Protection of cobalt-based refractory alloys by chromium deposition on surface. Part II: Behaviour of the coated alloys in oxidation at high temperature

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Abstract

A high chromium content, typically 30wt.%, is generally considered as necessary for cobalt-based alloys to allow them resisting oxidation by hot gases. Cobalt alloys with a bulk poorer in chromium may become resistant against high temperature oxidation if they are enriched in chromium on surface. The aim of this second part of the work is to expose to air at 1200°C three low-chromium cobalt-based alloys (Co-10Cr, Co-10Cr-0.25C-4.4Ta and Co-10Cr-0.5C-8.7Ta in wt.%), previously enriched in chromium on surface by pack-cementation, in order to examine if the applied cementation treatments are enough to ensure a good behavior on long time. The initial surface enrichment in chromium of the Ta-containing alloys, characterized by a maximal content on surface of about 30wt.%Cr and a depth of enrichment of several hundreds of micrometers, gives them a good resistance to oxidation at 1200°C, despite the very low chromium content in the bulk. This is also due to the interdendritic TaC carbides which may facilitate outward diffusion of chromium during oxidation as they facilitated its inward diffusion during cementation. In contrast, the CoCr alloy, enriched in chromium in the same conditions did not display a so good oxidation behavior.

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1. Introduction

The surface of the metallic pieces used at high temperature in gaseous aggressive environments is subjected to a more or less rapid degradation by high temperature oxidation and/or hot corrosion [1]. These phenomena, as well as other ones (creep deformation, fatigue cracks …), significantly contribute to the limitation of the lifetime. In order to delay the start of catastrophic oxidation or corrosion, refractory alloys must contain – at least in their sub-surface – a sufficient amount of Cr, Al or Si. Co-based alloys [2] and Ni-based alloys [3] are also concerned, as well as Mo or Nb-based [4] refractory alloys. In some cases the use of chromium is mandatory, for example when the application requires a resistance against corrosion by molten glass or molten salts as good as the resistance against oxidation by hot gases. In such cases it is considered that the chromium content needs to be at least about 20wt.% Cr in a nickel-based alloy, and as high as 30wt.% for a cobalt-based alloy. Such high Cr contents can be detrimental for other properties: refractoriness or metallurgical stability (risk of brittle phases' precipitation), for example. The presence of such high chromium contents is not necessary in the alloy's bulk since only the surface and sub-surface are exposed to the consequences of this degradation at high temperature. An inhomogeneous distribution of chromium (high near the surface and low in the bulk) can be envisaged to simultaneously keep on surface a good resistance to high temperature oxidation, and to prevent on long time precipitation of topologically close packed phases in the main part of piece thickness to avoid mechanical weakening. Such chromium distribution can be obtained by enriching in chromium the sub-surface of a low-chromium cobalt-based alloy, as realized in the first part of this study [5], and as usually done for several decades to enrich in Al the sub-surfaces of nickel-based [6], niobium-based [7] and cobalt-based [8] alloys.

In the first part of this work [5] such chromium enrichments were obtained in the sub-surface of a 10wt.%Cr- containing carbon-free binary cobalt alloy and of two other cobalt alloys containing exclusively TaC carbides. Such local chromium enrichment on surface may enhance the resistance of these alloys against high temperature oxidation and hot corrosion, by comparison with the uncoated bulk alloys.

In this second part of the present work the oxidation behaviour in air at 1200°C will be examined over several tens hours to verify if the cementation treatment applied to some of the studied 10wt.Cr-containing has resulted in a sufficient chromium enrichment on their surface to give them a good resistance against high temperature oxidation.

2. Experimental procedure

Characteristics of the studied alloys

A binary alloy named CoCr (targeted composition: Co(bal.)-10wt.%Cr) and two tantalum-containing alloys named CoTa1 and CoTa2 (targeted compositions: {Co(bal.) - 10wt.%Cr - 0.25wt.%C - 4.4wt.%Ta} and {Co(bal.) - 10wt.%Cr - 0.5wt.%C - 8.7wt.%Ta} respectively), were obtained by foundry from pure elements [5]. Their sub-surfaces were enriched in chromium by pack cementation at 1050°C (temperature chosen after thermodynamic calculations for optimizing the gaseous conditions), for two tested durations 7.5h or 15h (estimated from previous results for obtaining a significant Cr-deposit on surface), in a powders mixture containing the halide activator $CrCl_3$, the cement Cr and the inert filler Al_2O_3). The cementation step was followed by a heat-treatment step, for 75h at 1200°C in inert atmosphere to allow chromium diffusing deeper inwards (duration and temperature previously identified to allow a sufficient Cr-diffusion depth for such alloys).

A {7.5h-cemented; 75h-heat-treated} sample (named "C7.5HT75") and a {15h-cemented; 75h-heat-treated} sample (named "C15HT75") of each alloy were slightly polished with 1200-grit paper and put in a Carbolite STF 15/450 tubular furnace where they remained 50h at 1200°C (laboratory air). After cooling down to room temperature the oxidized samples were covered by electrolytic nickel in order to protect the formed external oxide scale against the mechanical stresses applied thereafter during metallographic preparation. These samples were cut and embedded in a cold resin mixture, then polished with paper from 240-grit to 1200-grit and finished with 1µm alumina paste.

To complete the oxidation results with kinetic data two thermogravimetric runs were performed at 1200°C for 50 hours in a flow of dry synthetic air (80%N_2 – 20%O_2) for the CoTa1 and CoTa2 alloys cemented during 15h and heat-treated. The used thermo-balance was a Setaram TG92. The mass gain measurements were exploited according to the {$dm \times dm/dt = Kp – Kv \times m$} treatment [9] to simultaneously specify the parabolic constant Kp and the chromia-volatilization constant Kv. At 1200°C it is effectively necessary to assess the kinetic of volatilization of chromia to avoid any minimization of the parabolic constant.

Microstructure and surface state characterizations

The metallographic samples were observed using a Scanning Electron Microscope (Philips XL30) in Back Scattered Electrons mode (SEM, BSE) to observe the microstructures and the surfaces states. Two concentration profiles were performed using Wavelength Dispersion Spectrometry – Electron Probe Micro Analysis (WDS-EPMA) for each oxidized sample, perpendicularly to surface and across the external oxide scale and the sub-surface (two microprobes were used: Cameca SX50 and Cameca SX100).

In parallel the determination of the local theoretic solidus temperature (which possibly varies with the local Cr content) was done using the Thermo-Calc version N software [10], working with a database derived from the SSOL database (SGTE) [11]. This {software + database} calculation tool is able to assess solidus temperatures consistent with experimental DTA measurements for tantalum-containing cobalt-based alloys [12]. The systems added to the initial SSOL database are Ta—C [13], Co—Ta [14], Cr—Ta [15] and Co—Ta—C [16].

3. Results

Microstructure states of the alloys before oxidation

The surface states and bulk microstructures of the cemented + heat-treated alloys before oxidation test are illustrated by the micrographs presented in Figure 1 and Figure 2. By comparison with the microstructures of the alloys before cementation, the cemented and heat-treated alloys are obviously affected by both rarefaction and fragmentation of their TaC carbides.

Surface states of the oxidized alloys.

The oxidized surfaces and affected sub-surfaces were observed using the SEM in BSE mode. The natures of the oxides were characterized by Electron Probe Micro Analysis.

After 50h of oxidation at 1200°C, the C7.5HT75 CoCr alloy is covered by a continuous layer of chromia. Internal oxidation also occurred here and there, seemingly along

the interdendritic spaces. In some places on surface, oxidation obviously started to become stronger (Figure 3a), which resulted in oxidized depths of several tens of micrometers.

A generalized catastrophic oxidation affected almost the whole surface of the C15HT75 CoCr alloy (Figure 3b). Indeed, under a first oxide scale composed of CoO (more than 100µm), there is a thick spinel oxide (several hundreds of µm) separating the cobalt oxide and the alloy.

After oxidation test, the C7.5HT75 CoTa1 (Figure 4a), C15HT75 CoTa1 (Figure 4b), C7.5HT75 CoTa2 (Figure 5a) and C15HT75 CoTa2 (Figure 5b) are covered by a continuous Cr_2O_3 scale. This external chromia layer was clearly identified by the most external part (on the left side) of the WDS-EPMA concentration profiles presented in Figure 6. Just under the chromia layer the most external part of the sub-surface is affected by internal oxidation. There is notably an almost continuous but irregular oxide of both chromium and tantalum ($CrTaO_4$), the thickness of which varies along the oxidation front.

General shapes of the new chromium distribution after oxidation test.

Oxidation for 50h at 1200°C has logically impoverished the alloys in chromium and the sub-surface has lost a significant part of the supplementary chromium which was previously added by cementation and diffusion heat treatment. Notably, the most external part of sub-surface, which was significantly richer in chromium than deeper, is now, on the contrary, poorer in Cr than several tens of micrometers deeper. Thus, except the CoCr alloy in the initial C15HT75 condition which is catastrophically oxidized on its main surface, all the oxidized samples present chromium profiles which display a bulge at about 50-100µm under the external surface. This is clearly visible on the WDS-EPMA chromium concentration profiles, superimposed with the initial profiles, in Figure 7 for the C7.5HT75 CoCr alloy, Figure 8 for the CoTa1 alloy in the C7.5HT75 (a) and the C15HT75 (b) conditions, and in Figure 9 for the CoTa2 alloy in the C7.5HT75 (a) and the C15HT75 (b) conditions. From the oxidation front, the chromium content increases from a low value (between about 8 and 11wt.%Cr). It reaches a maximal value (between about 13.5 and 14wt.%Cr) and it decreases slowly and finishes to join the initial chromium content of the alloy before cementation (about 10wt.%).

The characteristic values of chromium content and depth describing these new chromium distributions are presented in Table 1 (all C7.5HT75 alloys after oxidation) and Table 2 (all C15HT75 alloys after oxidation). The final chromium content on the external surface tends to be higher for the C7.5HT75 initial condition than for the C15HT75 one. This is true for CoTa1 (2wt.%Cr more), a little less true for CoTa2 (only 0.5 wt.% more, difference not significant with regard to the standard deviation values), and especially true for the binary alloy since the C15HT75 CoCr alloy lost its chromia-forming behavior before 50h. One can also remark that, for the same conditions of cementation and heat treatment, the minimal value of chromium on surface tends to be slightly higher for CoTa2 than for CoTa1, and more significantly higher for these two tantalum-containing alloys than for the binary CoCr alloy. The maximal chromium content (summit of the bulge) is almost the same for all the alloys (except the C15HT75 CoCr alloy which began to be catastrophically oxidized) but this maximal content is reached deeper for the CoTa2 alloy than for the CoTa1 alloy, and for the later deeper than for the C7.5HT75 CoCr alloy.

The chromium profiles have also changed in their inner part since the depth of chromium enrichment has slightly increased. Indeed, if the most external chromium has diffused towards the oxidation front, the chromium atoms situated deeper have logically pursued their inward diffusion, in the direction of the less Cr-enriched internal zones of the bulk. This led to post-oxidation chromium profiles which are partly above the initial ones, as

clearly evidenced in the WDS-EPMA Cr profiles of Figures 8b (shown by an arrow) for example. One can easily imagine that, after its appearance at the beginning of oxidation, the maximal chromium bulge was progressively shifted inwards (Fig. 8, arrow) while its height progressively decreased.

Thermogravimetry runs.

In order to enrich, with mass gain kinetic data, the previous metallographic results issued from the *post-mortem* characterizations done on oxidized samples, two thermogravimetry tests were performed at 1200°C for 50 hours with the samples of CoTa1 and CoTa2 alloys cemented in the C15HT75 conditions. The obtained mass gain curves are given in Figure 10. After a short initial linear part the mass gain became parabolic. Unfortunately this good behaviour allowing a slow oxidation rate, was lost after about 10 hours by the CoTa1 alloy for which the continuous protective Cr_2O_3 scale obviously encountered locally some damage (with as result a part of alloy surface exposed to rapid oxidation). In contrast the CoTa2 alloy remained protected by a chromia layer during the whole oxidation test. The values of the two kinetic constants, the parabolic Kp and the rate of chromia volatilization Kv, were extracted from the masss gain measurements by applying the $\{dm \times dm/dt = Kp - Kv \times m\}$ treatment [9]. This led to $Kp = 78 \times 10^{-12}$ g^2 cm^{-4} s^{-1} and $Kv = 212 \times 10^{-10}$ g cm^{-2} s^{-1} for the C15HT75 CoTa1 alloy (only for the parabolic part of the curve) and $Kp = 66 \times 10^{-12}$ g^2 cm^{-4} s^{-1} and $Kv = 118 \times 10^{-10}$ g cm^{-2} s^{-1} for the C15HT75 CoTa2 alloy (for the whole curve).

4.   Discussion

Chromium cementation and the following diffusion heat-treatment allowed obtaining increased chromium contents on the alloy surface and additional mass of chromium in the sub-surface. This represents a useful reserve in chromium which may allow low-chromium cobalt-based alloys resisting high temperature oxidation. Unfortunately it was probably at the expense of the mechanical properties at high temperature (notably creep-resistance) of the two TaC-containing alloys because of the fragmentation and rarefaction of their script-like eutectic carbides. These classical phenomena, mainly occurred during the diffusion heat-treatment (performed both at high temperature and for a long time), result from the minimization of the interfacial {matrix-carbides} energy and from the tendency of microstructures to converge to the thermodynamically stable equilibrium at the temperature applied during the heat treatment.

Despite of this pre-aging of the TaC carbides, detrimental for their strengthening effect, cementation and heat-treatment surely contribute to a longer life duration by delaying the catastrophic oxidation which surely threaten such low-chromium based-alloys after only few hours at high temperature in oxidizing atmosphere. Indeed, the presence of the chromium reservoir brought by the cementation treatment in the first tens of micrometers from the external surface allowed most of the alloys to resist against oxidation in air at 1200°C for several tens hours, despite that this temperature is especially high for a cobalt-based alloy, as well as for all alloys protected by a continuous chromia layer (alumina is generally preferred for oxidation resistance at very high temperature).

This benefit is rather limited for the cemented Co-10wt.%Cr alloy, since several deep penetrations of oxidation were noticed on the oxidized samples, revealing that it is threaten by an imminent catastrophic oxidation after 50 hours, especially for the C15HT75 CoCr sample. This illustrates firstly that the 7.5h-cementation is to be preferred to the 15h-cementation, and

secondly that this carbide-free alloy is not helped for the outwards diffusion of chromium to efficiently constitute and maintain a protective chromia scale.

In contrast the cementation of the two tantalum-containing alloys allowed them correctly resisting to oxidation by keeping a chromia-forming behavior since, after 50 hours at 1200°C, a protective chromia layer still covers the alloys, in which internal $CrTaO_4$ also appeared in the sub-surface. Such products of selective oxidation and internal oxidation are classical: they were for example earlier found after high temperature oxidation of more complex cobalt-based alloys containing strengthening Ta atoms in solid solution in their matrix or eutectic TaC carbides situated in the interdendritic spaces [17-19]. These oxidation features can be also encountered for chromium-rich nickel-based [20] or iron-based [21] alloys containing tantalum. Nevertheless, in some locations on the surface of an oxidized sample, oxidation penetration was deeper than in general all around of the sample (several µm more): this was the case of the CoTa1 alloy for the two {cementation + heat treatment} conditions and for the C7.5HT75 CoTa2 alloy.

This good behavior of the cemented Ta-containing alloys, significantly better than the cemented CoCr alloy one, is due to the eutectic carbides present in the interdendritic spaces of the CoTa1 and CoTa2 alloys. Indeed, these carbides obviously facilitated the outward diffusion of chromium during oxidation, although they are tantalum carbides and not chromium carbides. Such a favorable role of interdendritic TaC carbides for Cr diffusion towards the oxidation front during high temperature oxidation was earlier several times observed for 30wt.%Cr-containing TaC-reinforced cobalt-based superalloys. The Cr diffusion-helping role of tantalum carbides was here better for the CoTa2 alloy (the richest alloy in TaC carbides in this study) than for the CoTa1 alloy, as revealed by the Cr diffusion depths measured in the oxidized samples, but also by the better behavior of the CoTa2 alloy.

Moreover, the different diffusion depths existing after cementation and heat treatment showed here that a sufficiently dense network of tantalum carbides helps not only the diffusion of chromium towards the oxidation front for improving the resistance against high temperature oxidation, but also they helped sooner the incorporation of chromium deeper in the alloy [5]. Thus, tantalum carbides seem favoring both a rapid stockage of chromium in the sub-surface (long cementation and diffusion heat-treatment are thus not really necessary) and, after, a rapid releasing of this chromium for supplying the oxidation front with efficiency. If chromium carbides would be also able to play the second role, it was seen in the first part of this work [5] that they cannot play the first role because of their dissolution and the consecutive outward carbon diffusion which promotes the appearance of an external carbide layer instead a veritable metallic chromium-rich external zone.

Finally, the cemented alloy which showed the best behavior in oxidation at 1200°C in this study is the CoTa2 alloy, which was the more helped by its carbides network for chromium diffusion. This alloy was better than the others, in terms of: (1) sustainability of the covering role of the chromia scale (mass gain parabolic over the whole duration of the thermogravimetric test), (2) its protective efficiency (lower Kp constant) and (3) its resistance against volatilization by re-oxidation into CrO_3 gas (lower Kv rate).

One can remark that the values of volatilization constants which were determined in this study are consistent with other ones obtained earlier on other chromia-forming tantalum-containing nickel-based and cobalt-based alloys [19,22] or directly on sintered Cr_2O_3 [23,24]. Their determination allowed also obtaining not-minimized values of the parabolic constants, which are also at the same level as what is usually measured for chromia-forming cobalt-based superalloys

To finish one can remind that the possibility to obtain such sub-surface enrichment in chromium and the efficiency of protection against high temperature oxidation allow

diminishing the chromium content in the bulk, with interesting consequences about alloy cost and in some cases about refractoriness (then potentially mechanical properties at high temperature). Concerning the latter point, it is possible to assess the increase in solidus temperature allowed by a decreased chromium content, by performing Thermo-Calc calculations: when the Cr weight content of the binary CoCr (respectively CoTa1 and CoTa2) alloy decreases from 30wt.% to 10wt.%, the solidus temperature increases from 1424°C (resp. 1308°C and 1298°C) up to 1474°C (resp. 1361°C and 1358°C). Thus, the studied alloys are especially refractory and let expecting interesting mechanical properties. In contrast, the sub-surfaces, enriched in chromium, precisely up to about 30wt.% on the extreme surface after cementation and heat treatment, are less refractory but their role is only to resist oxidation.

5.   Conclusions

The sub-surface Cr-enrichments realized by pack-cementation in the first part of this work effectively brought a chromium reserve close to the future oxidation front and then to allow this reserve being rapidly available to deliver chromium to form and maintain a protective chromia scale on the surface of the cobalt-based alloys of this study, although their too low bulk chromium content was not compatible with such necessity of chromia-forming behavior. Thus increased solidus temperatures (+50°C to +60°C here), and then potentially high mechanical resistance at high temperature, can be achieved for the greatest part of the hot piece thickness while several hundreds of micrometers of less refractory but oxidation-resistant external alloy can protect the bulk even at a temperature as high as 1200°C. Chromium sub-surface enrichment achieved by pack cementation, obviously rarely used for cobalt alloys, can thus allow associating two antagonistic properties to present at high temperature: good resistance against oxidation and high refractoriness which is a favorable factor for a good mechanical resistance at high temperature. Concerning the structural hardening brought by tantalum carbides to two of the studied alloys, it was unfortunately seen that the long duration and high temperature of the diffusion heat-treatment had a harmful effect on the strengthening of this alloys since the TaC carbides got fractioned and lost their "script" morphology. Further work, for such alloys, can usefully concern optimization of heat-treatment to achieve both increase in oxidation resistance and maintaining of TaC strengthening effect.

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Table 1 Values of several characteristics of the Cr content profiles after oxidation for 50h at 1200°C (alloys cemented for 7.5h and heat-treated for 75h); average ± standard deviation from two profiles

Alloys		CoCr	CoTa1	CoTa2
Cr content on oxidation front (wt.%)		8.9 ±0.3	10.2 ±0.4	11.1 ±1.3
Maximal Cr content	Value (wt.%)	14.1 ±0.1	13.8 ±0.5	13.9±0.4
	Position (µm)	53 ±11	68 ±14	100 ±12
New depth of Cr enrichment (µm) (reminder of the depth of Cr-enrichment before oxidation)		195 ±2 (154 ±6)	214 ±7 (190 ±6)	259 ±11 (224 ±21)

Table 2 Values of several characteristics of the Cr content profiles after oxidation for 50h at 1200°C (alloys cemented for 15h and heat-treated for 75h); average ± standard deviation from two profiles

Alloys		CoCr	CoTa1	CoTa2
Cr content on oxidation front (wt.%)		2.5	7.9 ±1.3	10.6 ±1.0
Maximal Cr content	Value (wt.%)	11.7	13.9 ±0.1	13.7 ±0.4
	Position (µm)	48.5	80 ±6	94 ±26
New depth of Cr enrichment (µm) (reminder of the depth of Cr-enrichment before oxidation)		118 (156 ±3)	224 ±13 (196 ±2)	241±11 (231±13)
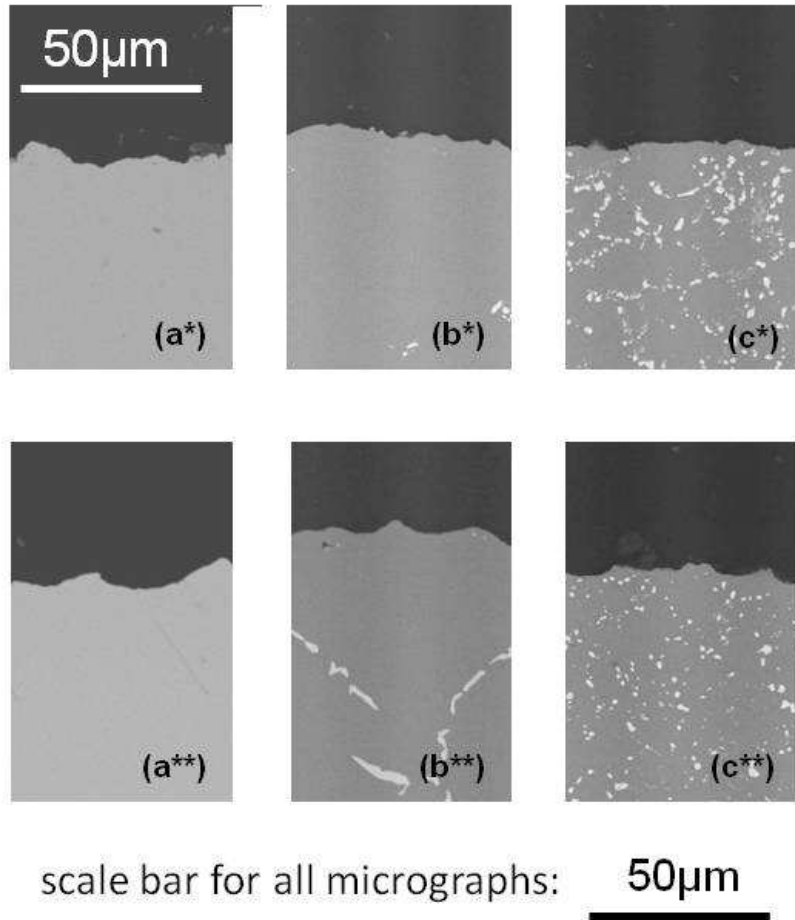
Figure 1 Surface states of the CoCr (a), CoTa1 (b) and CoTa2 (c) alloys after cementation for 7.5h (*) or 15h (**) and diffusion heat-treatment for 75h at 1200°C
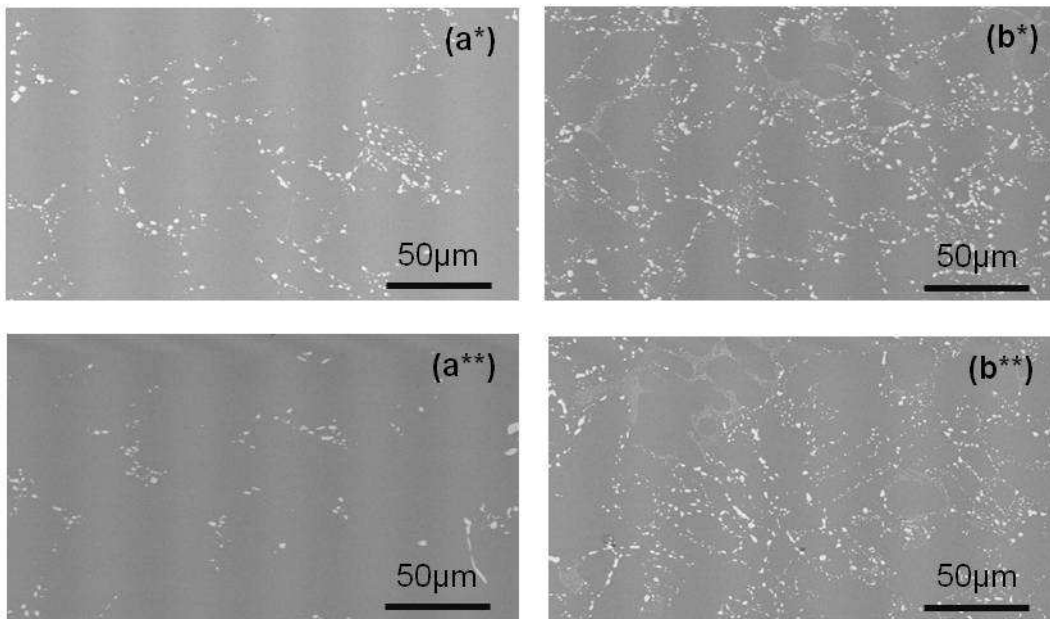

Figure 2 Bulk microstructures of the CoTa1 (a) and CoTa2 (b) alloys after cementation (*: 7.5h and **: 15h) and heat-treatment, before the oxidation tests; fractioned state of the TaC carbides
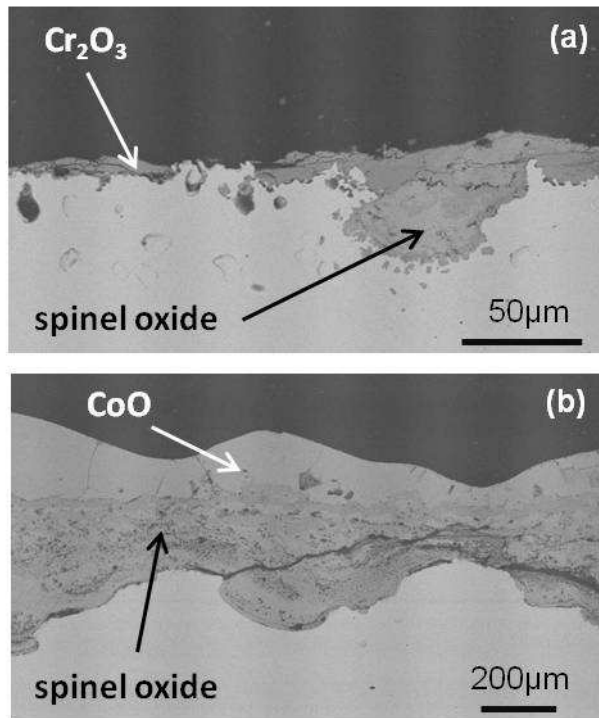
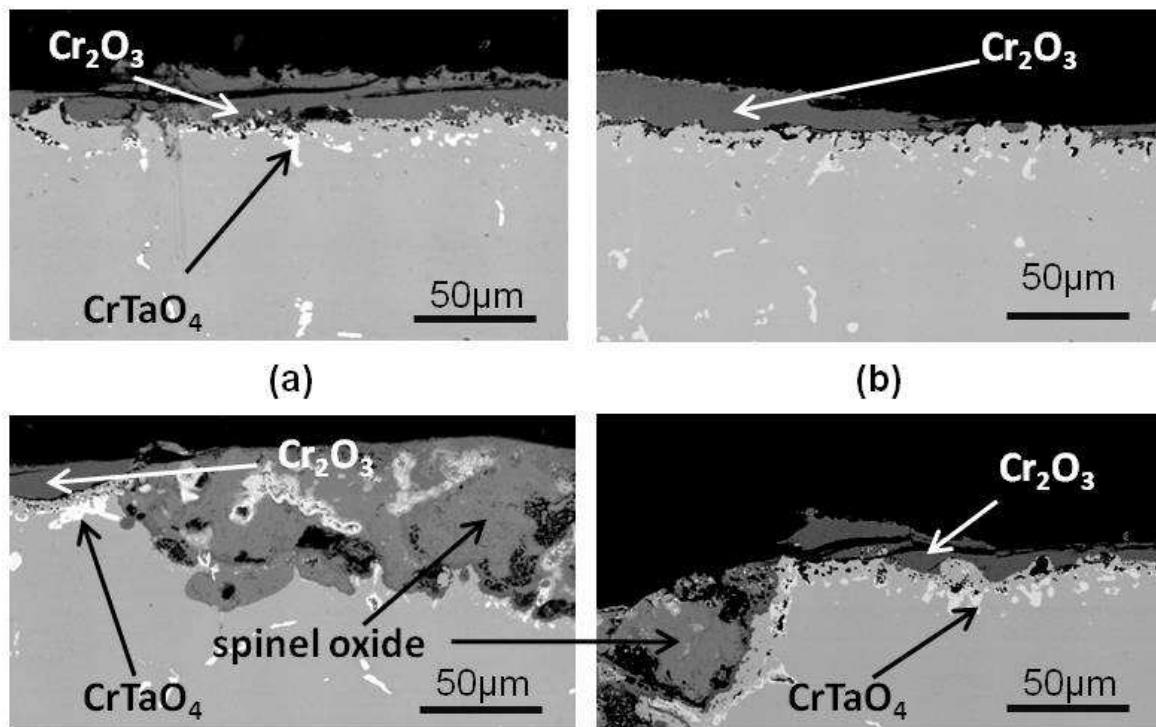Figure 3 Surface states of the C7.5HT75 (a) and C15HT75 (b) CoCr samples after oxidation for 50 hours at 1200°C

Figure 4 Surface states of the C7.5HT75 (a) and C15HT75 (b) CoTa1 samples after oxidation for 50 hours at 1200°C
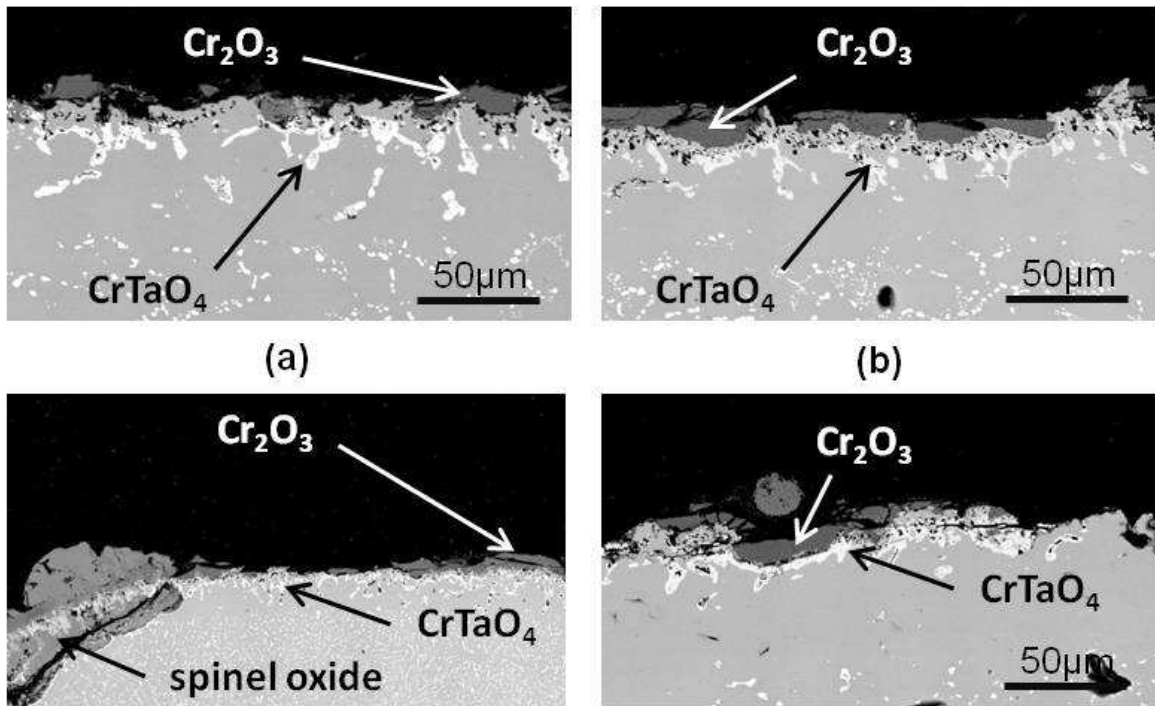
Figure 5 Surface states of the C7.5HT75 (a) and C15HT75 (b) CoTa2 samples after oxidation for 50 hours at 1200°C
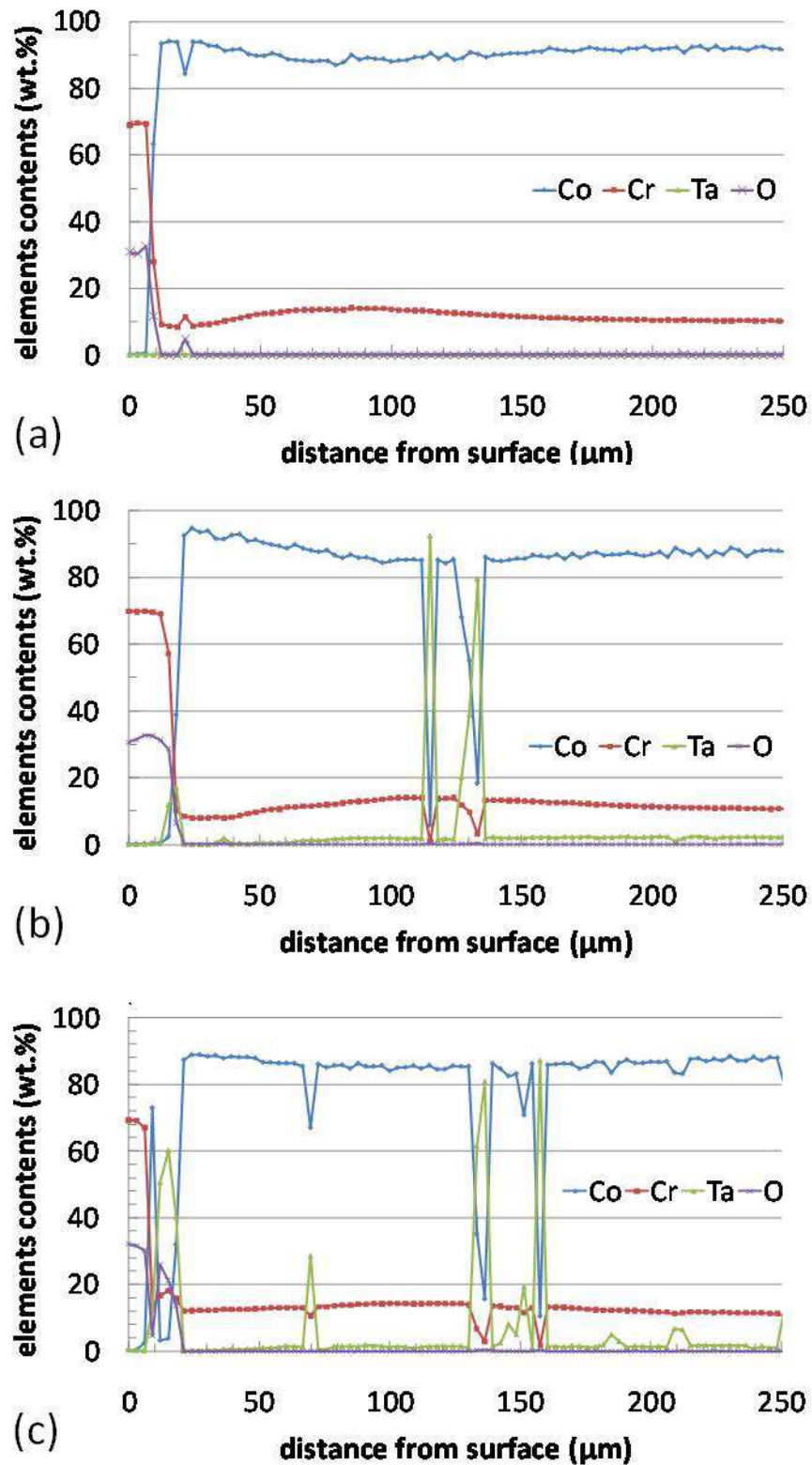
Figure 6 WDS-EPMA profiles from the external oxide scale to the bulk of the alloys oxidized for 50h at 1200°C: (a) CoCr in the C7.5HT75 condition, (b) CoTa1 in the C15HT75 condition, (c) CoTa2 in the C7.5HT75 condition
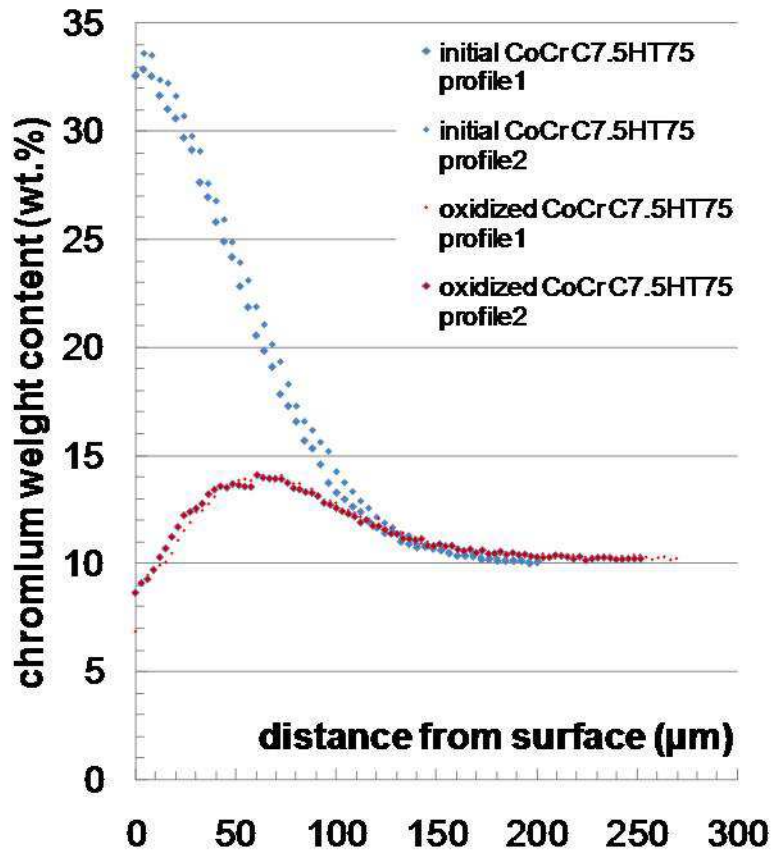
Figure 7 CoCr alloy before and after oxidation (two WDS-EPMA chromium profiles in each case, all superposed)
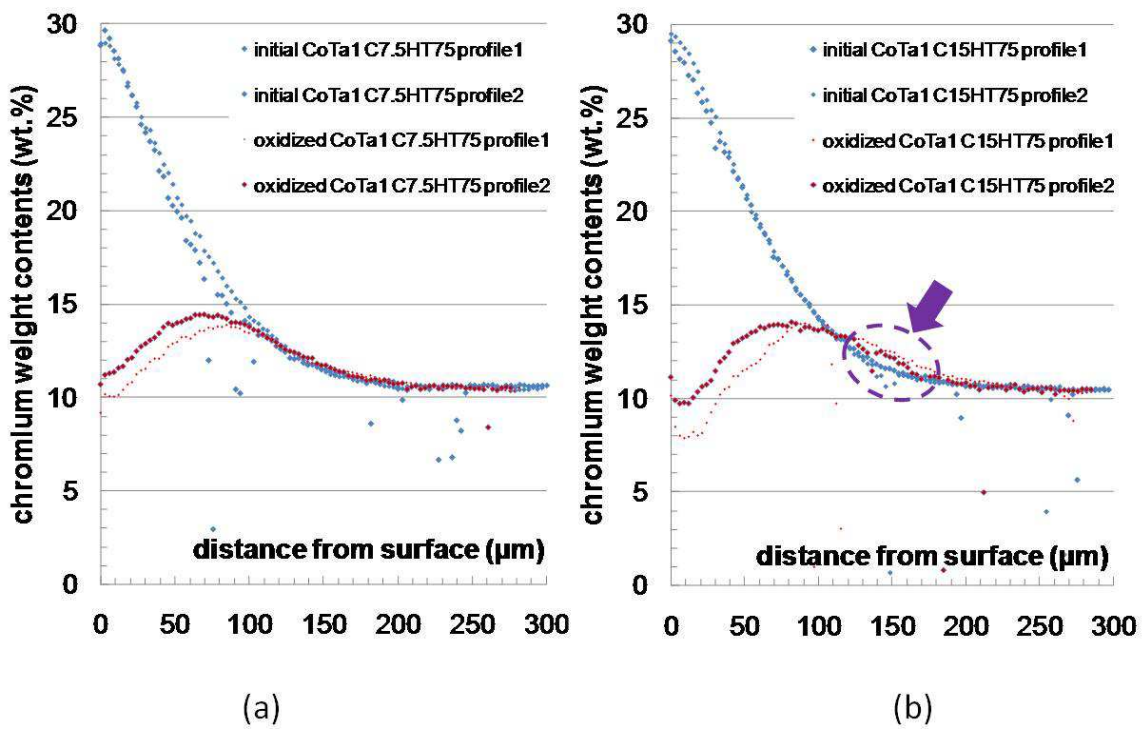

(a)

(b)

Figure 8 C7.5HT75 CoTa1 alloy (a) and C15HT75 CoTa1 alloy (b) before and after oxidation (two WDS-EPMA chromium profiles in each case, all superposed)
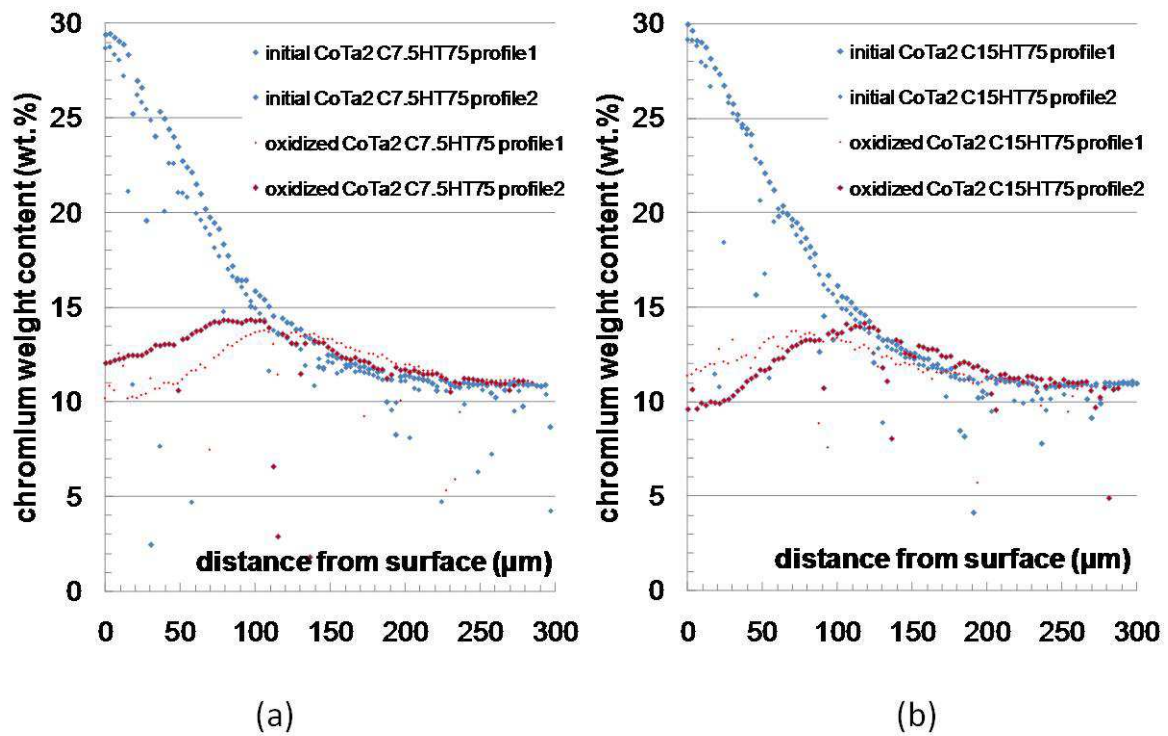
Figure 9 C7.5HT75 CoTa2 alloy (a) and C15HT75 CoTa2 alloy (b) before and after oxidation (two WDS-EPMA chromium profiles in each case, all superposed)
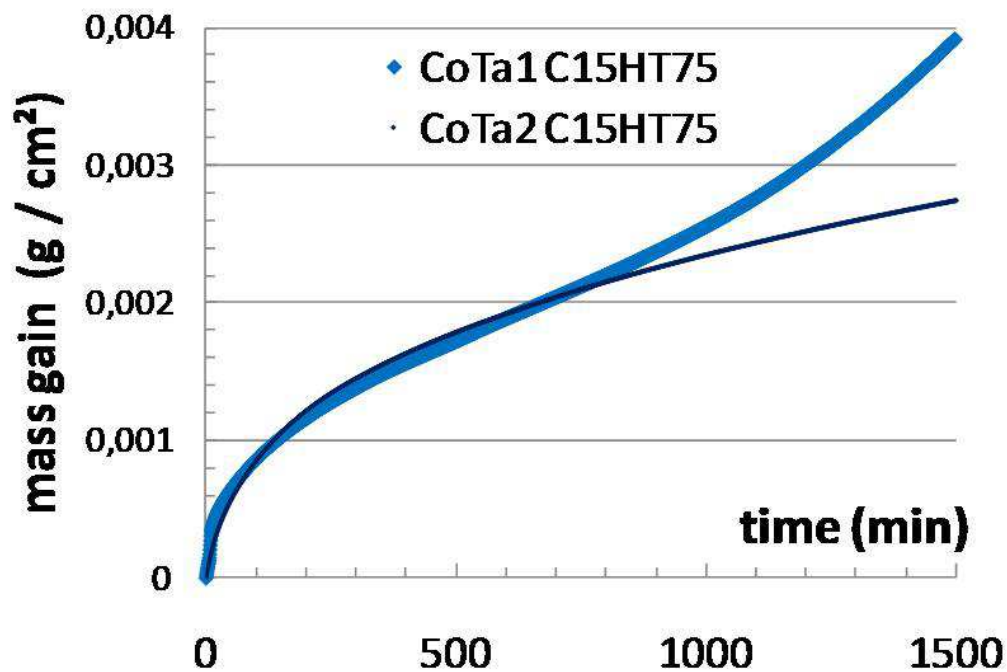

Figure 10 Superposed mass gain curves obtained by thermogravimetric oxidation for the C15HT75 CoTa1 and the C15HT75 CoTa2 alloys