

X-ray photoelectron spectroscopic study of a pristine millerite (NiS) surface and the effect of air and water oxidation

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ABSTRACT

Millerite, NiS, fractured under high vacuum and reacted with air and water has been analyzed by X-ray photoelectron spectroscopy (XPS). The pristine millerite surface gives rise to photoelectron peaks at binding energies of 853.1 eV (Ni 2p_{3/2}) and 161.7 eV (S 2p), thus resolving ambiguities concerning binding energies quoted in the literature. Air-reacted samples show the presence of NiSO₄ and Ni(OH)₂ species. There is evidence for polysulfide species (S_n²⁻, where 2 ≤ n ≤ 8) on air-oxidized surfaces. These may occur in a sub-surface layer or may be intermixed with the Ni(OH)₂ in the oxidized layer. The NiSO₄ species at the millerite surface occur as discrete crystallites whereas the Ni(OH)₂ forms a thin veneer covering the entire millerite surface. The NiSO₄ crystallites form on the surface of millerite but not on surfaces of adjacent minerals. Surface diffusion of Ni²⁺ and SO₄²⁻ across the millerite surface is thought to be responsible for the transport and subsequent growth of NiSO₄ crystallites developed on millerite surfaces. Although it is clear that Ni and SO₄²⁻ does not diffuse onto surfaces of adjacent minerals in sufficient quantity to form crystallites, the explanation is uncertain. XPS results for water-reacted surfaces show little difference from the vacuum fractured surfaces with the exception that minor amounts of polysulfide and hydroxy nickel species are present. Similar reaction products to those formed in air [NiSO₄ and Ni(OH)₂] are believed to be produced, but these are removed from the millerite surface by dissolution, leaving behind a sulfur-enriched surface (polysulfide) and hydroxyl groups chemisorbed to nickel ions at the millerite surface.