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Structural investigations of $CaO–CaF_2–SiO_2–Si_3N_4$ based glasses by Raman spectroscopy and XPS considering its application to continuous casting of steels

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ABSTRACT

Structural analysis of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass was conducted in order to understand its viscoelastic properties. $CaO–CaF_2–SiO_2–Si_3N_4$ based glass has been adapted in various industries because a small amount of nitrogen incorporation leads to enhancing many properties such as fracture toughness, viscosity and chemical durability. Recently, few metallurgists have begun to use $CaO–CaF_2–SiO_2–Si_3N_4$ based glass as a lubricant of continuous casting process of steel in order to maximize its viscoelastic property by controlling degree of polymerization (DP). The present study provides structural understanding of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass, specifically designed for the continuous casting process of steel by Raman spectroscopy and XPS. With Raman spectroscopy, the degree of polymerization (DP) was evaluated by the Q_3/Q_2 ratio. The qualitative analysis of nitrogen and non-bridging oxygen was conducted by XPS within a range between 0.1 and 6 wt.% of nitrogen. According to the results, the introduced nitrogen was incorporated with non-bridging oxygen of silicate network units, resulting in increase on degree polymerization (DP) of silicate network units. Such structural changes would potentially enhance shear thinning property of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass, resulting in a positive influence on continuous casting process of steel.

1. Introduction

$CaO–CaF_2–SiO_2–Si_3N_4$ based glass are amorphous solids derived from the silica structure by replacing part of the bivalent oxygen atoms by trivalent nitrogen atoms in a way that silicon is bonded simultaneously to oxygen and nitrogen atoms [1]. Due to the such superiority in bonding number, it is well known that replacement of small amounts of nitrogen in the glass by oxygen causes considerable changes in properties such as glass transition temperature, fracture toughness, viscosity, chemical durability and Young's modulus [2].

Such oxy-nitride glass, in particular, is attractive for glass fiber due to its outstanding electrical conductivity [3]. Apart from glass fiber industry, oxy-nitride glass has high potential applications in jointing or coating materials due to its high toughness and viscosity [3]. Especially, it is interestingly reported that oxy-nitride glass could be used for the containment of high level nuclear waste for their ultimate disposal due to its good chemical durability [3].

Recently, a rheological property of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass has been received attention in the steel industry. During the continuous casting process of steel, an amorphous liquid phase of synthetic oxy-fluoride glass or so called mold flux (MF) is sandwiched between oscillating water cooled copper mold and molten steel in order to lubricate the molten steel with achieving successful solidification of steel [4]. In this time, one of the important challenges to overcome is to design MF with a proper value of viscosity [4]. This is because the viscosity of MF has to be large enough at mold top surface (10–40 cm^{-1}) in order to alleviate slag entrainment and low enough at mold wall (100–1000 cm^{-1}) for maximizing lubricating capability [4].

Under such circumstances, metallurgists begun to study on rheological property of MF in order to design MF having Non-Newtonian behavior of shear thinning property in that viscosity decreases as a function of shear rate. With respect to Non-Newtonian behavior of MF, the author previously reported that MF itself shows a little bit of Non-Newtonian behavior of shear thinning property [4]. It was further suggested that the shear

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thinning property of MF is strongly dependent on DP [4]. Also, Watanabe et al. experimentally proved that nitrogen incorporation induce strong Non-Newtonian behavior of MF [5].

Albeit the previous researches by metallurgists including the author made huge progress in that they successfully achieved stronger shear thinning property with $CaO–CaF_2–SiO_2–Si_3N_4$ based glass and discovered correlation between shear thinning property and structure of MF, questions still exist concerning MF structure incorporated with nitrogen ($CaO–CaF_2–SiO_2–Si_3N_4$ based glass) because, as insisted by many researchers, the properties of glass are a function of structural features [6]. Therefore, the structural details of MF incorporated with nitrogen are absolutely needed in order to design MF with strong shear thinning property.

It is the purpose of this study to investigate the structural features of MF incorporated by nitrogen and to design $CaO–CaF_2–SiO_2–Si_3N_4$ based glass for improving shear thinning property. With Raman spectroscopy, DP of MF incorporated with nitrogen is evaluated by analyzing silicon discrete anion (Q_n) units. Subsequently, XPS analysis was conducted in order to understand quantitative features on nitrogen (N1, N2 and N3) and non-bridging oxygen. By combining the results from Raman and XPS, it should be able to understand the effect of nitrogen incorporation on structures of MF.

2. Experimental

2.1. Preparation of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass

There are mainly two methods to prepare $CaO–CaF_2–SiO_2–Si_3N_4$. The first and widely used method is the direct melting of all ingredients and nitrides under Ar atmosphere at high temperature [3]. The second way includes the preparation of the base oxide glass and followed by nitridation ammonolysis at high temperature [3]. For the present study, the second method is adapted in order to eliminate the feasibility of Si_3N_4 decomposition. Rajaram and Day reported that decomposition of Si_3N_4 is occurred due to the reaction of some gaseous product during melting a single step [7]. The flow chart for synthesis of silicon oxy-nitride glass for the present study is shown in Fig. 1. For the synthesis of $CaO–CaF_2–SiO_2–Si_3N_4$ based glass, firstly, oxy-fluoride glass with basicity(CaO/SiO_2) of 0.94 was prepared by melting a mixture, consisting of reagent grade SiO_2, CaO, MgO, Al_2O_3, Na_2O and F in a platinum crucible at 1572 K for 30 min to obtain homogeneous mixtures. Subsequently, molten mixtures in platinum crucible was quickly taken out from the furnace and followed by a rapid quenching process with water cooled steel mold. The chemical composition of oxy-fluoride glass was designed with a consideration of chemical composition for commercial MF. The specific chemical compositions are analyzed by using X-ray fluorescence (XRF) spectroscopy. For quantification of chemical composition wit XRF, a powder form of each sample was subjected to be melted with fusing agent (Di-Lithium tetraborate) at 1723 K and followed by quenching process. The quenched sample was grinded and mechanically mixed in order to achieve homogeneous condition. The prepared powder form of sample was tested by XRF (XRF-1800 model Shimadzu) to determine chemical composition.

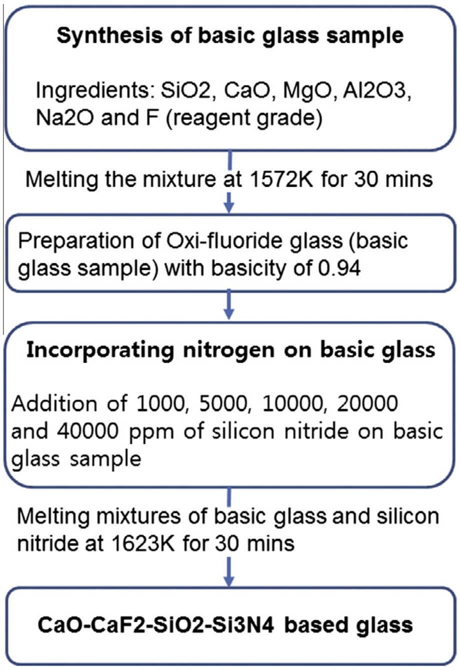

Fig. 1. Flow diagram showing the synthesis of silicon oxynitride glass.

After synthesizing oxy-fluoride glass, nitrogen is added to the precursor oxy-fluoride glass as a form of silicon nitride (Si_3N_4) at 1623 K for 30 min and followed by the quenching process. The additive silicon nitride amounts were between 0.11 and 6.57 wt.% respectively. The specific amounts of nitrogen in $CaO–CaF_2–SiO_2–Si_3N_4$ based glass were measured by N/O analysis (HORIBA Model: EMGA-930, Japan). The standard used for quantitative analysis of N was nitrogen (JSS370-1). All samples were crushed by vise and contained in a capsule. For each sample, 5 measurements were conducted to estimate the nitrogen homogeneity and average nitrogen content in the samples. The detailed chemical composition and analyzed nitrogen amounts are provided in Table 1.

2.2. Raman spectroscopy

The previously prepared $CaO–CaF_2–SiO_2–Si_3N_4$ based glass was analyzed by Raman spectroscopy (LabRaman High Resolution, Horiba Jobin-Ybon, France) in order to understand the structure of silicate discrete anions (Q_n) units. Studying on the structure of oxy-nitride units with quenched sample could be valid because Mysen and Richet experimentally proves that the structure of anionic unit is same before and after the quenching process [8]. Therefore, for the present study, Raman spectra of quenched $CaO–CaF_2–SiO_2–Si_3N_4$ based glass samples were collected at room temperature in the range of 200–1600 cm^{-1} with an Ar excitation laser source with a wavelength of 514.32 nm for 120 s. After collecting Raman spectra data, the Raman bands ranged between 800 and 1200 cm^{-1} were fitted by Gaussian function with PeakFit program version 4 within ±0.5 percent error. The relative amount of silicate discrete anions (Q_n) was measured by the area ratio of the best fitted Gaussian curves. As for the each silicate discrete anions, the bands highlighted at 855, 905, 964 and 1056 cm^{-1} correspond to Q_0, Q_1, Q_2 and Q_3 units respectively. The characteristic Raman assignments were listed in Table 2.

Table 1
Chemical composition of silicon oxynitride glass measured by XPS. Foundation stands for the basic silicon oxyfluoride glass for the continuous casting process. The samples labeled from N_1 to N_5 are prepared by synthesizing nitrogen with the foundation. The nitrogen contents were analyzed by Horiba N/O analysis.

Sample	SiO_2	CaO	MgO	Al_2O_3	Na_2O	CaF_2	N
Foundation	40.1	40.2	1	4.9	7.1	7.5	0
Sample			Nitrogen contents (wt.%)				
N_1			0.110				
N_2			0.371				
N_3			1.00				
N_4			2.45				
N_5			6.57				