



Electrochemical behaviour of copper–nickel alloys as immobilisation matrices for the storage of fission products in CO₂-enriched synthetic groundwater



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ABSTRACT

The surface properties of nickel and copper alloys exposed to simulated French Callovo–Oxfordien groundwater (aerated and CO₂-saturated solutions) have been evaluated from electrochemical impedance spectroscopy in conjunction with X-ray photoelectron spectroscopy.

The kinetic reactions and physical properties of the layers grown on the alloy's surfaces, change versus the Ni content in the alloys and the presence of CO₂ in the solution.

Nickel alloys retain favourable passive properties in such environments, whereas oxide products on copper alloys are insufficiently protective when formed in the absence of dissolved oxygen in the electrolyte. A maximum addition of 30 wt% of copper in nickel alloys provides good results with respect to corrosion resistance. Electrochemical measurements allow discriminating behaviour between oxide layers maintained by diffusion phenomena through layer and passive films which are maintained from migration phenomena.

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1. Introduction

In France, fission products are currently stabilised by vitrification processing. Because of the difficulties encountered in the incorporation of large amounts of “reducible” fission products (Pd, Mo, Ru, Rh, Tc, etc.) into a glass matrix, alternative immobilisation methods are now being investigated, in particular the feasibility of using metallic matrices.

The strategy involved in the use of a metallic matrix is to isolate nuclear waste from the biosphere through their incorporation into a material that can become passive [1]. Thus, in addition to the compatibility between irradiated particles and the matrix, the suitable waste loading and the possibility of manufacturing the material using a proven process (melting), the matrix material should exhibit satisfactory long term corrosion behaviour under geological disposal conditions. The material of the matrix should be chosen depending on the stability of its passive state in environments similar to those to which it will be exposed.

This paper presents part of our work undertaken to identify a material that is suitable for the trapping of fission products from reprocessed spent fuel (Pd, Mo, Ru, Rh, Tc, etc.) and that exhibits a highly resistant passive film. Obviously studies are in progress to consider the corrosion property of matrices containing incorporated fission products, especially the compatibility between the matrix and the second phase constituting fission products regarding galvanic corrosion. These aspects will not be considered in this paper.

Copper–nickel alloys are considered good candidate materials for the immobilisation of reducible fission products. The aim of this work is therefore to design nickel- and copper-based alloys that exhibit the required corrosion resistance against several simulated solutions (aerated solution, carbonated solution, etc. . .) that contain anions at relevant concentrations. Reducing conditions that take place under repository conditions will be considered in a subsequent paper. These materials exhibit an ability to become passive which protects them from corrosion.

The passive film is known to comprise an oxy-hydroxide layer grown from successive deprotonation, as described by Sato [2]. The inner layer of the passive film is mainly composed of a mixture of oxides of the alloying elements, and the outer layer is a precipitated layer of hydroxides of the elements. For example, a

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p-type semiconductor passive film of defective nickel oxide and a porous precipitated outer layer of a mixture of $\text{Ni}(\text{OH})_2$ and $\text{Cr}(\text{OH})_3$ were anodically grown on Ni–15%Cr polarised in sulphuric acid, and their behaviour was modelled by Urquidi-Macdonald [3]. Several authors have suggested that passive-film properties are dominated by the properties of nickel oxide in alloys containing 15% Cr and by Cr oxide in alloys containing 30% Cr [3,4]. Researchers have also shown that for Ni–15%Cr and Ni–30%Cr, the film properties are governed by the Cr more under acidic conditions (pH 2) than under alkaline conditions (pH 8.5). The selective dissolution of nickel in an acidic solution is assumed to be responsible for a film's properties being governed by Cr. Based on the Mott–Schottky analyses, other authors have demonstrated that the contribution of Cr in the passive film reduced the density of defects in the film [4]. pH also affects the properties of the film. For Ni–Cr alloys, Ni oxide dominated the film at pH 8.5, irrespective of the Cr content. At pH 2, the film was dominated by Cr oxide.

The corrosion behaviour of copper and copper–nickel alloys has been studied widely in several media, including pure water [5–8]. Pure copper is considered unstable in oxygen containing electrolytes, especially those that contain chloride ions. In these electrolytes, the adsorption of intermediate species ($\text{CuCl}_{\text{ads}}^-$) precedes alloy dissolution. However, interfacial pH evolution favours the hydrolysis of CuCl_2^- and the formation of Cu(I) oxide precipitates on the copper surface [9,10].

Because of their great mechanical strength, good thermal conductivity and good corrosion resistance, copper–nickel alloys with copper as the main component (Cu–10 at% Ni) are primarily used against flow-assisted corrosion [11]. This corrosion resistance is due to the formation of a thin adherent copper oxide (Cu_2O) phase and a thick porous copper hydroxide phase enriched with nickel within the film. However, the nickel content in the alloy must be sufficient to promote resistance to hydrodynamic effects. Higher corrosion resistance has been observed in alloys with 30 wt% Ni compared to 10 wt% Ni at 20 °C. Alloys with higher nickel contents therefore reduce in media at 50 °C [12]. The same effects have been observed in alkaline and acidic solutions. An increase in the nickel content up to 30 wt% promotes an increase in the thickness and the resistance of the passive film in acidic media. However, a nickel content greater than 30 wt% impairs corrosion resistance [13]. For chloride and sulphide electrolytes, the pit morphology and mechanism depend on the relative concentrations of both anions. When the sulphide concentration is stabilised, the chloride concentration modifies the susceptibility to pitting. When the chloride concentration is less than 5×10^{-4} M, sulphide promotes pitting, whereas it acts as an inhibitor at higher chloride concentrations [14]. In the presence of various anionic species in the groundwater environment, localised corrosion is observed at low temperatures [5]. Uniform corrosion is generated at low concentrations of bicarbonate, whereas this anion promotes a passive behaviour at high concentrations.

To evaluate the passive film properties of copper–nickel alloys as a metal matrix for the immobilisation of “reducible” fission products, this study is focused on the electrochemical behaviour of copper and nickel alloys in simulated groundwater with a composition approximately equal to that of the French Callovo–Oxfordien groundwater. Chemical groundwater analyses have indicated that electrolyte is principally composed of a constant concentration of carbonate, sulphate and chloride anions. The influence of pH modification induced by a saturation of CO_2 will also be described. XPS analyses were performed to identify the chemical nature of the passive film, and polarisation curves and electrochemical impedance spectroscopy (EIS) were performed to investigate the passive film properties and passivation kinetics. Finally, optical microscopy was used to investigate the morphology of corrosion.

2. Experimental

2.1. Specimens and surface preparation

The samples used in this study were composed of two sheets of pure materials – one copper (noted as Cu100) and one nickel (noted as Ni100) – and by two sheets of different composition of Cu–Ni alloys. The first copper alloy was composed of 70 wt% copper and 30 wt% nickel and is denoted Ni30. The second sample, a nickel alloy, was constituted of 70 wt% nickel and 30 wt% copper and is denoted Ni70. Samples were provided by Goodfellow Cambridge Ltd., UK. The chemical composition of the samples was checked using EDX measurements and was in good agreement with the specification table (i.e., they were high-purity materials).

Specimens were mechanically abraded through successive grades of SiC abrasive papers, from P 180 to P 4000 and were subsequently polished using several grades of diamond pastes down to 1 μm . The specimens were then ultrasonically cleaned in a distilled alcohol/acetone mixture. This working electrode was transferred immediately to the electrochemical cell to avoid surface ageing from contact with laboratory air.

2.2. Surface analysis

Surface analyses by X-ray photoelectron spectroscopy (XPS) were performed on samples after 2 h in aerated and CO_2 -saturated solutions. The XPS spectra were recorded using Versaprobe PHI 5000 apparatus operated in constant-analyser-energy mode (CAE; pass energy 117.4 eV for wide scans and 58.7 eV for regions) with monochromatized Al $K\alpha$ source (1486.7 eV). The linearity of the energy scale was calibrated using samples of pure copper, silver and gold. The pressure of the analysis chamber during acquisition was maintained at less than 10^{-7} Pa. No sputter-cleaning was performed prior to analysis. Spectra were acquired at 90° (normal angle with respect to the plane of the surface) and referenced to the adventitious hydrocarbon C_{1s} level set at 284.6 eV. Atomic quantifications of elements were performed from global XPS spectra; data was acquired in high-resolution mode for Cu_{2p} (927–974 eV), Cu_{LMM} (910–920 eV), Ni_{2p} (813–843 eV), $\text{Cl}_{2p_{3/2}}$ (192–213 eV), C_{1s} (277–294 eV), O_{1s} (522–543 eV) and S_{2p} (154–175 eV). Binding energies were compared to an open XPS database to identify the species present on the samples [15]. Gaussian and mixed Gaussian/Lorentzian functions, the Shirley background subtraction method and a least-square routine were used for fitting. The final results consisted of an evaluation of the quantities of oxo-hydroxide and adsorbed species as a function of the percentage of copper in the matrix under two gas conditions. At the end of the experiments, samples were stored in a vacuum desiccator after being rinsed with deionised water.

2.3. Electrochemical measurements

A conventional three-electrode cell was used to measure polarisation curves and impedance spectra. Pure metal and Ni–Cu alloys formed the working electrode with a surface area of 0.28 cm^2 . A graphite pin (with a specific area of 1 cm^2) and a saturated calomel electrode were used as a counter electrode and reference electrode ($E_{\text{SCE}} = +250$ mV/SHE), respectively. Electrochemical investigations were performed using a GAMRY™ Reference 600 potentiostat. In order to verify the reproducibility of the results, each experiment was performed three times. The curves reported on the figures correspond to the average of the measurements.

Samples were immersed in the solution for 2 h in order to obtain a steady-state OCP value. Electrochemical impedance measurements were then performed in the frequency range of 100 kHz to 50 mHz with a potential perturbation of 10 mV around the OCP.

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