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High temperature oxidation and corrosion by molten glass of refractory elements-base, Ni-base and Co-base alloys

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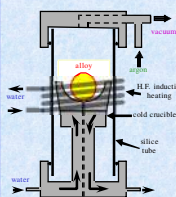
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INTRODUCTION

Many industrial applications require high-performance materials with good mechanical properties and high resistance to oxidation/corrosion at high temperatures. This is especially true in the glass industry, where metallic or ceramic materials suffer from high temperature oxidation and corrosion by molten glass at temperatures near 1000°C and sometimes much more. In the first case, conventional alloys belonging to cast nickel-base and cobalt-base families may be successfully used according to their sufficient mechanical properties. The major problem is the oxidation/corrosion phenomenon, the speed of which is both related to the characteristics of alloys and to those of the processes. To improve the resistance of these alloys it is essential to know the role of both alloy chemical composition and microstructure, and the one of the real process conditions. For higher temperatures, conventional alloys also meet mechanical deformation which become drastic if temperature reaches 1200°C or more. To solve this double problem of oxidation/corrosion and creep resistance, development of refractory alloys based on tungsten and/or molybdenum could be judicious. Oxidation resistance of these metals being very bad, they have to be alloyed with elements which form stoichiometric, protective oxide layers. Like for the conventional alloys, chromium has been chosen for this purpose, since chromia has a low solubility in most glasses.

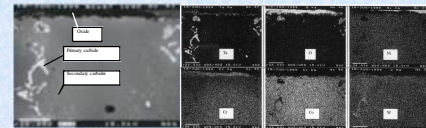
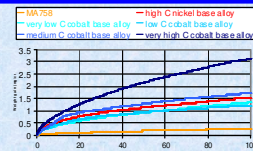
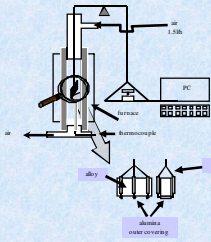
NICKEL AND COBALT BASE ALLOYS

EXPERIMENTAL

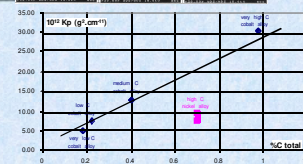


Alloy	Co	Ni	C	Cr	W	others
high C nickel alloy	/	bal.	0.7	28	6	7.5 Pt
very low C cobalt alloy	bal.	9	0.2	28	6	<1 Ta
low C cobalt alloy	bal.	9	0.2	28	6	3 Ta
medium C cobalt alloy	bal.	9	0.4	28	6	3 Ta
very high C cobalt alloy	bal.	9	1.0	28	6	6 Ta

OXIDATION

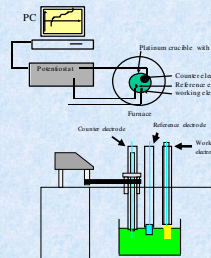


The behaviour of the five alloys has been studied by a thermogravimetric method. Tests were done at 1050°C during 100 hours. Parabolic oxidation constants obtained on cobalt-base alloys show a linear growth versus the carbon content. For a same carbon content, they are greater than the one of a nickel-base alloy. The examination of samples displays a protective chromia layer and an interdendritic oxidation of tantalum and a lack of chromium carbides.

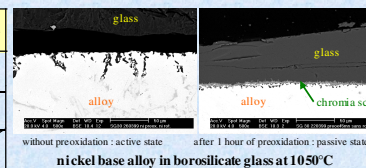
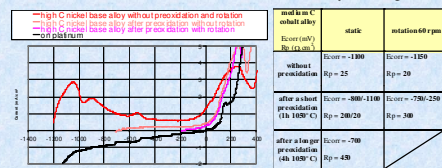
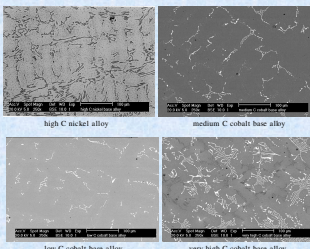
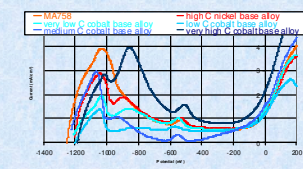


Alloys were obtained by high frequency induction melting, followed by a hardening heat treatment. Chemical compositions have been chosen in order to study both the role of the carbon content and the one of the base element.

CORROSION BY MOLTEN GLASS

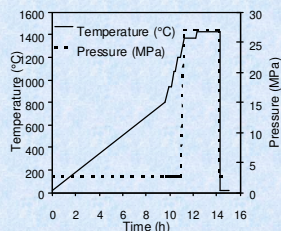
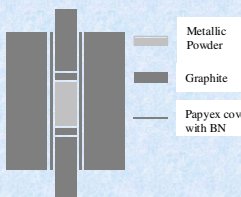


Electrochemical measurements have been done on each alloy as electrode inside molten glass. All of them can get a passive state, as it is shown by polarization curves. The passive state current can be very small as the one observed on the medium C cobalt-base alloy. Moreover it appears that a preoxidation by air before contact with molten glass leads to high values of both potential and polarization resistance. A similar effect is obtained with rotation of the working electrode, that moreover leads to a better stability of the passive state.



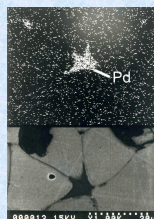
REFRACTORY ELEMENTS BASE ALLOYS

EXPERIMENTAL



The synthesis were carried out by uniaxial pressure sintering assistance. High pressure was applied with the use of a high temperature furnace equipped with a 10 tons uniaxial press.

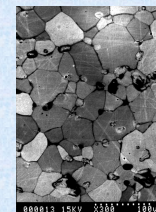
Due to the low diffusion coefficients, an activating agent has to be added to increase the interdiffusion of the alloy's constituted elements.



Palladium is the best activating agent

34Cr-32.5Mo-32.5W-1Pd alloy (w %)

	Wt %	At %
Chromium	64.31	79.54
Molybdenum	5.4	3.62
Palladium	24.52	14.82
Tungsten	5.77	2.02

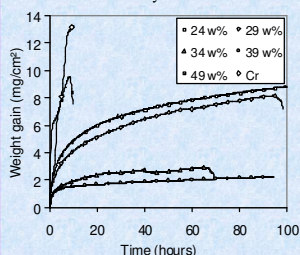


Formation of a α -Cr-Pd phase at the grain boundaries

No preferential grain orientation is displayed despite the uniaxial pressure

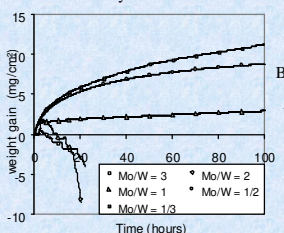
OXIDATION

Evolution of the oxidation resistance at 1300°C
XCr-YMo-ZW-1Pd alloys

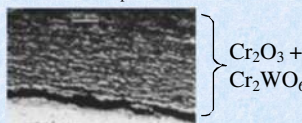


Catastrophic oxidation is observed both for the lower chromium contents and higher molybdenum contents alloys by formation of non-protective Cr₂WO₆ oxides and volatile MoO₃.

39Cr-XMo-YW-1Pd alloys

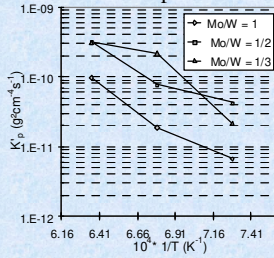


BSE micrography of the 39Cr-30Mo-30W-1Pd alloy oxidised at 1300°C for 100 hours: Visualisation of the protective chromia scale

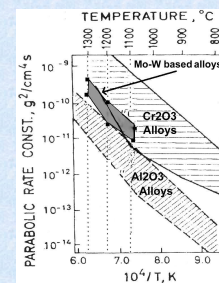


BSE micrography of the 34Cr-32.5Mo-32.5W-1Pd alloy oxidised at 1300°C for 70 hours: Visualisation of the catastrophic oxidation mechanism

Influence of the temperature



Evolution of the oxidation rate constant with the temperature and the Mo/W ratio



Calculated rate constant of chromia former Mo-W based alloys compared with Cr₂O₃ and Al₂O₃ former referring to Hindam and Whittle

CONCLUSIONS

Many conventional cast alloys as nickel-base and cobalt-base are candidate as materials of tools for molten glass working at medium temperatures. As it has been evidenced, the rates of both oxidation and corrosion by molten glass are related to the chemical composition and/or microstructure of the alloys (base element, kind and density of interdendritic carbides). It appears that an optimum could be found to minimize these phenomena, that are the most important for this temperature level. For higher working temperature, creep deformation can appear. It leads to select more refractory materials like CrMoW alloys. These ones have been obtained by a powder metallurgy way involving palladium as sintering agent, then investigated over a wide range of composition. Excellent oxidation behaviours are observed for alloys with a high chromium and tungsten contents. A comparison of the calculated parabolic rate constant for the alumina and chromia alloys shows that such chromia forming alloys can have an oxidation resistance similar to that of alumina forming alloys at high temperatures.