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# Microstructural and oxidation study of chromia forming Molybdenum-Tungsten based alloys



S.DILBERTO, C.RAPIN, P.STEINMETZ, P.BERTHOD

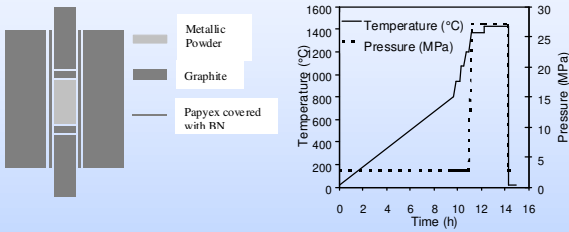


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## INTRODUCTION

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 as high as 1200°C or more. In this case, iron, or nickel based alloys cannot be used, due to their drastic loss of mechanical properties above 1200°C. Considering high temperature mechanical properties and corrosion resistance to molten glass, 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. Among the elements which can be used for this purpose, chromium is preferred since chromia has a low solubility in most glasses.

## EXPERIMENTAL

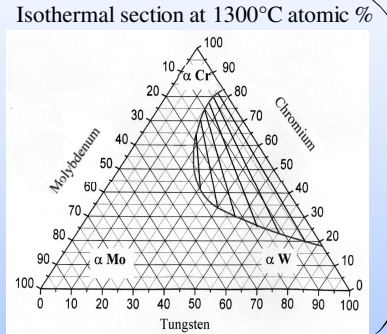


The synthesis were carried out by uniaxial pressure sintering assistance. High pressure was applied with the use of a high temperature furnace equipped with a 10 tons uniaxial press.

## Cr-Mo-W SYSTEM

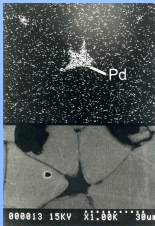
Experimental investigation of the ternary phase diagram and determination of the ternary cross and direct diffusion coefficients (1300°C).

Ternary diffusion coefficients	Composition range	Composition range
$\bar{D}_{12}$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )	60<Cr<65 10<W<15 Mo = 25	55<Cr<60 15<W<20 Mo = 25
for a constant molybdenum concentration	$\bar{D}_{CrMo}^{Mo}$ $\bar{D}_{CrW}^{Mo}$ $\bar{D}_{MoW}^{Mo}$ $\bar{D}_{CrCr}^{Mo}$ $\bar{D}_{CrMo}^{Cr}$ $\bar{D}_{CrW}^{Cr}$ $\bar{D}_{MoW}^{Cr}$ $\bar{D}_{CrCr}^{Cr}$ $\bar{D}_{MoMo}^{Cr}$	$\bar{D}_{CrMo}^{Mo}$ $\bar{D}_{CrW}^{Mo}$ $\bar{D}_{MoW}^{Mo}$ $\bar{D}_{CrCr}^{Mo}$ $\bar{D}_{CrMo}^{Cr}$ $\bar{D}_{CrW}^{Cr}$ $\bar{D}_{MoW}^{Cr}$ $\bar{D}_{CrCr}^{Cr}$ $\bar{D}_{MoMo}^{Cr}$
	0.83 0.39 -0.29 0.078 0.75 0.35 -0.31 0.09	
Ternary diffusion coefficients	60<Cr<65 20<Mo<25 W = 15	55<Cr<60 25<Mo<30 W = 15
for a constant tungsten concentration	$\bar{D}_{CrMo}^{W}$ $\bar{D}_{CrW}^{W}$ $\bar{D}_{MoW}^{W}$ $\bar{D}_{CrCr}^{W}$ $\bar{D}_{CrMo}^{Cr}$ $\bar{D}_{CrW}^{Cr}$ $\bar{D}_{MoW}^{Cr}$ $\bar{D}_{CrCr}^{Cr}$ $\bar{D}_{MoMo}^{Cr}$	$\bar{D}_{CrMo}^{W}$ $\bar{D}_{CrW}^{W}$ $\bar{D}_{MoW}^{W}$ $\bar{D}_{CrCr}^{W}$ $\bar{D}_{CrMo}^{Cr}$ $\bar{D}_{CrW}^{Cr}$ $\bar{D}_{MoW}^{Cr}$ $\bar{D}_{CrCr}^{Cr}$ $\bar{D}_{MoMo}^{Cr}$
	2.69 0.21 -0.18 0.73 2.1 0.47 -0.65 0.18	



## MICROSTRUCTURE

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

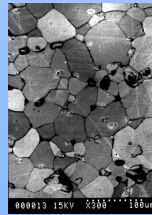


Palladium is the best activating agent

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

	Wt %	At %
Chromium	64.31	76.54
Molybdenum	5.4	3.62
Palladium	24.52	14.82
Tungsten	5.77	2.02

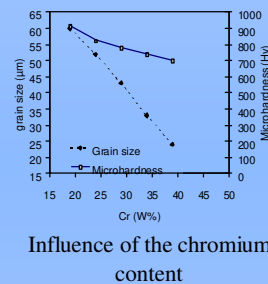
Formation of a  $\alpha$ -Cr-Pd phase at the grain boundaries



No preferential grain orientation is displayed despite the uniaxial pressure

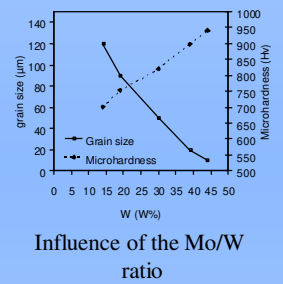
Grain size and microhardness evolution with composition

XCr-YMo-ZW-1Pd alloys



Influence of the chromium content

39Cr-XMo-YW-1Pd alloys



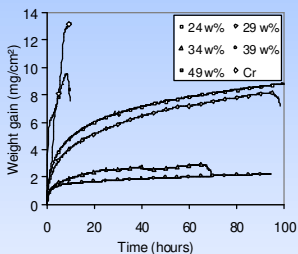
Influence of the Mo/W ratio

## OXIDATION

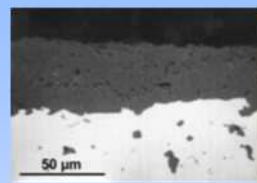
Evolution of the oxidation resistance at 1300°C

XCr-YMo-ZW-1Pd alloys

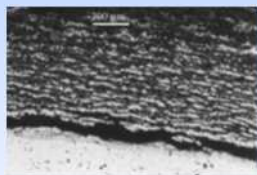
39Cr-XMo-YW-1Pd alloys



Catastrophic oxidation is observed both for the lower chromium contents and higher molybdenum contents alloys by formation of non-protective Cr<sub>2</sub>WO<sub>6</sub> oxides and volatile MoO<sub>3</sub>.

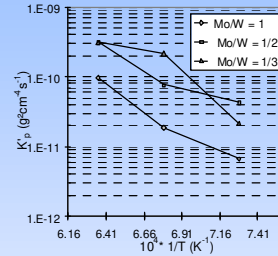


BSE micrograph of the 39Cr-30Mo-30W-1Pd alloy oxidised at 1300°C for 100 hours: Visualisation of the protective chromia scale



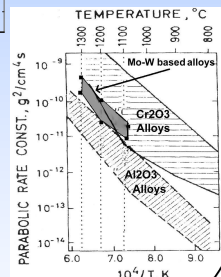
BSE micrograph of the 34Cr-32.5Mo-32.5W-1Pd alloy oxidised at 1300°C for 70 hours: Visualisation of the catastrophic oxidation mechanism

Influence of the temperature



Calculated rate constant of chromia former Mo-W based alloys compared with Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> former referring to Hindam and Whittle

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



## CONCLUSION

The microstructure and the oxidation behaviour of CrMoW alloys have been investigated over a wide range of composition. The sintering mechanism with palladium is based on the presence of a liquid CrPd phase at the grain boundaries, which allows a rapid diffusion of the elements. Excellent oxidation behaviours are observed for alloys with a high chromium and tungsten contents. A comparison of the calculated parabolic rates 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.