Glass matrix composite material prepared with waste foundry sand

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Abstract: The technology of glass matrix of the composite material manufactured through a sintering process and using waste foundry sand and waste glass as the main raw materials was studied. The effects of technological factors on the performance of this material were studied. The results showed that this composite material is formed with glass as matrix, core particulate as strengthening material, it has the performance of glass and ceramics, and could be used to substitute for stone.

Key words: waste foundry sand; waste glass; composite material

CLC mumber: TG 221+.1 Document Code: A Article ID:1672-6421(2006)04-0279-05

Water glass foundry sand has the advantages of being unreactive, low cost, easy acquisition, etc, thus its use is developing fast. In China, 12 million tons of castings are produced every year, of which 1.5 -1.7 million tons are produced using water glass sand, until now the waste foundry sand has polluted the environment if it has not been fully recycled. At present reclamation and utilization as a building material are applied to make use of waste foundry sand. Reclamation technology can save raw materials, decrease waste, and reduce the cost of castings. But the reclamation techniques for waste foundry sand have not been fully resolved, lots of dust and chippings inevitably appear during the process; these wastes contain alkali, which is the main environment pollution caused by waste sand. The method of resource recovery for waste foundry sand at present is to use it as a building material. For example, waste foundry sand has been used in asphaltum concrete in Finland; the size and chemical composition of waste foundry sand is the same as natural sand, so it can be substituted for natural sand in road surfaces of asphaltum concrete. Research of resource recovery of waste foundry sand began in the early 1990s in China, and a type of polymer composite material had been discovered. Well lids used in municipal engineering made from this material had been widely applied in the fields of drainage, telecommunication, gas, and feed water because of its high strength and with no metals in it. The technology of phosphate foam ceramic which uses waste foundry sand as a main raw material has been reported in recent years.

The technology of glass matrix of the composite material manufactured by a sintering process which uses waste foundry sand and waste glass as main raw materials is studied in this paper. This material has the performance of glass and ceramics, but avoids the more strict processing condition, such as high temperature melting and sinter. It's a green technology route.

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Received date: 2006-02-06; Adopted date: 2006-10-10

1 Principles, techniques, and investigation

1.1 The principle of preparation of glass matrix composite material

The chemical constitution of waste foundry sand is SiO_2, Na_2O, a little Al_2O_3, CaO, MgO, Fe_2O_3, Fe, and F. Na_2O, F-, and phosphate used as fluxes could reduce the melting temperature of the glass and accelerate sinter. Waste glass and waste sand can melt mutually and randomly at fused state due to the resemblance of their chemical components. Glass is a non-crystalline solid with no fixed melting point; it begins to soften at 600℃ and to flow at 900 ℃. While the crystal form of SiO_2 in waste foundry sand occurs to transform, the physical state basically stays stable. Thus, the continuum phase of the glass matrix composite is a kind of glass matrix made by sintering. The decentralization phase is granules of waste foundry sand. Macroscopically the conconfiguration of the glass matrix composite is waste foundry sand wrapped by waste glass. the improved properties of interface and glass matrix will result in a new kind of composite material with perfect performance.

1.2 Properties of raw materials

Waste foundry sand, waste glass, clay, water glass, coal dust, and additives were used as the main raw materials in the study. Their chemical and physical properties are shown in Table 1.

Table 1 Compositions of main raw materials wt.%

Raw materials	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	Other
Waste foundry sand	95.17	2.22	0.26	0.1	1.46	0.78	0.01
Waste glass	74.80	2.25	6.18	2.32	0.11	13.78	0.56
Clay	67.57	15.44	1.14	1.34	7.53	0.45	6.53

1.3 Apparatus

PE100X60 Jaw breaker, XMQ-67 ball mill, JJ-5 cement mortar mixer, 150 t pressure former, SRJX-8-13S high temperature stove, 20 kN universal test machine.

1.4 Experimental procedures

(1) First, waste foundry sand and the other raw materials were broken, ground and graded respectively. These powders were mixed with water in different proportions.

Subsequently, the mixtures were pressed to a certain shape, dried, and sintered. The effects of different proportions of the raw materials and different values of technical parameters on strength and appearance configuration were studied.

(2) Bending strength and exterior quality were adopted as assessment indexes of performance during this experiment.

2 Investigation and analysis

2.1 Effect of granularity of waste foundry sand on properties

Waste glass was ground as the matrix material and its granular size was less then 125 μm. Waste foundry sand of different granular sizes was mixed with the waste glass powder, in each case the two materials having the same weight. The results showed that the granular size had a distinct effect on the properties of the composite material. Looking at the exterior quality and bending strength, the composite material prepared from waste foundry sand of granular size 0.42 - 1.7 mm distorted greatly and the surface was coarse, while the composite material prepared from waste foundry sand of granular size 0.25 - 0.42 mm had perfect exterior quality without much distortion.

When the granular size of waste foundry sand is bigger, the interspaces of waste foundry sand are more. When stuffing is deficient or sintering temperature is lower, the waste glass will not melt and flow, so pores will exist in the interspaces. When the sintering temperature is higher, the waste glass will soften and flow, granules of waste foundry sand will distribute in the form of "island", leading to greater distortion of the waste glass matrix material. When the melting or sintering temperature is higher, this distortion phenomenon appears more marked. As shown in Fig. 1, in this experiment as the granular size gets smaller, the strength appears higher. Substantially, the pores decrease, the density increases, and the distortion reduce. But this effect of the granular size works only within a certain range of sizes. When the granular size is below a certain value the strength reduces instead. This is because as the granular size gets smaller, the surface area gets bigger, needing more waste glass to wrap the granules of waste foundry sand. When there is a shortage of waste glass, deficient continuum phases between the granules of waste foundry sand will result in the strength of composite material to be decreased.

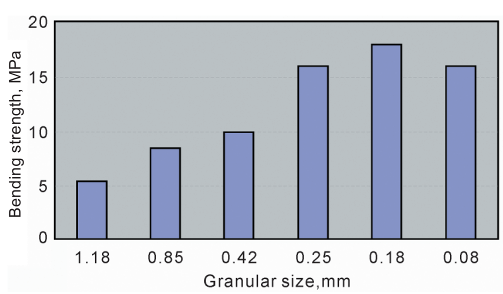

Fig.1 Effect of size of waste sand on strength

2.2 Effect of the amount of waste foundry sand on the properties of composite material

In the system of waste foundry sand-waste glass-water glass, the granular size of the waste foundry sand and waste glass was 125 μm. With the change of the proportions between waste foundry sand and waste glass, the composite material made at different sintering temperatures follows obvious laws as shown in Fig. 2. Waste foundry sand has a strengthening effect when the content of waste foundry sand is below 50 %. On the one hand, at a certain sintering temperature, glass soften at first, and its process is that long chain silicate networks in glass begin to deploymerize, becoming short chain configuration. It is the perfect fluidity and soakage of these oligomers that the surface of waste foundry sand is wrapped. In the course of wrapping, water glass film on waste foundry sand is compatible with glass. On the other hand, Na_2O in water glass film can break the glass network, decrease the soften point of glass, and increase fluidity. Furthermore, Na_2O and SiO_2 in waste foundry sand can form a vitreous body, with the same configuration and properties as waste glass added at first, which don't occur microseparate and lamellar precipitation. While silicate network formed due to water glass solidified functions as filling of the network, so fused and new vitreous body formed reveals perfect compatibility. Physical and chemical reactions of the liquid phase during the course of the sintering process only occur on the surface of waste foundry sand. This also fills lacunas and cracks in the waste foundry sand granules; subsequently the interface configuration is optimized. During the preparation of the composite, waste glass goes circularly through glass state-glutinous state-liquid state-glass state. Frequent temperature and phase state changes inescapably result in stress, and induce formation of microcosmic lacunas and cracks. Moreover, during the course of sintering, waste foundry sand goes through crystal transformation, but the phase state of the core granules doesn't change, thus limiting the distortion of glass, and reducing the negative effects on properties. Waste foundry sand granules have a strengthening effect within a certain spectrum, the higher the sintering temperature is, the better the strengthening effect is.

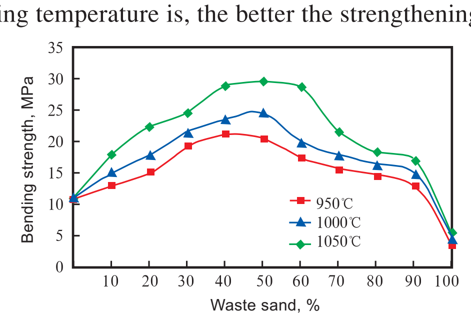

Fig.2 Effect of proportion of waste sand on strength

When the content of waste foundry sand exceeds 50 % with a sintering temperature of (1 000 ± 50)℃, the strength of the composite tends to decline. As shown in Fig. 2, when only waste foundry sand is moulded and sintered, the composite shows certain strength, because water glass used as adhesive helps to melt and form a vitreous body.

2.3 Effect of types of binders on properties of composite materials

The mixture of waste foundry sand and glass is a barren material and has no adhesion, so a binder must be added into the mixture to form the composite. There are various types of binders, the criteria in choosing one are that it first satisfies the forming needs and simultaneously participates in the chemical reaction of solid phase in the sinter process. In this experiment clay, sodium silicate, and phosphate were chosen. Their effects on the performance of the composite material are shown in Fig. 3. The phosphate binding admixture could not only satisfy the forming need, but also greatly contributes to the strength. The reason is that P_2O_5 as the oxide that forms the glass, has a better coring ability than the silicate glass, and easily forms the asymmetrical phosphoric acid polyhedron in the Si-O network, as the electric field of P^{5+} is stronger than Si^{4+}. It could separate from the Si-O network with the R^+ and R^{2+} in the glass and make the glass microseparate and become microcrystalline. In addition, the phosphoric acid can also react with the waste foundry sand, and the formation of phosphate make granules to be bonded firmly together that is of benefits to later sinter. The clay, having the oxide of iron and an alkali metal salt, has the ability of forming vitreous bodies in the sintering process. So it is beneficial to the sintering that appropriate amount of clay is added, but has less effect on the strength. The sodium silicate can promote a complete vitrification response, but if there is already enough glass in the mixture, its contribution to the strength is less.

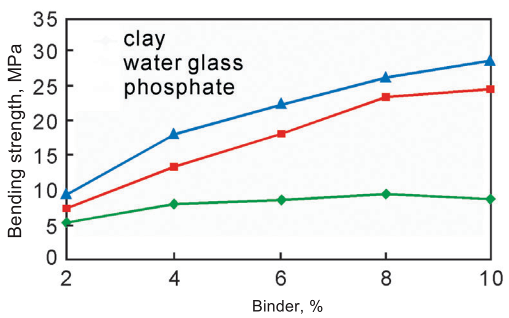

Fig.3 Effect of types of binders on strength

2.4 Effect of additive

Several additives, such as TE-1, TI-2, TC-3, TZ-4, were studied. when the quantity added is all 3 %. Figure 4 shows that there is obviously a strengthening effect. The mechanism perhaps is due to these additives including iron, titanium, chromium, phosphorus, or copper oxides could make the glass microseparate, and results in inhomogeneity nucleation in the interface, and thus produce fine crystal glass in the interfacial glass phase, and improve the strength of the composite material.

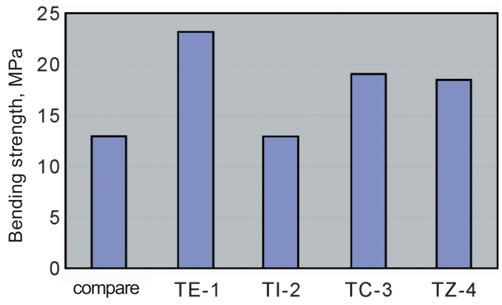

Fig.4 Effect of special oxide on strength

2.5 The influence of technical parameters on performance

The performance of the material was affected by technical parameters such as the content of water in the mixture, forming pressure, sintering system and the heat treatment method.

The right content of water is the major guarantee for the forming strength of the unsintered pressed compact, and it is difficult to form and the layer cracks easily if the water content is too low; if it is too high the unsintered pressed compact is seriously deformed, its strength is low, and it is difficult to transport. The amount of water relates to the particle size of the mixture. In the common sense, the finer the particle size, the higher the required water content; and the higher the pressure, the lower the required water content is for correct forming.

Through pressing, the loose particles gain specific shapes, the dispersed particles being in close touch reduces the amount of air, and the large volume change can be reduced in the sintering process. Pressure must be controlled within specific limits; if the pressure is too high, elastic impedance is produced in the mixture, with the unloading of pressure elasticity tends to revert and the expansion of compressed air will make the base body split. So, generally the pressure of operation should be under the pressure of limit moulding; within this range, if the pressure is higher the strength of unfired brick and the products would be improved steadily. Figure 5 clearly reflects this experimental phenomenon.

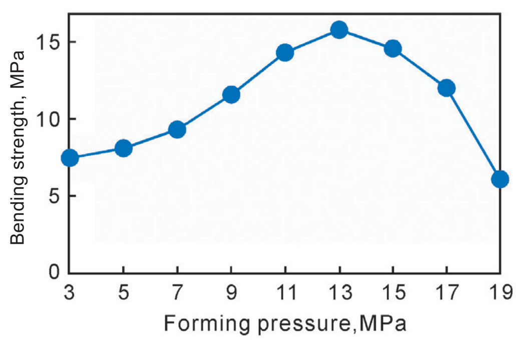

Fig.5 Effect of pressure on strength

The sintering process mainly includes drying, sintering and heat treatment, and it is the most important process in preparing the vitreous body material. At the drying stage, the water content escapes and the unsintered pressed compact hardens gradually; the chemical reactions do not occur yet. In the sintering stage, the waste glass in the raw material softens gradually, soaks into the non-vitreous particles, getting rid of the gas, filling in the holes, and gradually forming the vitreous body. The heat treatment is mainly to avoid the impact on quality of the products during the course of cooling after sintering. The sintering temperature relates to the proportion of glass in the raw materials, when the proportion of glass is higher, the required temperature is lower; when the proportion of glass is lower, the required temperature is higher. If the sintering temperature is too high, the matrix deforms seriously, producing a large number of bad air holes, and reduces the strength. Sintering time also has an effect on the performance of the material. For thin wall products, the time of sintering should be between 0.5 to 1.0 hour; if it is too short sintering is incomplete, if it is too long it will cause oversintering and lower the quality of the product.

After full sintering, generally cool within the furnace; when the furnace temperature falls below 80℃, the material can be removed from the furnace. However, the sample with the better quality appearance often cracked during milling of the surface. In order to reduce this phenomenon, the heat treatment method was changed during the experiment. The process is that after cooling within the furnace to a given temperature, hold the material for an hour, and then lower the temperature within the furnace again. The experimental results indicate (see Fig. 6) that under the different given temperature (560℃, 750 ℃, 850℃), the cracking phenomenon reduces, and the strength is higher than that under the conventional temperature. The reason may be two respects: firstly, the hot stress produced in the course of lowering the temperature could be dispelled by the heat treatment; secondly, if the glass still has the characteristics of stickiness and elasticity within the range of heat treatment temperature, crystal would take place in vitreous body, namely turn from the unstable state of thermodynamics and dynamics into the crystal form that is called glass ceramics. The transformation of the crystal form mainly takes place above 700 ℃; while the elimination of the hot stress mainly takes place below 700 ℃. So it is a comparatively effective measure to strengthen the material through the heat treatment.

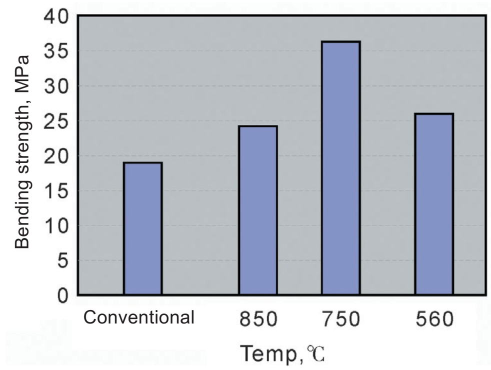

Fig.6 Effect of heat treatment on intension

3 Performance of glass matrix composite material

Table 2 shows that the mechanical performance of the glass matrix composite material prepared from waste foundry sand is close to that of the microcrystal glass and is superior to the natural stone.

It was proved that waste foundry sand as raw material was unstable, for the sodium silicate contained within the waste foundry sand could form the white frost in the dark and damp environment and make the aqueous solution assume strong alkaline properties. Several additives had been added to the mixture during the process of preparation to improve the strength and performance. They would exude easily and affect the security using if additive occur unstable in material. For this reason, the toxicity and causticity were analysed. Table 3 shows that the glass matrix composite material had the ability to firmly envelop any heavy metal and would not influence the health under the natural conditions.

Table 2 Performance of glass matrix composite material compared with others

item	glass matrix composite material	microcrystal glass	granite	marble
Bend strength, MPa	19 - 41	32 -70	9 - 25	6.7 - 20
Density, g/cm^3	2.3- 2.5	2.7	2.6 - 2.7	2.6 - 2.7
Rate of absorb, %	0.1	0	0.2 - 0.5	0.2 - 0.5
Ability of bearing alkaline/quality losing, %	98.5 %	99.95 %	> 96 %	
Wearability, g/m^2	0.15	0.07	0.21	
Microhardness	386	> 700	130 - 570	120 -140

Table 3 Analytical result of toxicity and corrosivity

	Heavy metal,mg/L							
	Hg	Pb	Cd	Cr	Cu	Ni	Zn	pH
Mixture of raw materials	0.005	0.16	0.08	0.78	0.096	0.047	0.36	13.5
Glass base composite material	Undetected	0.003	undetected	0.091	0.032	0.018	0.053	7.2
Standard value	0.05	3.0	0.3	10	50	10	50	12.52.0
Standard of test	GB5085.1-1996							

4 Analysis of technical and economic factors

The performance of glass matrix composite material prepared from waste foundry sand and waste glass is close to that of the building microcrystal glass; it could be used in large amounts in urban construction as a substitute for natural stone and concrete too.

To construct a production line of 100 000 m^2 annual output for microcrystal glass, would need a 3.8 million yuan investment, 1 200 m^2 floor space, and a 290 kW capacity electrical installation. The total manufacturing cost of glass matrix composite material is 30 yuan/m^2. This production line could dispose of about 10 000 tons of waste foundry sand annually, saving 300 000 yuan RMB directly in foundry work. The product would be worth above 5 million yuan RMB and the direct economic benefit would be 1.5 million yuan RMB annually.

5 Conclusions

(1) The glass matrix composite material could be prepared with waste foundry sand and waste glass as the main raw materials and through sintering. The major factors affecting the performance of this material are particle size of waste foundry sand, the proportions of the materials, the forming pressure, and the sintering method. In the material, strengthening of the sand particles is the key, and in the course of heat treatment, whether the increase of strength is the result of glass developing into a ceramic needs further research.

(2) The glass matrix composite material has good physical and mechanical performance and chemical stability. The production process is simple, the cost is low, and the material may be used widely as a substitute for natural stone in urban roadway construction.

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