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Corrosion mechanisms understanding in the environment of future reactors using molten salt fuel and coolant.

Abstract :

For the past decade, an increasing interest have been showed to molten chloride salts in the field of energy production and storage. Their physico-chemical properties, associated with the development of liquid-fuelled fourth-generation nuclear reactors, may be relied on to design efficient systems in terms of resource sustainability, actinide waste elimination and safety. The Oak Ridge National Laboratory (ORNL) program on the molten salt reactor experiment led to the development of the Hastelloy N alloy, a nickel alloy containing 7wt% of Cr and 16wt% of Mo. The composition of the alloy was optimized for corrosion resistance (both in low oxygen gas atmosphere and in molten fluorides), irradiation resistance and high temperature mechanical properties. Nevertheless, no notably resistant materials in molten chlorides have been identified and optimized so far, due to a less advanced research around nuclear systems exploiting chloride-based fuel salt. The main studies conducted in these environments have revealed the complexity of the corrosion mechanisms of materials in contact with molten chloride salts, which is due to the interaction between the dissolved species in the salt and the immersed materials, but also the interaction between atmospheric gases and the melted salt. The oxide ions activity (oxoacidity) in the salt is, for example, one of the key parameters regarding the behavior of materials in molten chloride salts. However, the determination of the oxoacidity is not frequently addressed among corrosion studies in molten chloride salt media. In the first part of the present study, various electrochemical techniques in molten salts were exploited and compared in order to quantify in the best way the oxoacidity of the NaCl-CaCl₂ binary salt molten at 600 °C. The obtained results demonstrated the good complementarity between the two main techniques for in-situ quantification of oxide ions in molten salts which are cyclic voltammetry and the yttria zirconia probe. Their use subsequently made it possible to monitor the enrichment in oxide ions of the NaCl-CaCl₂ mixture, by addition of CaO, as well as their depletion by separate addition of MgCl₂ and ZrCl₄. Obtaining these different oxoacidity conditions allowed to set the conditions for the immersion tests aimed at better understanding the impact of the oxide ion content on the corrosion of the immersed materials. The three selected test materials for the immersions are the 304 stainless steel, the nickel-based C276 alloy, and the ceramic Cr₂AlC. The corroded samples are characterized by gravimetric measurements, as well as by SEM-EDS observations and XRD analyses. The results obtained after static immersion for 336 h in NaCl-CaCl₂ at 600°C demonstrated that the corrosion resistance of the materials considered increased in the order: SS304 < C276 < Cr₂AlC, but also that the corrosion mechanisms for the two alloys differed according to the oxoacidity and the presence of reactive element in the salt. The Cr₂AlC ceramic behavior differs from the two alloys, by presenting a corrosion mechanism that is not significantly disturbed by the oxoacidity conditions, however the corrosion kinetics of the Cr₂AlC depend on the oxoacidity conditions. A third part was dedicated to the impact of the oxidizing species contained in the sweep gas, on the corrosion of the nickel-based alloy C276 immersed in the liquid salt NaCl-CaCl₂. These immersion studies, associated with gas chromatography analyses, revealed the role of O₂ and H₂O on the corrosion of the C276 alloy. These results, brought together with those concerning the influence of oxoacidity, have made it possible to outline a global mechanism of corrosion in NaCl-CaCl₂ at 600 °C.