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A kinetic study of the exsolution of pentlandite $(Ni,Fe)_9S_8$ from the monosulfide solid solution (Fe,Ni)S

BARBARA ETSCHMANN,[1] ALLAN PRING,[1,2,3,*] ANDREW PUTNIS,[4] BENJAMIN A. GRGURIC,[5] AND ANDREW STUDER[6]

[1]Mineralogy Department, South Australian Museum, North Terrace, Adelaide, South Australia. 5000, Australia
[2]Department of Geology and Geophysics, University of Adelaide, North Terrace, Adelaide, South Australia 5005, Australia
[3]School of Chemistry, Physics and Earth Sciences, The Flinders University of South Australia, GPO Box 2100 Adelaide, South Australia 5001, Australia
[4]Institut für Mineralogie, Universität Münster, Corrensstrasse 24, D-48149 Münster, Germany
[5]Geology and Resource Evaluation Department, WMC Resources Ltd., Mount Keith Operation, P.O. Box 238, Welshpool Delivery Centre, W.A. 6986, Australia
[6]Physics Division, ANSTO, PMB 1 Menai, NSW 2234, Australia

ABSTRACT

The kinetics of the exsolution of pentlandite from the monosulfide solid solution (mss) have been investigated using a series of anneal/quench and in situ cooling neutron diffraction experiments. Five mss compositions were examined by anneal/quench techniques covering the composition range $Fe_{0.9}Ni_{0.1}S$ to $Fe_{0.65}Ni_{0.35}S$ and using annealing temperatures between 423 and 773 K for periods from 1 h to 5 months. In situ cooling experiments were performed on four mss compositions in the range $Fe_{0.9}Ni_{0.1}S$ to $Fe_{0.7}Ni_{0.3}S$. The samples of these solid solutions were heated to 973 K, and then cooled to 373 K in steps of 50 K over a 24 h period. The extent of exsolution was monitored by Rietveld phase analysis using powder neutron diffraction data. The anneal/quench experiments established that initial exsolution of pentlandite from mss above 573 K is very rapid and is effectively complete within 1 h of annealing. However, the mss/pyrrhotite compositions remained Ni rich (17 at% Ni) after 5 months annealing, indicating that compositional readjustment at low-temperatures occurs over long periods. Below 573 K, exsolution is less rapid with rate constants in the range 6×10^{-6} to 1×10^{-5}/s and the activation energy for exsolution of pentlandite from mss $Fe_{0.8}Ni_{0.2}S$ between 473 and 423 K is 5 kJ/mol.

The in situ cooling experiments showed that the temperature at which exsolution commences upon cooling decreases from 873 K for $Fe_{0.7}Ni_{0.3}S$ to 823 K for $Fe_{0.9}Ni_{0.1}S$ and that exsolution effectively ceased on the time scale of the experiments at temperatures between 598 and 548 K. The kinetic data were analyzed using the Avrami model where $y = 1 - \exp(-k^n t^n)$ and the initial rates of exsolution were found to increase with Ni content from 2×10^{-6}/s for $Fe_{0.9}Ni_{0.1}S$ to 4×10^{-5}/s for $Fe_{0.7}Ni_{0.3}S$. Both high Ni content and high M:S ratio served to facilitate nucleation rate, indicating that nucleation occurs at S vacancies within mss crystals rather than at grain boundaries. Values of the Avrami geometric constant n vary during exsolution upon cooling indicating three possible changes in the growth mechanism during the reaction. The roles of impurities and S fugacity on reaction rates are discussed. The rate constants for exsolution of pentlandite from mss/pyrrhotite in nature are estimated to be 4 or 5 orders of magnitude slower than those reported here, still very rapid on a geological time scale. High metal mobility persists in this system at low temperatures, even at room temperature, and the textures and compositions observed in nature are a consequence of very low-temperature (<100 °C) equilibration of assemblages over geological time scales.