Climax Molybdenum
A Freeport-McMoRan Company

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PROPERTIES OF MOLYBDENUM DISULFIDE

MoS_2 (Molybdenite)

T. J. Risdon

The primary commercial source of molybdenum disulfide, as well as other molybdenum products is molybdenite, the mineral designation for MoS_2. Molybdenite is found in many parts of the world, but much of the world's supply originates in the Americas, either in primary deposits or as co-deposits with copper bearing minerals. The primary ores typically contain about 0.25% MoS_2, whereas in co-deposits, the MoS_2 content is <0.05%. The MoS_2 is recovered from the ore and purified by physical methods to a level of 99% for lubricant applications. In addition to its natural occurrence, MoS_2 can be prepared synthetically by several routes including direct union of the elements in pure nitrogen at 800 C,[1] thermal decomposition of ammonium tetrathiomolybdate or molybdenum trisulfide,[2] and by reaction of MoO_3 with H_2S or H_2S/H_2 mixtures at 500 C.[3] These preparative techniques result in hexagonal crystalline MoS_2, by far the most common form, but the rhombohedral form has been found in nature,[4] and prepared synthetically.[2] Natural and synthetic MoS_2 of both crystalline types possess lubricant properties, but the natural hexagonal material is preferred when cost and overall performance are considered. The properties of MoS_2 described in this bulletin are for hexagonal (2H) MoS_2 either naturally occurring or synthetically produced.

CRYSTAL STRUCTURE

Molybdenum disulfide exists in two crystalline forms, hexagonal and rhombohedral. The hexagonal form is by far the most common, being the only type found in commercial ores, but the rhombohedral form has also been found to occur in nature.

The hexagonal form is characterized by MoS_2 layers in which the Mo atoms have trigonal prismatic coordination of six sulfur atoms, with two molecules per unit cell. The crystal structure consists of "sandwiches" in which one planar hexagonal layer of molybdenum atoms is interspersed between two layers of sulfur atoms as shown in Figure 1.[5,6] Within the crystal, each S atom is equidistant from three Mo atoms and each Mo atom is surrounded by six equidistant S atoms at the corners of a trigonal prism with altitude and edge dimensions of 3.17 Å and 3.15 Å respectively, and a Mo to S spacing of 2.41 Å as shown in Figure 2.

The rhombohedral modification of MoS_2 also has trigonal prismatic coordination and differs from the hexagonal form only in the method of stacking. There are three molecules per unit cell. A schematic comparison of the hexagonal and rhombohedral modifications of MoS_2 is shown in Figure 3.

Molybdenum disulfide is classified as a transition

metal dichalcogenide (TMD) which includes the disulfides, diselenides and ditellurides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. These compounds exist in various crystalline forms but only the Mo and W compounds form the MoS_2 hexagonal type crystal structure.[7] Thus the excellent lubricant properties of MoS_2 are attributable to the large spacing (and weak Van der Waals bonding) between S-Mo-S sandwich layers. In supporting this statement, Jamison[6] has postulated that differences in lubricating behavior among the TMD compounds are attributable to the distribution of electrons on the constituent atoms. In MoS_2, there are six non-bonding electrons which can completely fill a band which physically confines the electrons within the crystal structure. This creates a net positive charge on the surface of the S-Mo-S sandwich layers which promotes easy shear through electrostatic repulsion. Gardos states that the ability of TMD particles to serve as building blocks of low shear strength surface layers is manifested by two