July 2008 Volume 4 Issue 4

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 4(4), 2008 [290-296]

Microstructure and hardness of several chromium-containing Co-based alloys reinforced by MC (TaC, NbC or HfC) carbides in as-cast or heat-treated conditions

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Received: 9th May, 2008 ; Accepted: 14th May, 2008

ABSTRACT

The cast Co-based superalloys are usually reinforced by carbides, notably of the MC type. If TaC are often used in this field, it is not the case of other MC carbides, e.g. NbC and HfC. The purpose of this work is to better know the fractions and shapes of these carbides when obtained by solidification and/or heat treatment in a cobalt-based alloy, with comparison with a similar alloy containing TaC carbides. Three alloys, Co-8Ni-30Cr-0.4C-3.3Nb, or 6.6 Ta/Hf, were cast and submitted to three different heat treatments. The morphologies, surface fractions and distribution of the primary and secondary carbides were examined and quantified. Macro- and micro-indentations were performed for all alloys in the as–cast and treated conditions. The results were analyzed versus the carbides fractions and distributions between grain boundaries and matrix. Primary TaC, NbC and HfC are all script-like eutectic carbides. The highest volume fractions are obtained for the HfC carbides while Nb and Hf, almost non-existent in the as-cast matrix, do not allow a real secondary precipitation of carbides.

KEYWORDS

Cobalt alloys;
TaC;
NbC;
HfC;
Heat treatment;
Hardness.

INTRODUCTION

The MC carbides are usually used in metallic alloys for hardening at room temperature as well as for higher temperatures. In the latter case tantalum carbides are probably the most used in cast superalloys[1] to which they bring high mechanical properties at high temperature, notably in the case of cobalt-based superalloys[2,3]. Since tantalum is a carbide-former element stronger than chromium, its presence easily leads to TaC carbides in Cr-rich cobalt alloys[4,5], and also in Cr-rich Fe or (Fe,Ni) -based alloys[6]. Other MC carbides are candidates for the strengthening of alloys at elevated temperatures. Niobium carbides, which are harder than chromium carbides and which can exist up to high temperatures, are able to increase the hardness and the wear resistance of different materials (steels[7,8], cermets[9]), their mechanical properties at high temperature (e.g. refractory intermetallics[10]) and even the shape memory effect in other alloys[11]. Hafnium carbides are among the most stable at very high temperature and are notably used for the mechanical strengthening of alloys which are especially refractory, for example alloys based on molybdenum, tungsten and/or rhenium[12-14]. This third type of MC carbides may also play a useful role in more conventional alloys, e.g. Ni-based ones[15].

If tantalum carbides are commonly used in cast cobalt-based superalloys, alone or together with chromium carbides, it is rarely the case for the two other MC carbides evocated above. The purpose of this study is to better know, for the as-cast condition or after heat treatment, the microstructures and hardness of two such Co-based alloys designed for high temperature applications. They contain 30 wt.%Cr for resisting high temperature oxidation and corrosion and the same medium content of carbon (0.4 wt.%) for promoting the carbide formation. But these alloys are reinforced by either NbC or HfC carbides. In addition, a more conventional alloy reinforced by TaC carbides was also elaborated and studied, for allowing comparison with the two first alloys.

EXPERIMENTAL

The chemical compositions of the three alloys were chosen in order to get the same atomic contents for, on the one hand carbon, and on the other hand Ta, Nb or Hf. The weight contents of carbon (fixed at 0.4 wt.%), tantalum niobium and hafnium were then calculated by considering the molar weights of these four elements (respectively 12, 181, 93 and 178.5 g Mol^{-1}). The three alloys were induction melted and cast under 300 mbar of pure argon, from pure elements (Co, Ni, Cr and Ta: Alfa Aesar, purity>99.9 wt.%, and C: graphite). Several parts (slightly less than 1 cm^3) were cut in the obtained ingots in order to prepare, for each alloy:

- A sample for the examination of the as–cast microstructure,
- Three sample for applying the heat treatments T1, T2 and T3.

The heat treatments which were applied using a resistive tubular furnace (in air) were:

- **T1**: Heating from room temperature (R.T.), stage at 1,100°C for 15 hours, and air quenching;
- **T2**:Heating from room temperature, stage at 1,200°C for 2 hours, air quenching, second heating from R.T., stage at 1,000°C for 10 hours, and air quenching,
- **T3**: T1 followed by T2.

All samples corresponding to the three alloys (as-cast, treated T1, treated T2 and treated T3), were embedded in a cold resin mixture, polished with paper from 120 or 240 grit up to 1200 grit, ultrasonic cleaned, and finally polished with 1µm-alumina paste to obtain a mirror-like surface state for examinations.

The microstructures of the mounted samples were characterized by using a Scanning Electron Microscope (SEM) in Back Scattering Electrons (BSE) mode for the general examination. BSE micrographs were taken for illustrating the microstructures or for measuring the surface fractions of carbides by image analysis (using the Photoshop CS software of Adobe). The quantification of the whole population of carbides (primary and secondary together) was done on four different micrographs (magnification: ×250), and the quantification of the secondary carbides only was done on four different micrographs (×1000) taken in matrix. In all cases the average value and the standard deviation were calculated and considered.

The global chemical compositions of the alloys were analyzed by using the Energy Dispersion Spectrometry (EDS) device of the SEM. A Cameca SX50 microprobe was used for analyzing carbides by Wavelength Dispersion Spectrometry (WDS) and for performing profiles across the microstructure.

Before hardness measurements, the samples were etched during a sufficient duration (90 seconds for the TaC-alloy and the HfC-alloy, 10 seconds only for the NbC-alloy) with the Murakami etchant (100mL of distilled water, 10g NaOH, 10g $K_3Fe(CN)_6$) for revealing the interdendritic MC carbides. Vickers macro-indentations, using a Testwell-Wolpert apparatus, were performed on the three alloys for the four conditions (as-cast or treated T1, T2 or T3), on the whole alloy with a load of 30kg (four measurements with calculation of the average value and the standard deviation). Vickers micro-indentations, using a Reichert D32 apparatus, were also performed in the matrix of all samples with a load of 32g (four measurements per sample, calculation of the average value and the standard deviation).

RESULTS AND DISCUSSION

The obtained chemical compositions

The average chemical contents of Co, Ni, Cr and

M (Ta, Nb or Hf) in the obtained alloys, resulting from EDS measurements performed with the SEM, are given in TABLE 1. On the contrary, it was not possible to measure the contents of carbon because of its too small atomic weight and its too low targeted content. Fortunately, it was previously verified that this type of elaboration of alloys (with this carbon content) usually respected the targeted values (determination done by spark spectrometry analysis). Thus it was reasonably supposed here that the targeted contents were really obtained, as confirmed by the carbide density which was seen in the as-cast microstructures of the obtained alloys.

TABLE 1: Chemical compositions of the three alloys (EDS, ±1wt.%; carbon content ≅0.4 wt.%; bal. Co)

Alloys	Ni	Cr	Ta	Nb	Hf
TaC -alloy	8	29.5	6.5	-	-
NbC-alloy	8	30	-	3.3	-
HfC-alloy	8	30	-	-	6.6

Microstructures of the alloys as-cast and after the three heat treatments

In the as-cast condition, the TaC-alloy displays a

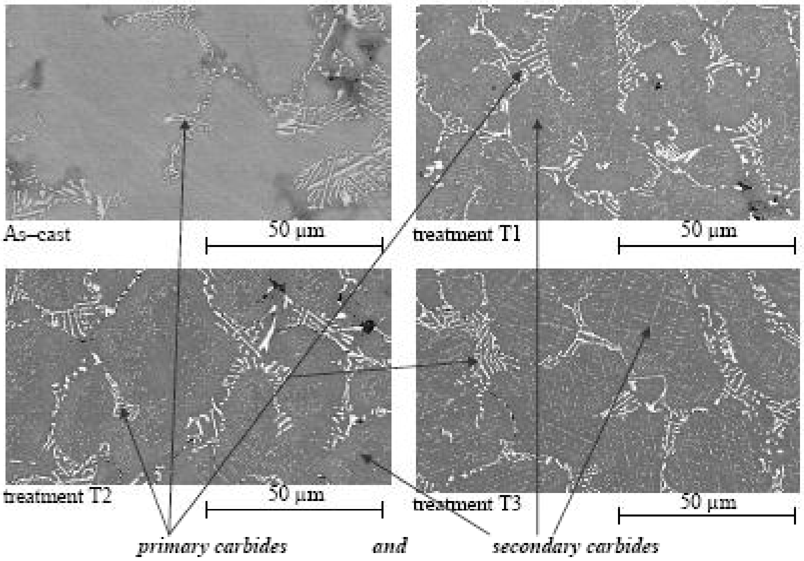


Figure 1: Microstructures of the TaC-alloy, as–cast and after the three heat treatments;(BSE micrographs); primary carbides only (secondary carbides are rare)

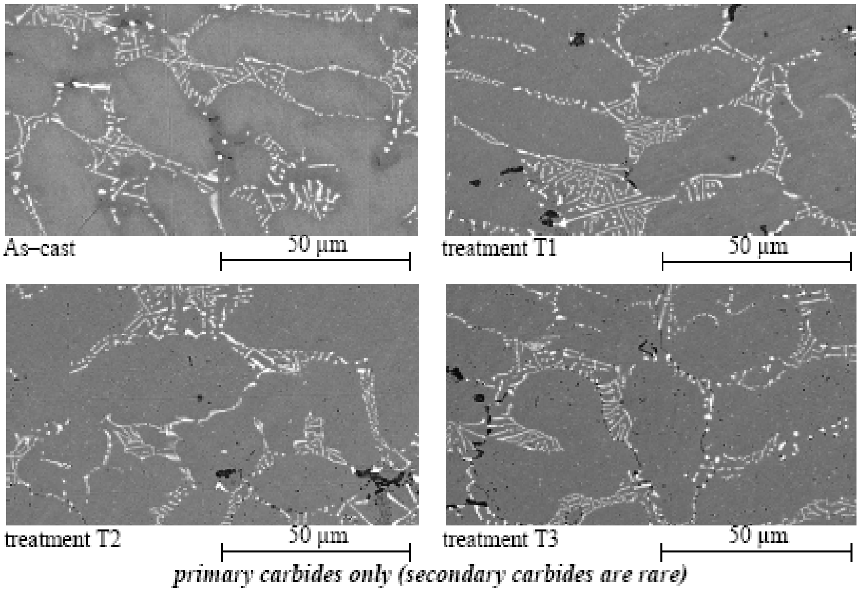
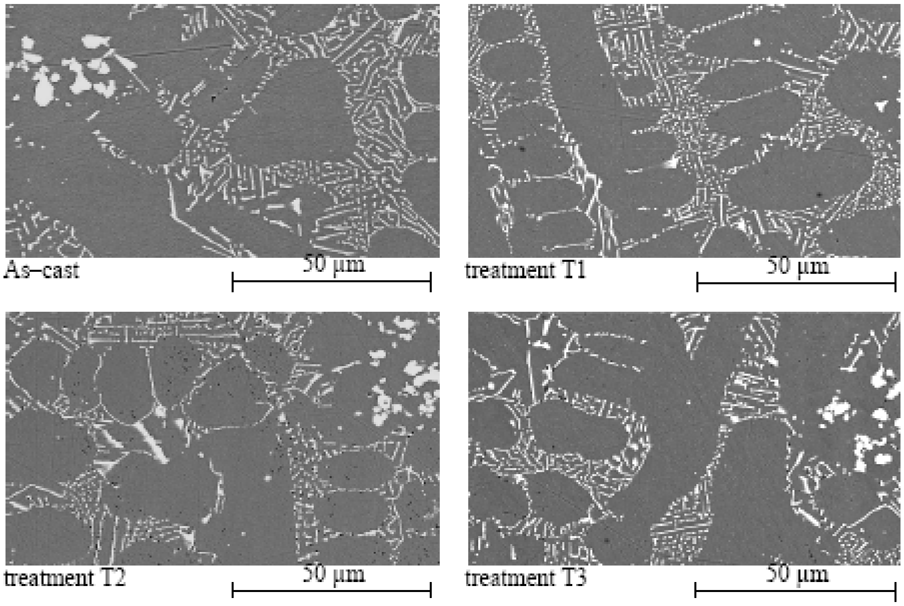


Figure 2: Microstructures of the NbC-alloy, as-cast and after the three heat treatments (BSE micrographs); primary carbides only (secondary carbides are rare)



primary carbides only (secondary carbides are rare)

Figure 3: Microstructures of the HfC-alloy, as-cast and after the three heat treatments (BSE micrographs)

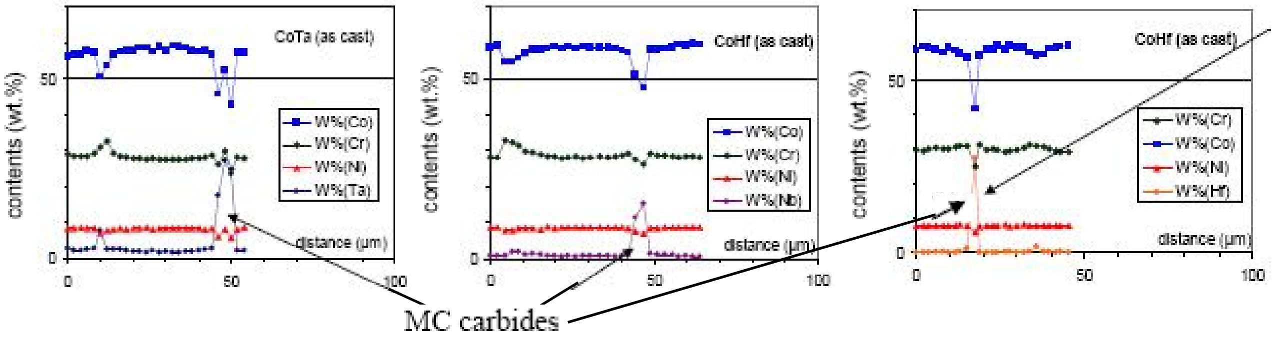


Figure 4: Examples of WDS profiles performed in the bulk of the three alloys in the as-cast condition

gray dendritic FCC matrix and eutectic tantalum carbides in the interdendritic spaces (figure 1). The TaC appear white in BSE mode because of their average atomic mass which is higher than the matrix one. In addition WDS pinpoint measurements performed on these carbides revealed very high concentrations of Ta. Some rare other carbides (probably chromium carbides), with a color which is darker than the matrix one, are also present but they were too small to be analyzed.

After heat treatment, the primary carbides are not modified but secondary carbides have precipitated in the matrix, with obviously three types of distribution. After the T1 treatment, the secondary carbides are more homogeneously spread in the matrix than after the T2 treatment. The T3 treatment led to a homogeneous distribution of carbides, but with a more elongated shape and with special orientations which are probably in relation with the crystallographic directions of the matrix. The same type of as-cast microstructure is visible in the NbC-alloy (figure 2), with also a dendritic matrix and white carbides (NbC) forming a eutectic compound with matrix in the interdendritic spaces. Contrary to the TaC-alloy, the heat treatments did not lead to the precipitation of numerous secondary carbides.

The HfC-alloy also contains a dendritic matrix and interdendritic eutectic carbides (figure 3), with some rare white blocky particles. Like for the NbC-alloy, the three heat treatments did not induce any changes for the primary carbides and did not promote the appearance of a lot of secondary carbides.

WDS profiles were performed across the microstructure of the three as-cast alloys (figure 4). The chromium is homogeneously present in the matrix (about 30 wt.%) while peaks of high M contents (M=Ta, Nb or

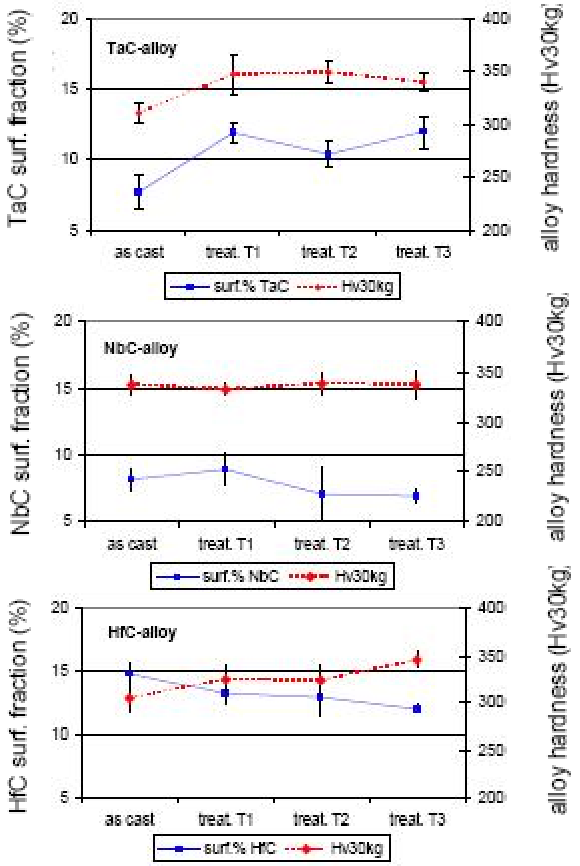


Figure 5: Carbide surface fraction and Vickers hardness versus the metallurgical state for each of the three alloys

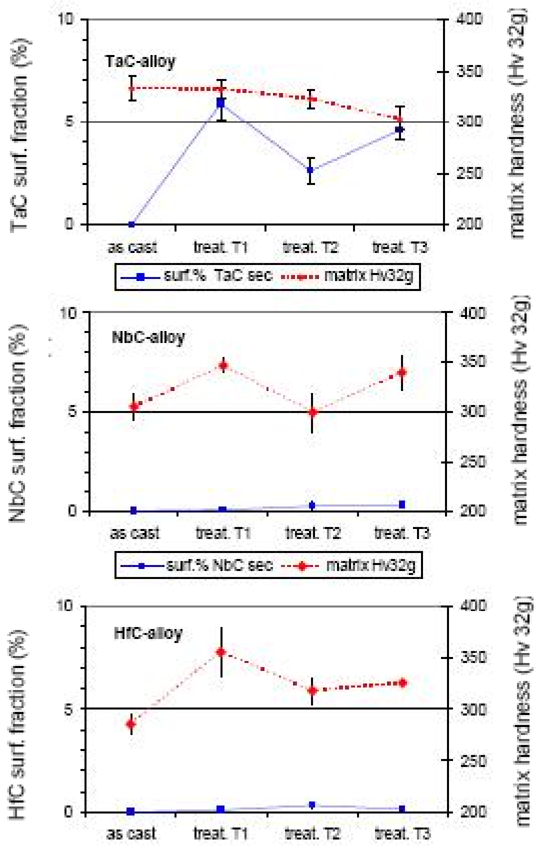


Figure 6: Surface fraction of secondary carbides in matrix and Vickers micro-hardness of the matrix versus the metallurgical state, for each of the three alloys

Hf) revealed the MC carbides. There are some differences about the M contents in the matrixes: if a significant part of Ta is still present in solid solution (typically 1.9 wt.%Ta), niobium is less present in the matrix of the NbC-alloy (typically 0.8 wt.%Nb), and hafnium is almost totally absent in the matrix of the HfC-alloy (less than 0.2 wt.%Hf).

Hardness and micro-hardness results in relation with the surface carbide fractions

Macro-indentation performed with a load of 30kg led to hardness values which can vary significantly with the metallurgical state of the alloy. It is particularly true for the TaC-alloy, the hardness of which increases when a heat treatment was applied (from about 310 up to about 350 Hv_{30kg}). It was attempted to correlate the hardness evolution with the whole surface carbide fraction measured by image analysis (figure 5). It appears that the hardness and the TaC surface fraction increase together between the as-cast condition and the three heat–treated states, an increase which is due to the precipitation of secondary carbides (about 3 to 5 surface percent in matrix). These macro-hardness values were completed by micro-hardness measurements in matrix (figure 6), plotted together with the surface fractions of secondary carbides in matrix. The hardness of matrix obviously stays at the same level when the as-cast, T1 and T2 metallurgical states are considered. In contrast it seems decreasing when the TaC-alloy was subjected to the heat treatment T3, which can be responsible of the slight decrease in macro-hardness seen between the T1 (or T2) treatment and the T3 treatment.

The macro-hardness of the NbC-alloy is higher than the TaC-alloy one in the as-cast condition (about 340 Hv_{30kg}) but the heat treatments did not induce a supplementary hardening (figure 5). Indeed, the obtained secondary carbides are rarer than in the case of the TaC-alloy after heat treatment (less than 0.5 surface percent of white NbC carbides). The hardness of matrix varies but without relation with the surface fraction of the precipitated carbides (figure 6).

The hardness of the HfC-alloy is increased by applying a heat treatment (figure 5), especially in the case of the T3 treatment which induces an increase in hardness from about 300-310 up to 340-350 Hv_{30kg}, i.e. like for the TaC-alloy between the as-cast condition and one of the three heat treatments. Contrary to what it was seen for the TaC-alloy, this is more related to a decrease in carbide fraction than to an increase. The hardness of the matrix (figure 6) also increases when a heat treatment is applied to the HfC-alloy, especially in the case of the T1 treatment, but there is seemingly no real relation with the surface fraction of secondary carbides (it is true that the latter is always very low).

General commentaries

Just after their elaboration by foundry, and for the same types of chemical composition (i.e. Co-8 wt.%Ni-30 wt.%Cr-0.4wt.%C-M with the same molar content as carbon) and of casting procedure, the three alloys qualitatively display the same type of microstructure: average grain size, dendritic FCC matrix, script-like carbides forming a eutectic compound with matrix, … Nevertheless, they are several differences between the as-cast microstructures and as–cast hardness of these three MC-containing alloys. Firstly, the volume fraction of carbides is obviously higher for the HfC-alloy than for the two others: with about 15 surf.% of HfC, the surface fraction of the as-cast HfC-alloy is twice the one of the NbC-alloy and the TaC-alloy (about 8 surf.%). Secondly the hardness of the NbC-alloy is seemingly higher than the hardness of the two other alloys, and thus the hardness cannot be easily correlated with the carbide fraction. Thirdly, among the three alloys, the TaC-alloy is the sole one displaying the presence of M element in solid solution with a significant content (about 2 wt.% Ta in matrix, to compare to less than 1 wt.% Nb and almost no Hf in the matrixes of the NbC-alloy and the HfC-alloy). This is probably the reason of the very limited precipitation of secondary carbides in the two latter alloys, even if several different heat treatments were tested in this study.

With the presence of a significant quantity of Ta atoms (and probably C atoms too) in solid solution in matrix, the TaC-alloy can be usefully subjected to heat treatments, the parameters of which can be chosen in order to achieve different densities and types of distribution of secondary carbides. This allows obtaining different levels of properties for the alloy, notably mechanical properties, as seen here with the hardness. Even if the hardness of the matrix seems to be lowered by the precipitation of secondary carbides (less tantalum in matrix then a lower hardening by big atoms in solid solution), the increase in carbide fraction due to the secondary precipitation induces a hardness enhancement for the alloy.

CONCLUSIONS

The TaC carbides, which are usually used in addition to chromium carbides for the strengthening at high temperature of cast cobalt-based alloys, can be obtained as script-like eutectic carbides (efficient to maintain the cohesion between neighbor grains or dendrites) and also as more or less numerous secondary carbides dispersed more or less homogeneously in matrix in which they obstruct dislocations movement and then limit creep deformation. The increase in volume fraction of TaC carbides noted after heat treatment revealed a hardening useful for mechanical properties, but maybe also that the machining of industrial parts made from this alloy should be easier before heat treatment than after. If niobium and hafnium are also able to promote the formation of script-like eutectic carbides in a cobalt-based alloy, with similar (for NbC), or even significantly more developed interdendritic carbide network (for HfC), than for tantalum, the matrix of the alloy is probably less reinforced by Nb and Hf atoms in solid solution and by secondary NbC and HfC carbides. If several more or less significant differences were found here concerning the room temperature hardness of alloy or matrix, it is probable that greater differences of mechanical properties (strength, creep deformation, ductility, …) would appear at high temperatures (1,000^{0}C and higher), between these as-cast or heat-treated TaC, NbC and HfC-containing Co-based alloys.

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