Electrochemical study of the multivalent systems of nickel, molybdenum and tellurium in molten glass

Littner A., Gaillard-Allemand B., Podor R., Rapin C., Steinmetz P., Vilasi M.
Laboratoire de Chimie du Solide Minéral-UMR7555-Université Henri Poincaré -
Nancy I, boulevard des Aiguillettes - BP 239 - 54506 Vandoeuvre Cedex - France

Multivalent systems of nickel, molybdenum and tellurium have been characterised at high temperature in molten glasses between 1273 and 1623 K. Electrochemical methods, polarisation curves, cyclic and square wave voltammetries, have been mainly used. The results obtained in the case of nickel have been interpreted thanks to other analytical techniques, such as PEELS, EPMA and magnetic susceptibility measurements. Ni^{+III} has been evidenced in oxidised molten glasses. Concerning molybdenum, two oxidation states have been pointed out. Moreover, the weak protection of molybdenum by silicides (Mo_xSi_y) which form on the surface of electrode, indicates that corrosion of $MoSi_2$-base materials should be detrimental. Finally, Te is characterised by only one electroactive system, Te^{+IV}/Te^0. Its study leads to an estimation of the Te^{+IV} diffusion coefficient.

Introduction

Glass making industries need metallic and intermetallic alloys with improved mechanical and chemical characteristics at high temperatures. As regards to chemical properties, a good resistance to the corrosion by molten glass is required and in consequence, platinum and platinum alloys are widely used even if they are very expensive. In order to find new suitable materials, less expensive than the noble metal alloys, the study of the corrosion resistance of several materials was performed at high temperature (1473K) in a simplified glass melt (noted SG). The electrochemical techniques were used because, as mentioned by many authors (1), they enable the measurements of the redox properties of metallic compounds as well as those of dissolved multivalent elements. Such measurements lead to the arrangement of redox couples into an electromotive force (emf) series which allows i) the predictions of reaction spontaneity between species or ii) the identification of possible oxidising and reducing agents in order to determine the corrosion mechanisms. In the present paper, the electrochemical features related to tellurium, molybdenum and nickel dissolved in molten glass are reported.

Experimental details

The conditions and the experimental equipment used in order to perform voltammetric measurements have already been described in detail in (2,3). The working- (wire ϕ = 1mm) and the counter- (plate S = 6 cm^2) electrodes were made in platinum and an yttria stabilised zirconia electrode flushed with air was used as the reference electrode. Thus, all the potentials mentioned in this paper are referred to this ZrO_2 electrode.

The electrochemical investigations were performed in a SG with the composition 16.55 wt% Na_2O, 58.6 wt% SiO_2, 24.75 wt% B_2O_3, equilibrated in argon U (max. O_2 content = 50ppm) during 15 hours at 1423K. This inert atmosphere was chosen in order to prevent the atmospheric corrosion of the metallic materials which are studied elsewhere. In these conditions, tellurium is in its reduced state and can interact with platinum constituting the experimental device. Moreover, as shown by the binary Pt-Te phase diagram (4), the particular two phase mixture (0.356Pt-0.644PtTe) corresponds to an eutectic composition with low melting point (1133 K). Its formation could be responsible of the breakdown of the platinum crucible. Thus, a particular nikel-superalloy container protected by cathodic polarisation was developed and therefore, allowed the study of molybdenum and tellurium systems (figure 1).

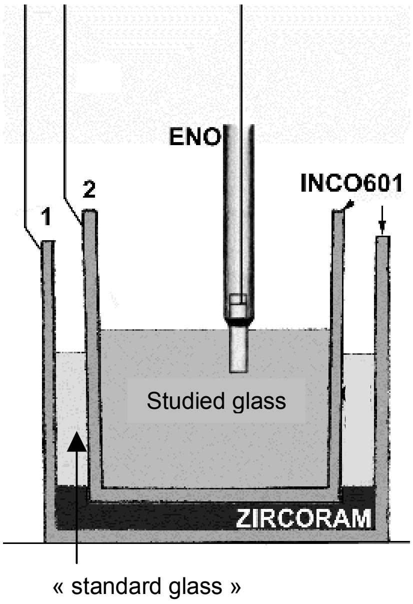


Fig.1 : Crucible made with nickel-superalloy INCO601. The configuration like a “double envelope” enables the polarisation of the inside container. A stabilised zirconia electrode and the two walls (1) and (2) are used as a conventional three electrodes system ; the standard glass has the following composition : 16.55 wt% Na_2O, 58.6 wt% SiO_2, 24.75 wt% B_2O_3; "zircoram" is a ceramic separator made with 80 wt% Cr_2O_3, 20 wt% ZrO_2.

Results and discussion

System of tellurium

The results of cyclic voltammetric measurements performed by linear and square-wave potential sweeps led to the following main features :

- in the electroactivity domain of the glass melt, Te^0 and Te^{+IV} are the only two achievable oxidation states (figure 2) ;
- the half wave potentials of the oxidation and reduction peaks are equal to E_{ox} = - 0.16V and E_{red} = - 0.5V, respectively ;
- the Te^{+IV}/Te^0 couple appears to be an irreversible system because the oxidation and reduction peaks are separated by more than 0.34 V ($\Delta E \rangle \frac{RT}{nF}$) ;
- according to the linear variation of E_{red} versus the potential scan rate (figure 3), an approximate value of the diffusion coefficient of Te^{+IV} can be deduced owing to Randles-Sevcic equation ($i_p = K.n.\Im.C_o^{Ox}.\sqrt{\frac{n.\Im}{R.T}}.\sqrt{v.\pi.D_{Ox}}$ and 0.25< K < 0.28) $^{(5)}$: the value of D_{Te+IV} is in the range of $2.5x10^{-7}$ $cm^2.s^{-1}$.

Thus, the oxidising ability of Te^{+IV} is equivalent to that of Fe^{+III} generally measured in molten glass.

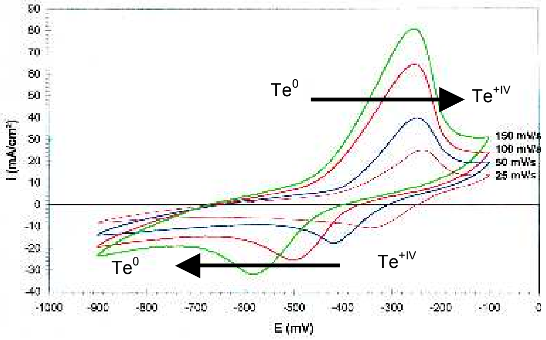


Fig. 2 : cyclic voltammogram recorded as a function of the potential scan rate (scan rate = 150, 100, 50 et 25 mV.s^{-1}) ; performed at 1423 K in SG melt, doped with 1wt%TeO_2

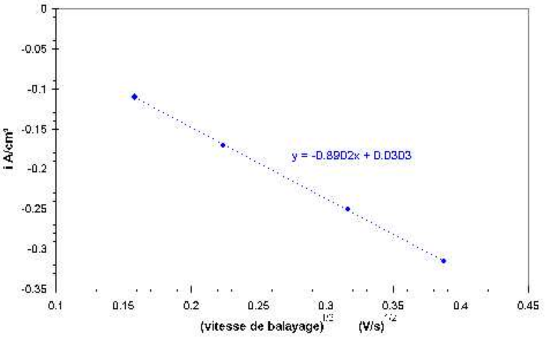


Fig. 3 : current densities of the cathodic peaks versus the square root of the potential scan rate. The values of current densities are measured on the figure 2.

System of molybdenum

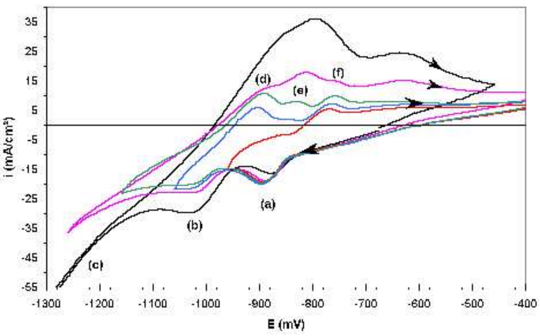
The voltammograms shown on figure 4 were performed on a platinum electrode by successive cathodic sweeps for which the final potential is increased at each cycle. The results obtained in these conditions are in perfect agreement with those of Balaz and Rüssel (6) :

- the (a) and (f) peaks are due to the Mo^{+VI}/Mo^{+III} system. Its related $E_{1/2}$ is equal to -0.83V ;
- the (b) and (d) peaks are characteristic of the Mo^{+III}/Mo^{0} system. Its related $E_{1/2}$ is equal to -0.96V ;
- when the final potential reaches values lower than -1.2V (c), the silica is reduced into silicon ; the latter forms molybdenum silicides which are oxidised subsequently at higher potentials (e).

These results were completed with those of the Mo and $MoSi_2$ corrosion studies performed in the SG doped with 1.5 wt% Fe_2O_3 :

- at 1423 K, the free potential of pure molybdenum is equal to -1V and thus, it validates the characteristic value $E_{1/2}$ = -0.96V determined for the Mo^{+III}/Mo^{0} system ;
- the cathodic polarisation of pure molybdenum electrode yields to the formation of silicides, but their efficiency as protective coating is very poor. This was confirmed by the electrochemical and metallographic studies of pure $MoSi_2$ tested in molten glass at higher temperature (1623 K) : i) the current density of corrosion estimated by polarisation resistance measurements remains high even after long time of immersion ($R_p = 20\ \Omega.cm^2$ and related $I_{cor}^{MoSi_2} = 1{,}2\ mA.cm^{-2}$; thickness reduction of intermetallic material measured after 50 h of immersion test $\Delta e = 35\ \mu m$), ii) the weak adhesion and the porosity of the corrosion products can not prevent the attack of this material by the molten glass (figure 5).

Thus, the oxidising abilities of both Mo^{+III} and Mo^{+VI} are relatively low compared to that of Fe^{+III} generally measured in molten glass.



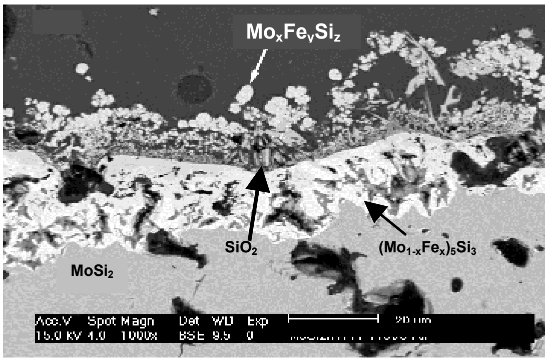
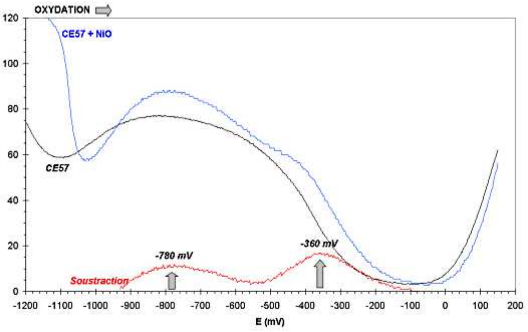


Fig. 4 : cyclic voltammograms recorded at 1423K in a glass doped with 1wt% MoO_3 (scan rate $v_b = 50$ mV.s^{-1}) Cathodic sweep : (a) and (f) due to Mo^{VI}/Mo^{III} ; (b) and (d) due to Mo^{III}/Mo^0 ; (c) due to Si^{IV}/Si^0 and (e) to Mo_xSi_y

Fig. 5 : surface of the $MoSi_2$ electrode after immersion in molten glass at 1623 K during 6h. Superficial layer of $(Mo_{1-x}Fe_x)_5Si_3$ - needles of silica at the glass/electrode interface - precipitates of $Mo_xFe_ySi_z$ in the glass.

System of nickel

The redox behaviour of nickel species was investigated in a platinum crucible. The cyclic voltammetry performed by use of a platinum working electrode revealed clearly the existence of two distinct redox systems at -0.780V and -0.360V, respectively (Figure 6).



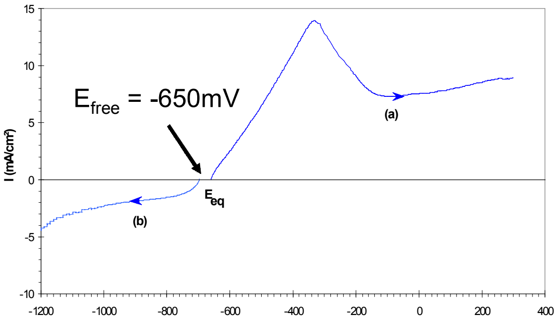


Fig. 6 : square wave voltammogram recorded at 1423K in SG melt, doped with 1wt% NiO ($\Delta E = 100$mV, $f = 50$ Hz, $v_b = 0.1$ V.s^{-1})

Fig. 7 : dynamic polarisation of a Ni electrode recorded at 1423K in SG doped with 5 wt% NiO. ($v_b = 0.16$ mV.s^{-1})

Thanks to the linear polarisation of a nickel electrode, the first value was accurately attributed to the Ni^{+II}/Ni^0 system because the free potential of metal is equal to -0.650V (Figure 7).

The use of complementary analytical techniques was helpful for the identification of the second system. In a first step, glasses were polarised respectively at -0.4V and -0.1V during 1 hour, then quenched in water. In a second step, Energy Electron Loss Spectroscopy (EELS) and magnetic susceptibility measurements were carried out on each kind of glass sample. The results obtained by EELS are reported on figure 7 : i) both spectra of NiO standard and polarised glass at -0.4V are similar, ii) the spectra of the two types of glasses exhibit a shift of 2 eV equal to that observed when spectra of NiO and Ni_2O_3 are compared, iii) the L_{III}/L_{II}

peak ratio is lowered in the case of the -0.1V polarised glass. Concerning magnetic measurements, the results obtained in the case of glass polarised at -0.1V led to values of magnetic susceptibility compatible with the existence of whether single Ni^{+III} or a mixture of Ni^{+II} and Ni^{+III} where the latter species is predominant.

In consequence, all these experimental features lead to the following conclusions : i) the value of the characteristic potential $E_{1/2}$ of the Ni^{+II}/Ni^{0} couple is equal to –0.780V and is lower than those mentioned by K. Takahashi et al.(7) and Rüssel et al.(8), ii) Ni^{+III} can be stabilised in glass melts contradicting the conclusions of many authors who calculate that the characteristic potential $E_{1/2}$ of the Ni^{+III}/Ni^{+II} couple is higher than the potential of glass melts oxidation(9). Moreover, one can note that the experimental result interpretations do not refer to the possible existence of tetra- or octa-coordinated Ni^{+II} in the glass(10), but they do not contradict this assumption.

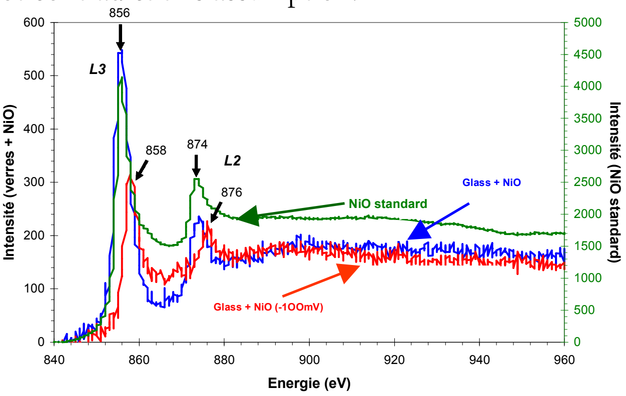


Fig. 8 : EEL spectra of pure NiO, glass with NiO and -0.1V polarised glass with NiO

Acknowledgements

The authors gratefully acknowledge A. Vernière (Maître de Conférences - Université H. Poincaré) for the magnetic measurements and F. Diot and S. Barda (Service Commun d'Analyses par Sondes Electroniques – Université H. Poincaré) for the electron microprobe microanalyses.

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