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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

IV. LUBRICATION PROPERTIES OF THE GRAPHITIC CHALCOGENIDES

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By F. K. McTaggart* and A. Moore†

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Summary

The majority of the chalcogenides of Ti, Zr, Hf, and Th having layer lattice structures and/or graphitic nature were tested for possible lubricating properties. Although none of these materials adheres to the common metals, it was shown that the shearing forces necessary to cause sliding between layers are in general low and comparable to those involved in molybdenum disulphide and graphite.

I. Introduction

The good lubricating properties of graphite and molybdenum disulphide, which are layer lattice-type materials, have been known for some time. Peterson and Johnson (1954) measured the frictional properties of a number of other substances and found that the layer lattice compounds $CdCl_2$, CdI_2, $CoCl_2$, $CuBr_2$, PbI_2, and WS_2 give low coefficients of friction when placed between sliding steel surfaces. These compounds also appear to form films on the metal surfaces. However, none was as effective as MoS_2, although WS_2 seemed to merit further investigation as a lubricant. The present paper describes the frictional properties of some of the graphitic compounds found among the chalcogenides of titanium, zirconium, hafnium, and thorium.

II. Materials

The preparation and structures of the titanium, zirconium, and hafnium chalcogenides used in this work have been described by McTaggart and Wadsley (1958). The thorium compounds have recently been prepared and examined (McTaggart, unpublished data). Of the chalcogenides prepared by these authors, those presented in Table 1, when rubbed between the fingers, produced a smooth lustrous texture similar to that produced by graphite and MoS_2. Those marked with an asterisk were chosen for investigation. For comparison a high-grade commercial molybdenum disulphide of fine particle size and a commercial graphite were used.

Comparison of the electronmicrographs (Plates 1 and 2) of the compounds chosen for investigation shows clearly how the trichalcogenides rub out to thin

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ribbonlike particles. This ribbonlike structure appears to persist in one or two of the di-compounds, for example, $ZrSe_2$, probably due to the fact that the latter were all made by thermal degradation from the corresponding tri-compounds. The graphitic structure typical of the dichalcogenides is shown in TiS_2, $TiSe_2$, $TiTe_2$, and $ZrTe_2$.

TABLE 1

GRAPHITIC CHALCOGENIDES

Chalcogenide	Titanium	Zirconium	Hafnium	Thorium
Sulphides	TiS_3* TiS_2*	ZrS_3* ZrS_2	HfS_3 HfS_2	
Selenides	$TiSe_2$*	$ZrSe_3$* $ZrSe_2$*	$HfSe_3$ $HfSe_2$	
Tellurides	$TiTe_2$*	$ZrTe_3$* $ZrTe_2$		$ThTe_{2\cdot5}$

III. EXPERIMENTAL PROCEDURE AND RESULTS

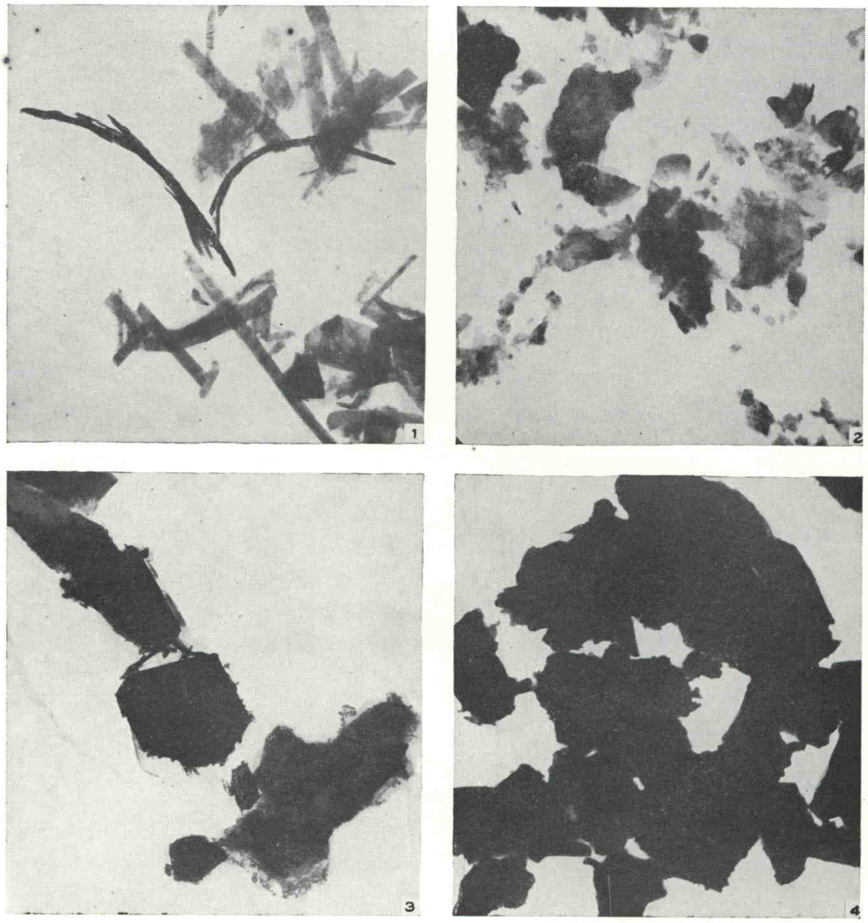
The friction apparatus which was similar to that described by Bowden and Leben (1939) consisted of a ¼ in. diameter steel hemisphere DPH 258 sliding over a flat steel surface DPH 145 under a load of 4 kg and at a speed of about 0·1 mm/sec. The steel surfaces were cleaned by abrading on wet carborundum paper, washing in hot water, and allowing the water film to evaporate.

Initial tests were made with up to 10 per cent. solid lubricant (MoS_2, TiS_3, TiS_2, etc.) suspended in pure paraffin oil. Under such conditions it was almost impossible in one passage of the slider to establish a layer of the solid lubricant on the metal and the frictional behaviour resembled closely that of pure paraffin by itself. Attention was then turned to establishing tracks of solid materials by dry rubbing ; molybdenum disulphide adhered readily and formed a smooth track after 30 to 40 passes of the plate beneath the hemispherical slider, usually carried out under increasing loads up to a maximum of 4 kg. The coefficient of friction was then about 0·04. When the sulphides, selenides, and tellurides of titanium and zirconium were used in the same way it was found impossible to establish a track. These materials would not adhere to the metal plate and were simply pushed out of the way of the slider. The coefficient of friction was about 0·5.

In order to ensure that sliding between the solid lubricant and the steel should take place, the steel slider was replaced by a compact of the lubricant pressed at 80,000 lb/in². Before sliding, it was lightly ground on fine emery paper. The coefficient of friction for graphite was 0·16, for MoS_2 0·2, and for the other materials between 0·30 and 0·54 (see Table 2). Finally, the sliding of the solid lubricant on itself was investigated by using a flat compact of the lubricant as the lower surface. The compact surfaces were rubbed lightly with fine emery paper before use. Under these conditions MoS_2 showed approximately

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM CHALCOGENIDES. IV

Electronmicrographs (×10,000) of graphitic chalcogenides: 1, ZrS_3; 2, $ZrSe_3$; 3, $ZrSe_2$; 4, $ZrTe_3$.



Electronmicrographs (× 10,000) of graphitic chalcogenides : 1, TiS_3 ; 2, TiS_2 ; 3, $TiSe_2$; 4, $TiTe_2$.

the same coefficient of friction as many of the other chalcogenides, namely, *c.* 0·20 to 0·25; graphite gave a lower value, namely, 0·08 to 0·09; and the telluride values were higher (Table 2).

The value for MoS_2 confirms a previous measurement of $\mu=0\cdot20$ to $0\cdot22$ by Feng (1952) for the sliding of a thick layer of this material.

The chalcogenides under investigation were found not to adhere well to copper, brass, stainless steel, silver, titanium, or zirconium.

TABLE 2

COEFFICIENTS OF FRICTION

Lubricant Material	Coefficient of Friction (μ)		Lubricant Material	Coefficient of Friction (μ)	
	Compact of Lubricant on Steel	Compact of Lubricant on Compact of Lubricant		Compact of Lubricant on Steel	Compact of Lubricant on Compact of Lubricant
MoS_2	0·2	0·22	ZrS_3	0·42	0·25
Graphite ..	0·16	0·08–0·09	$ZrSe_3$	0·46	0·25
TiS_3	0·34	0·24	$ZrSe_2$	0·35	0·22
TiS_2	0·31	0·26	$ZrTe_3$	0·54	0·45
$TiSe_2$	0·30	0·21			
$TiTe_2$	0·40	0·37			

IV. DISCUSSION

It is now well established (see, for example, Bowden and Tabor 1950) that the frictional force is dependent on the area of real contact between the sliding surfaces and the shear strength of the junctions found at those points of contact. It has been shown that the combination of low shear strength and small area of real contact, which is obtained with a thin, low-strength film on a hard substrate, will give very low values of the coefficient of friction. This principle, which is applied in the use of thin soft metal films in bearing metals and other bearing surfaces, is also of interest in the use of solid lubricants. Thus MoS_2 will give a low value of friction when present as a thin film between steel surfaces because (i) it adheres to the metal strongly, replacing metal-metal junctions by sulphide-sulphide junctions of approximately equal area, and (ii) in the direction perpendicular to the planes of the crystal layers the bonding is weak and hence low shearing forces will cause movement. However, when sliding as a solid substance on itself the deformation of the relatively soft MoS_2 compacts results in a large area of contact and hence an increase in the coefficient of friction.

The fact that the other chalcogenides tested, except the tellurides, yield coefficients of friction of much the same magnitude as MoS_2, when sliding on themselves, would indicate that bond strengths of similar magnitude exist between their crystal planes. Hence they may be regarded as potential lubricants. They fail, however, to satisfy the second condition for practical lubrication, namely, the ability to adhere to metal surfaces and so provide junctions other than metal-metal ones.

It is not clear why MoS_2 bonds to metals so readily while such similar compounds as TiS_2 etc. do not. The phenomenon may be related to the adsorption of water vapour. Thus Savage (1948) has shown that graphite loses its lubricating properties in a very dry atmosphere; on the other hand, Peterson and Johnson (1953) demonstrated that MoS_2 is not always effective in humid conditions. It is possible that some of the materials reviewed here may become effective lubricants over certain ranges of water vapour concentration, or by chemical or other modification. If that occurred, some of them offer advantages over MoS_2 for ease of production and grinding.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

BOWDEN, F. P., and LEBEN, L. (1939).—*Proc. Roy. Soc.* A **169**: 371.

BOWDEN, F. P., and TABOR, D. (1950).—"The Friction and Lubrication of Solids." (Oxford Univ. Press.)

FENG, I. MING (1952).—*Lubric. Engng.* **8**: 285.

MCTAGGART, F. K., and WADSLEY, A. D. (1958).—*Aust. J. Chem.* **11**: 445.

PETERSON, M. B., and JOHNSON, R. L. (1953).—Tech. Notes Nat. Adv. Comm. Aero. Wash. No. 3055.

PETERSON, M. B., and JOHNSON, R. L. (1954).—Tech. Notes Nat. Adv. Comm. Aero. Wash. No. 3334.

SAVAGE, R. H. (1948).—*J. Appl. Phys.* **19**: 1.

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