



Kinetic studies of some solid-state reactions of metal sulfides

by

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**A dissertation submitted for the degree of Doctor of Philosophy
at the**

University of Adelaide

Adelaide

Australia

August 2005

From the Author



I think I had a brilliant idea for the “Preface” but I forget what it was. Thoughts flashed through my mind and just vanished. Perhaps I am overwhelmed at the thought of finishing my thesis or by the thought that my "student-hood" is becoming history and my life is about to enter a new phase. As I am leaving the University of Adelaide after 2 years and 6 months study as a PhD student, my mind is filled with fond memories of the people that work with and the experiences that gave me the courage to seek an academic career. My heart holds all these experiences as treasures.

I count myself lucky to have been a member of the University Adelaide. The University has given me a unique opportunity to explore the "unknown world" and my journey of exploration continues.

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August 2005

THESIS BY PUBLICATIONS

This doctoral thesis is submitted as a portfolio of peer-reviewed publications according to the 'PhD Rules & Specifications for Thesis' of the University of Adelaide. The journals in which these papers were published or accepted are closely related to the research field of this work. The citation information is listed and the journals are ranked in the order of impact factor in reference to their scientific significance (*Journal Citation Report 2004*, Thomson ISI).

Journal Title	Impact factor	Total Cites	Immediacy Index *	Cited Half-life **
<i>Geochim. Cosmochim. Acta</i>	3.811	26862	0.68	> 10.0
<i>Am. Mineral.</i>	1.785	8845	0.438	>10.0
<i>Thermochim. Acta</i>	1.161	6048	0.234	8.1

* Immediacy Index measures the average number of times that an article, published in a specific year within a specific journal, is cited over the course of the same year; ** Cited Half-life measures the number of years, going back from the current year, that account for half the total citations received by the cited journal in the current year.

The thesis is based on the following papers.

1. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) A low-temperature kinetic study of the exsolution of pentlandite from the monosulfide solid solution using a Refined Avrami method, *Geochim. Cosmochim. Acta*, **69**, 415-425.
2. Wang H., Pring A., Xie, Y., Ngothai Y., O'Neill B. (2005) Phase evolution and kinetics of the oxidation of monosulfide solid solution under isothermal conditions, *Thermochim. Acta*, **427**, 13-25.
3. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) The kinetics of the $\alpha \rightarrow \beta$ transition in synthetic nickel monosulfide, *Am. Mineral.*, (accepted).
4. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) The mechanism and kinetics of α -NiS oxidation in the temperature range 670 – 700°C, *Am. Mineral.*, (in press).

The following additional publications of relevance in the present work included in the appendixes of this thesis are:

- A. Tenailleau C., Etschmann B., Wang H., Pring A., Grguric B.A., Studer A., (2005) Thermal expansion of troilite and pyrrhotite determined by *in situ* cooling (873 to 373 K) neutron powder diffraction measurements, *Mineral. Mag.*, **69**, 205-216.
- B. Wang H., Ngothai Y., O'Neill B., Etschmann B., Pring A. (2003) The effects of S fugacity on the exsolution of pentlandite (Ni,Fe)₉S₈ from the monosulfide solid solution (Fe,Ni)S, CHEMECA 2003, the 31st Annual Australian Chemical Engineering Conference, Adelaide, Australia.
- C. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) X-ray study of the transition kinetics of α - to β -nickel monosulfide, CHEMECA 2005, the 33st Annual Australian Chemical Engineering Conference, Brisbane, Australia.
- D. Ngothai Y., Wang H., Pring A., O'Neill B. (2005) A review on the controversial phase relations of pyrrhotite group minerals in low temperature ranges, CHEMECA 2005, the 33st Annual Australian Chemical Engineering Conference, Brisbane, Australia.
- E. Wang H., Pring A., Xie, Y., Ngothai Y., O'Neill B. (2005) Phase evolution during the oxidation of monosulfide solid solution under isothermal conditions, CHEMECA 2005, the 33st Annual Australian Chemical Engineering Conference, Brisbane, Australia.
- F. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) Model-free kinetics of the pentlandite exsolution from monosulfide solid solution, the 7th World Congress of Chemical Engineering, Glasgow, U.K.
- G. Wang H., Pring A., Ngothai Y., O'Neill B. (2005) A mineralogical kinetic note: Negative activation energy or misinterpretation of Avrami method, the 7th World Congress of Chemical Engineering, Glasgow, U.K.

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Declaration

I declare that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. The publications included in this thesis have not been previously submitted for the award of any degree at University of Adelaide or other university.

I give consent for this copy of my thesis, when deposited in the library of the University of Adelaide, being available for loan and photocopying.

Haipeng Wang

September 2005

Acknowledgement

I had so much enjoyment in working with my colleagues and supervisors that I almost feel sorry when realize the completion of this project is imminent. During these unforgettable years, many people have enlightened and encouraged me through their wisdom and support, without their input the success of this project would have been impossible. I am indebted to numerous people who have helped me; I apologize if not all of them are specially mentioned.

Thanks to my supervisors, Prof. Allan Pring, Dr. Yung Ngothai, and A/Prof. Brian O'Neill for your faith in me, and your unreserved help. Your enthusiasm in science has encouraged me to pursue my career in research.

I would like to thank Dr. Barbara Etschmann, Dr. Christophe Tenailleau for their assistance in collecting data and giving enlightening advices. Grateful appreciation is due to Dr. Joël Brugger for introducing me to the computational and simulation programs, MatLab, CrystalMaker. To all those who have helped with experimental and/or computational problems, thank you! I like to thank the Australian Education, Science and Training Department for the APA award, which has allowed this work to be carried out.

Finally, thanks to my parents.....

爸爸妈妈:

谢谢你们们的养育之恩，对我的关怀和教育。回首整整二十二年的求学生涯虽然有艰辛，有困惑，但是更多的是精神上的充实和获得成功时的喜悦。我将博士毕业，却思绪万千，突然想到应借我博士论文即将出版的机会，把我对您们的感谢写入这本书的“前言”。谨将此书献给您们，它标志我学生生涯的结束，也“纪录”了您们多年来对我付出的心血。没有您们的信任和鼓励，也不会有现在的我。

王海鹏

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Abstract

For many geochemical systems, reaction kinetics determines the system's current status and evolution. It might also be the key to unraveling their thermal history. In metal sulfide systems, kinetic studies have been carried out on four sets of solid-state transitions/transformations in Fe-Ni-S and Ni-S systems. In this work, a new kinetic model, the *Refined Avrami* method, has been developed to account for reactions involving changes in reaction mechanisms. Nonstoichiometric compounds are commonly present in these reactions.

The exsolution of pentlandite from the monosulfide solid solution (*mss*) is an important reaction in the formation of nickel ores. For near equimolar *mss* compositions, the reaction rate is rapid even in the low temperature ranges. For bulk composition $\text{Fe}_{0.77}\text{Ni}_{0.19}\text{S}$, the experimental results show the reaction rates (*mss* \rightarrow pentlandite) vary from 1.6×10^{-5} to $5.0 \times 10^{-7} \text{ s}^{-1}$ at 200 °C and from 9.4×10^{-5} to $4.1 \times 10^{-7} \text{ s}^{-1}$ at 300 °C. The activation energy, E_a , varies during the course of reaction from 49.6 $\text{kJ}\cdot\text{mol}^{-1}$ at the beginning of reaction (nucleation mechanism is dominant) to 20.7 $\text{kJ}\cdot\text{mol}^{-1}$ at the end (crystal growth mechanism is dominant).

Monosulfide solid solution (*mss*) is a common intermediate phase observed during the oxidation of nickel ores, such as violarite and pentlandite. The investigation of *mss* oxidation is of benefit in understanding the thermal behavior of economically important metal sulfides during smelting. The oxidation products of *mss* vary in our samples depending on their compositions. Apart from the common oxidation products hematite and $\text{Ni}_{17}\text{S}_{18}$, $\text{Fe}_2(\text{SO}_4)_3$ was observed during the oxidation of $\text{Fe}_{7.9}\text{S}_8$, and pentlandite for $\text{Fe}_{6.15}\text{Ni}_{1.54}\text{S}_8$. The activation energy was determined using a model-free method. The

oxidation of $\text{Fe}_{6.4}\text{Ni}_{1.6}\text{S}_8$ exhibited a higher E_a than $\text{Fe}_{6.15}\text{Ni}_{1.54}\text{S}_8$ over the course of the reaction. The E_a increases with reaction extent (y) from 67.1 to 103.3 $\text{kJ}\cdot\text{mol}^{-1}$ for *mss* composition $\text{Fe}_{6.15}\text{Ni}_{1.54}\text{S}_8$ and from 76.1 to 195.0 $\text{kJ}\cdot\text{mol}^{-1}$ for $\text{Fe}_{6.4}\text{Ni}_{1.6}\text{S}_8$.

The kinetic study of the $\alpha\text{-Ni}_{1-x}\text{S} \rightarrow \beta\text{-NiS}$ transition shows that initial compositions of $\alpha\text{-Ni}_{1-x}\text{S}$ plays an important role in the kinetics of the transition. The activation energy (E_a) for this α - to β -phase transition is 16.0 (± 0.5) $\text{kJ}\cdot\text{mol}^{-1}$ for NiS in the temperature range 70 to 150 $^\circ\text{C}$, and 13.0 (± 0.5) $\text{kJ}\cdot\text{mol}^{-1}$ in the temperature range 250 to 350 $^\circ\text{C}$. For $\text{Ni}_{0.97}\text{S}$, however, E_a decreases from 73.0 (± 0.5) to 17.0 (± 0.5) $\text{kJ}\cdot\text{mol}^{-1}$ over the course of the reaction in the temperature range 300 to 320 $^\circ\text{C}$. The relationship between E_a and extent of transition (y) for the initial bulk $\text{Ni}_{0.97}\text{S}$ was derived using the *Refined Avrami* method. For Ni deficient compositions, $\alpha\text{-Ni}_{1-x}\text{S}$, the transformation to $\beta\text{-NiS}$ is accompanied by the exsolution of either a progressively more Ni deficient $\alpha\text{-Ni}_{1-x}\text{S}$ and Ni_3S_4 , and the reactions become more sluggish for more metal deficient compositions.

The study of oxidation kinetics of $\alpha\text{-NiS}$ is of metallurgical interest, as $\alpha\text{-NiS}$ related phases may occur when nickel ores are flash smelted to produce nickel matte. In an open-air environment, the oxidation mechanisms of $\alpha\text{-NiS}$ are constant at 670 and 680 $^\circ\text{C}$, dominated by the direct oxidation of $\alpha\text{-NiS} \rightarrow \text{NiO}$. The dominant oxidation mechanism changes to a chain reaction: $\alpha\text{-NiS} \xrightarrow{k_1} \text{Ni}_3\text{S}_2 \xrightarrow{k_2} \text{NiO}$ at 700 $^\circ\text{C}$. Therefore, different kinetic models need to be applied to these two distinct reaction mechanisms. Activation energy for the oxidation, $\alpha\text{-NiS} \rightarrow \text{NiO}$, in the temperature range 670 to 680 $^\circ\text{C}$ was calculated to be 868.2 $\text{kJ}\cdot\text{mol}^{-1}$ using *Avrami/Arrhenius* method. Rate constant k_1 and k_2 are approximated to be $3 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ s}^{-1}$ for the first part and second part of the chain reaction respectively at 700 $^\circ\text{C}$.

The study of the variation in reaction rate with oxidation time illustrates the optimum oxidation time zone for each temperature, where NiO can be produced at the fastest rate.

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