Metallurgical Reaction
Engineering Series

Kinetics and New Technology in Nonferrous Metallurgy

Liu Chunpeng

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Preface

The present book deals with the fundamentals of extracting metals or compounds from various ores and refining crude metals or compounds in nonferrous metallurgy. In recent years in the field of research work of metallurgy much more attention has been paid to the kinetics of the metallurgical process. The process kinetics is an important basis for effective process control and new technology development. In the present volume there are 34 papers concerning in mineral processing and its theory are summerized in six chapters, two of them dealing with the application of microwave and thermal plasma techniques, three of them dealing with the reduction and oxidation kinetics of various sulfide and oxide ores, and with processing technologies. The interaction kinetics between oxide and sulfide during their processing is discussed in chapter 4. It would give a reference to metallurgists, chemists and research students or workers.

In organizing these papers into volume, the author first of all thanks Drs. Hua Yixin, Liu Zhonghua, Peng Jinhui, Guo Xianjian, Lan Yaozhong, Lu Yaohua, Tao Dongping, Li Cheng, Su Yongqing and Song Ning, who had put much effort to complete a

part of those papers which are included in present volume. Thank Editorial Board of Metallurgical Reaction Engineering Series for their much care and support on publishing. Thanks are also given to Kunming University of Science and Technology and its Department of Metallurgy for their financial support.

Liu Chunpeng
March, 2000

Introduction

In recent years, the basic structure of flowsheet of metallurgy is changed not very much, especially the production of non-ferrous metals is continued to use traditional method although metallurgical technology has been innovated considerably with the improvement of mechanical equipment and the application of computer. The disadvantages of the traditional method are serious pollution of the air, tedious flowsheet, high energy consumption and high cost. Therefore, the topics of first importance to research in metallurgy are to simplify flowsheet, to prevent pollution, to lower cost and to increase efficiency.

The contents of this book comes from treatises on kinetics and new technology in non - ferrous metallurgy published in recent decades. It has six chapters, including four chapters in sulfuration, desulfuration, kinetics of hydrogen reduction and related new technology, and reaction kinetics of interaction of sulfide and oxide, last two chapters in chemical metallurgy with microwave and application of hot plasma in non-ferrous metallurgy. The contents and structure of every chapter are organized based on kinetics and related technology, and Chapter 1 and Chapter 2 can be taken as examples. In

Chapter 3 the introduction of new technology and suggestion are stated simultaneously in describing the kinetics of hydrogen reduction of sulfide minerals. The reactions proceeded in blowing process of copper converter, in QSL process of spraying lead sulfide concentrates, etc are expounded by the kinetics and the mechanism of interaction of sulfide and oxide. As for the application of hot plasma technology in non-ferrous metallurgy, it is elucidated by smelting of ore with high melting point (such as preparation of rutile from ilmenite), producing high nickel matte from nickel bearing pyrrhotite, concentrating Co-Fe alloy (containing same matte) from Co-Ni slag. Because of application of above technology, the metallurgical effects is improved, the technological flowsheet is shortened, and the direct recovery of metal is increased. It is better than the traditional technology.

Due to the limited academic knowledge of the author, there may have some un-appropriate, or even mistakes in selecting the contents of some topics and processing the data in this book. The comments are welcomed by the author. Thanks!

Contents

Chapter 1
Sulfidizing Reaction and Technological Application

As it is well known that the natural low grade sulfide ores are readily floated by ore dressing to concentrate the metal sulfides up to a much higher grade benefiting for subsequent metallurgical process. Based on the floatation technique it is advantageous to sulfidize the low grade refractory copper oxide ore and then to concentrate the obtained sulfide by floatation. This combined process has been successfully applied to treat the low grade refractory oxide copper ore of Tangdan from Dongchuan Mines[1], Yunnan Province.

Except above combined process, there are at least two similar processes successfully applied in industry as follows:

(1) Sulfidation-evaporation or fuming process to enrich tin from tin bearing materials, such as tin slag, the hard-head (Sn-Fe alloys) from reduction smelting of tin concentrates and middling from the ore dressing plant[2].

(2) Secondary sulfidation-floatation process in treating Ni-Cu alloys separated from converter high grade matte to enrich Pt-group metals.

From above examples it is clear that the sulfidation-floatation combined process is very a useful technique in nonferrous extractive metallurgy.

1.1 Kinetics of sulfidation of natural copper oxide minerals with elemental sulfur and mineralogical phase transformation[3]

It is unprofitable and inefficient to directly treat the low grade refractory copper oxide ore either by ore dressing or by hydrometallurgical process due to a host gangue minerals must be removed from a minor copper content randomly embedded in the dolomitic rocks. A combined process based on transforming the state of copper oxide to sulfide by roasting with elemental sulfur at lower temperature and treating the product in a subsequent step by floatation has been practiced successfully and profitably.

Based upon the industrial application of this combined process it is essential to investigate the kinetics and mechanism of sulfidizing process of the natural copper oxide minerals, such as chrysocolla, malachite and melaconite which are originally contained in the ore.

1.1.1 Chemical composition and mineralogical constituents of copper oxide ore

The dolomitic combined copper oxide ore for the test is originated from Dongchuan Mines. Its major chemical and mineralogical components are shown in Table 1-1 and Table 1-2 respectively.

Tab.1-1 Major composition of copper oxide ore from Dongchuan Mines

Components	Cu	$CaCO_3$	$MgCO_3$	SiO_2	S
Weight/%	0.62	43.88	32.20	18.30	0.070

Tab.1-2 Mineralogical components of copper oxide ore from Dongchuan Mines

Minerals	Malachite	Chrysocolla	Melaconite	Sulfides (total)
Weight/%	70	18	—	8~10

The samples of natural minerals of malachite, chrysocolla and melaconite originated from Dongchuan Mines for the test were prepared by hand picking. In order to imitate the original ore, the dolomite or limestone was added to the picked minerals, all materials were ground and then mixed with sulfur powder in case for each experiment.

1.1.2 Sulfidizing reaction of minerals and efficiency of sulfurization

The reactions of minerals sulfidized with sulfur are shown by following equations:

$$2CuO + S_2 = Cu_2S + SO_2 \tag{1-1}$$

$$2CuSiO_3 + S_2 = Cu_2S + SO_2 + 2SiO_2 \tag{1-2}$$

$$Cu(OH)_2 \cdot CuCO_3 + S_2 = Cu_2S + SO_2 + H_2O + CO_2 \tag{1-3}$$

The amount of produced SO_2 from the reactions is determined by iodimetric method:

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI \tag{1-4}$$

Main parameters influencing the efficiency of sulfurization are the amount of sulfur mixed in the test charge and the reaction temperature. The effect of sulfur amount and reaction temperature on the efficiency of sulfurization described by x, fraction of sulfurization, for various minerals are respectively shown in Figs. 1-1 ~ 1-3 and Figs. 1-4 ~ 1-6.

1.1.3 Derivation of kinetic equation

According to the experimental condition the constant temperature of experiment will be attained after 20 minutes due to the time required for heating the crucible and the test charge to the level of predetermined temperature. Therefore, a part of solid sulfide will be formed with the sulfidizing reaction before the given constant temperature reached.

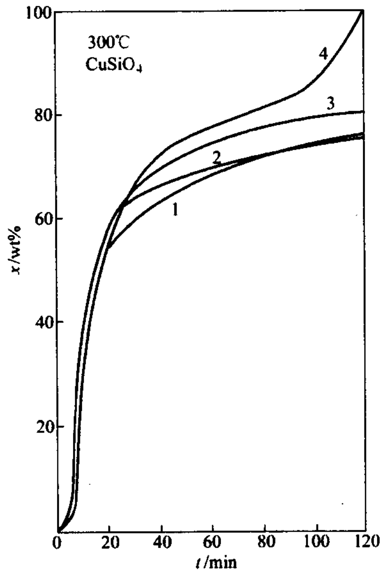

Fig. 1-1 The effect of sulfur amount on sulfurization rate of pure chrysocolla at $T = 300℃$, $N_2 = 100\ mL \cdot min^{-1}$

1—0.7%S; 2—0.9%S; 3—2.7%S; 4—1.0%S

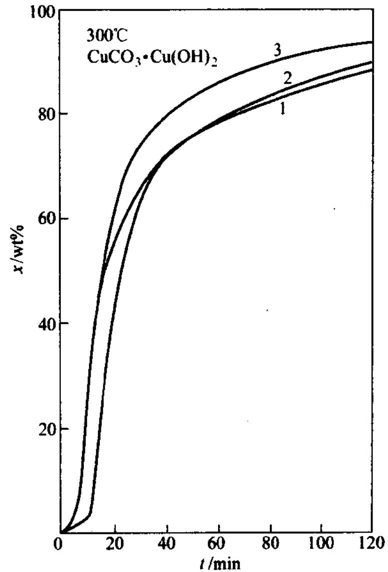

Fig. 1-2 The effect of sulfur amount on sulfurization rate of malachite mixed with limestone powder, copper content in mixed sample = 0.56% at $T = 300℃$, $N_2 = 100\ mL \cdot min^{-1}$

1—0.5%S; 2—0.7%S; 3—0.9%S

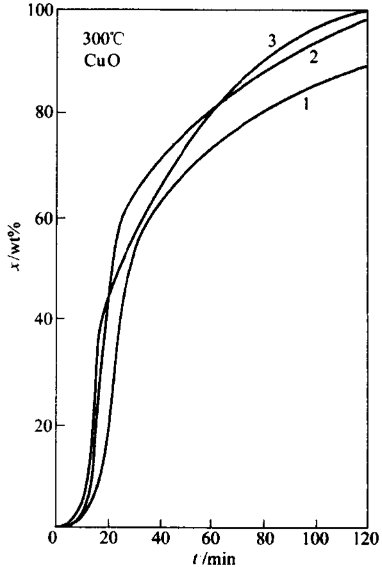

Fig. 1-3 The effect of sulfur amount on sulfurization rate of melaconite mixed with limestone powder, copper content in mixed sample = 0.85% at $T = 300℃$, $N_2 = 100\ mL \cdot min^{-1}$

1—0.7%S; 2—1.0%S; 3—1.1%S

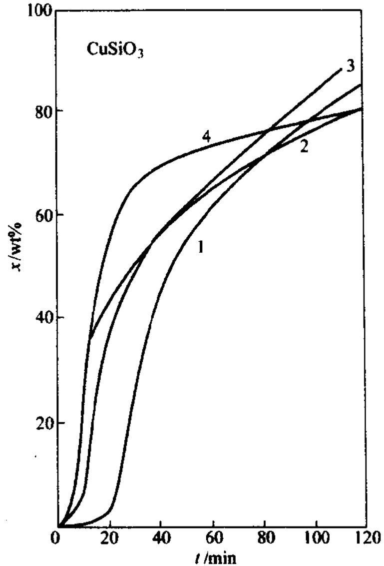

Fig. 1-4 The effect of temperature on sulfurization rate of chrysocolla with amount of sulfur addition = 1.0%, $N_2 = 100\ mL \cdot min^{-1}$

1—250℃; 2—300℃; 3—350℃; 4—400℃

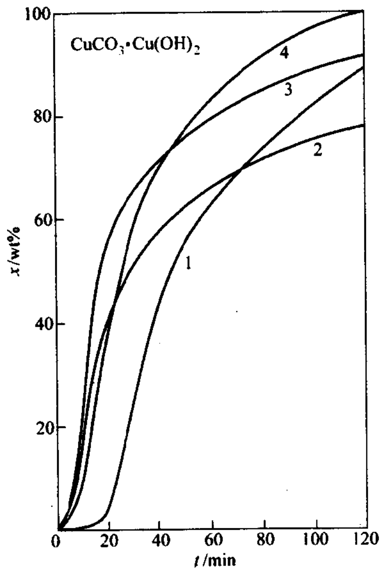

Fig. 1-5 The effect of temperature on sulfurization rate of malachite with amount of sulfur addition = 1.0%, N_2 = 100 mL·min^{-1}

1—250℃; 2—300℃; 3—350℃; 4—400℃

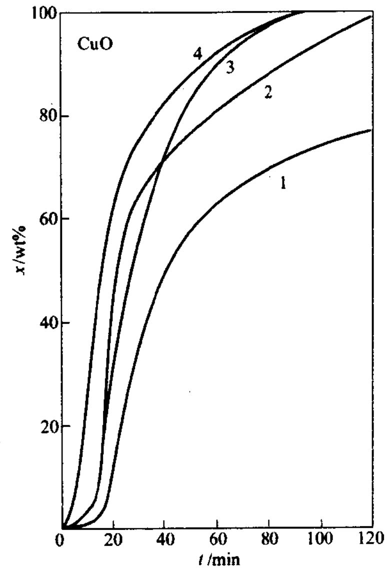

Fig. 1-6 The effect of temperature on sulfurization rate of melaconite with amount of sulfur addition = 1.0%, N_2 = 100 mL·min^{-1}

1—250℃; 2—300℃; 3—350℃; 4—400℃