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High temperature oxidation of HEAs and MC-strengthened HEAs in presence of water vapor

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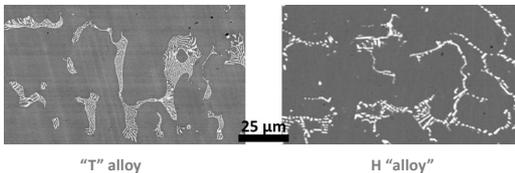


Introduction

Exposed to air at high temperature, chromia-forming alloys, and even alumina-forming alloys, may behave differently in presence of water vapor by comparison to dry air. Notably, chromia volatilization may be accelerated for a given constant temperature and even it may take place at temperatures lower than 1000°C. Usually not really concerned by volatilization, alumina may start to be affected by volatilization in case of humidified air. Due to the presence of manganese in their chemical compositions, Cantor's alloys and derivatives oxidize with the development of complex oxide scales including mixed {Cr,Mn}-oxides, which may behave differently than pure chromia. In this work, oxidation tests in hot humidified air are carried out, followed by kinetic treatment of the mass gain files. Characterization focuses not only on the isothermal mass gain at the stage temperature (1000°C) but attention is also paid to the mass variations during heating and to the ones during cooling. Differences in mass variation behavior will be evidenced and interpreted in term of influence of the presence of water vapor and also in term of effect of the alloy's chemical composition.

Presentation of the HEA-based single-phased (C), TaC-containing alloy (T) and HfC-containing alloy (H) concerned by this study [1]

- "C" is the original Cantor's alloy (equimolar in Co, Ni, Fe, Cr and Mn) in a conventionally cast version modified by a decrease in Mn (× 0.5 → 10 at.%) and an increase in Cr (× 1.5 → 30 at.%); it is single-phased
- "T" is based on the "C" alloy described above, but it contains additionally Ta and C (to reach the 0.25 %C and 4 %Ta weight contents); its matrix is similar to the "C" alloy (with about 1 wt.%Ta in solid solution) and it contains eutectic TaC carbides located in the interdendritic spaces
- "H" is also based on the "C" alloy and it contains also Hf and C (added to reach the 0.25 %C and 4 %Hf weight contents); its matrix is identical to the "C" alloy (no Hf inside) and it contains interdendritic eutectic HfC carbides and some blocky HfC (seemingly of a pre-eutectic origin).

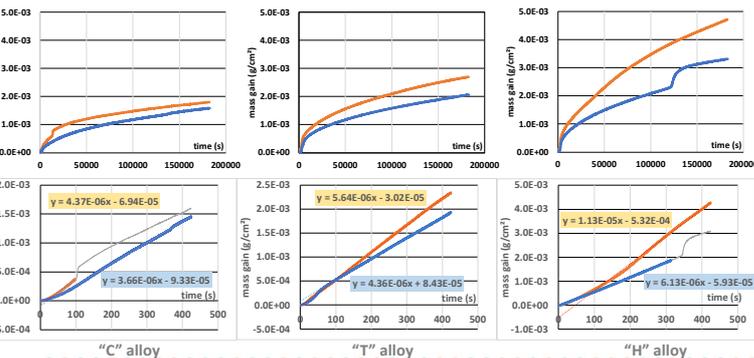


Details concerning the oxidation tests

- Sample geometry and size: parallelepipeds with square main faces, about 2 mm × 8 mm × 8 mm, all faces ground with #1200-grit SiC papers and all edges and corners smoothed
- Temperature for the isothermal stage: 1000°C; isothermal duration: 50 hours; hot air flow: 20 mL/min
- Apparatus for the tests in dry air (80%N₂-20%O₂): SETARAM TG92 thermobalance
- For the tests in humidified hot air: SETARAM SETSYS thermobalance with a WETSYS vapor generator; partial pressure of water vapor = 179 mbars (achieved by producing 90% of relative humidity at 60°C)

Results: isothermal oxidation

- All isothermal mass gain curves globally parabolic; in some cases: jumps caused by local unsticking of the oxide scale followed by new fast oxidation of the corresponding denuded part of alloy
- In ascending order of global mass gain kinetic: "C" < "T" < "H" whatever the oxidizing atmosphere
- Water vapor: slower mass gain than in dry air

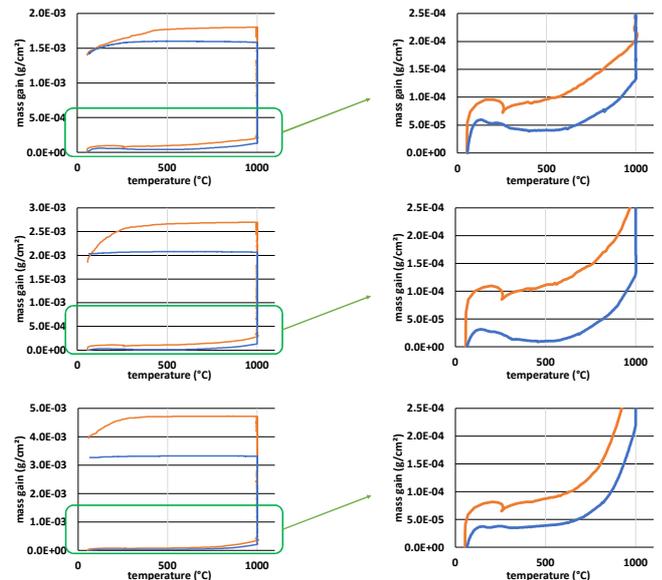


- Plot of the mass gain versus the square root of time: straight lines → seemingly no volatilization of oxide (≠ Cr₂O₃ which can be re-oxidized into gaseous CrO₃ in the case of chromia-forming alloys)
- In the table below, values of the total mass gain achieved during the whole isothermal stage and values of the parabolic constant deduced from the slopes of the straight lines obtained by plotting mass gain versus the square root of time (in some cases only from the straight curve part preceding the first significant mass gain jump)
- By comparison with Ni-25/30Cr (wt.%) alloys oxidized in the same conditions of temperature and atmosphere (dry air: $K_p \approx 3 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, $K_v \approx 1 \times 10^{-12} \text{ g cm}^{-2} \text{ s}^{-1/2}$; wet air: $K_p \approx 3 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, $K_v \approx 50 \times 10^{-12} \text{ g cm}^{-2} \text{ s}^{-1/2}$) the parabolic oxidation is faster but no linear mass loss (e.g. due to oxide volatilization) can be evidenced

Alloy:	C alloy		T alloy		H alloy	
Oxidant atmosphere:	dry air	wet air	dry air	wet air	dry air	wet air
Total isothermal mass gain (mg cm ⁻²):	1.595	1.438	2.407	1.927	4.335	3.088
K_p (× 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹):	9.55	6.70	16.13	9.50	64.98	18.79

Results: oxidation during heating, scale spallation during cooling

- Plotting mass variation versus temperature instead time allows observing the mass phenomena during heating and during cooling
- Heating: no difference due to the presence of water vapor can be evidenced for the mass gain by oxidation in the high temperature part of heating
- Cooling: water vapor seems totally inhibiting the small oxide spallation occurring in dry air (change in oxide nature? better plasticity of the oxide scale?)
- Heating and cooling: possible difference of artificial mass variation due to gas buoyancy (consequence of a density difference between dry air and wet air?)



Conclusion

The presence of water vapor, with the content tested here, obviously lowered significantly the isothermal mass gain kinetic by oxidation at 1000°C of these {Mn,Cr}-modified Cantor-type cast alloys (but without change of the hierarchy among the carbide-free and the MC-containing alloys). Another beneficial effect is perhaps also to notice, concerning the mass loss during cooling, according to the present kinetic results. This thermogravimetry part of the study of the effect of water vapor on the high temperature oxidation behavior of these alloys will be soon completed with the results of the ongoing post-mortem metallography investigation of their oxidized states. One can hope that these results will explain the present observations.

Acknowledgements:

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References :

- [1] N. Chenikha, P. Spaeter, C. Gay, A. Vernière, P. Berthod: Microstructures in as-cast condition of Medium Entropy Alloys designed to contain eutectic carbides TaC or HfC. *Journal of Engineering Science and Innovation* (2023) 8(2) 159–170. <https://hal.science/hal-04281563>
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