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Glass composition dependence of metal corrosion by molten glass

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➲ The knowledge of the corrosion behavior of metals in molten glass is an important challenge for the glass industry. If the corrosion reactions can be predicted from both immersed material and glass composition, this would be a great advance in this field. A series of four metals have been immersed in six different glasses. The results reported herein point out the effect of the addition of an oxidant to the glass and of the glass basicity upon metal corrosion.

EXPERIMENTAL PROCEDURE

➲ The metallic plates are directly immersed in molten glass in order to limit its oxidation before diving.
➲ After the immersion test, cross-sections are realized in order to determine :

➲ Substrate thickness from direct measurements (optical microscope, SEM)

➲ Corrosion layer morphologies (SEM)

➲ Determination of the corrosion layer and substrate compositions (EPMA)

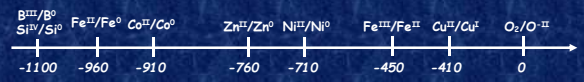
Glass compositions expressed in weight percent

	SiO_2	B_2O_3	Al_2O_3	Li_2O	Na_2O	K_2O	CaO	ZnO	Fe_2O_3	ZrO_2
G-Zn	58.8	18.2	4.3	2.6	7.0	-	5.2	3.2	-	0.7
G-Fe	46.5	18.5	10.0	-	20.0	-	-	-	5.0	-
G-S	64.5	4.5	3.40	-	16.0	1.20	7.2	-	0.15	-
G-A	70.5				29.5					
G-B	66				34					
G-C	59.2				40.8					

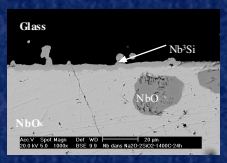
STUDY OF THE METAL/GLASS INTERFACES

➲ Determination of the phases formed at the metal/glass interface during the immersion (T=1400°C)
➲ Interpretation of the morphologies referring to both redox couple scale and diffusion paths through the phase equilibria diagrams

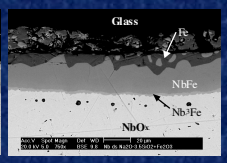
Partial scale of redox couple potentials



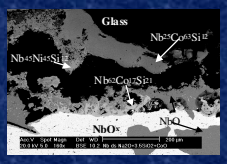
Nb in G-A
➲ Si^{IV}/Si^0



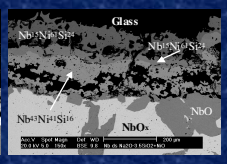
Nb in G-A + Fe_2O_3
➲ Fe^{II}/Fe^0



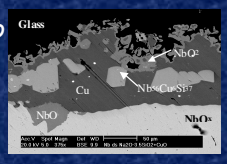
Nb in G-A + CoO
➲ Co^{II}/Co^0



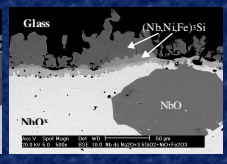
Nb in G-A + NiO
➲ Ni^{II}/Ni^0



Nb in G-A + Cu_2O
➲ Cu^I/Cu^0

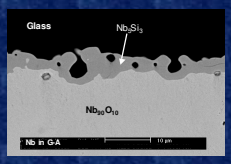


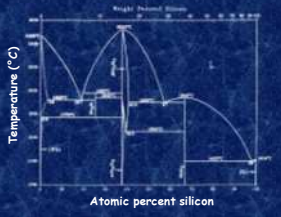
Nb in G-A + NiO + Fe_2O_3
➲ Ni^{II}/Ni^0
➲ Fe^{II}/Fe^0



➲ Metals react with the redox couples present in the glass which potential is the higher in the scale
➲ Two elements can be deposited at the same time on the metal

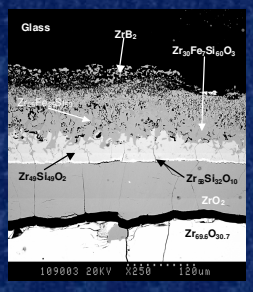
Simple case : Niobium in G-A

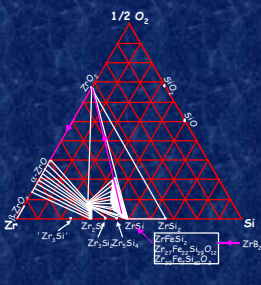




➲ Metallic silicon reacts with Nb to form Nb_5Si_3
➲ Oxygen diffuses in Nb to form NbO_x

Complex case : Zirconium in G-Fe

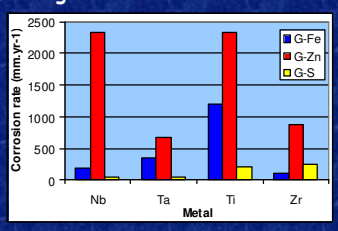




➲ Fe,Si and B form during redox reactions
➲ Complex layers develop according to the Zr-Si-(Fe-B)-O phase diagram

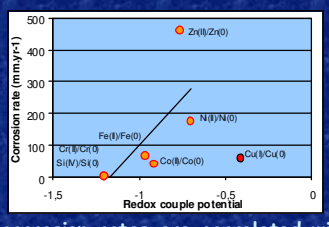
CORROSION KINETICS

➲ The corrosion rates are reckoned thanks to thickness measurements determined after two hours of metal/glass contact.



➲ Corrosion rates in G-Zn > G-Fe > G-S
➲ Corrosion rate depends on the considered metal/glass couple, that is to say, of the corrosion mechanism.

➲ Case of niobium immersion in Na_2O - $3.5SiO_2$ (G-A) modified by metal oxide additions



➲ The corrosion rates are correlated with the redox potentials of the M^{II}/M^0 couples. The higher the difference between the Nb^{II}/Nb^0 potential and the M^{II}/M^0 potential is, the higher the corrosion rate is.

CONCLUSIONS

➲ The morphology of the metal/glass interface depends on immersion duration, immersion temperature, the metal and the glass composition.

➲ The corrosion rates depend on the redox reactions involved in the metal corrosion by molten glass.

➲ The first results trying to correlate the corrosion rates and glass basicity are not self-consistent.

➲ The metal corrosion by molten glass can be used to deposit complex layers at the metal surface or to partially oxidize the metal.