MoS_2 in the temperature regime at least encompasses an endothermic decomposition to amorphous MoS_2 (only composition change), and a subsequent exothermic amorphous–crystalline transition of MoS_2 (structure modification). It is known that MoS_2 is usually amorphous upon formation [6, 7]. Similar phenomena were observed during the decomposition of MoS_3 to MoS_2 [11] and some workers attributed this abnormal exothermic effect to possible recrystallization of the obtained MoS_2 [12]. Obviously, fully crystallized MoS_2 could be formed after appropriate annealing.

It has been further noticed, from Fig. 1, that the decomposition (3) proceeds over a temperature interval of about 80 °C and the DTG curve for this reaction suggests a number of discontinuous subreactions which proceed very rapidly. In order to reveal more details of these peak blips, further results are obtained in Fig. 2 with a reduced heating rate (2 °C min^{-1}). It is seen that, after demoisturisation, the ATT again underwent a similar four-stage reaction, with the first two being the same as those of Fig. 1; the third was the further decomposition of MoS_2 to Mo_3S_4, and the fourth was the oxidation of Mo_3S_4 to Mo_2O_3

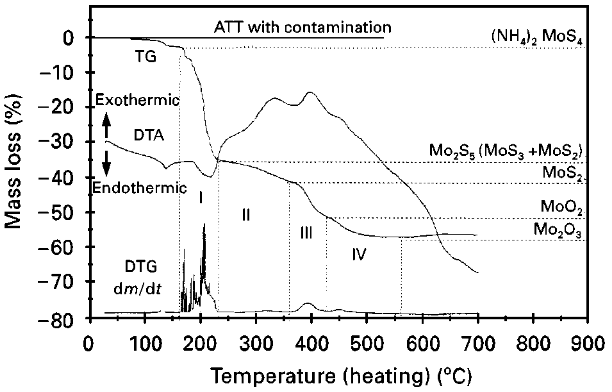

Figure 1 TG, DTA and DTG diagrams for the decomposition of ATT solids at a heating rate of 10 °C min^{-1}. The reaction product at each stage of decomposition is indicated in the figure.

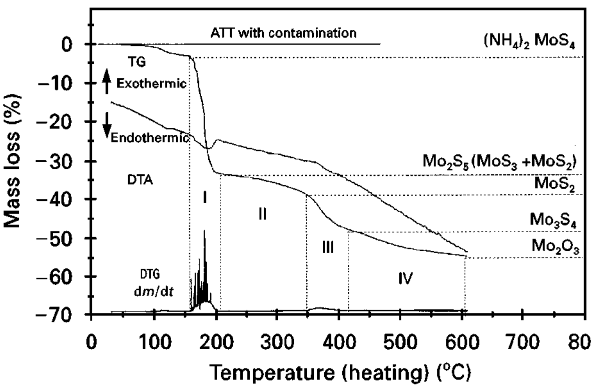

Figure 2 TG, DTA and DTG diagrams for the decomposition of ATT solids at a heating rate of 2 °C min^{-1}. The reaction product at each stage of decomposition is indicated on the figure.

according to the reactions

$$3\mathrm{MoS_2} \xrightarrow{T_5 = 350\text{–}420\,^\circ\mathrm{C}} \mathrm{Mo_3S_4} + 2\mathrm{S}\uparrow \qquad (7)$$

$$2\mathrm{Mo_3S_4} + 9\mathrm{O_2} \xrightarrow{T_6 > 420\,^\circ\mathrm{C}} \mathrm{Mo_2O_3} + 8\mathrm{S}\uparrow \qquad (8)$$

The decrease in the DTA peak intensity is due to enhanced heat dissipation of the sample at reduced heating rates, and hence less information is obtained than previously. Despite the difference of reactions (7) and (8) from reactions (5) and (6), they are regarded as the same in a sense that they are all the eligible occasional subsequent reactions, the occurrence of which almost depends upon the typical quality of the atmosphere (how and to what extent is oxygen involved). Of particular interest again is the reproduction of $\mathrm{MoS_2}$ and $\mathrm{Mo_2S_5}$, although the identity of the latter could be a subject of controversy [1, 13, 14].

The thermograms in Fig. 2 again reveal quite a few peaks in the region of reaction (3) which, on expansion of the relevant temperature range (Fig. 3), tend to fall within two envelopes centred at approximately 173 and 183 °C. The narrow temperature regimes, not quite clear regime boundaries, and small peak intensities are characteristic of these reactions, which leave no clear possibility for the products to be isolated and studied *ex situ*. However, from the diagrams only, three additional reaction stages (i–iii in Fig. 3) could still be determined from the mass loss ratios, accounting for the sequential losses of ammonia from ATT, in barely separated stages, and the loss of hydrogen sulphide to produce, in turn, intermediate products $\mathrm{(NH_4)HMoS_4}$, $\mathrm{H_2MoS_4}$ and $\mathrm{MoS_3}$

$$\text{Stage i: } \mathrm{(NH_4)_2MoS_4} \xrightarrow{t_1 = 160\text{–}173\,^\circ\mathrm{C}} \mathrm{(NH_4)HMoS_4} + \mathrm{NH_3}\uparrow \qquad (9)$$

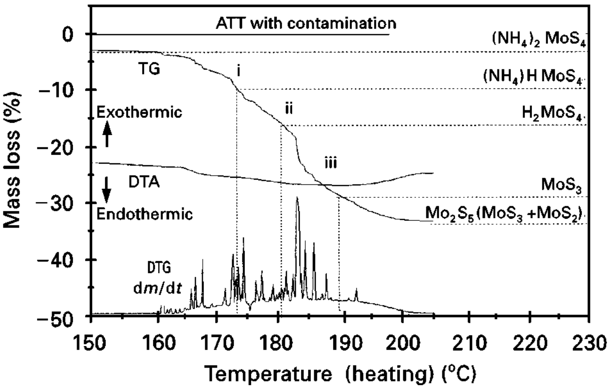

Figure 3 Enlarged plot of Fig. 2, revealing in more detail the decomposition in the range 150–230 °C.

$$\text{Stage ii: } \mathrm{(NH_4)HMoS_4} \xrightarrow{t_2 = 173\text{–}189\,^\circ\mathrm{C}} \mathrm{H_2MoS_4} + \mathrm{NH_3}\uparrow \qquad (10)$$

$$\text{Stage iii: } \mathrm{H_2MoS_4} \xrightarrow{t_3 = 180\text{–}190\,^\circ\mathrm{C}} \mathrm{MoS_3} + \mathrm{H_2S}\uparrow \qquad (11)$$

These reactions explain the persistent presence of those minor peaks on the DTA diagrams. Each of the above reactions are specific and separate, in theory, to their temperature regimes indicated, but in practice they turn out to be more like a single reaction, like the previously reported reaction (1), because of difficulties in the precise control of temperature within a very limited regime. That is probably why these intermediate reactions, although they might be of little significance in practice, have never been reported before. The blipping of peaks of these reactions could be accounted for by a number of microscopic transient events which possibly involve cracking of the solid phases, leading to bursts of reactivity.

Reactions (9–11) also confirm the possibility of preparation of $\mathrm{MoS_3}$ from ATT but show that this is not a direct process. Further, the decomposition of $\mathrm{MoS_3}$ to $\mathrm{MoS_2}$ is also rather an indirect process, containing the following intermediate process

$$2\mathrm{MoS_3} \xrightarrow{t_4 = 190\text{–}220\,^\circ\mathrm{C}} \mathrm{Mo_2S_5} + \mathrm{S}\uparrow \qquad (12)$$

The full sequence of decomposition processes studied above is summarized in Fig. 4. The formation of $\mathrm{MoS_3}$ and $\mathrm{MoS_2}$ from ATT is confirmed. Those reactions following formation of $\mathrm{MoS_2}$ are not considered further, because of their irrelevance to the present study; they appear to be occasional results affected by experimental conditions, such as argon drying. Our results show that decompositions of ATT to $\mathrm{MoS_3}$ is not a direct process, different from previous findings [11]. Instead, intermediate products, namely $\mathrm{(NH_4)HMoS_4}$ and $\mathrm{H_2MoS_4}$, are produced which have not been reported before. However, $\mathrm{H_2MoS_4}$ as a compound has been recognized and a similar decomposition of $\mathrm{H_2WS_4}$ to $\mathrm{WS_3}$ and $\mathrm{H_2S}$ is known [15]. This might be supportive to our findings. Furthermore, we find that the decomposition of $\mathrm{MoS_3}$ to $\mathrm{MoS_2}$ also has an intermediate compound, $\mathrm{Mo_2S_5}$. The reason that decomposition reactions of ATT can be used to produce molybdenum sulphides is considered to be associated with the inherent structural similarities of ATT and the solid decomposition products, which assist and direct the decomposition stage

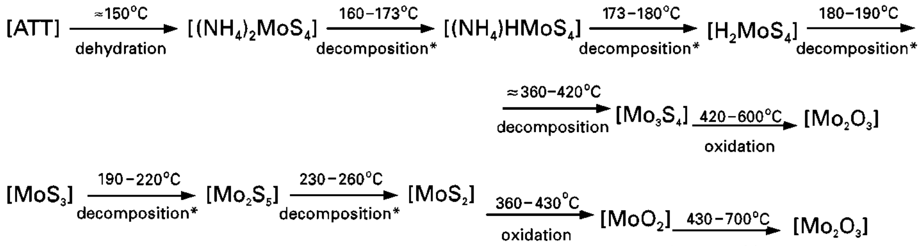

Figure 4 Decomposition sequences of ATT solids.

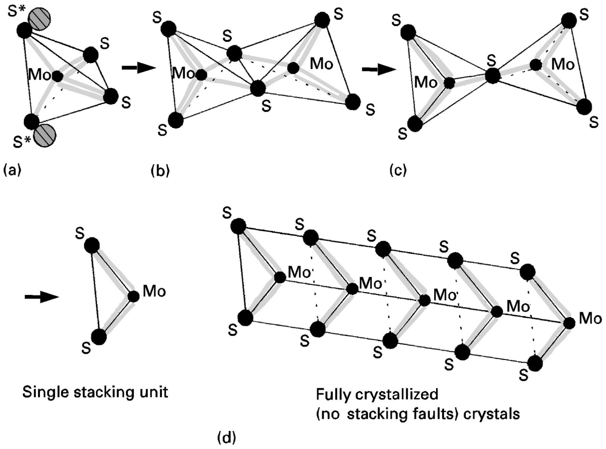

Figure 5 Models revealing structural similarities of (a) $(NH_4)_2MoS_4$ ($S^* = SNH_4$), (b) MoS_3, (c) Mo_2S_5 and (d) MoS_2. The development of these compounds from $(NH_4)_2MoS_4$ is believed to stem from their inherent structural similarities.

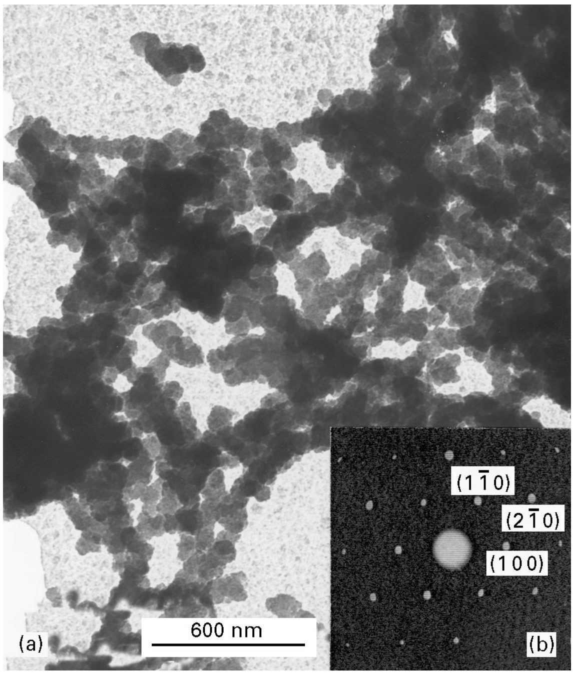

Figure 6 (a) Bright-field transmission electron image of Mos$_2$ crystals; (b) the [0 0 1] zone axis reflection pattern of crystals shown in (a). See text for details.

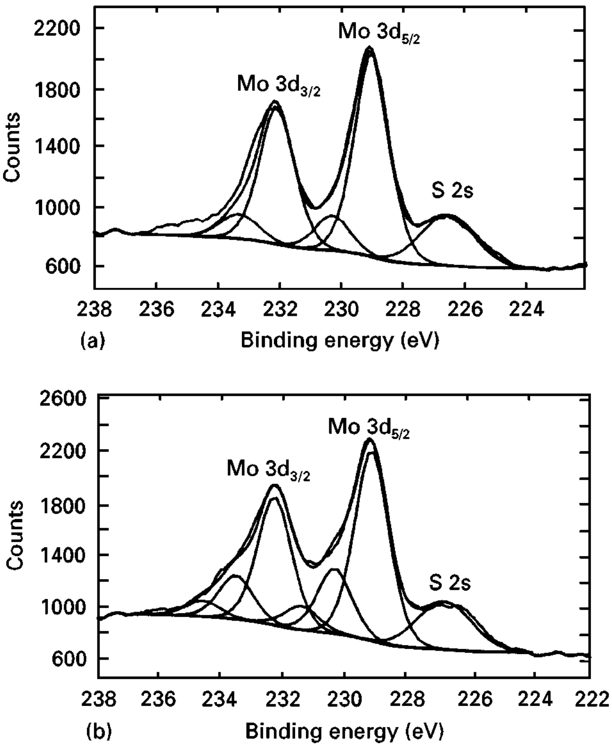

Figure 7 High resolution X-ray photoelectron spectra for Mo 3d orbital doublets of (a) MoS_2 prepared by thermal decomposition of $(NH_4)_2MoS_4$ at 450 °C in a vacuum of 1.33×10^{-6} Pa and (b) MoS_2 prepared by vacuum annealing (450 °C; 1.33×10^{-6} Pa) of MoS_2 precursors formed by anodizing [19]. The S 2s peak at 226.7 eV and the Mo $3d_{5/2}$(229.1 eV) and $3d_{3/2}$ (232.3 eV) doublet are all consistent, in terms of their peak shift values from zero-valence states, doublet peak relative intensity ratios and peak separation energies, with that of MoS_2 [20–22]. Other minor peaks are from residual MoS_3 or Mo_2S_5 [19].

by stage, with a minimum free-energy change of the reactant–product system, to the products of each stage. The tetrathiomolybdate anion has a tetrahedral molecular structure [16, 17], as shown in Fig. 5a, the MoS_2 has a well-known layered triangular molecular structure [6] (Fig. 5d) and the structures of MoS_3 and Mo_2S_5 are illustrated in Fig. 5b and c, respectively. It could be recognized that the layered triangular structure of MoS_2 (Fig. 5d) is inherently a partial remnant of Mo_2S_5 (Fig. 5c), MoS_3 (Fig. 5b) and $(NH_4)_2MoS_4$ (Fig. 5a). This is similar to the case for Mo_2S_5 when compared with MoS_3 and $(NH_4)_2MoS_4$, and for MoS_3 when compared with $(NH_4)_2MoS_4$. We propose that the well-established ways for the formation of MoS_2 from $(NH_4)_2MoS_4$, including that used in this study, and the occurrence of a number of intermediate compounds found in this study, are a direct consequence of the above structural similarities, through which a natural progression of structural and compositional changes of $(NH_4)_2MoS_4$ are guaranteed, resulting in the sequential development of $(NH_4)HMoS_4$, H_2MoS_4, MoS_3, Mo_2S_5 and MoS_2. It should be emphasized that the present study is directly relevant to the preparation of the MoS_2 solid lubricant through the solid-state decomposition of ATT during heating under the protection of inert gases (argon in this case). The above findings and suggestions should assist in the mechanistic understanding of such a decomposition process by revealing a number of intermediate sequential subevents and by demonstrating the inherent structural similarities of the various products of decomposition. The MoS_2, as formed in the present experiment, could provide certain lubricity, and further improved lubrication properties could be expected by modifying it into a fully crystallized form, by annealing under better-quality atmospheric protection, such as a sufficiently high vacuum. Fig. 6a shows, by transmission electron microscopy, an example of the morphology of the MoS_2, synthesized by a similar thermal process (annealed for 5 h at 450 °C in a vacuum of 10^{-6} torr). The lubricant particles developed are roughly 100–200 nm in size. The crystallinity is confirmed by selected-area diffraction of these particles, as revealed in Fig. 6b. The involvement of oxygen in reactions at temperatures higher than about 350 °C, shown in Figs 1 and 2, is prevented in this case, evidently by the higher-quality protection of the vacuum used. The crystal is found to be hexagonal 3H type in structure. The MoS_2 formed in this study is of direct reference for other techniques for preparing solid lubricants, such as anodizing [18], although the processes by which the lubricants formed (i.e. from solutions) are usually amorphous MoS_2 precursors rather than crystalline MoS_2. However, the XPS studies of the product of Fig. 6, shown in Fig. 7a, are the same as the MoS_2 precursors with the same heat treatment, as shown in Fig. 7b. This encourages investigation into the formation of solid lubricants by anodizing which can produce composite self-lubricating films of anodic oxides and solid lubricants and can be an advantage in many cases [19].

Acknowledgements

The authors wish to thank the Engineering and Physical Science Research Council for financial support and an award of a postdoctoral research associateship to H.W.W. Special thanks are due to M. Tout, S. Cadogan and Professor F. R. Sale, Manchester Materials Science Centre, for their technical assistance with the calorimetric experiments.

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Received 9 May 1997
and accepted 18 March 1998