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One-step glass-ceramics production process using iron smelting slags of spent automotive catalysts

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ABSTRACT
The most important secondary resources of platinum group metals (PGMs) are spent automotive exhaust catalysts, which are called “mobile PGM mines.” Low-temperature iron-capture technology is a promising technology for recovering PGMs due to its high efficiency and low pollution. Because of the content of aluminosilicates and toxic heavy metals (Cr, Ba, Ni, and Mn), the disposal of iron-capture smelting slag is necessary. This paper is devoted to the solidification of heavy metals and the resource utilization of iron-capture smelting slag. Glass-ceramics were made by a one-step method using aluminosilicates as network formers. Heavy metals and CaF_2 are employed as nucleating agents in pickling sludge. According to the analysis of differential scanning calorimetry, the glass transition temperature and crystallization temperature of samples are in the range of 650 ℃–700 ℃ and 800 ℃–920 ℃, respectively. The gap between the glass transition temperature and crystallization temperature of samples decreased from 211 ℃ to 150 ℃ when increasing the amount of pickling sludge from 7% to 28% (mass fraction). The devitrification activation energy decreased from 321.8 to 303.5 $kJ·mol^{-1}$, while the Avrami index increased from 1.7 to 3.7. It demonstrates that pickling sludge can reduce the temperature difference between nucleation and crystallization, which is beneficial in realizing the one-step process. The effects of pickling sludge and heat treatment systems on glass-ceramics were investigated. The diopside phase is the main crystalline phase of glass-ceramics. Nepheline and Magnetite phases were detected when the amount of pickling sludge (mass fraction) reached 28%. The physical properties of the glass-ceramics were improved with the increase in heat treatment temperature and time. When the addition amount of pickling sludge (mass fraction) was 21%, the glass-ceramics prepared by heat treatment at 900 ℃ for 1.2 h had the best properties; namely, the density was 3.04 $g·cm^{-3}$, the water absorption (mass fraction) was 0.11%, and the Vickers hardness and flexural strength were 742.72 HV and 119.32 MPa, respectively. The Toxicity Characteristic Leaching Procedure (TCLP) leaching standard was met by heavy metals such as Cr, Ba, and Ni in the toxicity test. Glass structure analysis revealed that the pickling sludge increased the nonbridging oxygen content in the base glass while reducing the degree of glass network polymerization, resulting in an enhanced crystallization tendency. The pickling sludge proved to have potential as an inexpensive nucleating agent in the preparation of glass-ceramics with excellent performance. The glass-ceramics with these unique properties are promising to be applied as building materials.

KEYWORDS:
spent catalysts pickling sludge glass-ceramics one-step process crystallization

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1. Introduction

Since the 1980s, countries have formulated strict vehicle emission standards to cope with the global greenhouse effect, and automobile exhaust catalysts have been mandatory since then [1]. According to data from the National Bureau of Statistics, as of June 2020, my country's motor vehicle ownership reached 360 million, ranking first in the world [2]. The replacement of automobiles produces a large amount of waste catalysts rich in platinum group metals, which belong to HW50 hazardous waste and have potential environmental risks [3]. The recovery and resource disposal of platinum group metals from waste automobile catalysts can bring huge economic and environmental benefits, and at the same time is of great significance to the sustainable development of platinum group metals in my country.

The recovery of platinum group metals from waste automobile catalysts is mainly divided into two categories: hydrometallurgy and pyrometallurgy [4], [5]. In industry, pyrometallurgy has become the mainstream process due to its advantages such as high efficiency and pollution control [6]. The author team proposed a low-temperature iron capture platinum group metal method by reducing the smelting temperature through slag design. Based on the principle that platinum group metals and iron form a solid solution, the density difference between the alloy and slag phases is used to achieve platinum group metal enrichment and separation. The platinum group metal content in the slag is 10 $g \cdot t^{-1}$ As follows [7], [8]. Waste catalyst cordierite carrier and flux form a large amount of smelting slag. Most of the smelting slag is piled up or buried, causing problems such as land occupation and resource waste. Using smelting slag to prepare green and environmentally friendly building materials can not only reduce environmental pressure, but also make up for the shortage of natural resources. The main components of smelting slag, such as Al and Si, can be used as glass network formers or intermediates, and alkali metals such as Ca and Na can be used as modifiers. Based on the special chemical composition of smelting slag, high value-added microcrystalline glass can be prepared by melting-heat treatment. There are three main methods for preparing microcrystalline glass: (1) melting-two-step method; (2) melting-sintering method; (3) melting-one-step method [9]. The two-step method includes two-step heat treatment of nucleation and crystallization; the sintering method is to crush and shape the basic glass obtained by water quenching, and then sinter and crystallize it. The process is long and energy-intensive [10]; the one-step method is to expand the overlapping range of the nucleation and crystallization temperatures of the glass. The two processes of nucleation and crystallization are completed within the same temperature range, which has the advantages of energy saving and high efficiency. At present, there are few studies on the one-step process of microcrystalline glass, especially the one-step crystallization kinetics and thermodynamics. [11] used nickel-iron slag from electric furnace and ordinary blast furnace slag as raw materials, and realized the one-step preparation of microcrystalline glass by adding a small amount of Mg^{2+} and TiO_2. MgO can promote the precipitation of pyroxene mineral phase, but excessive amount will lead to the precipitation of forsterite, which reduces the mechanical properties of microcrystalline glass. Zhao Guizhou et al. [12] used steel slag as the main raw material and prepared calcium aluminum feldspar phase microcrystalline glass by increasing the alkalinity using a one-step process. The basic glass was heat treated at 1100 ℃ for 120 min, and the flexural strength was 56.4 MPa. [13] added TiO_2 as a nucleating agent to laterite ore to prepare microcrystalline glass in one step. With the increase of TiO_2 addition, the main crystal phase began to transform from μ-cordierite to pseudosapphire phase. The crystallinity, grain size and acid and alkali resistance of glass-ceramics have been improved. [14] used blast furnace slag as raw material and manganese-containing spinel phase as nucleating agent to prepare glass-ceramics in one step and studied the orientation of grains.

This study used pickling sludge as nucleating agent and waste catalyst iron capture smelting slag as raw material to prepare glass-ceramics in one step. Pickling sludge can provide CaF_2, Fe_2O_3 and Cr_2O_3 as nucleating agents, which reduces the cost of nucleating agents [15], [16]. The effect of pickling sludge dosage on the crystallization mechanism of glass-ceramics was studied from three perspectives: crystallization kinetics, glass structural unit and microstructure, and the effect of heat treatment system on the microstructure and properties of glass-ceramics was discussed.

2. Conclusions

This study aims to realize the resource utilization of waste automobile exhaust catalyst iron capture smelting slag through a simple and inexpensive method. The effective components in the pickling sludge were used as nucleating agents, and microcrystalline glass with excellent performance was successfully prepared by a one-step method after melting. The main conclusions are as follows:

(1) The crystallization kinetics study shows that with the increase of the amount of pickling sludge, the gap between the glass transition temperature and the crystallization temperature of the basic glass decreases, and nucleation and crystallization can occur at the same temperature. The activation energy of crystallization of the basic glass decreases, the Avrami index increases from 1.7 to about 3, and the crystallization mechanism gradually changes from two-dimensional crystallization to three-dimensional crystallization.

(2) The microcrystalline glass with a pickling sludge dosage (mass fraction) of 21% has the best comprehensive performance. The sample obtained by heat treatment at 900 ℃ for 1.2 h has a density of 3.04 $g \cdot cm^{-3}$, a water absorption of 0.11%, a Vickers hardness of 742.72 HV and a flexural strength of 1.347. 119.32 MPa.

The acid and alkali resistance are 99.16% and 99.79% respectively. The performance meets the requirements of industrial microcrystalline glass plate (JC/T 2097-2011). The leaching mass concentrations of Cr, Ba, Ni and Mn are 0.50, 0.47, 0 and 0.72 $mg \cdot L^{-1}$ respectively, which are lower than the threshold value of GB5085.3-2007 standard.

(3) Pickling sludge increases the non-bridging oxygen content, destroys the [SiO_4]/[AlO_4] glass network structure, and reduces the degree of polymerization of the glass network. When the amount of pickling sludge is 21%, the non-bridging oxygen content in the base glass is the highest (NBO/T=1.96) and the crystallization tendency is the strongest.

3. References

[1] Xue H, Dong H G, Zhao J C, et al. Research progress in recovery of platinum group metals from spent automotive exhaust catalysts. Precious Met, 2019, 40 (3): 76

[2] Zhang F Y, Lu S J. Research progress on recovery of platinum group metals from spent automotive catalysts supported on cordierite. Rare Met Mater Eng, 2021, 50 (9): 3388

[3] Ding Y J, Zhang S G. Status and research progress on recovery of platinum group metals from spent catalysts. Chin J Eng, 2020, 42 (3): 257

[4] Ding Y J, Cui Y J, Zhang S G. Mechanism and process of zinc fragmentation-acid leaching of platinum group metals concentrates from iron capture method. Chin J Rare Met, 2022, 46 (1): 57

[5] Zheng H D, Ding Y J, Wen Q, et al. Separation and purification of platinum group metals from aqueous solution: Recent developments and industrial applications. Resour Conserv Recycl, 2021, 167: 105417

[6] Ding Y J, Zhang X Y, Wu B Y, et al. Highly porous ceramics production using slags from smelting of spent automotive catalysts. Resour Conserv Recycl, 2021, 166: 105373

[7] Ding Y J, Zheng H D, Zhang S G, et al. Highly efficient recovery of platinum, palladium, and rhodium from spent automotive catalysts via iron melting collection. Resour Conserv Recycl, 2020, 155: 104644

[8] Zheng H D, Ding Y J, Wen Q, et al. Slag design and iron capture mechanism for recovering low-grade Pt, Pd, and Rh from leaching residue of spent auto-exhaust catalysts. Sci Total Environ, 2022, 802: 149830

[9] Chen Y X, Gao N, Wang X, et al. Structure and properties of MgO−Al2O3−SiO2 glass-ceramics made from laterite and sea sand ore. Shanghai Met, 2021, 43 (4): 98

[10] Li B Q, Guo Y P, Zheng Z R, et al. Preparation and crystallization influence of ceramic waste residuebased glass ceramics with one- step sintering process. China Ceram, 2019, 55 (5): 37

[11] Li Y, Yi Y D, Chen K Y, et al. Optimization of performance and composition for glass ceramics prepared from mixing molten slags. Chin J Eng, 2019, 41 (10): 1288

[12] Zhao G Z, Li Y, Dai W B, et al. Preparation and processing parameter research of high basicity steel slag-based glass-ceramics with one-step sintering process. Chin J Eng, 2016, 38 (2): 207

[13] Wang C Y, Jia H C, Wang A P, et al. Effect of TiO2 on the crystallization and properties of MgO−Al2O3−SiO2 glass-ceramics prepared by an " one-step" method from laterite ore. Ceram Int, 2019, 45 (4): 5133

[14] Ma J, Shi Y, Zhang H X, et al. Crystallization of CaO−MgO−Al2O3−SiO2 glass ceramic derived from blast furnace slag via one- step method. Mater Chem Phys, 2021, 261: 124213

[15] Pei F J, Zhu G H, Li P, et al. Effects of CaF2 on the sintering and crystallisation of CaO−MgO−Al2O3−SiO2 glass-ceramics. Ceram Int, 2020, 46 (11): 17825

[16] Li H X, Li B W, Zhang X F, et al. Influence of Fe2O3 on the microstructure and properties of the nanocrystalline tailing-based glass-ceramics. J Synth Cryst, 2016, 45 (1): 176

[17] Zong Y B, Chen W H, Fan Y, et al. Complementation in the composition of steel slag and red mud for preparation of novel ceramics. Int J Miner Metall Mater, 2018, 25 (9): 1010

[18] He Y, Shen X F, Jiang Y, et al. Effects of Li2O replacing Na2O on glass forming, structure and properties of Na2O−MgO−Al2O3−SiO2 glass and glass-ceramics. Mater Chem Phys, 2021, 258: 123865

[19] He D F, Ma H, Zhong H. Effect of different nucleating agent ratios on the crystallization and properties of MAS glass ceramics. J Eur Ceram Soc, 2021, 41 (16): 342

[20] França R, Bebsh M, Haimeur A, et al. Physicochemical surface characterizations of four dental CAD/CAM lithium disilicate- based glass ceramics on HF etching: An XPS study. Ceram Int, 2020, 46 (2): 1411

[21] Sun Y S, Ma L Y, Cui J D, et al. Effects of heat-treatment temperature and holding time on the microstructure and mechanical properties of lithium disilicate glass-ceramics. J Non Cryst Solids, 2021, 553: 120502

[22] Zhang J J, Zhang X Y, Liu B, et al. Phase evolution and properties of glass ceramic foams prepared by bottom ash, fly ash and pickling sludge. Int J Miner Metall Mater, 2022, 29 (3): 563