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Influence of Tourmaline on DPC Pore Structure and Removal Effect on Malachite Green

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ABSTRACT

Taking diatomite as the main material, the DPC was obtained by solid-phase sintering and low-temperature calcination craft. The study focused on the content of tourmaline to influence of materials' microstructure, pore size distribution and the decolourization ability for malachite green aqueous solution. Samples in different tourmaline content were characterized by scanning electron microscopy, Hg porosimetry and so on. The results indicate that sample with 12% tourmaline has the smallest average aperture of 177.5 nm and biggest specific surface area of 6.83 m^2/g; tourmaline content is enhanced from 0% to 16%, the materials' porosity decreased from 49.3% to 36.5% and materials' decolourization ability to malachite green solution's strengthens gradually. When tourmaline content is 16%, malachite-green aqueous solution is completely decolourized in 6h and the absorption peaks disappear at 412 nm and 618 nm.

INTRODUCTION

The porous material has a certain size and quantity pore structure that is taken as a useful structure to exist. The hole's size, quantity and distribution are the primary factors of influence on porous material performance. The porous ceramics is a kind of new materials taking the pore structure as characteristic, which is widely applied in the metallurgy, chemical industry, environmental protection, energy, medicine, serves as material of filtration, separation, heat insulation, chemical padding, biological ceramics, catalyst and catalyst carrier by good permeability, low density, high specific surface area, low heat-conductivity, thermostable, anticorrosive fine characteristic and so on (Grandjean et al. 2006, Dong et al. 2006).

The diatomite is a kind of non-metallic mineral formed gradually by the diatom-wreckages that grew and deposited in the sea or lakes and via geological processes. In recent years, the diatomite is noticed by widespread origin, low price, as well as the unique diatom shell structure. Using diatomite primitive pore structure and low-temperature calcination craft, diatomite-based porous ceramics (DPC) with tiny aperture, cost inexpensive was prepared (Li et al. 1999, Vasconcelos et al. 2000).

Tourmaline is a kind of ring-like silicate crystal mineral including water, fluorine, Al, Na, Ca, Mg, B, Fe and so on, which has the functions of spontaneous permanent polarity, shield electromagnetic wave, release negative ions, purifying environment and so on (Kakamu et al. 2000). Tourmaline can ionize and activate the hydrone, has the strong radiation ability in 4~14μm far infrared wave bands, and produces the active oxygen (Nakamura & Kubo 1992, Ji et al. 2002). Tourmaline as a new industry mineral has received universal recognition for its unique nature and the product high added value in environmental protection, medicine, chemical industry, light industry, building materials and so on (Dong et al. 2005). In many application domains, tourmaline powder is dispersed with difficulty in the nonpolar materials because of tourmaline ultra fine strong polarity and pellet micro refinement. By the nonpolar beautification, fossilization to tourmaline powder, to solve disfigurements of its bad dispersivity, recycling difficulty and bad adsorptive capacity, which is an important direction in tourmaline research domain. In this work, the study has focused on the content of tourmaline to influence its microstructure, pore size distribution and the decolorization ability for malachite green aqueous solution, and malachite green solution's decolorization mechanism.

MATERIALS AND METHODS

Materials: Commercial diatomite powders (Linjiang Meston Powdery Material Co., Ltd. in Jilin province) with median particle size 7.8 μm, primitive aperture size 20-500 nm and specific surface area 20.88 m^2/g; commercial ultra-fine tourmaline powders with median diameter 2.80 μm; sintering assistant (feldspar, quartz, kaolin); cementing agent (poly-

vinyl alcohol); dispersing agent (polyacrylate sodium).

Sample preparation and characterization: This experiment's agglutination assistant is 8%, and tourmaline contents are 0%, 8%, 12% and 16%, and diatomite content is decided according to tourmaline and agglutination assistant's content. Diatomite, tourmaline and sintering assistant by certain percentage are mixed with water, the dispersing agent and the cementing agent, and the mixtures were milled with the spherical grinding medium (zirconium oxide ball diameter of 3~5 mm, material and ball ratio 1:4) in the laboratory circular sand mill to 1.2 μm average particle size and oven-dried at 105°C for 2 h, and then scattered, formed (pressure: 40 MPa), and sintered at 960°C for 2 h.

The microstructure of DPC was observed by scanning electronic microscope (SEM Japanese, ST-2000). The pore size distribution and specific surface area of samples were observed by Hg porosimetry (American, Auto Pore IV 9500). Samples' absorbance for malachite green solution were investigated with spectrophotometer (Shanghai, UV-2000). The samples' porosity was detected according to the GB/T 1966-1996.

Malachite green solution decolorization experiment: DPC' block bodies (1 g) at different tourmaline content were put in conical flasks having 100 mL initial density 20 mg/L malachite green aqueous solution, and then put in the water bath constant temperature oscillator to shake. Malachite green solution (initial and in 6 hours) was carried on entire journey scanning in the 380~740 nm scope with the UV-2000 spectrophotometer.

RESULTS AND DISCUSSION

Influence of tourmaline to DPC microscopic appearance: Microscopic analysis of DPC at different tourmaline content indicate (Fig. 1): When samples with tourmaline content are 0% and 8% (quality percentage, the following homology), primitive holes on the diatomite plate-type pellets are maintained completely in the materials, and secondary holes formed by the solid-phase sintering are bigger, and the conglutination are few between the aggregate pellets (Fig. 1 a and b). When tourmaline content is 12%, the primitive holes on the diatomite pellets diminish, the finely particles increase simultaneously, the diatomite plate-type pellets are connected by the small pellets and formed three dimensional network structure (Fig. 1c). When tourmaline content is 16%, the plate-type pellets have had distortion, the diatomite primitive holes vanish, the finely particles conglutinate to grow up (Fig. 1d).

This is because of the superfine tourmaline powder introduces the massive strains, the lattice imperfection, as well as the nanometer level microstructure in the DPC, which

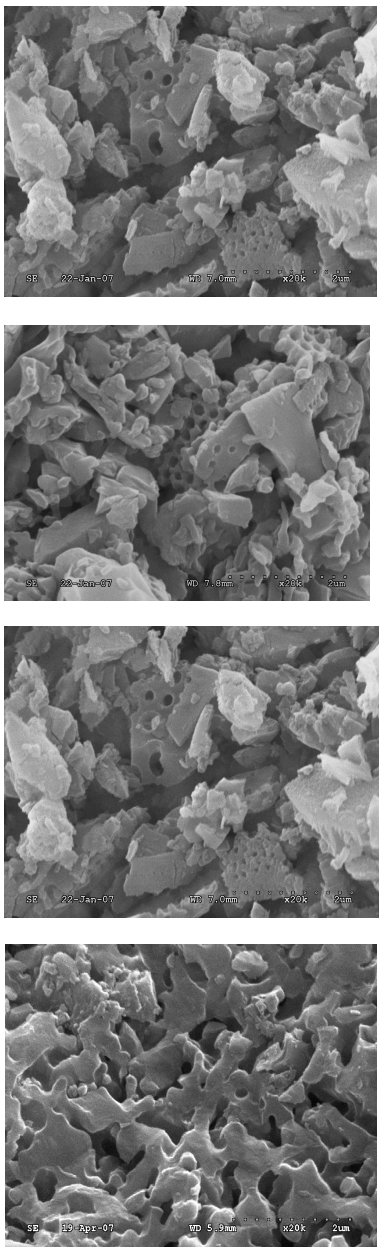

Fig. 1: SEM photograph of DPC in different tourmaline contents. a) 0%; b) 8%; c) 12%; d) 16%

makes the average grain diameter wane, and the powder's specific surface area increase. This causes the powder to have high Gibbs surface energy and low-sintering temperature. So materials with tourmaline content 0% and 8% are not sintered in 960°C (2 h), and the inter-granular crevice is yet bigger. But DPC with tourmaline content of 16% is roasted at 960°C, the pores in the diatomite diminish gradually because of melting. The partial aggregate pellets break into fragments, and then the particle size decreases. Moreo-

ver, according to the agglutination mass transfer mechanism (Dong et al. 2006), the primitive powder is thinner, its force surface energy is bigger, the agglutination propelling is stronger, the particle proliferation range is shorter, and the solubility pellet in liquid phase is higher, and the agglomeration transfer speed is higher, thus the crevice formed by the pellet stack is smaller under the same calcination temperature.

Influence of tourmaline to DPC' pore size distribution : Fig. 2 is the pore size distribution of diatomite porous ceramic in different tourmaline content. The aperture of DPC without tourmaline (Fig. 2a) distributes between 100~550 nm, and the most probable pore diameter is 351.9 nm. Curves of samples with tourmaline content of 8% and 12% move towards left evidently (Fig. 2b and c). The aperture distribution shifts to 80~400 nm and 30~350 nm respectively, and the most probable pore diameter also shifts to 213.6 nm and 178.8 nm respectively. When material with tourmaline content is 16%, aperture distribution range expands to 50~450 nm and the most probable pore diameter move rightward to 232.8 nm (Fig. 2d). Owing to the superfine tourmaline powder content introduced excessively, primitive powder's average grain diameter reduces. Some researches indicated (Wu et al. 1999) that under the high temperature, the fine particle percentage is more, the agglomeration system's specific surface area is higher, the diffuse interface is bigger, and the diffusion is stronger. The fine particles are easier to proliferate toward the big pellet gaps and to divide the big blow hole into several small blow holes. Therefore, after appending the superfine tourmaline powder, the pore size distribution shifts toward left, and the most probable pore diameter decreases. When the superfine tourmaline powder content is 16%, the small blow holes merge as a result of the sintered body over-roasting, and diatomite primitive hole vanishes, which causes the materials' aperture enhance, and the aperture distribution and the most probable pore diameter move towards right.

Influence of tourmaline to DPC pore performance: Table 1 gives the material average aperture, specific surface area and the porosity of the samples at different tourmaline content. As given in Table 1, the tourmaline content increased from 0% to 16%, and its porosity decreased from 49.3% to 36.5%. When tourmaline content is 12%, the smallest average aperture and the biggest specific surface area are 177.5 nm and 6.83 m^2/g respectively. Superfine tourmaline content increases or decreases, the average aperture and specific surface area have varying degree's rise and drop. According to the agglutination mass transfer mechanism, the superfine tourmaline content is higher, the body contraction is bigger. The apertures between the pellet and the

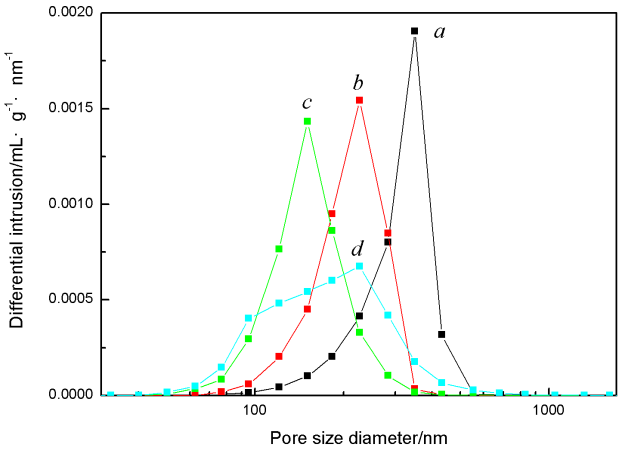

Fig. 2: Pore size distribution of DPC at different tourmaline content. a) 0%; b) 8%; c) 12%; d) 16%.

diatomite primitive hole reduce, thus the materials' porosity drops. This is that the introduction of superfine tourmaline powder increases the proportion of fine particles, which makes the aperture decided by the grain size reduction. Superfine tourmaline powder also makes the primitive powder fine, the surface energy enhance and the agglutination propelling force to increase. The liquid-phase produced by sinter at 960°C makes the diatomite primitive pore size to decrease as a result of the capillarity permeating, so the materials' average pore size reduces with superfine tourmaline powder content increasing. Simultaneously the massive tiny holes in the sintered body also make the materials' specific surface area to increase. When tourmaline content surpasses 12%, diatomite primitive holes vanish by microscopic structure impact of tourmaline. Moreover, in the condition of the liquid-phase participation agglomeration, the pellet displacement and rearrangement observe the smallest energy principle. Surface of superfine tourmaline pellet has higher surface energy and agglutination assistant (at the molten state) connection's pate between the pellets at the high temperature. The pellets close mutually by the surface tension to increase the contact area, and to reduce the relative surface energy, which causes massive adhering in materials. The fine particles grow up and the holes reduce between the pellets, which causes the materials' average aperture to increase and specific surface area to drop.

Influence of tourmaline to malachite green solution decolorization effect: Fig. 3 is the absorbency curve of samples treating malachite green solution at different tourmaline content. It can be seen that the malachite green has the obvious absorption in 618 nm and 412nm and the absorption peak is strongest in 616 nm. The diatomite porous ceramics at different tourmaline content prepared by the same technological conditions, all have high surface area and big contact area

Table 1: Average aperture, specific surface area and porosity of diatomite-based porous ceramics at different tourmaline content.

Tourmaline (%)	0	8	12	16
Average pore diameter* (nm)	323.4	240.1	177.5	223.2
Specific surface area* ($m^2 \cdot g^{-1}$)	4.23	5.12	6.83	6.42
Porosity** (%)	49.3	46.8	39.0	36.5

*Measured by mercury injection apparatus, **Measured by Archimedes method.

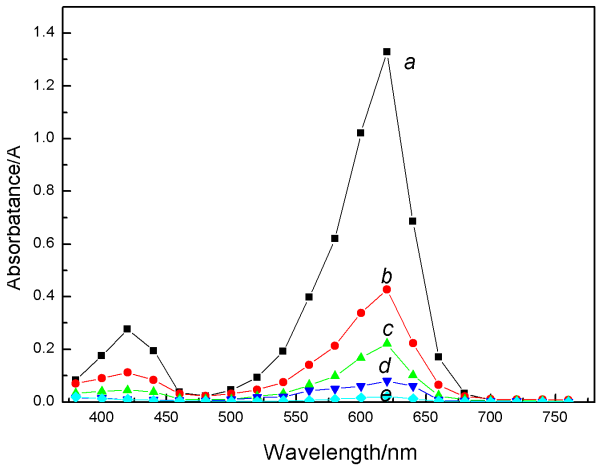

Fig. 3: Samples' absorbency curve for malachite green solution in different tourmaline content. a) Standard sample; b) 0%; c) 8%; d) 12%; e) 16%.

with the solution, so the massive malachite green molecules are adsorbed to the materials' surface or the opening wall. The experiment displays that decrease of malachite green solution absorbency is more obvious with tourmaline content increase in material. The malachite green solution absorbency that is processed by tourmaline content of 16% sample is very small (Fig. 3e, nearly zero).

The reason why tourmaline enhance the decolorization ability of diatomite porous ceramics to the malachite green solution is as follows:

1) Tourmaline spontaneous electrode's existence has been confirmed by the experiment: Tourmaline particle's periphery existing the electrostatic field with the c axis axial surface as the two-pole, and the superficial field intensity achieves 10^7 V/cm^3. Its polar structure enables it to have ability of the two-pole spontaneous adsorption external electric charge and charged particle, to have the intense adsorption to the polar molecule. This makes the material to have the very good adsorption performance, and thus enhances the malachite green numerator' adsorption on the porous ceramics passageway.

2) Tourmaline electrical effect is the electric field to water's electrolysis and electrostatic field to charged ion adsorption and neutralization. Under the electrostatic field function, the electrolysed hydrone forms H^+ and OH^-. OH^- and the hydrone union to produce active molecular $OH^-(H_2O)_n$ that stimulates the electron in malachite green molecular orbit, causes it to the high energy level jump, and then has the electron transport. The molecule itself forms the high-activity granule carrying electron-hole, and $OH^-(H_2O)_n$ to its attack is easier. The malachite green oxidized degradation is decomposed finally into the small member or mineralized completely. Moreover, tourmaline radiation's remote infrared ray can activate hydrone and reduce the hydrone associated strength. When the proper motion frequency of material fundamental particle illuminated by the far infrared matches to the far infrared, it can absorb radiant energy and bring intense resonance, and then cause the object flash to be heated. Quite parts of inorganic substance and majority organic high-molecular compounds have the intense absorption band in the far infrared area, so this can promote the organic matter degradation reaction to carry on fast (Meng et al. 2004). Next, tourmaline may make the dissolved oxygen in the water to increase and the dissolved oxygen's existence also is an important reason that the organic dye is degraded (Cao et al. 2007).

CONCLUSIONS

1. Taking diatomite as the main material, the diatomite porous ceramics was obtained by solid-phase sintering and low-temperature calcination technology. The study focused on the content of tourmaline to the influence of materials' microstructure, pore size distribution and the decolorization ability for malachite green aqueous solution.
2. Sample with 12% tourmaline has smallest average aperture of 177.5 nm and biggest specific surface area of 6.83 m^2/g. As the tourmaline content is increased from 0% to 16%, the materials' porosity declined from 49.3% to 36.5%.
3. Materials' decolorization ability, to malachite green, strengthens gradually with tourmaline content increasing. When tourmaline content is 16%, malachite-green aqueous solution is completely decolourized in 6 h and the absorption peaks disappear at 412 nm and 618 nm.

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