Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Decomposition of persistent luminescent microparticles in corrosive phosphate glass melt

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ARTICLE INFO

Keywords:
Phosphate glasses
$SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles
Persistent luminescence
Corrosion
Decomposition

ABSTRACT

Findings on the decomposition of persistent luminescent (PeL) $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticles (MPs) in phosphate glass melt under static condition are reported. PeL phosphate glasses with the composition ($50P_2O_5$-$10Na_2O$-40SrO) (in mol%) were prepared by adding the MPs in the glass melt. The decomposition of the MPs occurs during the preparation of the glass and leads to changes in the Eu^{2+} sites and to the formation of Eu^{3+} which decreases the PeL properties of the glasses. The decomposition of the MPs depends on the temperature at which the MPs are added in the melt and also on the time before casting the melts.

1. Introduction

There has been some interest during the past few years to process glass-ceramics (GCs) with persistent luminescence (PeL) properties as such GCs emit light for a long time (from seconds to hours) after the removal of the irradiation source [1]. These new materials can find applications as, for example, fluorescent light sources due to their high luminous efficiency, energy-saving, long lifetime and good features for protection of the environment [2].

PeL glass-ceramics were successfully obtained using the so called "Frozen sorbet method" developed by Nakanishi et al. [3]. This method was applied to the SrO-Al_2O_3-B_2O_3 glass system in which $SrAl_2O_4:Eu^{2+},Dy^{3+}$ crystals precipitate [4]. These crystal seeds, which grow into microparticles (MPs), are formed by the ions from the glass. In these $SrAl_2O_4:Eu^{2+},Dy^{3+}$ crystals, both Eu^{2+} and Dy^{3+} substitute for Sr^{2+}. The Eu^{2+} ions act as luminescent centers while the Dy^{3+} ions are used to increase the duration of the persistent luminescence as they increase the number of energy traps in the structure [5]. However, with this "Frozen sorbet method", the composition of the MPs depends on the composition of the glass matrix. Therefore, we developed an alternative route for the preparation of phosphate glasses with persistent luminescence properties [6]: PeL phosphate glasses were obtained by adding $SrAl_2O_4:Eu^{2+}$, Dy^{3+} microparticles (MPs) in glass batches prior to the glass melting. However, the MPs aggregate in the glasses leading to glasses with inhomogeneous persistent luminescence properties. Based on these results, our work has now been focused on the preparation of glasses with uniform persistent luminescence.

Recently, an alternative approach, the direct doping of particles into tellurite-based glass melts, was developed to prepare glasses with better dispersion of particles in the glass [7,8]. The first step consists of melting the glass batch. Then, the temperature is reduced to the doping temperature to increase the glass viscosity. The particles are, then, added at this doping temperature, mixed into the melt and finally cast after a short dwell time to allow dispersion of the particles. Recently, we showed, for the first time to our knowledge, that this direct doping method could be used to process phosphate glasses with upconversion (UC) while using a low amount of Er^{3+} and Yb^{3+} (0.01 at% of Er^{3+} and 0.06 at% of Yb^{3+}) [9]. Our study suggested that it is crucial to understand how the particles are corroded in the molten glass in order to control the dispersion and survival of the particles in the glass and so to prepare glasses with homogeneous luminescence properties.

Surprisingly, the works concerning the corrosion behavior of glass melts have been realized only since the late 1950s and on pure metals such as Pt [10] and Fe [11] just to cite a few. The behavior of pure metals immersed in molten glasses in terms of corrosion rates and corrosion layers was found to depend on the glass composition and melt temperature [12]. Therefore, the investigation of the corrosion of other materials in phosphate glass melt is of great interest and brings new knowledge on the corrosion behavior of the glass melts.

Here, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ microparticle (MPs) were added in

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https://doi.org/10.1016/j.corsci.2018.02.050
Received 30 August 2017; Received in revised form 15 February 2018; Accepted 21 February 2018

Table 1
Summary of the doping parameters used to prepare the glasses, sample codes and Standard deviation (SdtDev) of the pixel intensity from the analysis of the glass pictures (Fig. 1). The SdtDev was obtained using ImageJ, Java-based image processing program.

Melting condition			
Dwell time (t) (min)	Doping Temperature (T_{doping}) (°C)	Sample code (T_{doping}-t)	SdtDev
3	975	975 – 3	10
	1000	1000 – 3	11
	1025	1025 – 3	9
5	975	975 – 5	10
	1000	1000 – 5	8
	1025	1025 – 5	6
10	975	975 – 10	20
	1000	1000 – 10	12
	1025	1025 – 10	11

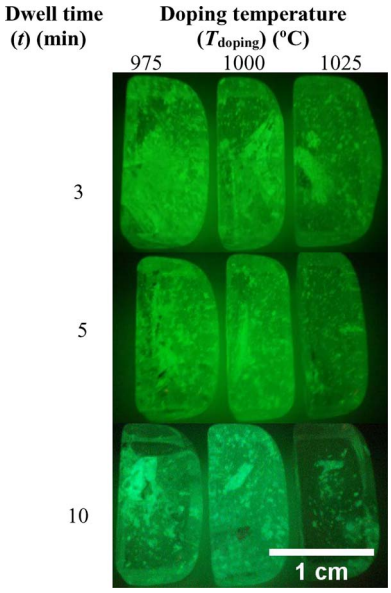

Fig. 1. Pictures of the glasses prepared using different (T_{doping}-t) parameters after stopping the UV irradiation.

phosphate glass melt after melting. The impact of different doping temperatures and dwell times on the corrosion of the MPs is discussed. In the context of this paper, corrosion can refer to the decomposition of the MPs in the glass. The decomposition of the MPs is correlated to the changes in the persistent luminescence properties of the glasses induced by the changes in the Eu^{2+} sites and to the formation of Eu^{3+} at the expense of Eu^{2+}.

2. Experimental procedure

2.1. Glass processing

Glasses with the composition $50P_2O_5$-$10Na_2O$-40SrO (mol%) were prepared using a standard melting method. $NaPO_3$, $SrCO_3$ and $(NH_4)_2HPO_4$ were used as the starting raw materials. $Sr(PO_3)_2$ precursors were first independently prepared from mixtures of the alkaline earth carbonates and $(NH_4)_2HPO_4$ using slow heating rate up to 900 °C. A 10 g batch glass was melted for 30 min at 1050 °C. After melting, 1 weight-% of commercial $SrAl_2O_4$: Eu^{2+},Dy^{3+} microparticles (MPs) (Jinan G.L. New Materials, China, BG-01) was added at a specific doping temperature (T_{doping} ranging between 975 and 1025 °C) and the glass was finally quenched after 3–5 min after adding the MPs (doping parameter called dwell time reported as t). Each glass was prepared from a specific batch and using specific (T_{doping} − t) doping parameters. Finally, the resulting glasses were annealed at 400 °C, which is 40 °C below the glass transition temperature, for 4 h in air. The different trials are summarized in Table 1.

2.2. Composition analysis

A scanning electron microscope (Carl Zeiss Crossbeam 540) equipped with Oxford Instruments X-Max^N 80 EDS detector was used to image and analyze the composition of the samples. The polished glasses were coated with a thin carbon layer before EDS mapping. As commonly performed when analyzing the composition of glasses, the at% were converted in mol%. The accuracy of the composition analysis was ± 1.5 mol%.

2.3. Luminescence

The persistent luminescence properties of the crushed microparticle-containing glasses were measured at room temperature using a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Hamamatsu R928 photomultiplier (PMT). The conventional luminescence (λ_{exc}: 266 nm, Nd:YAG pulse laser, 8 ns, TII Lotis) was measured at room temperature using a CCD camera (Avantes, AvaSpec–2048 × 14). For persistent luminescence measurements, the samples were irradiated for 5 min at room temperature with a compact UV lamp (UVGL-25, 4 W, λ_{exc}: 254 nm). The persistent luminescence spectra were recorded 1 min after ceasing the irradiation with a 4 s data collection time.

3. Results and discussion

To succeed in doping the glasses homogenously with the MPs, it is crucial to identify a suitable temperature for doping and dispersing the MPs in the glass melt as explained in [8]. MPs were found to decompose in the investigated glass system when melting the glass at 1100 °C for 10 min while the MPs maintain their PeL properties in the glass when the glass is melted at 1000 °C for 10 min as reported in [13]. Therefore, 1100 °C is already an upper limit of the doping temperature. The lower limit of the doping temperature is determined by the glass melt viscosity; as the temperature decreases, the viscosity of the glass increases. As a result, there is a temperature at which the glass melt is too viscous for the MPs to disperse homogeneously as explained in [8]. Therefore, in this study, the MPs were added at 975, 1000 and 1025 °C after the melting to avoid the decomposition of MPs. As the doping temperatures are near the melting temperature, the viscosity of the glass does not change dramatically when the temperature of the melt is reduced between 975 and 1025 °C. This was confirmed by measuring the viscosity of the glass from 10^5 to 10^{11} Pa s using beam bending and parallel plate viscometers (not shown here) and by fitting the viscosity curve using the Vogel-Fulcher-Tamman equation to estimate the viscosity of the glass at the different doping temperatures. In addition to the doping temperature, the dwell time is another crucial parameter to identify in order to disperse homogeneously the MPs into the phosphate glass. As for the doping temperature, a better dispersion of the MPs can be