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MODIFYING EFFECT OF ELECTRON BEAM IRRADIATION ON MAGNETIC PROPERTY OF IRON-BEARING MINERALS

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Abstract: The effect of electron beam irradiation on magnetic property of iron bearing minerals was investigated by susceptibility measurements. The results show that the magnetic susceptibility of iron bearing sulfide minerals can be enhanced remarkably by strong beam current irradiation, while the magnetic susceptibility of oxidized iron minerals keeps unchanged and even is slightly reduced. The magnetic susceptibility of arsenopyrite can reach the ferromagnetic level. The particle size of irradiated minerals makes notable effects on magnetic susceptibility. The magnetic susceptibility of irradiated minerals is enhanced greatly with reduction of particle size, and the irradiation dose corresponding to the maximum magnetic susceptibility is decreased simultaneously. Exposure of pyrite to small beam current electron irradiation can only enhance its magnetic susceptibility from 4 to 5-fold. Enhancement of magnetic property by radiation induced defects and excitation in minerals is limited. Strong beam current electron irradiation provides a novel approach to enlarge the magnetic property differences between iron bearing minerals.

Keywords*: magnetic susceptibility, iron bearing mineral, sulfide, electron beam irradiation*

Introduction

Exposure of solids to high-energy radiation is known to result in radiation-induced defects and leads to related process acceleration, such as diffusion controlled reaction in solid and solid phase synthesis (Gribkov et al.,1995; Auslender et al., 1997,1999). It also makes possible to create new conditions for changes in solid materials properties e.g. the mechanical strength, electric, magnetic and surface properties, floatability of minerals and others. The difference between minerals with close physical and physicochemical properties can be markedly enlarged (Florek, 1995; Bochkarev et al.,

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1997; Milkhilov et al., 1998; Kovalyov et al., 1999; Chanturiya et al., 1999; Wang et al., 2002a; Wang et al., 2002b; Wang et al., 2002c). The study of the effect of accelerated electron energy on magnetic separation of iron bearing ores showed that the preliminary treatment of raw ores by electron beam irradiation enables to increase the concentrate grade and decrease the loss of valuable constituents in tailing. This promising technique was successfully used to treat in laboratory scale iron, iron containing tin and chalcopyrite and others ores (Bochkarev et al., 1992, 1997; Florek et al., 1992; Ostopenko et al., 1992).

The objective of this work is the study of the electron irradiation effect on magnetic property of iron bearing minerals such as pyrite, arsenopyrite, chalcopyrite, marmatite, hematite and siderite. The magnetic susceptibility change of weakly magnetic iron bearing minerals induced by electron beam irradiation is investigated and analyzed.

Experimental

Materials

The iron-bearing minerals such as pyrite, arsenopyrite, chalcopyrite, marmatite hematite and siderite were picked from real ores and purified using suitable mechanical measures. The pure mineral samples were first ground in mortar and then classified into several size fractions. The minerals samples with size range of -180+75, -75+53 and -53 μm were subjected to electron irradiation treatment.

Methods

The samples were irradiated with an electron accelerator at a steady-state regime. The low irradiation dose experiments were conducted on the type BF-5 experimental accelerator installed at Beijing Normal University. The electron beam parameters were as follows: the incident electron energy 1.5 MeV, irradiation dose rate 100 Gy/s (Gray, $Gy = m^2/s^2$), current intensity were altered from 90 to 150 μA . The high irradiation dose experiments were conducted on the type GJ-15 industrial accelerator installed at Tianjin Institute of Technical Physics. The fixed electron beam parameters were as follows: electron energy 1.5 MeV, current intensity 6 mA. The irradiation dose was varied in accordance with the problems stated. The magnetic susceptibility was measured on a multi-purposes magnetism analyzer model WCF2-65. The exciting current was set at 1.0 A for all tests.

Results and discussions

Small beam current irradiation

Arsenopyrite and two types of pyrite (sample A from Hunan Leiyang mine, sample B from Zhejiang Longyou mine) were exposed to electron beam irradiation under low dose and small beam current. Under such irradiation conditions the thermal effect on

irradiated minerals is negligible. As shown in Table1, the magnetic susceptibility of arsenopyrite after irradiation increases. At beam current 115 μA and dose $23 \cdot 10^3$ m^2/s^2, the magnetic susceptibility of arsenopyrite increases 5 times than that prior to irradiation. The beam current and irradiation dose are the major parameters for changes in magnetic properties.

Table 1. Effect of current density and irradiation dose on magnetic susceptibility of arsenopyrite. Magnetic susceptibility of arsenopyrite prior to irradiation is $5.39 \cdot 10^{-6}$ cm^3/g and particle size –180 μm

Current density (μA)			115		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	2.3	4.6	6.9	9.2	11.5
Susceptibility 10^{-6} (cm^3/g)	12.72	15.52	18.83	14.28	9.38
Current density (μA)			115		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	13.8	16.1	18.4	20.7	23.0
Susceptibility 10^{-6} (cm^3/g)	11.16	13.14	26.77	28.35	30.72
Current density (μA)			90		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	12	14	16	18	20
Susceptibility 10^{-6} (cm^3/g)	7.35	19.68	9.28	20.17	22.94

The magnetic properties of irradiated pyrite A and B are given in Tables 2 and 3, respectively. The results show that the changes in magnetic susceptibility fluctuate. At electron current density 150 and 115 μA, the magnetic susceptibility even decreases under low irradiation dose. Under high irradiation dose (above $10 \cdot 10^3$ m^2/s^2 for 150 μA, and above $20.7 \cdot 10^3$ m^2/s^2 for 115 μA) the magnetic susceptibility of pyrite A becomes higher than the initial value. Under current density 120 μA the result is

Table 2. Effect of current density and irradiation dose on magnetic susceptibility of pyrite A. Magnetic susceptibility of pyrite A prior to irradiation is $7.89 \cdot 10^{-6}$ cm^3/g and particle size –180 μm

Current density (μA)			150		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	2	4	6	8	10
Susceptibility 10^{-6} (cm^3/g)	0.7	1.46	1.68	4.89	22.69
Current density (μA)			120		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	2	4	6	8	10
Susceptibility 10^{-6} (cm^3/g)	15.83	20.47	16.50	18.03	7.09
Current density (μA)			115		
Irradiation dose ($kGy = 10^3$ m^2/s^2)	13.8	16.1	18.4	20.7	23.0
Susceptibility 10^{-6} (cm^3/g)	3.01	3.65	4.17	9.26	22.69

different as the magnetic susceptibility increases under the irradiation dose from $2 \cdot 10^3$ m^2/s^2 to $8 \cdot 10^3$ m^2/s^2, and then decreases at higher irradiation dose $10 \cdot 10^3$ m^2/s^2. Generally, the magnetic susceptibility of irradiated pyrite B increases, however, a significant decrease can be observed for the current density 120 μA with irradiation dose $6 \cdot 10^3$ m^2/s^2, 115 μA with $16.1 \cdot 10^3$ m^2/s^2 and 90 μA with $14 \cdot 10^3$ m^2/s^2. The reason of such fluctuating changes for mineral pyrite A and B is still unclear. It may be related to the extent of crystalline perfection, specific defects and geologic environment of mineralization of pyrite. Further study is needed.

Table 3.Effect of current density and irradiation dose on magnetic susceptibility of pyrite B. Magnetic susceptibility of pyrite B prior to irradiation is $7.89 \cdot 10^{-6}$ cm^3/g and particle size –180 μm

Current density (μA)			150		
Irradiation dose (kGy = 10^3 m^2/s^2)	2	4	6	8	10
Susceptibility 10^{-6} (cm^3/g)	12.17	15.14	16.26	20.17	16.05
Current density(μA)			120		
Irradiation dose (kGy = 10^3 m^2/s^2)	2	4	6	8	10
Susceptibility 10^{-6} (cm^3/g)	29.58	22.04	4.51	13.5	22.77
Current density (μA)			115		
Irradiation dose (kGy = 10^3 m^2/s^2)	13.8	16.1	18.4	20.7	23.0
Susceptibility 10^{-6} (cm^3/g)	12.59	6.4	11.85	19.95	12.37
Current density (μA)			90		
Irradiation dose (kGy = 10^3 m^2/s^2)	12	14	16	18	20
Susceptibility 10^{-6} (cm^3/g)	10.91	4.68	38.43	15.57	15.03

Strong beam current irradiation

The effect of strong beam current irradiation on magnetic susceptibility of arsenopyrite, pyrite, chalcopyrite and marmatite is given in Figs. 1a–d. From Fig. 1 it can be seen that magnetic susceptibility of irradiated minerals under strong beam current irradiation changes remarkably. However, the response of minerals to irradiation is different. With increase in irradiation dose the magnetic susceptibility of minerals increases sharply reaching its maximal value and then decreases. Hence, there is a critical irradiation dose for each mineral. Furthermore, the critical irradiation dose is dependent upon the particle size. The coarser particle size, the higher value of the critical irradiation dose.

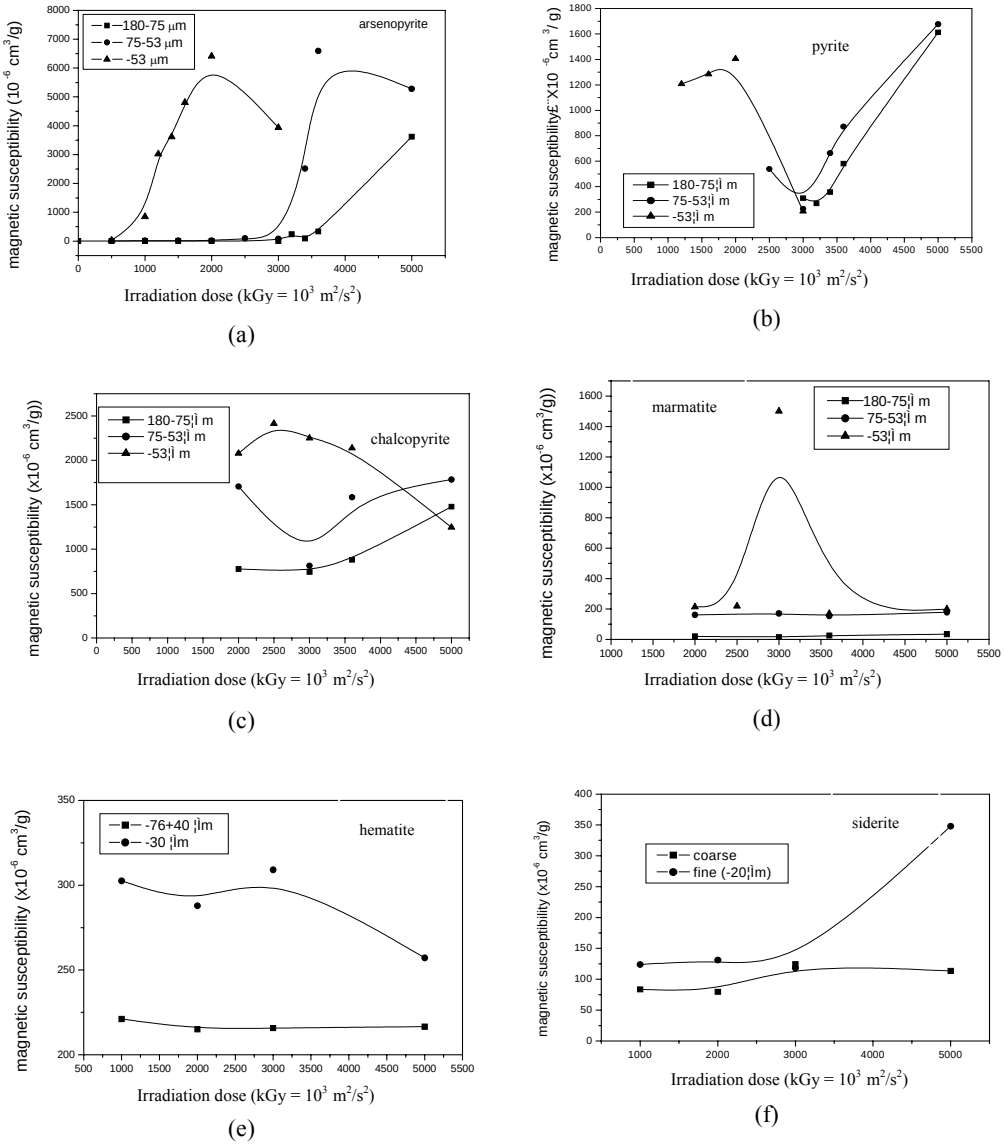

Fig. 1. Magnetic susceptibility of arsenopyrite (a), pyrite (b), chalcopyrite (c), marmatite (d), hematite (e) and siderite (f) as a function of irradiation dose

The magnetic susceptibility of arsenopyrite with size –75+53 μm increases sharply with the irradiation dose, reaching the maximum value at $6.6 \cdot 10^{-3}$ cm^3/g, which is higher than the minimum level of ferromagnetic scope $3 \cdot 10^{-3}$ cm^3/g (Liu, 1994). After irradiation the magnetic susceptibility of pyrite sized 75-53 μm reaches maximum at $1.7 \cdot 10^{-3}$ cm^3/g (Fig. 1b). For chalcopyrite the maximum magnetic susceptibility is

obtained for particle size –53 μm and is equal to $2.4 \cdot 10^{-3}$ cm^3/g (Fig. 1c). The magnetic susceptibility of marmatite remains almost unchanged, except for –53 μm fraction (Fig. 1d).

The results show that the particle size has a notable effect on the magnetic susceptibility of the irradiated minerals. For arsenopyrite as an example, the corresponding irradiation dose is $2000 \cdot 10^3$ m^2/s^2 for –53 μm, $3600 \cdot 10^3$ m^2/s^2 for –75+53 μm and $5000 \cdot 10^3$ m^2/s^2 for –180+75 μm. Further increase in the irradiation dose causes sharply decreases in the magnetic susceptibility. It may be due to greater specific surface and reaction rate constant for finer particles. Exceeded irradiation may result in overoxidation of minerals and in decrease of magnetic susceptibility of irradiated minerals (Wang, 2002 d).

The irradiation effect of the magnetic susceptibility of hematite and siderite in given in Figs. 1e–f. It can be seen that the magnetic susceptibility of hematite after irradiation remains almost unchanged and even slightly reduced. The magnetic susceptibility of siderite fine particles increases to a great extent under irradiation dose of $5000 \cdot 10^3$ m^2/s^2.

Collision of incident electron with mineral crystal lattice causes temperature rising and leads to the thermolysis of mineral (Bochkarev et al., 1997; Milkhilov et al., 1998; Wang, 2002 d; Wang et al., 2004). Under certain conditions, the ferromagnetic phases are formed that enhances magnetic property of minerals.

Decomposition of chalcopyrite in atmosphere occurs in the manner of oxidation and sulfation. The oxidation and sulfation processes may be markedly intensified at higher temperature. The partial and complete oxidations of chalcopyrite by conventional heating occur at temperature of 680 °C and 850 °C, respectively. The sulfation process of chalcopyrite at 600 °C can be expressed as follows:

$$2CuFeS_2 + \frac{17}{2}O_2 \xrightarrow{T} 2CuSO_4 + Fe_2O_3 + 3SO_2 ,$$

while complete oxidation occurs at temperature 850°C:

$$2CuFeS_2 + \frac{13}{2}O_2 \xrightarrow{T} 2CuO + Fe_2O_3 + 4SO_2 .$$

Ferric oxide (Fe_2O_3) produced in both reactions enhances the magnetic properties of chalcopyrite. Furthermore, Fe_3O_4 phase may also form as a product of chalcopyrite thermolysis when the temperature exceeds 500 °C. The thermolysis products of chalcopyrite excited by radiation-thermal treatment using XRD spectrum were previously studied by Florek et al. (1992) and Wang et al. (2004). The results of XRD analysis (Fig. 2) indicate that other iron oxide phases such as γFe_2O_3 and Fe_3O_4 also appear. Therefore, the thermolysis process of chalcopyrite excited by radiation-

thermal treatment is distinct from conventional thermolysis and might be expressed by the following reaction:

$$5CuFeS_2 + 16O_2 \xrightarrow{e,T} 5CuO + \gamma Fe_2O_3 + Fe_3O_4 + 10SO_2 .$$

In addition, the thermolysis process is largely excited by radiation-thermal treatment. The partial and complete thermolysis occurs at lower temperature at about 400 °C and 600 °C, respectively. Consequently, temperature of thermolysis can be reduced about 280 °C and 250 °C, respectively. Intensification of thermolysis is probably due to that the defects resulted by electron beam irradiation may accelerate the diffusion and reaction process inside the solid phase.

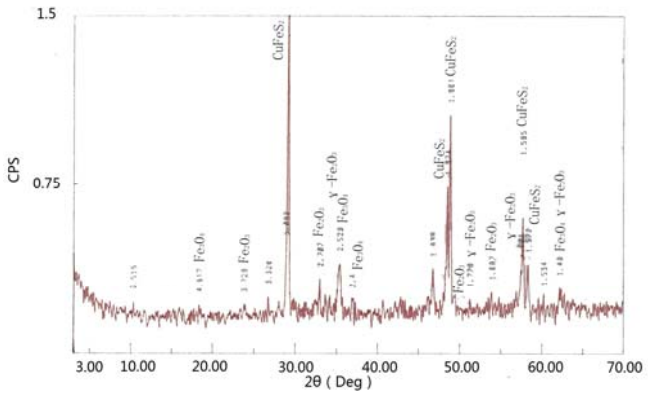

Fig. 2. XRD analysis of chalcopyrite after irradiation pretreatment at maximum temperature 600 °C

Conclusions

Changes of magnetic properties of pyrite by electron beam irradiation under small beam current and low irradiation dose resulted from radiation induced defects and excitation in minerals. As a result, the magnetic susceptibility enhancement is limited.

Strong beam current electron irradiation enhances the magnetic susceptibility remarkably. The magnetic susceptibility of iron bearing sulfide is easier to enhance by irradiation than that of oxidized iron minerals.

The particle size of minerals has notable effect on the magnetic susceptibility. The magnetic susceptibility of irradiated minerals is enhanced greatly with finer particle size, the irradiation dose corresponding to maximal magnetic susceptibility can be decreased.

Radiation defects diffusion and radiation enhanced diffusion process should be responsible for the difference between electron beam radiation induced phase conversion and conventional heat one.

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