3rd International Conference on Self-Healing Materials
Bath, UK. 27-29 June 2011

INFLUENCE OF THE ACTIVE PARTICLES ON THE SELF-HEALING EFFICIENCY IN GLASSY MATRIX

F.O. Méar[1], S. Castanié[1], D. Coillot[1], R. Podor[2] and L. Montagne[1]

[1] Université Lille Nord de France F-59000 Lille, France ; Unité de Catalyse et de Chimie du Solide, UMR-CNRS 8181 ; USTL F-59652
Email : francois.mear@univ-lille1.fr

[2] Institut de Chimie Séparative de Marcoule, UMR 5257 CEA-CNRS-UM2-ENSCM Site de Marcoule, BP 17171, F-30207 Bagnols-sur-Cèze cedex, France

Keywords: Self-healing; Glassy matrix; High Temperature Environmental Scanning Microscopy (HT-ESEM); Oxidation

ABSTRACT

To prevent leakage induced by crack in glass seals, we developed a new concept of self-healing [1, 2], derived from that proposed for polymeric materials. Healing particles are dispersed within the glass or glass-ceramic matrix, such as that when a crack occurs on the surface, the particles react with oxygen and produce a new glass that heals the crack. This self-healing is called “autonomous” since it does not require any external action. This is opposite to “non-autonomous” self-healing, which needs to operate under an external action like an increase in temperature.

In previous papers, we described the autonomous self-healing process [2-4], and showed how the different atmospheres present in fuel cell (SOFC) may influence the glass healing. A judicious choice will then enable to optimize the self-healing efficiency.

When a crack occurs, healing particles located in the crack react with oxygen. Subsequently, the crack is fully healed as oxidation progresses. The annealing atmosphere has thus an evident influence on crack healing. It was shown that the presence of oxygen is necessary to the self-healing phenomenon, as it is driven by the oxidation of healing particles. However, the threshold in partial oxygen pressure to get the healing effect can be quite low.

We first reported that vanadium boride can be used as an efficient self-healing particle since it reacts with oxygen leading to vanadium pentoxyde V_2O_5 and boron dioxide B_2O_3, respectively [2]. These two glass-former oxides present a low viscosity at a SOFC operating T of 700°C, and are thus able to fill the crack. The use of four other elements or compounds, vanadium (V), boron (B), vanadium-carbide (VC), and boron-carbide (B_4C) as active particles has been studied [4]. To produce enough quantity of healing oxide, ca. 10 vol% active particles are needed to get a strong crack-healed zone.

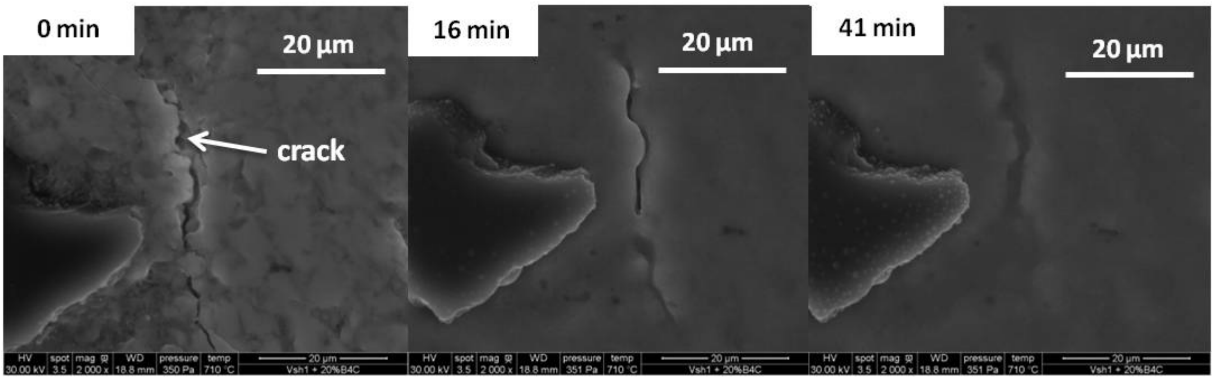

Figure 1: HT-ESEM pictures of SG1+20 vol%B_4C crack healing under air atmosphere at 700°C for the times indicated.

The HT-ESEM micrographs corresponding to the glass SG1+20vol%B_4C sample are shown in figure 1. It is observed that the B_4C particle that is present at the left side of the crack oxidizes and produces B_2O_3 that covers the glass matrix. This effect is evidenced by the change of the sample morphology. At the beginning of the oxidation test, the surface of the sample is indeed irregular. The formation and spreading of B_2O_3 yield to the smoothing of the sample surface. This oxide flows into the crack to fill it completely after 40 minutes of heating.

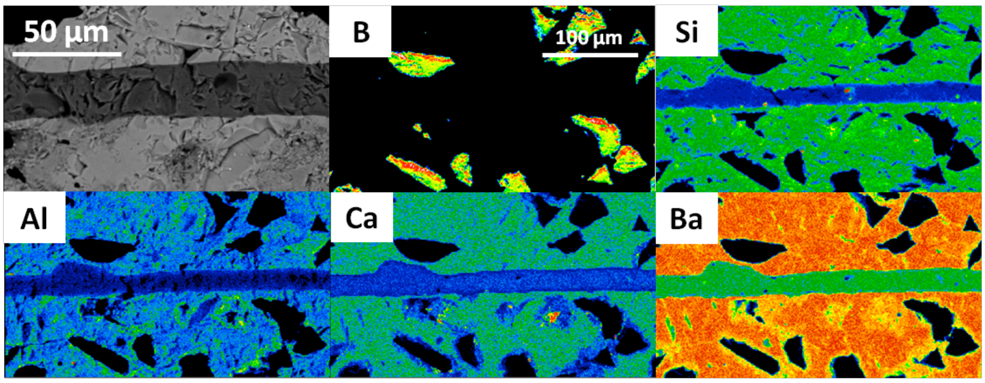

Figure 2: *Ex situ* Castaing microprobe analysis of a fracture of SG1+20vol%B_4C sample healed under air at 700°C for 1h: SEM picture and X-ray element maps after heat treatment.

The analyses of the composite (SG1+20vol%B_4C) obtained using electron microprobe (Fig.2) show that the crack is completely filled by a homogeneous phase containing all the elements of the glassy matrix. (i.e. alkaline earth boroaluminosilicate). Additionally, the interface between the matrix and the healed crack is well defined, meaning a limited reactivity.

The electron probe microanalyser facility in Lille (France) was funded by the European Regional Development Fund.

REFERENCES

[1] D. Coillot, F.O. Méar, and L. Montagne, Self-healing vitreous composition, method for preparing same, and uses thereof. WO2010/136721, 2010.

[2] D. Coillot, F.O. Méar, R. Podor, and L. Montagne Autonomic self-repairing glassy materials. *Advanced Functional Materials* **20**, 2010, pp. 4371-4374.

[3] D. Coillot, R. Podor, F.O. Méar, and L. Montagne, Characterization of self-healing glassy composites by high-temperature environmental scanning electron microscopy (HT-ESEM). *Journal of Electron Microscopy* **59**, 2010, pp. 359-366.

[4] D. Coillot, F.O. Méar, R. Podor, and L. Montagne. Influence of the active particles on the self-healing efficiency in glassy matrix. *Advanced Engineering Materials, 2011* In press.