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An study on preparation and utilization of tourmaline from tailings of an iron-ore processing plant

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Abstractt

This paper deals with a systematic research on preparation and utilization of tourmaline from tailings of an iron ore processing plant in Xinjiang, China. Tourmaline has the characteristics of piezoelectricity, thermoelectricity, spontaneous polarization and far-off infrared radiations. Ultra-fine powders of tourmaline have extensive applications in the fields of electrical, chemical and environment protection, as well as health protection. Tourmaline with finer particle size or larger specific surface area will have better industrial performance. After a brief introduction about the applications of tourmaline for functional material, the combined process with gravity separation, ultra-fine dry grinding, and ultra-fine wet grinding is introduced and the preparation technology of ultra-fine tourmaline powder discussed. Using this technology it is possible to produce tourmaline powder with particle size smaller than 100 nm, and a continuous production process can be realized. The final powder product has much superior performance such as high whiteness and large specific surface area, and its negative ions emission can reach the value of 7190 ions per cubic centimeter.

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Keywords: Tourmaline; Ultra-fine grinding; Jet mill; Stirred ball mill; Particle size; Negative ion

1. Introduction

As the most abundant industrial waste material, the tailings from mines in China have amounted to a total mass of more than 20 billions tons, which occupy a lot of precious farming land. The utilization of tailings as new resources has become one of the hotspot topics and presents a real challenge for the Chinese mining industry. This paper deals with a systematic study on the recovery and enrichment of tourmaline from tailings of an iron-ore

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processing plant in Xinjiang, China by high-intensity magnetic separation and gravity concentration, and the utilization of the prepared tourmaline product.Being called as "Emerald jade seal", tourmaline is a boron-bearing silicate mineral, with trigonal and trigonalrhombohedron crystal structure. The molecular formula of tourmaline is $Na(Mg,Fe,Mn,Li,Al)_3Al_6[Si_6O_{18}]\cdot[BO_3]_3(OH,F)_4$, containing trace elements such as: V，Cr，Zr，Mn，Ti，Sr and Ga. Based on its main components, tourmaline can be characterized into aphrizite, tsilaisite, uvite and buergerite. Occurring in prismatic form, tourmaline is produced in granite pegmatite or high temperature-gas hydrothermal minerals[1, 2]. Tourmaline has the characteristics of infrared emission, piezoelectricity, pyroelectricity and spontaneous polarization, and widely applied in electronics, chemical, environment protection and health field. A lot of experimental data showed that the effects of piezoelectricity and pyroelectricity increase as the fineness and the specific surface area of the tourmaline powder increase.

As a noble nature functional material, the application and preparation of tourmaline is still under development. Chen Xubo and etc[3]. made a review and prospection on the applications and development of modified tourmaline powder, while Huang Yunlong, zheng Shuilin[4] and others researched on the tourmaline processing techniques and its application prospects. Ji Liyuan[5] applied a technology of two stages grinding with a low-speed-stirring grinding circuit and a high-speed-stirring grinding circuit, obtaining an ultra-fine tourmaline powders with the fineness of d95 $\leqslant$-2 μ m. Zheng Shuilin[6] and others obtained the super fine tourmaline powders with the fineness of d50 $\leqslant$0.8 μ m and d97 $\leqslant$2.0 μ m by using the agitating mill. Song Yu[7] studied the effect of the wet grinding in different conditions, such as different milling time, ratio of solid to liquid, solvents and amounts of grinding aid.

This paper mainly introduced the possible fields of applications of tourmaline powder, and studied gravity-pneumatic ultra-fine dry grinding-stirred ball milling composite process, which potentially can produce super-fine tourmaline powder with particle size in micron, sub-micron and nanometer range with narrow particle size distribution. By optimization techniques, high whiteness, fine particle size（$d_{50} \leqslant$ 0.5 μ m), narrow particle size distribution($d_{max} \leqslant$ 3.0 μ m), and regularly particle shaped ultra fine tourmaline product can be produced.

2. The applications of tourmaline powder

The main production countries of tourmaline are Russia, USA, Burma, Brazil and etc. Africa is also rich in tourmaline. In China, tourmaline resources mainly distributed in Xinjiang, Inner Mongolia, Yunnan, Jilin, Shangdong and other pegmatite developing area. As a new type of mineral in the industry, stem from its unique properties, tourmaline is widely applied in electronics, chemical, environment protection and health field.

2.1. Water and waste water treatment

Tourmaline has permanent spontaneous electrode in nature, as well as the electrode produced from tourmaline has strong adsorption on heavy metals ions（Cu^{2+}、Pb^{2+}、Zn^{2+}、Cd^{2+}）and other impurities[8]. Infrared ray emitted from tourmaline can resonance with hydrogen bond in water and essentially activates the water molecular into small clusters, which could inhibit the proliferation and reproduction of bacteria in water. Therefore, tourmaline has widely application in activation of drinking water and sewage treatment. Industry applications are environmental washing ball, drinking water purification ceramic ball and so on.

2.2. Functional textile fibre

Tourmaline has the ability to emit negative ions and far-infrared radiation. Apply tourmaline powder with maximum particle size less than 3μm in the production of artificial fibre wire, producing "anion fibre", which have heat preservation and deodorizing effects. It can also enhance blood circulation inside human body, which could increase human physiological functions.

2.3. Medical care

Tourmaline can emit far-infrared electromagnetic wave with wavelength of 4-14μm, which matches the absorption spectrum of human body, and hence absorbed by human tissues, increase the temperature of human tissue, and speed of blood flow, improve microcirculation, and as a result, improve body immunity[9]. It is has been applied in Chinese medicine treatment for rheumatoid arthritis.

2.4. Negative ion paint

Apply as interior wall paint, tourmaline can permanently emit negative ions, which could purify indoor air. Apply for exterior wall paint, it can prevent buildings from acid rain damage or corrosion. Synthetic with organic silane resin, it is feasible to coat on the surface of automobile to improve corrosion resistance. Apply as protective coating material on the surface of ship body, it can absorb anionic, and electrolysis with water molecular, forming monolayer to prevent marine organism attach or grown on ship body, enhancing the corrosive resistance of the ship body.

2.5. Applications on electronic industry and electromagnetic shielding material

Tourmaline can be used as wavelength adjustment device, and polarizer tab in polariscope in radio industry, It can also be used as piezometer for measuring stamping press in air or water. Tourmaline can also react with water molecular in air, forming anion, which can neutralize emitted cation, and block the electromagnetic waves emitted by household appliances, protect human body from radiation.

2.6. Energy saving, emission reduction and other aspects

Studies showed that[10], tourmaline can activate gasoline and diesel, its far-infrared radiation can prompt C=C and C≡C bond resonance of the fuel cells, thereby increase the combustion efficiency and reduce harmful emissions. Synthesis ultra-fine tourmaline powder with organic adhesive to make tourmaline composite coating material. This material can be used in cigarette production, which can reduce the harmful substances in cigarette smoke.

3. Preparation of ultra-fine tourmaline powder

Tourmaline is high hardness, high wearing strength, difficult to crush material. Currently, for the preparation of tourmaline powder, the grinding fineness is normally between 325 mesh to 1250 mesh, and cannot effectively separated from mica, quartz and other impurities. It is therefore hard to prepare the high purity, ultra-fine product, which limit the scope of application of tourmaline. Based on long term exploration tests and researches, applicable technical routine have been discovered to prepare high purity ultra-fine tourmaline powder, and industry application was also achieved.

3.1. Material

The raw tourmaline samples were collected from an iron-ore processing plant in Altai Region of Xinjiang, China. Due to various reasons the tourmaline mineral contained in the tailings of the plant had not been utilized. With a processing flowsheet of high-intensity magnetic separation followed by gravity concentration, tourmaline in the tailings was enriched.

The raw tourmaline samples were collected from Altai Region in Xinjiang of China. Specific gravity of the tourmaline is 3.024 g/cm^3 and the Mohr's hardness is 7.5. The raw material were formed in granite pegmatite type orebody and deposit generated by pneumatolytic-hydrothermal process. It is a typical pegmatite deposit of pneumatolytic mineral. The genetic ore type is the type of magnesium tourmaline. The chemical constituents are given in table 1.

Table 1 The chemical components of tourmaline

Compositions	Content /%
SiO_2	37
TiO_2	0.734
Al_2O_3	31.4
Fe_2O_3	4.64
FeO	2.72
B_2O_3	12.56
MnO	0.0048
MgO	4.87
CaO	0.66
K_2O	0.045
Na_2O	1.987
Li_2O	0.003
P_2O_5	0.013
H_2O^+	2.76
H_2O^-	0.09

3.2. Process and equipments

The ultra-fine tourmaline powder preparation process, with gravity-pneumatic ultra-fine dry grinding-wet stirred ultra-fine grinding composite techniques. See figure 1 for more details.

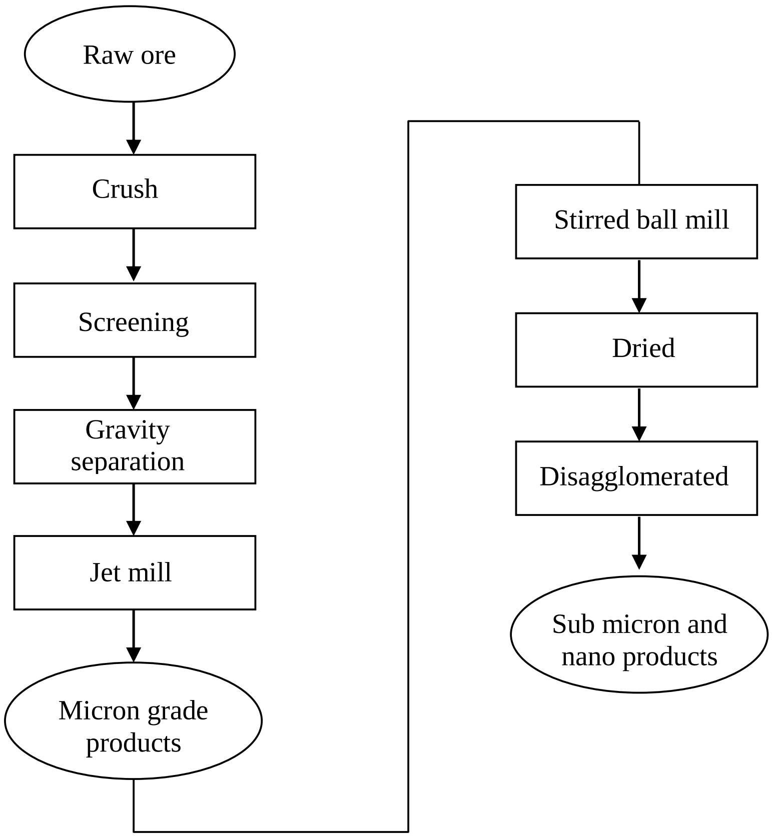

Fig.1 Flowsheet for ultra-fine grinding of tourmaline

3.3. Equipments and grinding medium

For gravity separation, the equipments are: PE400*600 jaw crusher, Φ600*450 roller briquetting, XZY2100*1050 shaking table and etc.

The QLM-Ⅳ fluidized-bed counter-stream jet mill was used to produce super fine powder under dry processing condition. Manufactured by Shenyang Aircraft R&D Institute, this equipment is mainly composed of air compressor, gas source system, feeding system, abraders, products collection system and control system. The total installed power is 307.75 kW.

The SJ-90 stirred ball mill was used to produce super fine powder under wet processing condition, which was manufactured by Beijing General Research Institute of Mining and Metallurgy. This equipment is mainly composed of stirred mill system, circulatory system, cooling system and discharge system. The total installed power is 36 kW.

The grinding medium was zirconia ball, which was provided by Nanbo Structure Ceramic Limited, Shenzhen. The specifications: density 6.0～6.05 g/cm3 , mechanical strength 1000 Mpa, ball size 10 mm and 5 mm in the mass ratio of 1:1.

3.4. Performance measuring equipments

LMS－30(Japan) laser diffraction scatter light particle-size analyzer; 3014X-ray diffractive small-angle scatter light instrument; St-03 specific surface area measurement instrument; HITACHI S-3500N scanning electron microscope; pHSJ-3F pH meter; WSD-III whiteness meter and 5DX Fourier transform infrared spectroscope and so on.

4. Ultra-fine product and testing

4.1. Preparation of ultra-fine tourmaline powder by jet mill

After washing, crushing and screening, the tourmaline raw material is fed to the Jet Mill, the average particle size of the feed is less than 1mm. Keeping other technical parameters constant, and the product fineness of Jet mill was mainly controlled by the speed of the classifying rotator. By using spray nozzle with the diameter of □13 mm and adjusting the rotating speed from low to high, particle size of the product changes from large to small coming out of the cyclone separator. See figure 2 for more details.

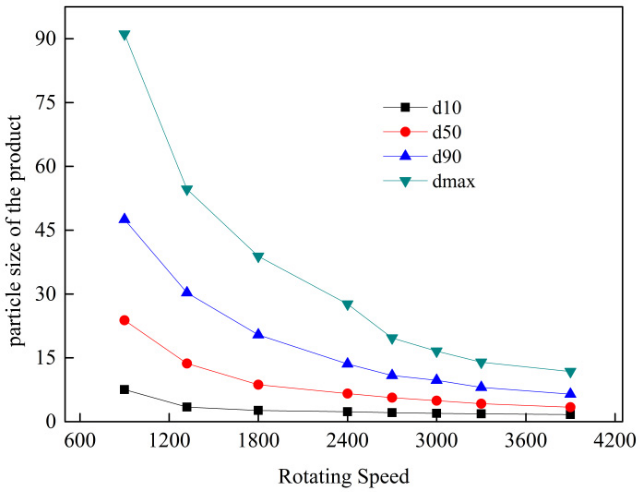

Fig.2 Influence of classification wheel rotating speed on product size of cyclone classifier

4.2. Preparation of ultra-fine tourmaline powder by stirred ball mill

Tourmaline powder prepared by jet mill was used as feed to the stirred ball mill. Use water as grinding solvent, the grinding medium to material ratio was between 3~3.5, the solvent was water. As the grinding fineness decreased, the viscosity of the pulp increased gradually. To ensure a full dispersion of the material, water was added to the pulp and the pulp concentration decreased from 50% to 30%. The pulp was then discharged from the stirred ball mill after 40h of grinding, dried and disagglomerated to obtain the final product of ultra-fine tourmaline powder. Chemical essaying showed that the purity of final product is above 99%. Figure 3 showed the measuring results of laser particle size analyzer.

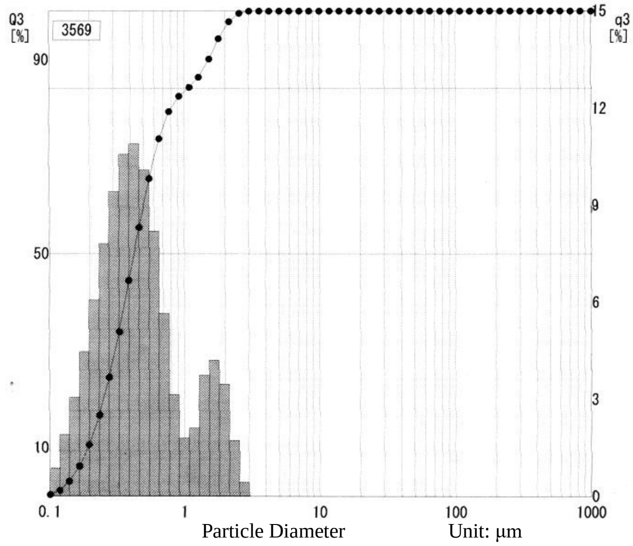

Fig. 3. Particle size distribution of super fine tourmaline.

4.3. Product measurement by scattering and small-angle diffraction

The result of measurement by LMS-30 laser particle size has some limitations in measuring size range and reducing error. Therefore the product JB80 was also analyzed by scattering and small-angle diffraction with the 3014X-ray analyzer, the results are shown in Table 2.

Table 2 Test results of X-ray diffraction for super fine tourmaline

Size Interval（nm）	f(D)(%/nm)	Mass Fraction%	Cumulative%
1～5	0.32	1.3	1.3
5～10	0.68	3.4	4.7
10～18	0.77	6.2	10.8
18～36	0.68	12.2	23.0
36～60	0.61	14.7	37.7
60～96	0.42	15.2	52.9
96～140	0.32	14.0	66.9
140～200	0.23	14.1	81.0
200～300	0.19	19.0	100.0
Mean Size D=111.4(nm)	Median Size d=89.0(nm)	Distribution Spread B=82.9(nm)	

It can be seen from Table 2 that by using the combined grinding technology a product of ultra-fine powder with average diameter of 89 nm, d_{max} diameter of 300 nm was obtained.

4.4. Measurement of specific surface area

The ultra-fine tourmaline product was analyzed with the ST-03 specific surface area analyzer. The specific surface area measured was 53.3 m^2/g . The formula (1) was used:

$$d_{average} = 6 / (S \cdot \delta) \tag{1}$$

Where δ is the mineral density (g/cm^3), the average particle size can be calculated. With the mineral density 3.02 g/cm^3, the average particle size calculated was 37.2 nm, indicating a powder product with particles in 100 nanometer was obtained using the combined grinding process.

4.5. Analyze with SEM

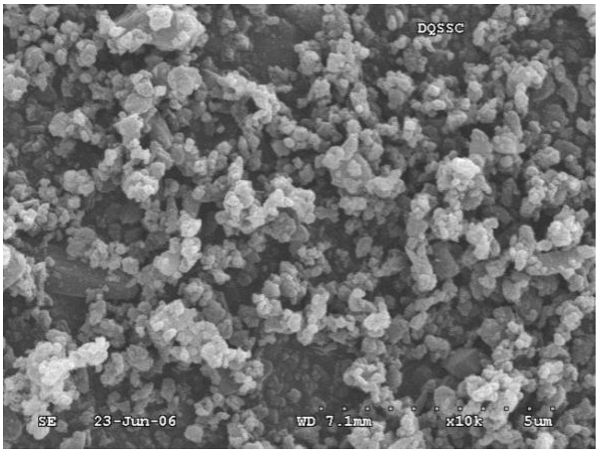

Fig. 4. SEM picture of super fine tourmaline.

The ultra-fine tourmaline product was analyzed with the HITACHI S-3500N SEM. The SEM picture of the product is shown in Fig.4, the product particle is uniformly distributed and the average particle size is less than 100 nm.

4.6. Measurement of PH

The pulp of the product was measured with the pHSJ-3F pH-meter. The pulp prepared with the tap water in Beijing has a pH value of 8.80 under the condition of the pulp density 30% and the temperature 20 ℃.

4.7. Measurement of whiteness

The whiteness of the product JB80 was measured with the WSD-III whiteness meter, and the whiteness value (Wh) obtained was 76.70.

4.8. Measurement of occurrence density of negative ion

Ultra-fine tourmaline powder was analyzed at Quality Supervision Center of Shanghai Textile Industry. It was found that the number of negative ions generated can reach the value of 7190 per cubic centimeter.

4.9. Detection of far-infrared radiation

Ultra-fine tourmaline powder was analyzed by the 5DX Fourier-transformed infrared spectrometer emission/transmission spectroscopy, and the result showed that the infrared emission of the powder in the waveband of 8～15 μm was 0.88.

5. Ultra-fine product and testing

The results presented indicate that, (1) Tourmaline is widely applied in electronics, chemical, environment protection and health field, and the effects of piezoelectricity and pyroelectricity increase as the fineness and the specific surface area of the tourmaline powder increase. (2) With a processing flowsheet of high-intensity magnetic separation and gravity concentration followed by ultra-fine grinding (dry and wet), tourmaline powders of various sizes as functional materials can be prepared from the tailings of an iron-ore processing plant. (3) The pulp of the ultra-fine tourmaline powder obtained has following specifications: Average particle size less than 100 nm, the specific surface area of the tourmaline powder 53.3 m^2/g; the whiteness value (Wh) 76.70; the number of negative ions emission 7190 per cubic centimeter and the infrared emission of the powder in the 8～14 μm waveband 0.88. (4) The processing flowsheet was reliable and easy to operate. The tourmaline powder obtained has superior performance. (5) The study showed it is possible to recover tourmaline mineral from the tailings with the given processing flowsheet, obtaining salable products with high added value.

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