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Surface modification of soda–lime–silicate glass via the high-temperature electrochemical injection of tin ions

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ABSTRACT

Under float glass process mimicking conditions, the surface modification of soda–lime–silicate glass was achieved via the electrochemical injection of tin ions. A voltage of 10 V was applied to the 7 mm thick glass at 1000 °C for 5 min between molten tin and graphite electrodes. The chemical composition, phase, and microstructure of the glass after cooling were studied using optical, scanning electron and transmission electron microscopies, X-ray diffraction, and Mössbauer spectroscopy. After applying the voltage, the glass was found to exhibit a five-layered structure with different compositions and microstructures, e.g., a glass–ceramic layer consisting of SnO_2 crystalline particles dispersed in a SiO_2–SnO–Al_2O_3 glass and a phase-separated spinodal microstructured glass layer, within ~200 µm in depth from the glass/molten tin anode. The depth dependent composition of the surface and the formation of a multilayered structure are discussed and explained in terms of the migration of ions according to the applied electric field and the chemistry of the glass. The properties that the glass is expected to have and the potential of using this method as a novel online surface modification process that can be incorporated into industrial float glass manufacturing are also discussed.

1. Introduction

Sheet glass is often functionalized using surface modification techniques to improve its properties, such as its heat reflection, which can be improved using a metallic thin film coating, and mechanical strength, achieved via chemical strengthening/ion exchange. Various surface modification methods have been developed and used in industrial manufacturing, including thin film coating [1], mechanical processing [2–4], chemical and electrochemical processing [5–18], and laser processing [19–21]. The surface modification process is generally carried out on a separate production line after the manufacture of the sheet glass. However, recently, the incorporation of an online surface modification technique into sheet glass manufacturing was studied with the aim of improving the function and productivity of the sheet glass and saving energy, thus reducing the environmental burden of the manufacturing process [22–23].

Among the manufacturing processes used to produce sheet glass, the float glass process is widely used for manufacturing large-sized sheet glass, in which the glass melt is poured onto molten tin (float bath) and formed into a sheet with a smooth surface. As the molten tin conducts electricity, the float glass process has the potential to incorporate a surface modification technique using electrochemical methods, where the molten tin acts as an electrode. In fact, electrochemical surface modification using molten tin as an electrode has already been studied as a method for the online surface modification of sheet glass [24–26]. In the previously reported technique, a molten tin float bath was used as the cathode. However, we have recently reported the use of molten tin as an anode, where electrochemical proton injection into soda–lime–silicate glass was carried out at 1000 °C using the molten tin and a graphite plate cathode placed on the molten glass [27]. In that study, reduction of hydroxyl (OH) concentration in the glass near to the glass/molten tin interface due to dehydration was successfully suppressed arising from the application of a 3 V DC voltage during the float process. However, in the same study, it was also found that when a DC

Abbreviations: DC, Direct current; SEM, Scanning electron microscope; BSE, Backscattered electron; EPMA, Electron probe micro analyzer; TEM, Transmission electron microscope; EDS, Energy dispersive X-ray spectroscopy; PXRD, Powder X-ray diffraction; ICDD, International Center for Diffraction Data; CEMS, Conversion electron Mössbauer spectroscopy; IS, Isomer shift

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