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# Electrochemical study of cobalt base superalloys' corrosion by a molten glass ; influence of alloy's microstructure and of the chemical composition of the glass

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## INTRODUCTION

Superalloys are among the materials used in the hottest parts of glass making machines. These metallic alloys bring their high mechanical properties where tensile resistance and fracture toughness are of a great importance. Unlike many refractory oxide materials, superalloys are affected by both high temperature oxidation and corrosion by molten glass, which limit their life duration. On the second point, it is possible to increase the resistance of superalloys against glass corrosion, by reaching and keeping a passive state. The aim of this paper is to characterize the behavior of cobalt base superalloys in molten glass, and to determine the influence of alloys and glass characteristics, and of some process parameters.

## EXPERIMENTALS

### SYNTHESIS OF THE ALLOYS

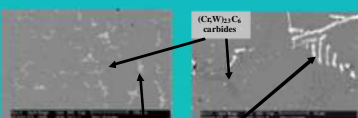
Chemical compositions of the studied alloys (%wt)

Alloy	Co	Ni	C	Cr	Ta	W
Co2 cobalt alloy	bal.	8.5	0.4	29	3	6
Co1 cobalt alloy	bal.	8.5	0.4	29	6	/
Co0 cobalt alloy	bal.	9.0	/	27.9	0.81	5.1

The cobalt base alloys studied are mainly three alloys. Co1 is strengthened by TaC carbides and Co2 by both TaC and  $(Cr,W)_{23}C_6$  carbides. These carbides form an eutectic with matrix at the grain boundaries. The third one, Co0, is an alloy of the same composition of Co2 matrix. It allows to underline the specific role of carbides.

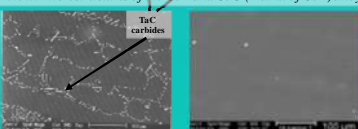
All alloys were synthesised by high frequency induction melting. Their solidification took place inside a ceramic crucible. The grain size obtained is about 50  $\mu m$ .

In some cases, a Ni base superalloy (Ni-30Cr-0.7C-7Fe-7W in %wt) and pure chromium were also tested for comparison.



Above: microstructures of the Co2 alloy at two magnifications

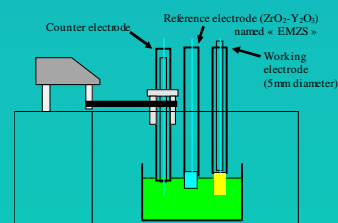
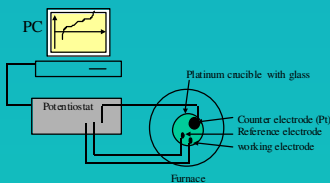
Below: microstructures of the Co1 and Co0 (matrix of Co2) alloys



### CHARACTERIZATION OF ALLOYS' CORROSION BY MOLTEN GLASS

The alloys' corrosion behavior was characterized using an electrochemical apparatus. It is adapted for molten glasses from the classical three-electrodes one usually used for aqueous corrosion studies.

Polarization curves, corrosion potential and polarization resistances were measured for several alloy-glass couples and different air oxidation conditions before immersion into glass.



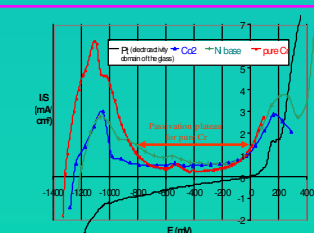
Chemical compositions of the glasses (%wt)

Glass	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
SL Glass	bal.	16	7.2	3.4	4.5	0.15
SA Glass	bal.	6.7	15	22	/	4.9
BS Glass	bal.	0.6	22	14	7.4	0.31

## RESULTS

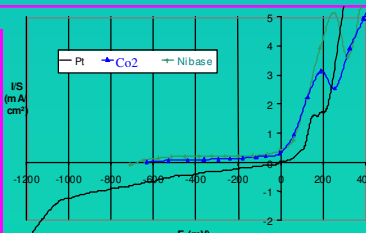
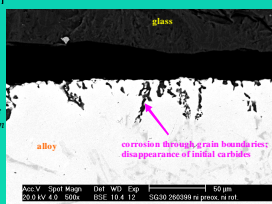
Generally, Co base and Ni base superalloys are in an active state when directly dived into molten SL glass without any air oxidation before. Corrosion is then fast, corresponding to about a few cm/year of alloy dissolved in glass. Corrosion potential ( $E_{corr}$ ) and polarization resistance ( $R_p$ ) are about -1.2V / EMZS and 20  $\Omega \cdot cm^2$ . The anodic reaction is  $Cr \rightarrow Cr^{III} + 2e$  and the cathodic one is  $Si^{IV} + 4e \rightarrow Si^0$ .

Polarization curves showing a passivation plateau after the anodic peak, all alloys, as pure Cr, are able to become passive.



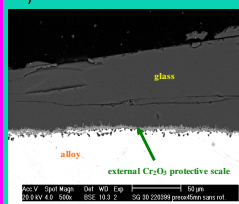
Above: alloys are active but passivable

Below: example of a Ni base superalloy being in an active state (2h in SL glass at 1050°C, no preoxidation before immersion, no rotation)

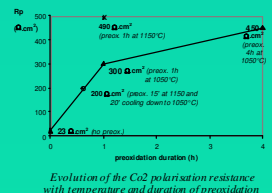


Above: alloys are passive after a preoxidation before immersion

Below: example of a Ni base superalloy being in a passive state (14h in SL glass at 1050°C, preoxidation before immersion, no rotation)

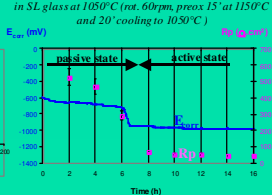


Obtaining a passive state depends on both preoxidation parameters and microstructure of the alloys. The higher the oxidation temperature is and the longer its duration is, the higher  $R_p$  is and the better the resistance against corrosion is. Minimal values of  $T(^\circ C)$  and  $d(h)$  exist for each alloy, when the glass allows passivation. For instance, Co2 is easier to passivate than Co1 which needs a longer preoxidation for a same  $T$ , probably because it contains no tungsten and only one type of carbide. Carbides seem to play an important role.

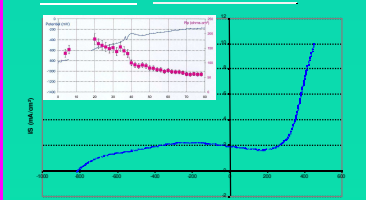
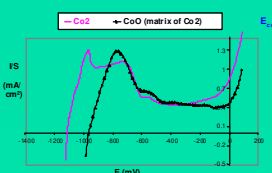


Left: polarization curves of Co2 and Co0 (matrix of Co2) in SL glass at 1050°C (rot. 60 rpm)

Right: evolution with time of  $E_{corr}$  and  $R_p$  of Co0 in SL glass at 1050°C (rot. 60rpm, preox. 15' at 1150°C and 20' cooling down to 1050°C)

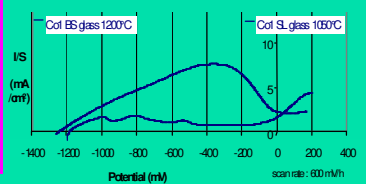


Indeed, Co0 which represents only the matrix of Co2, shows a different behavior, with notably a worse stability of the passive state.



Above: polarization curve of Co1 dived in SA glass without preoxidation (in left upper corner; following of both  $E_{corr}$  and  $R_p$  on 80 hours); rot. 60rpm

Below: polarization curve of Co1 in SB glass at 1250°C compared to the one in SL glass at 1050°C (no rotation)



If oxidised by air at high temperature before immersion ("preoxidation"), our high chromium superalloys can be stabilised in a passive state. It is characterised by the presence of an external chromia layer which protects the alloy from fast corrosion.  $E_{corr}$  and  $R_p$  are higher ( $> -0.7V$  / EMZS and  $> 200 \Omega \cdot cm^2$ ), corresponding to corrosion rates of a few mm/year.

The anodic reaction is  $Cr \rightarrow Cr^{III} + 3e$  and the cathodic one is reduction of other oxidant species than  $Si^{IV}$  (dissolved  $O_2$ ,  $Fe^{III}$ ). The  $E_{corr}$  values give in each case some indications about the main acting oxidant.

Glass chemical composition can also influence the behavior of the alloys. In some cases no preoxidation is necessary for alloys to be passive as early as immersion. For example, Co1 directly dived into SA glass at 1200°C is immediately in a passive state, thanks to the presence of  $Fe^{III}$  oxidants.  $E_{corr}$  and  $R_p$  evolutions show that  $Fe^{III}$  acts first, then oxidation continues with  $O_2$ .

At the opposite, Co1 appears not to be able to become passive in the BS glass at 1250°C, even after a preoxidation. There is no real passivation plateau and corrosion current is largely higher at all potentials. A possible reason is a too high solubility of  $Cr_2O_3$  in this glass.

## CONCLUSIONS

Thus, high chromium superalloys are generally passivable in molten glass. They can be protected against glass corrosion by an external chromia scale, the corrosion rate strongly decreasing. In some cases no precaution is required for such alloys to reach the passive state, as it was observed for a glass containing strong oxidant species ( $Fe^{III}$ ). In other glasses, the alloys need to be helped. In this field, a preliminary oxidation in air at high temperature gives them a first chromia scale and they get immediately the passive state. Minimal values of temperature and duration of this preoxidation have to be respected, depending of the alloy's characteristics. Among these latter, it appeared that existence and types of carbides can influence the reaching easiness of the passive state and its everlastingness on long times. Finally, certain glasses do not allow chromia-former alloys to become passive, maybe because a too high solubility of chromia into the glass melt.