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HEATING RATE OF MINERALS AND COMPOUNDS IN MICROWAVE FIELD①

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ABSTRACT More than 40 kinds of selected minerals and compounds were individually irradiated by microwaves under an inert atmosphere, and the temperatures of samples were measured with a metal-sheathed thermocouple inserted into the samples directly. The results indicated that most sulphide and some oxide minerals and compounds could be heated to high temperatures in a short time, whereas the common gangue minerals, some oxide and oxy-salt minerals or compounds could not. The sulphide minerals had faster heating rate than the oxide minerals containing the same cations. The impurities of minerals had significant effect on the heating rate. The selective heating characteristics of microwaves on different minerals and compounds could be attributed to the differences between their conductivities or dielectric loss factors and bonding properties.

Key words microwave heating minerals and compounds mineral processing extractive metallurgy

1 INTRODUCTION

Microwave heating has found wide applications in the production of engineering materials, especially in the field of drying, curing and sintering. The applications of microwave in mineral processing and extractive metallurgy are still at the development stage, but many attractive research results have been made, which include the drying of coal, the grinding of ores, the pretreatment of refractory gold concentrate and the recovery of gold from low grade ores and tailings, the extraction of rare earths and heavy metals from ores, the carbothermic reduction of iron ores and titanomagnetite, the processing of lunar materials and industrial wastes and the like, demonstrating the potential applications of microwaves in mineral processing and extractive metallurgy, although many practical problems remain to be solved.

Microwave heating as an alternative to conventional heating has many advantages. It does not rely entirely on the heat conduction from surface of the materials to the interior as conventional heating does with most other forms of energy, because heat is generated directly due to the dissipation of microwave energy within the materials. Depending on the properties of materials (conductivity, permeability and permittivity), microwave can effectively and instantaneously generate heat throughout materials, selectively heat materials[1] and stimulate certain chemical reactions[2]. Besides, smelting and some high-temperature chemical reactions seem to take place at significantly lower temperatures when using microwaves instead of conventional heating[2]. The special features of microwave heating are obviously of practical importance for mineral processing and extractive metallurgy. So it is very necessary to study the microwave heating properties of minerals and compounds as a first step towards investigating the applications of microwaves in metallurgical industry. Although the microwave heating characteristics of some minerals and compounds were reported[3], the heating rate of a

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mineral may vary from place to place due to the differences of its impurities. A further study on the microwave heating rates of minerals and compounds is still needed. The present study has been conducted to determine the microwave power absorbed by various minerals and compounds by measuring temperatures of the samples.

2 EXPERIMENTAL

2.1 *Materials*

The minerals used in the present work were selected from natural ores, and the associated gangue minerals were removed by handpicking. The minerals selected were examined by X-ray diffraction analysis. The purity of the minerals was greater than 95% by weight. The chemical compounds used were analytically pure reagents. The particle size of samples was in $-100+180$ meshes and the sample weight was 30 g.

2.2 *Procedures*

Experiments were conducted in a 650 W, 2 450 MHz microwave oven (NE-6790). Each sample was placed in a quartz crucible (7 cm × d3 cm) which was inclosed in a quartz container (13 cm × d5 cm) with an inlet and an outlet for gas flow. Purified argon was blown into the quartz container at 2.5 mL/s during microwave irradiation so that samples were heated under an inert atmoshpere. A schematic diagram of the apparatus used is shown in Fig. 1.

In the past, the surface temperatures of minerals during microwave irradiation were determined by an infrared technique. The precision of the measurement was unsatisfied because the surface temperture is usually lower than that of the interior of samples. For this reason, a metal-sheathed Ni(Cr)-Ni(Si) thermocouple (WRNK-102) was used instead of infrared pyrometer. However, the thermocouple can not be inserted into the sample during microwave irradiation because microwaves may discharge on the surface of thermocouple and hence a positive deviation will be caused.

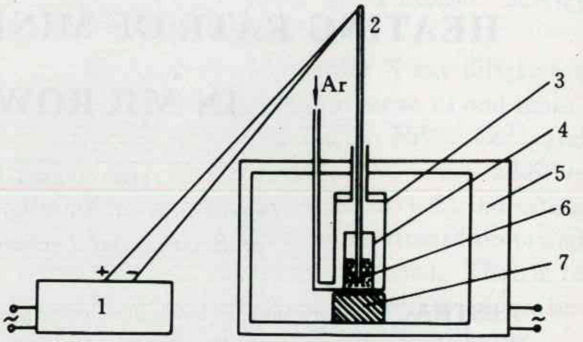

Fig. 1 Schematic diagram of the apparatus

1—recorder; 2—thermocouple; 3—quartz container; 4—quartz crucible; 5—microwave oven; 6—sample; 7—corundum supporter

In each run, therefore, the thermocouple was immediately inserted into the sample through the outlet of gas for the direct measurement of temperature as soon as the microwave irradiation was stopped.

The temperatures measured were recorded by a function recorder (LZ3-104). The results determined by this method are slightly lower than the real temperatures of samples, but the errors are acceptable and the interference of thermocouple with microwave heating is eliminated. According to the blank test made on boiling water, the measurement error is less than 2%.

3 RESULTS AND DISCUSSION

The temperatures of selected minerals and compounds heated by microwaves were summarized in Tables 1 ~ 3, respectively. It can be seen that the temperatures achieved for various minerals and compounds in a definite time are obviously different. Most sulphides and some oxide minerals and compounds which absorb microwaves readily can be heated to high temperatures in a short time. However, silicate, some oxy-salt and oxide and a few of sulphide minerals, which can not or only partially absorb microwaves, can only be heated to low temperatures. The gangue minerals coexisting with the ore minerals such as quartz (SiO_2) and calcite ($CaCO_3$) can hardly be heated. Therefore, valuable minerals within the host rock can be selectively heated without the necessity of heating the whole rock mass.

Table 1 Effect of microwave heating on the temperatures of sulphide minerals and compounds

Minerals or compounds*	Chemical composition	T /K	t /s	$\Delta T:\Delta t$ /K·s^{-1}
silver sulfie*	Ag_2S	422	150	0.83
cobalt sulfide*	Co_9S_8	892	150	3.96
cuprous sulfide*	Cu_2S	1 026	160	4.55
carrollite	$Cu(Co, Ni)_2S_4$	970	150	4.48
chalcopyrite	$CuFeS_2$	980	60	11.37
bornite	Cu_5FeS_4	1 250	150	6.35
ferrous sulfide*	FeS	800	100	5.02
pyrrhotite	$Fe_{1-x}S$	955	40	16.43
pentlandite	$(Fe, Ni)_9S_8$	752	150	3.03
nickel pyrrhotite	$(Ni, Fe)_7S_8$	956	150	4.39
molybdenite	MoS_2	1 060	150	5.08
nickel sulfide*	Ni_3S_2	690	150	2.61
galena	PbS	1 010	120	5.93
jamesonite	$Pb_4FeSb_6S_{14}$	800	30	16.73
lead-zinc sulfide concentrate	PbS-ZnS	720	150	2.81
stibnite	Sb_2S_3	450	150	0.51
stannous sulfide*	SnS	1 090	100	7.92
sphalerite	ZnS	432	150	0.89

Table 2 Effect of microwave heating on the temperatures of oxide minerals and compounds

Minerals or compounds*	Chemical composition	T /K	t /s	$\Delta T:\Delta t$ /K·s^{-1}
alumina*	Al_2O_3	430	150	0.88
calcium oxide*	CaO	449	150	1.01
cuprous oxide*	Cu_2O	1 395	120	6.87
magnetite	Fe_3O_4	1 026	150	4.85
hematite	Fe_2O_3	455	420	0.37
ilmenite	$FeTiO_3$	1 260	150	6.41
vanadium titanomagnetite	$(V, Ti, Fe)Fe_3O_4$	1 260	190	5.06
magnisia*	MgO	362	150	0.43
manganese dioxide*	MnO_2	1 378	100	10.80
lead oxide (yellow)*	PbO	489	150	1.27
antimony oxide*	Sb_2O_3	370	120	0.60
quartz	SiO_2	346	150	0.32
cassiterite	SnO_2	1 480	60	19.70
stannic oxide (pure)*	SnO_2	1 010	150	4.75
titania*	TiO_2	323	240	0.10

Table 3 Effect of microwave heating on the temperatures of oxy-salt minerals and compounds

Minerals or compounds*	Chemical composition	T /K	t /s	$\Delta T:\Delta t$ /K·s^{-1}
calcium carbonate*	$CaCO_3$	498	150	1.33
siderite	$FeCO_3$	546	150	1.65
cerussite	$PbCO_3$	510	180	1.18
smithsonite	$ZnCO_3$	406	180	0.60
calcium hydroxide*	$Ca(OH)_2$	440	150	0.95
limonite	$FeOOH.\ nH_2O$	350	150	0.35
acbolite	$(Mn, Co, Ni)(O, OH)$	670	200	1.86
wulfenite	$PbMoO_4$	475	180	0.98
chrysocolla	$(Cu, Al)_2H_2Si_2O_5 \cdot (OH)_4 \cdot nH_2O$	440	180	0.79
garnierite	$(Ni, Mg)_3Si_2O_5 \cdot (OH)_4$	525	180	1.26
serpentine	$Mg_6Si_4O_{10}(OH)_3$	460	180	0.90

3.1 *Effect of Conductivity on Heating Rate*

The energy dissipation of microwaves in unit volume of a material can be given in terms of the power density as[4]:

$$P = 2\pi f \varepsilon_0 \varepsilon'' E^2 \qquad (1)$$

where P —power density absorbed by materials, W/cm^3; f —frequency of microwaves, s^{-1}; ε_0 —dielectric constant in vacuum, 8.854 $\times 10^{-14}$ F/cm; ε'' —dielectric loss factor of complex dielectric constant, $\varepsilon = \varepsilon' - j\varepsilon''$; E —electric field strength, V/cm.

If the heat loss due to radiation is not taken into consideration, the heating rate of the material in the microwave field can be determined by:

$$\mathrm{d}T/\mathrm{d}t = 2\pi f \varepsilon_0 \varepsilon'' E^2 / \rho C_p \qquad (2)$$

where ρ —bulk density of the material, g/cm^3; C_p —specific heat capacity, J/g·K.

Substituting the relationship between ε'' and conductivity[5]

$$\varepsilon'' = \sigma / 2\pi f \qquad (3)$$

into Eqn. (2) gives:

$$\mathrm{d}T/\mathrm{d}t = \sigma E^2 / \rho C_p \qquad (4)$$

Since only throughout its interior can a material be heated efficiently by microwave, the penetration depth into the material where the power falls to one half its value on the surface should be considered. The penetration depth D_p, when ε'' is small, is given by:

$$D_p \propto \lambda_0 \sqrt{\varepsilon' / \varepsilon''} \qquad (5)$$

where λ_0 —wavelength of microwave, cm.

The above equations demonstrate that the heating rate of a material and the penetration depth of microwave into the materials are determined by dielectric loss factor or conductivity. Based on the experimental results of this work and the electrical conductivity of minerals given by Keller[6], the conductivity dependence of microwave heating rate can be obtained, as shown in Table 4. It can be seen that the insulator-type minerals and compounds ($\sigma = 10^{-8}\ \Omega^{-1} \cdot m^{-1}$) absorb little microwave energy and appear almost transparent to microwaves; while for those with high conductivities ($\sigma < 10^6\ \Omega^{-1} \cdot m^{-1}$), the energy loss is high, penetration depth is low and most energy is reflected; and the semiconductor-type minerals and compounds ($\sigma = 10^{-8} \sim 10^6\ \Omega^{-1} \cdot m^{-1}$) can be heated well because their dielectric loss factors are considerably large and the penetration depth of microwave into these minerals and compounds is not small.

3.2 *Effect of Composition and Structure*

According to Eqns. (2) and (4), the heating rates of minerals mainly depend on ε''

Table 4 Effect of conductivity on heating rate

Minerals or compounds*	Chemical composition	Conductivity/$\Omega^{-1}\cdot m^{-1}$	$\Delta T : \Delta t$ /$K\cdot s^{-1}$
magnesia*	MgO	1.61×10^{-11}	0.42
sphalerite	ZnS	$2.5\times10^{-5}-2.5\times10^{-4}$	0.89
molybdenite	MoS_2	$1.0\times10^{-6}-8.3$	5.08
haematite	Fe_2O_3	$1.0\times10^{-4}-4.8\times10^{2}$	0.37
cassiterite	SnO_2	$1.0\times10^{-4}-2.2\times10^{3}$	19.70
stibnite	Sb_2S_3	$1.0\times10^{-2}-1.0\times10^{2}$	0.51
chalcopyrite	$CuFeS_2$	$6.3\times10^{-1}-5.0\times10^{4}$	11.40
jamesonite	$Pb_4FeSb_6S_{14}$	$6.67-5.0\times10^{1}$	16.70
silver sulphide*	Ag_2S	$5.0\times10^{2}-6.6\times10^{2}$	0.83
ilmenite	$FeTiO_3$	$2.5\times10^{-1}-1.0\times10^{3}$	6.41
manganese oxide*	MnO_2	$1.0-6.67\times10^{2}$	10.80
cuprous sulphide*	Cu_2S	$2.4\times10^{1}-1.3\times10^{4}$	4.55
magnetite	Fe_3O_4	$1.4-6.7\times10^{4}$	4.86
bornite	Cu_5FeS_4	$1.7\times10^{2}-6.3\times10^{5}$	6.35
pyrrhotite	$Fe_{1-x}S$	$6.3\times10^{3}-5.0\times10^{5}$	16.40
galena	PbS	$1.7-1.0\times10^{6}$	5.93
pentlandite	$(Fe, Ni)_9S_8$	$9.1\times10^{4}-1.0\times10^{6}$	3.03

or σ, which are determined by compositions and structures of minerals. Thus, the heating rate is directly related to ionic type, ionic radius, bond type and impurities of minerals.

3. 2. 1 Sulphide Minerals

As shown in Table 1, most of the sulphide minerals and compounds has fast heating rate, which is in good agreement with their greater dielectric constants($\varepsilon' = 4.44 \sim 600$, $\varepsilon'' = 0.025 \sim 90.0$[7]) at microwave frequency band. However, the heating rates are different for different positive ions in the minerals and compounds. The sulphide minerals and compounds containing Fe^{2+}, Co^{2+}, Ni^{2+}, Mo^{4+}, Cu^{+}, Sn^{2+} and Pb^{2+} have fast heating rate, whereas those containing Sb^{3+}, Zn^{2+} and Ag^{+} can not be heated well by microwaves. The reason may be attributed to the differences between the bonding properties of these minerals and compounds.

Sulphur anion S^{2-} is easily polarized by cations due to its larger radius (18. 4 nm). When S^{2-} and a metallic cation combine to form a mineral or compound, the polarization between the anion and cation will be significant. The ionic polarization adds the partial covalent character to the ionic bond[8]. As a result, most of the sulphide minerals and compounds such as those containing Fe^{2+}, Co^{2+}, Ni^{2+}, Mo^{4+}, Cu^{+}, Sn^{2+} and Pb^{2+} would have bond-type transition from ionic to covalent. If cations such as Ag^{+}, Zn^{2+} and other cations with d^{10} electrons are also easily polarized by anions, the inter-polarization of anion and cation may result in the obvious deformation of electron cloud and change ionic bond to covalent bond[8]. Since the minerals and compounds with bond-type transition are good conductors and purely covalent or ionic minerals and compounds are insulators under most circumstances[7], the dielectric loss factor is greater for the former, and smaller for the latter. Accordingly, the microwave heating rates are faster for the sulphide minerals and compounds with bond-type transition such as Cu_2S, SnS, PbS and transition-metal sulphide minerals and compounds, and slower for those with covalent bonds such as ZnS, Ag_2S and Sb_2S_3.

3. 2. 2 Oxide Minerals

For oxide minerals and compounds which contain Mn^{2+}, Fe^{3+}, Fe^{2+}, Cu^{+}, Sn^{4+}, Pb^{2+} and Sb^{3+}, as shown in Table 2, the effect of cation type on the heating rate is similar to that for the corresponding sulphide minerals and compounds. However, the oxide minerals and compounds containing rare-gas cations (Mg^{2+}, Al^{3+}, Si^{4+}, Ca^{2+}) can not be heated well and their heating rates are the slowest among the oxide minerals and compounds determined. This result is correspondent to the fact that their positive nuclei are effectively shielded, their radii and polarizabilities are smaller, and hence they can combine with O^{2-} to form ionic minerals and compounds, making electrical conductivity or dielectric loss factor smaller.

Comparing Table 1 with Table 2, it can be found that most oxide minerals and compounds have slower heating rates than the corresponding sulphide minerals and compounds with the same cations. Hence the effect of anion type on the heating rate is significant also.

3. 2. 3 Oxy-salt Minerals

The heating rates of oxy-salt minerals and compounds are usually slower in comparison with those of other minerals and compounds, as shown in Table 3. This is due to their smaller dielectric constants($\varepsilon' = 3.58 \sim 4.0$, $\varepsilon'' = 0.025$[7])

3. 2. 4 Impurities of Minerals

The heating rate is also influenced by the impurities of minerals apart from the types of positive and negative ions. When a mineral contains impurities, there are structure defects in it, such as vacant lattice, interstitial atoms and dislocation. Though the amount of these defects is often small, they can sharply decrease the energy gap between valence and conduction bands and thus increase the electrical conductivity[9]. So the heating rates of minerals will be changed due to the presence of impurities. For instance, it is due to the differences between the impurities that the heating rate of cassiterite is different from that of the pure stannic oxide, although their chemical compositions are the same (SnO_2) (see Table 2).

4 CONCLUSIONS

(1) The abilities for minerals and compounds to absorb microwaves are mainly determined by their compositions, structures and impurities. In respect to the electrical conductivity, the semiconductor-type minerals and compounds are more effective than the insulator-type in absorbing microwaves. In respect to the bonding properties, the minerals and compounds with metallic bonds can more effectively absorb microwaves than those with purely ionic or covalent bonds.

(2) Most sulphide minerals and compounds have faster heating rates than do the oxide minerals containing the same cations.

(3) Impurities of minerals and compounds have significant influence on the heating rate.

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