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Study on the plasticity and sintering properties of electrolytic manganese residue

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Abstract: Electrolytic manganese residue (EMR) is an acid filter residue and contains a large amount of hazardous substances. The plasticity and sintering properties of EMR heated at 920-1020˚C are measured. EMR primarily consists of quartz (SiO_2) and chemical gypsum ($CaSO_4 \cdot 2H_2O$), and has a high plasticity. The water absorption and porosity increased but the density and the bending strength decreased with the sintering temperature rising at 920–980˚C. Inversely, the water absorption and porosity of sample decreased but the density and strength increased at 980–1020˚C, and it has the maximum density (1.439 g/cm^3) and maximum strength (8.7 MPa). Once sintered above 980˚C, some liquid phases appear and lead to shrinkage and cracking, indicating the failure of continuous sintering.

Introduction

Electrolytic manganese residue (EMR) belongs to a kind of acid filter residue produced in the production process of electrolytic metal manganese[1]. EMR contains a large number of the heavy metallic ions, the solubility salts and other solid mineral compositions such as sulphates, ammonia-nitrogen and water solubility Mn^{2+}, Cu, Zn, Cr, Pb, As, Co et.al hazardous substances. The damaging exploitation and excessive digging of the manganese-ore have given rise to the increasingly decline of manganese-ore grade, and per 1 ton electrolytic manganese can produce 9-11 tons acid-soaking EMR[2]. If landfilled directly in air, Mn-residue even shows the slurry-like due to the higher water content. At present, there is still no good ways to treat the Mn–residue, and the large–scale stacking and landfill is still the valid and direct method for Mn–residue. As a result, it brings to many harms such as the land occupation, the pollution of underground/surface water, and the serious deterioration of soil/air environment due of some poisonous elements inside the Mn–residue[3], which restricts the healthy and sustainable development of the manganese industry.

Experimental procedures

After dried at 80˚C for 8 h and thoroughly mixed by ball milling, the raw Mn–residue powder was then uniaxially pressed into a cylindrical compact (Φ80×8 mm) under 40 MPa pressure and a cubical compact (37mm×6.5mm×6.5mm) under 25 MPa pressure, respectively. The phase was identified by X–ray diffractometer (Model DX–2700), and the plasticity index was measured by plasticity tester (Model KSB). The sample was pressurelessly sintered at 920–1020˚C and then soaked at the peak temperature for 2h. The water absorption (W_a), porosity (P_a) and density (D) were measured by Digital Ceramic Water–absorption tester (Model TXY) with the Archimedes method. The bending strength was measured by the electric general materials instrument (Model RGM–4100), and the microstructure was observed by scanning electron microscope (Model JSM–5610LV).

Results and discussion

XRD analysis

Fig. 1 shows the phase identification of the Mn–residue powder, which exhibits its phase constituents mainly including the quartz (SiO_2, PDF no.: 65–0466) and gypsum, namely calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$, PDF no.: 33–311). The both characteristic spectral lines keep rather keen-edged, indicating the Mn-residue having a well crystal habit. Due to the higher calcium sulphate content, the Mn–residue belongs to the industrial gypsum waste. Additionally, some weaker wide peaks among the XRD patterns probably result from the noncrystalline ores among the diverse compositions of raw manganese mine, or other trace mines not detected by XRD because the production process of electrolytic manganese did not generate new noncrystalline ores. Qian's[4] work declared that Mn-residue mainly contains quartz and gypsum, and small hehatite, and can replace plaster using as the cement retarder.

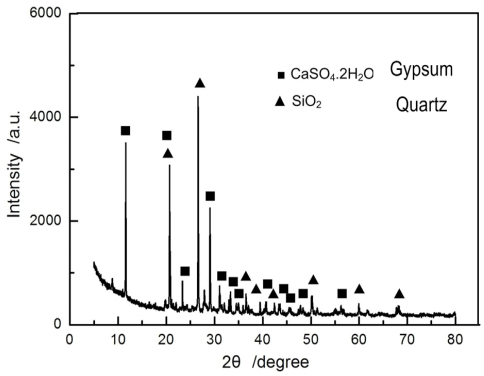

Fig. 1 XRD pattern of raw Mn–residue.

Plasticity

The plasticity of ceramic mud-pie plays an important role in controlling the forming process for ceramic green body. Generally, the plasticity of clay mud-pie is denoted by plasticity index. The plasticity index exceeds 3.6 for the high plasticity clay, lies at 2.5–3.6 for the middle plasticity clay, and is less than 2.5 for the low plasticity clay[5].

Three Mn-residue mud-balls with various water contents (75 g per ball with Φ45±1 mm diameter) were aged various times (0, 1, 2, 3 and 5 days). *Fig*. 2 shows the plasticity index of Mn-residue mud-balls with various aged times and water contents. As seen, with the aged time increasing, the plasticity indexes of mud-balls decreased linearly. All plasticity indexes of mud-balls aged within 2 days exceeded 3.6, and those of mud-balls aged within 5 days exceeding 3.6 were over 21%, which means Mn-residue exhibiting rather high plasticity. Furthermore, the water content reveals the evident influence on the plasticity of Mn-residue, and too high or too low water content is not always advantageous for the plasticity. The mud-pie plasticity is closely linked to the mineral type, the particle size and shape, and the categories of adsorbing cation, namely to the hydration shell thickness formed around the particles. The too much water will generate fluxion and thus lose the plasticity. Otherwise, the too low water will lead the continuous hydration shell to fracture, the internal friction to elevate, the plasticity to fall, even to emerge the loose state under the lower pressure.

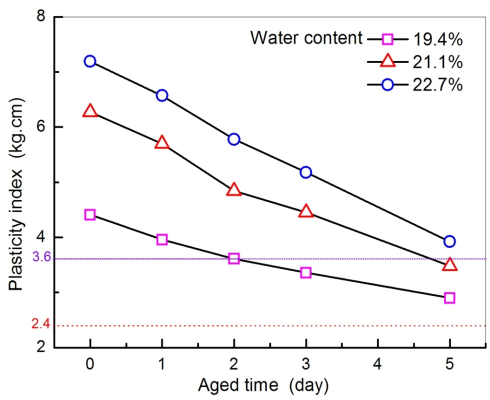

Fig. 2 Plasticity index of Mn–residue with various aged time and water content.

Sintering properties

Fig. 3 shows the appearance of sample sintered at 920–1020˚C. As seen, the appearance primarily takes on the drab. Relative to the upper surface, the lower surface shows the thick puce owing to the heterogeneous sintering atmosphere, which is maybe concerned with the gas emitting and discharging produced by sintering process. The decomposed SO_3 gas easily volatilize and is a kind of poisonous and thick pungent smell gas, if letting out to the air will bring to the serious environment pollution. So burning the Mn-residue, it must consider the SO_3 discharging, in case the

second pollution generated by Mn-residue sintering. When the temperature exceeds 1000˚C, the sample occurred the obvious shrinkage, cracking and deformation, meaning the continue sintering failure.

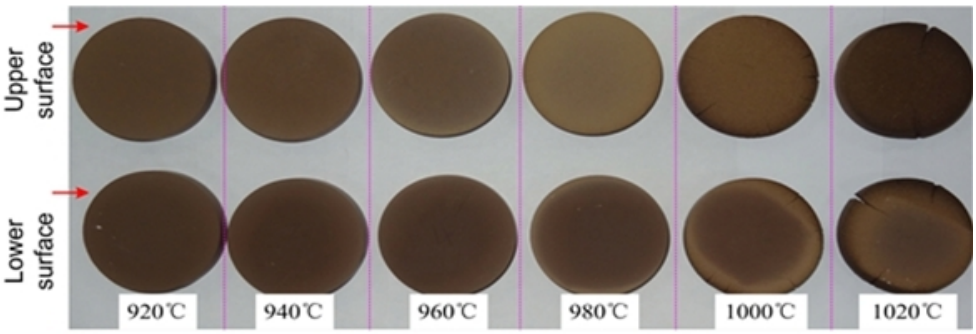

Fig. 3 Macro-shapes of Mn–residue compacts at various sintering temperature.

The water absorption, porosity and bulk density are the key parameters to evaluate the ceramic sintering materials, especially for those of industrial slag compact. The crystal water in the Mn-residue is rather difficult to remove in spite of the free water can remove through the long-time drying. *Fig*. 4 shows the water absorption, porosity and bulk density at various sintering temperature. At 920–980˚C, the W_a and P_a of Mn-residue burning samples gradually increased with temperature rising and reached the maximum at 980˚C, which is linked to the dehydration of calcium sulphate dihydrate and the ceaseless volatilization of SO_3 gas from calcium sulphate decomposition. However, the W_a and P_a gradually decreased instead once temperature exceeds 980˚C. When sintered at 1000˚C and 1020˚C, the volatilization of SO_3 gas has finished, and the liquid phase melting became more and more. These liquid phases will endlessly infiltrate and diffuse, and hence fill and stuff the formed much pores, which makes the W_a and P_a fall down. Due to the same reason, the bulk density of sample appears opposite change trend, and obtains the maximum of 1.439 g/cm^3. However, during the temperature falling, these liquid phases will solidify and generate the stronger internal stress to make the burning compact produce more cracks and fractures. As a result, for the single burning of Mn-residue, it is not always favorable for the sintering properties once temperature exceeds 980˚C.

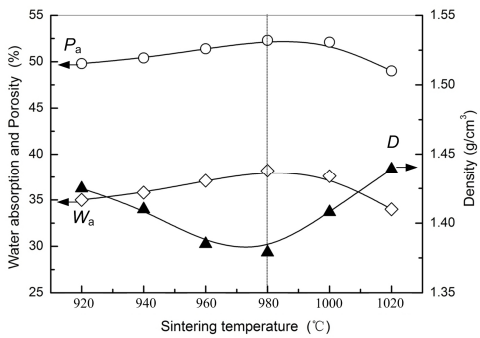

Fig. 4 Water absorption, porosity and density of sintered Mn–residue at various temperatures.

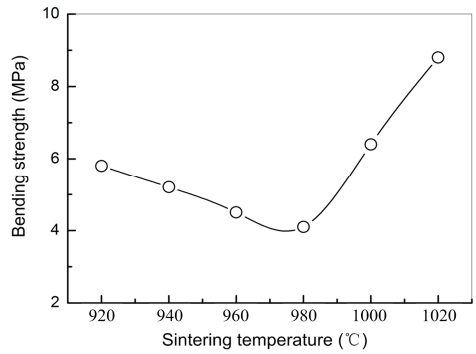

Fig. 5 Bending strength of sample at various temperatures.

Bending strength and microstructure

Fig. 5 shows the bending strength at various temperatures. Clearly, the bending strength gradually decreased at 920–980˚C, but increased sharply at 980–1020˚C and reached the maximum value (8.7 MPa). This bending strength reversion is related to the porosity change and the liquid phase appearance. Commonly, the strength of ceramic materials reduces with the porosity rising and increases with the liquid phase increasing. The amount, size, shape and distribution of pore all have the evident influence on the strength. At 920–980˚C, no appearance of liquid phase and the increasing porosity will lead the bending strength to lower down. At the same time, because of the volatilization of impurity connected with other particles inside Mn-residue and the $CaSO_4$ decomposing into CaO

and SO_3, the binding force among Mn-residue particles lower down and the internal stress resistance to deformation fall too, which leads the bending strength to gradually decrease. On the contrary, at 980–1020˚C, the porosity gradually reduces. In particularly, the presence and increase of liquid phase can fill into the pores and adhere the particles each other to form a uniform and tight structure, and thus increase the bending strength. On the other hand, when the rapid increased molten phase cooled down, the coefficient difference of linear expansion within the sample will tear the sintered body during solidification, which results in the sintering sample producing more and larger macro-cracks.

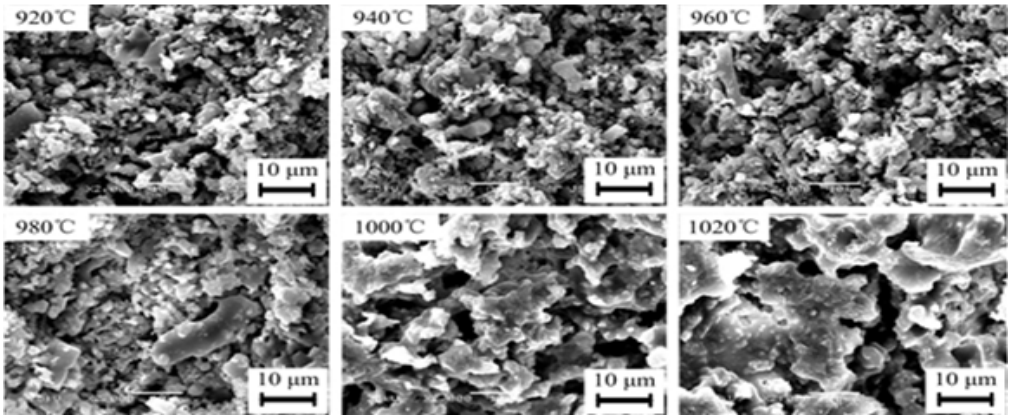

Fig. 6 Fractured Microstructures of samples sintered at various temperatures.

The fractured microstructure of sample sintered at different temperatures is revealed in *Fig*. 6. At 920–980˚C, the particles in the fractured surface take on the loose status and the pores become more and larger. But at 980–1020˚C, the pores decrease obviously and there appears many coagulated clumps filling into the pores and adhering with each other, meaning the Mn–residue melting. It is suggested that the mineral composition of Mn-residue should contain some transparent or semitransparent glassy body. After sintered, a few of the well-developed crystalline phase means that Mn-residue belongs to an industrial solid waste with some potential activity. It is the liquid phase increase that leads the W_a and P_a of sintered samples to unceasingly lower down once above 980˚C, inversely the bulk density and bending strength continuously elevate. It is unfavorable for only Mn-residue to continuously heat above 1000˚C owing to the appearance of many macro-cracks.

Summary

The Mn–residue mainly consists of quartz and gypsum and reveals the high plasticity. Sintered at 920–1020˚C, the W_a , P_a, densification and bending strength of samples are closely linked to the Mn–residue melting. It is unfavorable for only Mn-residue to continuously heat above 1000˚C.

Acknowledgements

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