The chalcogenides (sulfides and selenides) of molybdenum (particularly MoS$_2$) and also of tungsten, niobium, and tantalum combine useful antifriction and electrical properties with high radiation resistance—a feature which has attracted the attention of many investigators [1, 2]. Some of these compounds are already widely used as solid lubricants, especially for operation in a vacuum, at high temperatures, and in cryogenic engineering. The chalcogenides of W and Mo, which are semiconductors, find their application as thermoelements. Some Nb and Ta chalcogenides possessing metallic conductivity are beginning to be employed as additions to sliding contact materials [3, 4].

In the future, we may expect these substances to be used much more extensively. However, the reactions of such chalcogenides with metals have received little study, although information on this subject is of vital importance in the development of sintered composites containing these compounds. The reason for this is that many physical properties, especially the antifriction characteristics, of the chalcogenides are associated with their lamellar structure, and can be retained only if this starting structure remains unchanged during the heat treatment of a composite material. Apart from this, a knowledge of the interaction between these chalcogenides and metals is required for the evaluation of the tribochemical reactions which may occur on friction surfaces between these compounds and metallic mating parts.

The results are presented in this article of an x-ray diffraction investigation of the reactions of MoS$_2$, WS$_2$, WSe$_2$, NbSe$_2$, TaSe$_2$, and TaS$_2$ with copper, silver, nickel, and cobalt. The raw materials employed were a molybdenite to TU-35MU No. 8092-65 Technical Specification (99.76% MoS$_2$); tungsten and tantalum disulfides prepared at the Institute of Materials Science, Academy of Sciences of the Ukrainian SSR, by reacting WO$_3$ and tantalum powder with hydrogen sulfide [5]; and tungsten, niobium, and tantalum diselenides produced by the capsule synthesis technique at the Moscow Institute of Steel and Alloys. The MoS$_2$, WS$_2$, and WSe$_2$ had a 2H-MoS$_2$ type structure [6], the NbSe$_2$, a 2H-NbS$_2$ type structure, the TaSe$_2$, a 4H-TaS$_2$ type structure, and the TaS$_2$ a 1H-TaS$_2$ type structure [7, 8]. The particle size of these compounds was 50–100 μ.

The chalcogenides, taken in the amount of 20 wt. %, were mixed with Cu, Ni, Ag, and Co powders and compacted under a pressure of 5 tons/cm$^2$ into 10-mm-diameter tablets, which were then held successively at temperatures of 500, 600, 700, 750, 800, 850, 900, 950, and 1000° C for 1 h. The heating was performed in an MPV–3 vacuum furnace. The residual pressure in the heated furnace was $10^{-4}$–$2\cdot10^{-5}$ mm Hg. After each heating period, the tablets were subjected to x-ray structural phase analysis in a URS–50I apparatus. Photographs were obtained in the filtered radiation of a cobalt anticathode. It was established that, with the exception of the compounds MoS$_2$ and WS$_2$ with silver, whose structure is preserved right up to the melting point of silver, all the chalcogenides investigated react with these metals.

In all the chalcogenides studied except TaS$_2$, the sulfur or selenium atoms are disposed on the points of trigonal prisms (trigonal coordination). In TaS$_2$, the sulfur atoms occupy the points of octahedra (octahedral coordination) [7, 8]; MoS$_2$, WS$_2$, and WSe$_2$ are semiconductors, while NbSe$_2$, TaSe$_2$ and TaS$_2$ possess...
metallic conductivity [2]. Our experimental data have shown that these structural and physical characteristics of the chalcogenides determine the character of their reaction with the metals.

None of the compounds with semiconducting properties and the 2H-MoS$_2$ structure forms solid solutions with the metals. Molybdenum disulfide does not react with copper up to 750°C, with nickel up to 600°C, and with cobalt up to 800°C; the corresponding temperature limits are 800, 600, and 900°C for WS$_2$ and 600, 500, and 700°C for WSe$_2$. Tungsten diselenide does not react with silver up to 700°C, while MoSe$_2$ and WS$_2$ do not react with silver, as already mentioned above, right up to the melting point of this metal. When the temperatures shown above are exceeded, reactions take place between the metals and chalcogenides, resulting in the formation of ternary compounds having neither a lamellar structure nor antifriction properties. The products yielded by the reaction of copper with MoS$_2$ were studied in greater detail. It was found that the reaction produces a compound containing about 22 wt.% S, 33 wt.% Mo, and 45 wt.% Cu, which has a spinel-type cubic lattice with the parameter $a = 19.48 \pm 0.01 \text{ Å}$. As a result of the reactions of WS$_2$ and WSe$_2$ with copper at temperatures above 850 and 700°C, respectively, metallic tungsten is precipitated.

Niobium diselenide and TaSe$_2$, which also have the trigonal coordination of their selenium atoms but slightly different structures [8, 7] and metallic conductivity, form solid solutions with all the metals investigated. The dissolution of a metal in the diselenide lattice generally begins at temperatures of 500°C or lower. As a result of the dissolution of copper in NbSe$_2$, the lattice parameter $c$ substantially increases, from $12.552 \pm 0.004$ to $13.700 \pm 0.01 \text{ Å}$; the parameter $a$ also increases, although less appreciably: from $3.444 \pm 0.001$ to $3.480 \pm 0.005 \text{ Å}$. A solid solution of copper in NbSe$_2$ is stable at least up to a temperature of 1000°C.

The reactions of NbSe$_2$ with Co and Ni at temperatures of 600°C and higher lead to the formation of solid solutions of Co and Ni in NbSe$_2$; as a result, the lattice parameters $c$ slightly decrease (to $12.36 \pm 0.01$ and $12.40 \pm 0.01 \text{ Å}$, respectively), while the parameters $a$ remain almost unchanged ($3.450 \pm 0.005$ and $3.460 \pm 0.005 \text{ Å}$ respectively). At temperatures above 750 and 700°C, respectively, the lamellar structures in these composites disappear.

Silver dissolves in NbSe$_2$ even at room temperature. Solutions of Ag in NbSe$_2$ are stable up to 700°C, but their structure, while remaining lamellar, changes considerably compared with the original NbSe$_2$, the 2H-NbS$_2$ type becoming transformed into the 6H-TaS$_2$ type with the parameters $a = 3.470 \pm 0.005$ and $c = 42.5 \pm 0.1 \text{ Å}$. This structure [7] contains elements of both the trigonal and octahedral coordinations. Some x-ray diffraction pictures exhibit reflections due to the 1H-TaS$_2$ type structure with the octahedral coordination. After holding at temperatures in excess of 700°C, the lamellar structures in these composites disappear.

Tantalum diselenide also dissolves all the metals investigated, but the dissolution begins at higher temperatures than in the case of NbSe$_2$. As a result of the dissolution of copper in TaSe$_2$, the parameter $a$ increases from $3.380 \pm 0.005 \text{ Å}$ after holding at 500°C to $3.475 \pm 0.005 \text{ Å}$ after holding at 850°C (for pure TaSe$_2$, $a = 3.434 \pm 0.001 \text{ Å}$). The parameter $c$ also increases, from $27.04 \pm 0.02$ to $27.80 \pm 0.02 \text{ Å}$ (for the starting TaSe$_2$, $c = 25.51 \pm 0.004 \text{ Å}$). After heating to temperatures above 850°C, the lamellar structures are no longer observed. During the dissolution of nickel, the constant $c$ decreases to $24.70 \pm 0.002 \text{ Å}$, while the constant $a$ increases to $3.57 \pm 0.005 \text{ Å}$ (after treatment at 600°C). At higher temperatures, the lamellar structure in this composite material disappears. The dissolution of Co in TaSe$_2$ reduces the constant $c$ to $24.96 \pm 0.02 \text{ Å}$ (850°C), but does not affect the constant $a$. At temperatures in excess of 850°C, this composite loses its lamellar structure.

Tantalum disulfide possesses metallic conductivity, but nevertheless differs substantially from NbSe$_2$ and TaSe$_2$ in structure. Its structure is characterized by the octahedral coordination of sulfur atoms. This characteristic appears to affect its ability to dissolve metals. Silver, nickel, and cobalt are insoluble in TaS$_2$, which is preserved in contact with these metals up to temperatures of 700, 500, and 600°C, respectively. Copper begins to dissolve in TaSe$_2$ at temperatures below 500°C. The resulting solid solution has the parameters $c = 13.20 \pm 0.01$ and $a = 3.350 \pm 0.005 \text{ Å}$. Under these conditions, the structure of TaS$_2$ becomes transformed from the 1H-TaS$_2$ type with the octahedral coordination of atoms into the 2H-TaS$_2$ type with the trigonal coordination. In all probability, it is this transformation that is responsible for the dissolution of the metal. The Cu-TaS$_2$ solid solution is stable at least up to 1000°C.

*Analysis of this structure was performed by S. K. Maksimov.