PACK-CEMENTATION OF CHROMIUM ON Co, Ni AND Fe-BASED CARBIDES-STRENGTHENED ALLOYS: INFLUENCE OF THE CARBIDES NATURE ON THE Cr-ENRICHMENT

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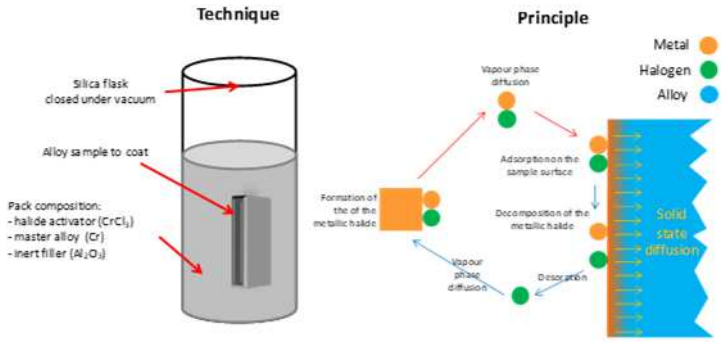
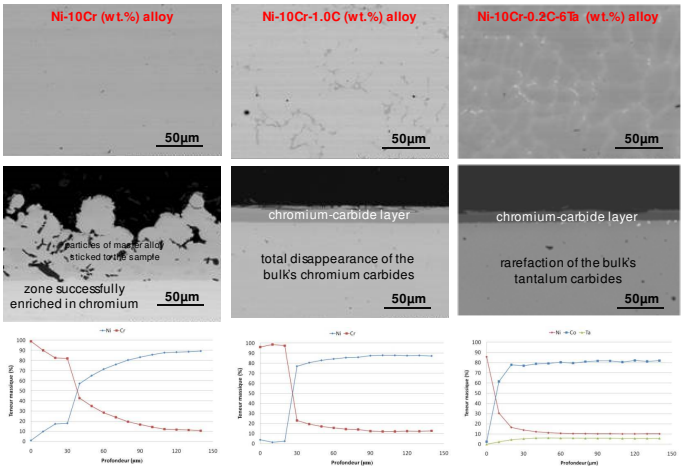
Superalloys, which are mainly based on cobalt, nickel and/or iron [1], are usually exposed to high temperature oxidation. To resist this phenomenon they are designed to contain high amounts in Cr, Al or Si to develop external protective oxide scales [2]. These elements must be in quantities high enough in the bulk, or only in the sub-surface where they are really useful to combat hot oxidation. In the later case a surface enrichment can be achieved by using pack-cementation, a CVD technique used since many years ago to superficially enrich cobalt alloys with chromium [3], nickel alloys with aluminium [4] or iron alloys with silicon [5], for example. The success of such operation depends on thermodynamic and kinetic conditions, but also on some microstructure characteristics of the alloy. The aim of this work is to explore the possible influence of the nature of the carbides which are in some cases used to mechanically reinforce some refractory cast alloys (notably against creep deformation).

Experimental details

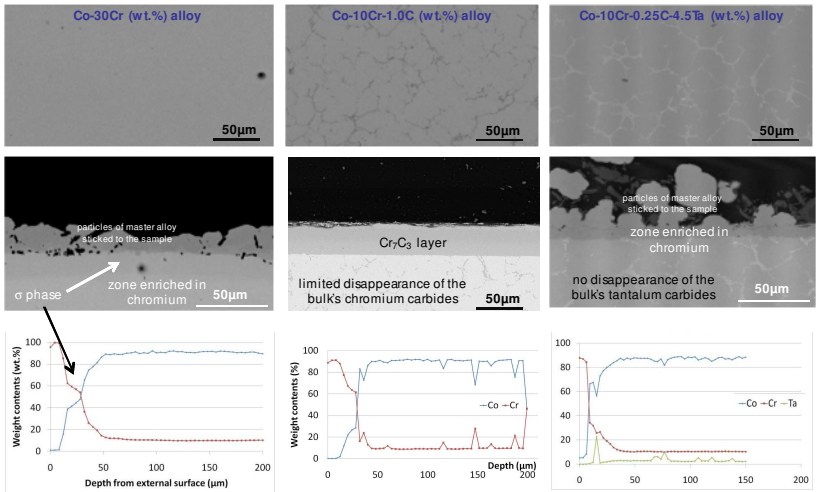
Several alloys based on Co, Ni or Fe, all with a chromium content equal to 10wt.%Cr and containing either chromium carbides or tantalum carbides were elaborated by foundry and subjected to chromium deposition by pack cementation at 1050°C during about 10 hours (7h30 for the Ni alloys, 7h30 and 15h for the Co alloys, 15h for the Fe alloys). The samples were cut and metallographically prepared, before observation of their surface using electron microscopy and acquisition of transversal Cr-profiles using microprobe.



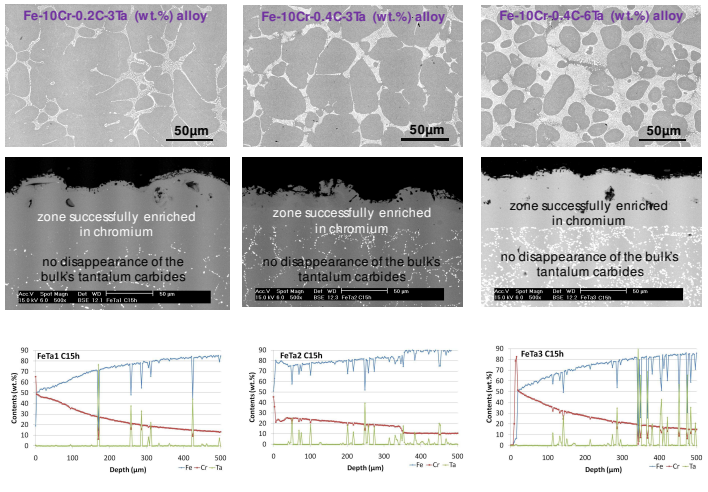
Results obtained on nickel alloys [6]



Results obtained on cobalt alloys [7]



Results obtained on iron alloys [8]



It appears that the Cr-enrichment failed in the case of all alloys which initially contained interdendritic chromium carbides as single reinforcing phase or present together with tantalum carbides. Whatever the base element, this was due to the formation of a chromium carbide involving the carbon atoms diffusing from deeper, released by the dissolution of the bulk chromium carbides. In contrast, when TaC were the single carbides present in a Co-based or Fe-based alloy, the inward chromium diffusion was never inhibited and a sub-surface really enriched in chromium (up to 30wt.% in some cases) was observed. This difference results from the higher stability of the TaC at high temperature. In contrast, the lack of stability of tantalum carbides earlier observed in Ni-based alloys [9] led again to the development of a carbide layer along the surface of the TaC-containing nickel alloy. In the cases where the Cr-enrichment of the sub-surface was successful, the incorporation in the sub-surface of the cement grains still sticked to surface and a deeper inward diffusion of the added chromium can be achieved by applying an additional long high-temperature heat-treatment.

To conclude, one can say that the success of the sub-surface enrichment in chromium by pack-cementation of carbides-reinforced alloys thus supposes that the bulk's carbides are very stable, even in presence of a neighbour high Cr activity. It appeared here that TaC are to be prefered to Cr_7C_3 or $Cr_{23}C_6$, at least in cobalt-based or iron-based alloys.

References:

[1] Superalloys: A Technical Guide 2nd Edition (2002), ASM International, edited by M.J. Donachie and S.J. Donachie, pp. 2.
[2] High Temperature Oxidation and Corrosion of Metals (2008), Elsevier, ed. by D.J. Young.
[3] G.H. Faber, "The role of chromium in corrosion and oxidation resistant alloys and coatings", High Temp. Alloys Gas Turbines, Proc. Conf., 1978, pp. 225-230.
[4] C. Choux, S. Chevalier, Y. Cadoret, "Elaboration of nickel aluminide diffusion coatings: application to oxidation resistance", Mater. Sci. Forum, vol. 595-598, 2008, pp. 41-49.
[5] M.J. Mukherji, P. Prabhakaram, "Diffusion coatings on steel", Anti-corros. Method, vol. M25(1), 1978, pp. 4.
[6] G. Michel, P. Berthod, M. Vilasi, P. Steinmetz, « Influence de la densité et de l'orientation du réseau de carbures des alliages base nickel de fonderie sur la cinétique de leur enrichissement en chrome par cémentation en caisse », proceeding of the congress « Matériaux 2010 » held in Nantes (France) on October 18th-22nd 2010.
[7] G. Michel, P. Berthod, Michel Vilasi, S. Mathieu, P. Steinmetz, "Protection of cobalt-based refractory alloys by chromium deposition on surface. Part I: Sub-surface enrichment in chromium by pack-cementation and diffusion", Surface & Coatings Technology, 205, 2011, pp.3708–3715.
[8] G. Michel, P. Berthod, M. Vilasi, "Refractoriness, microstructures and high temperature oxidation of TaC-reinforced iron-based alloys protected by chromium-rich coatings", Advances in Science and Technology, vol. 72, 2010, pp. 53-58.
[9] P. Berthod, L. Aranda, C. Vébert, S.Michon, "Experimental and thermodynamic study of the high temperature microstructure of tantalumcontaining nickel-based alloys", Calphad, 28, 2004, pp.159–166.