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Some examples of microstructure modifications induced by high temperature oxidation in cast chromium-rich refractory alloys strengthened by carbides

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ABSTRACT

Some of the cast metallic alloys for use at high temperature contain reinforcing carbides to notably resist creep. These may be eutectic carbides appeared during solidification, present in grain boundaries, with various volume fractions depending on the carbon content and with various compositions depending on the natures of the carbides-forming elements present. Such strong carbides-forming elements are generally also easier to oxidize than the base elements of the alloys and they play an important role in the high temperature oxidation of the alloy, often leading to special phenomena in the external oxide formed as well as in the alloy just under the oxide-metal interface. In this work the oxidation behaviour at high temperature of selected alloys and superalloys reinforced by carbides of different types was investigated by notably considering these phenomena. © 2013 Trade Science Inc. - INDIA

INTRODUCTION

The great family of refractory alloys and superalloys for high temperature applications contain, in addition to the γ/γ' nickel-based superalloys or to the Oxide Dispersion Strengthened superalloys for example, the polycristalline chromium-rich cobalt-based, nickelbased or iron-based superalloys strengthened by carbides elaborated by foundry^[1]. Such refractory superalloys coming from this particular family present special characteristics possibly being of importance in case of high temperature oxidation. In this work it is wanted to recapitulate the characteristics of the carbides such as

KEYWORDS

Foundry alloys; High temperature oxidation; Effect of carbides; Sub-surface modifications.

composition possibly leading to microstructure changes in the sub-surface of the alloys, as well as the different curious phenomena affecting the sub-surface of the oxidized alloys varying with the characteristics of the interdendritic carbides.

EXPERIMENTAL DETAILS

The studied alloys are various ones, based on nickel, cobalt and/or iron and containing carbon in more or less high quantity as well as different carbides-forming elements (Cr, Ta,...), the first listed carbide-forming element (Cr) being present with a content of 30wt.% in



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all alloys to allow potentially a good resistance against high temperature oxidation^[2,3]. All the alloys were elaborated under an argon atmosphere, with the melting of pure elements (coming from Alfa Aesar, purity higher than 99.9%) together by high frequency induction melting (about 100 kHz) and the solidification took place in the water-cooled crucible of the furnace (CELES). The ingots (all of about 40g) were cut and polished (final paper: 1200-grit) to obtain samples for the oxidation tests. Some of the exposures to high temperatures were performed in atmospheric air in simple furnaces (followed thereafter by the metallographic characterization of the oxidized samples), or in synthetic 80%N₂-20%O₂ gas mixture in the furnace of a Setaram TGA92 thermobalance (also followed by metallographic characterization of the oxidized samples).

RESULTS AND DISCUSSION

Different oxides formed with chromia

In case of the presence of another carbide-forming element stronger than chromium the solidified alloys may contain other carbides partly or totally replacing the chromium carbides. This occurs for example if the other carbide-forming metal is tantalum, hafnium, niobium or zirconium^[4], for example. This M element may be then also oxidized, this inducing different behaviours. In a TaC-containing alloy exposed to oxidant gases (air for example) at temperatures comprised between 1000 and 1200°C, oxidation induces the formation of a chromia continuous scale, but also of other oxides such as a sub-layer of the mixte oxide CrTaO₄ between the alloy and the external chromia oxide. A zone of disappearing TaC carbides develops inwards and the Ta atoms initially belonging to the disappearing carbides diffuse toward the external surface where they are oxidized in $CrTaO_4$ islands growing in the sub-surface.

In case of the presence of hafnium in the alloy, eutectic HfC carbides very stable, at high temperature^[4], can be obtained. They display a script-like morphology similar to the TaC in other alloys. The oxidation is worse than in the case of tantalum (early loss of the chromia-forming behaviour) and oxidation may rapidly become catastrophic, because of the lack of chromium diffusion due to the presence of interdendritic hafnium carbides not favourable to the diffusion of chromium. The situation is worse for the NbC-containing alloys in which the Nb₂O₅ oxide forms and probably perturbs the chromia growth, this favouring catastrophic oxidation), as well as for the ZrC-containing alloys with which similar degradation of the behaviour can be encountered (Figure 1).



Co-30Cr-10Ni -0.4C-7Ta alloy oxidized 100h at 1200°C

100 µm

Co-29Cr-8Ni

-0.4C-5Nb

alloy oxidized

100h at 1200°C)



Co-30Cr-9Ni -0.4C-3Hf alloy oxidized 100h at 1200°C)



Co-30Cr-9Ni -0.2C-5Zr alloy oxidized 75h at 1200°C}

Figure 1 : Surface states of different MC-reinforced Cobased alloys oxidized at high temperature.

The presence of $CrTaO_4$ films in the external continuous chromia layer covering the oxidizing TaC-containing Co-based, Ni-based, NiFe-based or Fe-based alloys may partly obstruct the volatilization of chromia by re-oxidation of Cr_2O_3 in gaseous CrO_3 , phenomenon existing for more than 1000°C. Indeed one can

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think that these films of tantalum-chromium oxide may act as a protective layer isolating chromia from the hot oxidizing gas. Lower values of the volatilization constant Kv, determined together with the value of the parabolic constant Kp according to the formula { $m \times (dm/dt) = Kp - Kv \times m$ }^[5], may be obtained in presence of TaC. A similar influence was also reported^[6] concerning CoO or (Co,Ni)O oxides mixed with chromia (e.g. for Co-30Cr-xC alloys), as well as for Fe-30Cr-yC alloys for which Fe was partly substituted to Cr in the external M_2O_3 .

Disappearance of the carbides in the sub-surfaces

In situation of oxidation at high temperature, the carbides just under the extreme surface may be directly attacked by oxidation. Internal oxides may then form over a low depth which can become much more important if the interdendritic boundaries are almost perpendicular to the external surface. A little deeper, the oxidation progress has sufficiently lowered the matrix contents in carbon and in metal M belonging to the M_vC_v secondary carbides (precipitated in the matrix during a preliminary heat treatment) and/or to the primary M_vC_v carbides (precipitated at the end of solidification and often forming an eutectic compound with matrix), to destabilize these carbides. The latter dissolve and liberate carbon and metal M atoms and these ones diffuse thereafter toward the oxidation front where they are then oxidized. This leads to the appearance of a carbide-free zone on the most external sub-surface and to its development inward the bulk. The inward extension of this carbide-free zone depends on the temperature of isothermal oxidation: the higher this temperature, the deeper the carbide-free zone (example in Figure 2).

The carbide-free zone depth also depends on the



Figure 2 : Effect of the oxidation temperature on the depth of the carbide-free zone (and of the external oxide thickness).

exposure duration (the longer the duration, the deeper the carbide-free zone), on the initial carbide fraction of the alloy (the higher the carbon content, the less deep the carbide-free zone) as illustrated in Figure 3.

It also depends on the oxidation kinetic (the faster the oxidation rate, the deeper the carbide-free zone until the alloy eventually loses its chromia-forming behaviour), as well as on the alloy family (if oxidation rapidly becomes catastrophic: oxidation of not only Cr but also of Co, Fe,..., i.e. presence of CoO neighbour to Cr_2O_3 , spinel $CoCr_2O_4$,...). In the latter case the oxidation front may penetrate in the alloy and its movement follows more or less the frontier separating the carbide-free zone and the still carbide-containing zone. This phenomenon, metallographically revealed by an irregular alloy/external oxide boundary or by a chromia content surprisingly high on the extreme surface, tends to minimize the depth of the apparent carbide-free zone as illustrated by Figure 4: Co-30Cr-0.8C oxidized during 50h at 1100°C (ir-

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regular alloy/oxide separation and external oxide composed of Cr_2O_3 and of CoO) and Fe-30Cr-0.8C oxidized at 1200°C during 50 hours (irregular alloy/

oxide separation and $(Fe,Cr)_2O_3$ oxide with varying contents in Fe and Cr along the external oxide). Figure 5 also illustrates the catastrophic oxidation



Figure 3 : Effect of the carbon content (carbide fraction) on the depth of the carbide-free zone (and of the external oxide thickness).



Co-30Cr-0.8C 50h 1100°C Fe-30Cr-0.8C 50h 1200°C Figure 4 : Oxidation phenomena concerning the external oxides and the sub-surfaces of a cobalt-based alloy and a ironbased alloy (irregular interface between oxide and alloy).

of a Co-30Cr-0.8C alloy after 50 hours of oxidation at 1200°C: the external oxides are mainly of cobalt (CoO in the most external part of the thick scale and spinel $CoCr_2O_4$: its (main) internal part). The whole bulk has lost the carbon which was initially contained (into CO_x gases): this carbon has diffused outwards and has been oxidized while the chromium released by the carbides dissolution remains in solid solution at the 30wt.% value

on the main part of the whole sample thickness^[6]. Thus, this is not really like a carbide-free zone developed from the external surface to the sample core since the carbide-free zone is usually also a Cr-depleted zone.

Modification of the carbides present in the subsurface

Another curious phenomenon which can occur in the oxidized carbides-containing chromia-forming alloys is the existence, after oxidation at about 1000°C, of an intermediate zone of alloy separating the carbidefree zone and the bulk. Here the carbides seem coarsening^[7] (Figure 6), or displaying a change of stoichiometry (from a low carbon one to a higher carbon one). A third possible phenomenon is the precipitation of new carbides. The carbides dissolving in an outer neighbour band of alloy, previously enriched in carbon by the dissolving carbides near the oxidation front, give their carbon atoms deeper where carbides coarsen by combining the new carbon atoms with the local chromium atoms present in high content in matrix (25-30wt.%, de-

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pending of the carbide population). This sometimes occurs in the sub-surface of some carbides-strengthened alloys but only at 1000°C or even 1100°C, as it can be seen after 50 or 100h of oxidation in air as well as in some more complex oxidizing atmospheres such as combustion gases. At higher temperatures, no such phenomenon can be seen, the carbon released by the dissolving carbides having probably left the alloy in gaseous oxidized species (CO_v).



Figure 5 : Co-30Cr-0.8C after oxidation during 50h at 1200°C (catastrophic oxidation and loss of all carbides, even in the bulk).



Figure 6 : Sub-surface changes for carbides induced by the oxidation at high temperature (here: Ni-30Cr-1.2C oxidized for 50 hours at 1000°C).

General commentaries

The carbides network reinforcing the interdendritic spaces of the cast equiaxed alloys and superalloys designed for high temperature applications requiring high chromium contents to resist not only oxidation by gas but also hot corrosion by molten substances (what alumina scales are not able to do) may thus behave differently in high temperature oxidation for some carbides and for other carbides. If the chromium carbides (which may form in absence of metallic elements stronger in their carbide-forming properties or in presence of more carbon as required for the contents in strong carbideforming elements) are present in the microstructure, they show a beneficial effect by releasing chromium participating to the maintenance of a chromia continuous external layer efficient to protect the alloy against fast oxidation. This is the reason why a carbide-free zone develops from the oxide-alloy interface following an almost parabolic kinetic law. The development of this carbide-free zone may be accompanied by the formation of a curious more internal zone separating it from the bulk in which new carbides precipitate (leading then locally to a higher carbide fraction), eventually with simultaneously a change of stoichiometry for a carbonrichest one. With the resulting local enrichment in carbon, this phenomenon, which occurs at temperatures near 1000°C, may decrease the local refractoriness of the alloy and may potentially lead to a local internal melting in case of an accidental sudden increase in temperature. The other carbides also dissolve progressively from the oxide-alloy interface, their constitutive atoms diffusing thereafter toward the oxidation front to be oxidized: it is the case of the tantalum atoms coming from the TaC carbides but not of the Hf atoms remaining trapped in the too stable HfC carbides. In the first case another oxide, Ta₂O₅ or CrTaO₄, forms: it can be detrimental for the chromia adherence on the substrate (easier spallation in case of thermal cycling) but it may also partly protect chromia from volatilization in case of temperatures higher than 1000°C. The CoO or NiO, or (Fe,Cr)₂O₄ oxides may have a similar role if such elements are present as base elements, but no carbides are indirectly responsible of the protecting effect in their cases.

CONCLUSION

By possibly involving strong carbide-forming ele-

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ments which are also strong oxide-forming elements, the oxidation of cast alloys and superalloys strengthened by interdendritic and/or secondary carbides of various natures may lead to interesting phenomena, additional to the chromia development on surface. Since the rate of carbide-free zone growth is dependent on both the temperature of oxidation and of the oxidation duration, as well as some of other phenomena characteristic of a level of temperature (carbides reprecipitation between the carbide-free zone and the bulk: near 1000°C), the metallographic study of industrial pieces made of such carbide-strengthened alloys may give indication about the local conditions of use, as well as the thickness of oxide scales which are unfortunately often lost during cooling, differently to the internal phenomena concerning the carbides which are still available for observation and characterization.

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