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Influence of the chromium content on the as-cast microstructures of ternary alloys very rich in carbon part I: Cobalt-based alloys with 3, 4 or 5 wt.%C

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ABSTRACT

Three ternary alloys based on cobalt and containing chromium (12, 15.5 and 23wt.% Cr) and very high amounts of carbon (3, 4 and 5wt.% C) were first subjects of preliminary thermodynamic calculations, and second they were really elaborated by foundry under inert atmosphere. The obtained ingots were metallographically prepared then characterized by electron microscopy, X-ray diffraction and surface fractions measurements. The calculations and metallographic results were compared to the ones previously obtained for ternary cobalt alloys with the same carbon contents but all containing 30wt.%Cr. In some case the position of the new alloys with regard to the eutectic composition is modified consecutively to the change in chromium content. Their microstructures showed especially high quantities of lamellar graphite, obviously formed during solidification, together with the expected high fractions of carbides. As the presence of such graphite was not in conform with the first calculated results, new calculations were performed after having forbidden the appearance of cementite. The new calculated results were much closer to the microstructures experimentally obtained. Furthermore there was a rather good agreement between the predicted mass fractions of carbides and graphite and the ones deduced from the measured surface fractions of these phases in the real alloys.

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INTRODUCTION

Cobalt-based alloys rich in chromium may be met in prosthetic dentistry^[1] (for example as the metallic frameworks bringing the required mechanical resistance to fixed partial dentures), in aeronautics and power

KEYWORDS

Cobalt alloys; High chromium; Very high carbon; Thermodynamic calculations: Carbides; Graphite.

generation^[2,3] (notably for the turbine's blades and disks) as well as in the glass industry^[4] (e.g. the metallic tools used for fiberizing molten glass for insulation purpose). The presence of high quantities of simultaneously carbide-forming elements and carbon may lead to the development of many carbides able to increase the

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mechanical strength and the hardness of the alloys, properties which are very useful for other practical application of cobalt alloys, as cutting tools^[5] consisting in a cobalt matrix reinforced by high amounts of dispersed WC carbides, and as Co-W₂C coatings^[6] deposited on steels by thermal spray. Such carbides may also be obtained by using chromium as carbideforming element and then high values of hardness can also be achieved thanks to the high hardness of the different types of chromium carbides (much more than 1000 Hv)^[7] which may develop at solidification for example. However, when the $\{Cr/C\}$ ratio is too low, a new phase may appear: graphite. This phase, which is detrimental for notably the tensile strength of the alloys, can be in contrast of a good help for their thermal diffusivity. Graphite was already encountered in a Co-30Cr-5C alloy for example, one of the {Cr, C}-rich cobalt alloys studied in a previous work^[8], and the purpose of this paper is to explore new compositions favourable for graphite in Co(Cr)-based alloys, not richer in carbon but with chromium contents lower than the one previously tried (30wt.%): Co-12Cr-3.0C ("Co30 with 12wt.%Cr"), Co-15.5Cr-4.0C ("Co40 with 15.5wt.%Cr") and Co-23Cr-5.0C ("Co50 with 23wt.%Cr").

EXPERIMENTAL

Initial thermodynamic calculations

Before the real elaboration of the alloys, thermodynamic calculations were performed to predict the microstructures which may appear, as is to say the natures and quantities of the solid phases (carbides, graphite and eventual intermetallic phases). For this purpose the Thermo-Calc software (Nversion)^[9], working with a database containing the descriptions of the ternary system Co-Cr-C and its sub-systems^[10-15], was used for determining the theoretic stable microstructures for the temperatures 1500°C, 1400°C, 1300°C, ..., 200°C, 100°C and 0°C. The lowest ones, typically bellow 500°C, are not of course of a good representativeness of reality): this is the reason why the right side of the graphs of phase's evolution versus temperature will be thereafter shaded in blue.

Elaboration and metallographic characterization of the alloys

The three alloys were elaborated by foundry under inert atmosphere. The initial charges were composed of pure elements (cobalt and chromium: Alfa Aesar, purity higher than 99.9 wt.%; carbon: graphite). They were melted and solidified in the water–cooled copper crucible of a CELES high frequency induction furnace in pure argon (300mbars). The obtained ingots, which were of about forty grams, were thereafter cut, embedded in a cold resin mixture (manufacturer ESCIL) and polished with SiC papers from 240 to 1200 grit, with final polishing done using a textile disk enriched in 1µm alumina particles.

The metallographic observations were done using Scanning Electron Microscopy (SEM: Philips, model XL30), in the Back Scattered Electrons mode (BSE, 20kV). Several micrographs were taken at different magnifications between $\times 250$ and $\times 1000$. These ones were exploited to illustrate the microstructures and to measure the surface fractions of carbides and of graphite by image analysis (software Adobe Photoshop CS). X-Ray Diffraction runs were additionally performed to specify the natures of the carbides, using a Philips X'Pert Pro diffractometer (wavelength Cu K α : 1.5406 Ansgtröms).

RESULTS AND DISCUSSION

Thermodynamic calculations

Co-12Cr-3C (with comparison to Co-30Cr-3C of a previous work⁸)

This first alloy (Figure 1, bottom) should begin its solidification between 1300 and 1200°C by the crystallization of both the Face Centred Cubic matrix (about 93Co-6Cr-1C in wt.%) and cementite (M_3C with about 72Co-22Cr and 6.5C in wt.%). These two phases, which are present in similar quantities (about 60%-55% for austenite and 40-45% for cementite), cool together bellow 700°C until cementite disappears for the benefit of a new part of austenite (which rises to about 85% in mass) and of M_3C_2 (about 14% in mass). At the same time a small mass fraction of graphite may also appear (a little more than 1.1% in mass). A new major change may occur between 500 and 400°C: the

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Figure 1 : The stable metallurgical states, versus temperature, of the two "Co30" alloys: the previously studied one⁸ with 30wt.%Cr (top) and the new one with 12wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

allotropic transformation of austenite (almost pure Co) into the cobalt Hexagonal Compact Phase.

The main differences with the microstructure evolution of the Co-30Cr-3C alloy are the absence of M_7C_3 carbides at high temperature (for 12 wt.%Cr only cementite exists as carbide) and the presence of only the chromium-poor M_3C_2 carbides at low temperature against mainly M_7C_3 and very small fractions of $M_{23}C_6$ and M_3C_2 when the chromium content in alloy was 30wt.%.

Co-15.5Cr-4C (with comparison to Co-30Cr-4C of a previous work⁸)

This first alloy (Figure 2, bottom) behaves similarly to the Co-12Cr-3C alloy above, with a solidification also beginning between 1300 and 1200°C by the crystallization of austenite (about 92Co-7Cr-1C in wt.%) and cementite (M_3C with about 71Co-23Cr and 6.6C in wt.%). These two phases also co-exist between 1200 and 700°C in similar quantities but with an order inversed by comparison to the previous case (about 45-40% of austenite and 55-60% of cementite). Here too cementite ought disappear between 700 and 600°C while the part of austenite increases up to about 80% in mass and M_3C_2 appears (about 18% in mass). A small mass fraction of graphite should simultaneously appear (a little more than 1.6% in mass). The austenite, now almost of pure cobalt, is replaced by the cobalt Hexagonal Compact Phase between 500 and 400°C.

The main differences with the microstructure evolution of the Co-30Cr-4C alloy are the absence of the M_7C_3 carbides at high temperature (for 15.5



Figure 2 : The stable metallurgical states, versus temperature, of the two "Co40" alloys: the previously studied one⁸ with 30wt.%Cr (top) and the new one with 15.5wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress



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wt.%Cr the single existing carbide is here too cementite) and the presence of only the chromium-poor M_3C_2 carbides at low temperature against both M_7C_3 and M_3C_2 for 30wt.% Cr.

Co-23Cr-5C (with comparison to Co-30Cr-5C of a previous work⁸)

The behaviour of the first alloy (Figure 3, bottom) is similar to the Co-12Cr-3C and Co-15.5Cr-4C alloys above, with the solidification between 1300 and 1200°C to form austenite (about 91Co-8.5Cr-0.8C in wt.%) and cementite (M_3C with about 65Co-28Cr and 6.6C in wt.%), and the cooling of these two phases which are not now in similar quantities (about 75% of cementite against only 25% of austenite, in mass percents). The mass fractions of Cr₃C₂ and graphite appearing at the cementite' disappearance, are 26.5% and 1.5% respectively.



Figure 3 : The stable metallurgical states, versus temperature, of the two "Co50" alloys: the previously studied one⁸ with 30wt.%Cr (top) and the new one with 23wt.%Cr (bottom), as calculated by Thermo-Calc; qualitative illustration of the microstructures development during the solidification progress

The main differences with the microstructure evolution of the Co-30Cr-5C alloy are here too the absence of the M_7C_3 carbides at high temperature since only cementite is present as carbide for this 23wt.%Cr – containing alloy. In contrast, at low and room temperatures, the microstructures are qualitatively similar for the two 5wt.%Cr alloys: HCP matrix, Cr_3C_2 and graphite. These are less Cr_3C_2 (27% against 34% in mass) but more graphite (1.5% against 0.4% in mass) in the 23wt.%Cr-containing alloy than in the 30wt.%-containing one.

Microstructures of the real alloys

Co-12Cr-3C (with comparison to Co-30Cr-3C of a previous work⁸)

Whereas the "Co30" (with 30wt.%Cr) was graphite-free (Figure 4 top), the decrease of the chromium content down to 12wt.%Cr obviously promotes the appearance of a great quantity of graphite (Figure 4 bottom), with a "rosette" shape. This shape suggests that these graphite lamellae precipitated at solidification and not by solid state transformation as predicted by calculations. However there is a common point between the two alloys: they are both of a hypoeutectic type, since they both contain dendrites of matrix.

Co-15.5Cr-4C (with comparison to Co-30Cr-4C of a previous work⁸)

For the alloys containing 4wt.% of carbon (Figure 5), the impoverishment in chromium induces not only the appearance of a high quantity of lamellar graphite but also a change of microstructure type, from a hypereutectic one (top) to a hypo-eutectic one (bottom). Indeed, if the Co-30Cr-4C alloy contained primary coarse acicular carbides in addition to the {matrix + carbide} eutectic compound, the alloy with chromium lowered to 15.5wt.%Cr presents dendrites of matrix, formed at the beginning of solidification, probably together with the particles of lamellar graphite, the rosette shape of which clearly shows that they also precipitated during solidification.

Co-23Cr-5C (with comparison to Co-30Cr-5C of a previous work⁸)

The microstructures of the 5wt.%C-containing alloys are qualitatively similar (Figure 6). Indeed, the hypereutectic character of the initial alloy (with

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Figure 4 : Microstructures of the alloys Co30-30Cr (top)⁸ and Co30-12Cr (bottom) in their as-cast conditions (two magnifications; left x250, right: x1000); SEM/BSE micrographs



eutectic carbides

Figure 5 : Microstructures of the alloys Co40-30Cr (top)⁸ and Co40-15.5Cr (bottom) in their as-cast conditions (two magnifications; left x250, right: x1000); SEM/BSE micrographs





Figure 6 : Microstructures of the alloys Co50-30Cr (top)⁸ and Co50-23Cr (bottom) in their as-cast conditions (two magnifications; left x250, right: x1000); SEM/BSE micrographs







Figure 8 : XRD spectra obtained on the as-cast alloys Co40-30Cr (top)⁸ and Co40-15.5Cr (bottom)



Figure 9 : XRD spectra obtained on the as-cast alloys Co50-30Cr (top)⁸ and Co50-23Cr (bottom)

30wt.%Cr) is kept for the new alloy since they both contain coarse pro-eutectic carbides, the {matrix + carbide} eutectic compound and graphite particles. If this chromium content lowered to 23wt.% did not change the microstructure type, the content decrease for the stronger carbide-former element present in the alloy induced a significant increase in graphite quantity. This one is obviously lamellar but less with a "rosette" shape than in the Cr-lowered Co30 and Co40 alloys.



Since graphite is here more mixed with the {matrix + carbide} eutectic compound, it probably precipitated during solidification simultaneously with the {matrix + carbide} eutectic, maybe as a {matrix + graphite} eutectic in competition with the latter one.

Results of X-Ray Diffraction

To better know the natures of the carbides, experiments of X-Ray diffraction were done. This led to the spectra presented in Figure 7, Figure 8 and Figure 9 for the "old" (30wt.%Cr) and new (lowered Cr content) "Co30", "Co40" and "Co50" alloys respectively. Similarly to the three 30wt.%Cr-containing alloys these spectra show that the as-cast microstructures of the Cr-impoverished alloys are more complex than expected since:

- two types of matrix are simultaneously present: the FCC (Face Centred Cubic) type (austenite) and the Hexagonal Compact Phase type (HCP),
- two types of chromium carbides also co-exist: Cr₇C₃ and Cr₃C₂,
- and other peaks of diffraction, which were not really identified, also appear (maybe cementite).

General commentaries

The as-cast microstructures which were obtained for these three new alloys are significantly different by comparison with their 30wt.%Cr-containing initial versions, notably because of the presence of significant amounts of graphite. The presence of graphite, and of more graphite than the 30wt.%-containing Co50 alloy, was effectively predicted by thermodynamic calculations but its appearance was expected during the cooling in the solid state. The graphite particles observed in the real microstructures obviously appeared during solidification. Furthermore, if the presence of both M₂C₃ and M₃C₂ carbides were predicted in the 30wt.%Crcontaining Co30 and Co40 alloys (and also in the 30wt.%Cr-Co50 since this carbide was predicted above 600°C but probably transformed only partly in $M_{3}C_{2}$ during the cooling at low temperature, as the FCC matrix in the HCP one), the presence of M_7C_3 was detected by X-Ray Diffraction not only in the three 30wt.%Cr-containing alloys but also in the Co30, Co40 and Co50 alloys with lower Cr contents although only $M_{3}C_{2}$ were predicted over the whole temperature range



Figure 10 : New thermodynamic calculations performed with the condition of "suspended cementite"

of interest here. This shows that the thermodynamic calculations were not representative of the reality, not only quantitatively as previously encountered for the very high carbon alloys^[8] but also qualitatively. Since one can remark that the M_7C_3 carbides did not appear at any moment according to Thermo-Calc and that this was possibly due to the appearance of cementite, it was decided to perform new calculations after having added conditions to forbid the cementite appearance (cementite declared as "suspended phase").



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The new calculated results are presented in Figure 10. One can see that, with this condition applied to cementite, graphite appears during solidification (and is stable at all the lower temperatures) and the $M_{\gamma}C_{3}$ carbides also exist, at high temperature. But they may also partly exist at room temperature if the cooling was fast enough to limit their transformation in the low temperature M_3C_2 carbides. Thus, for not too high cooling rate one can effectively obtain the complex microstructures as metallographically observed (solidification-type graphite in "rosettes" or at least with a lamellar shape) and as characterized by X-Ray Diffraction (matrix FCC partly transformed in HCP and M_2C_3 partly transformed in M_3C_2). In addition it is possible that small quantities of cementite also really precipitated since some peaks of the XRD spectra obtained in the Cr-impoverished alloys as well as in the 30wt.%Cr-containing ones, remain not identified.

Furthermore, after having deduced the mass fractions from the surface fractions (assumed close to the volume fractions) of graphite and carbides measured by image analysis, using the same values of graphite and carbides densities as in the previous study about high carbon Co-30Cr-xC alloys^[8], it appears that a rather good agreement between thermodynamic calculations and characterization of real microstructures is also found about the phase quantities:

Co30 with 12wt.%Cr

1.5 (high temperature) to 1.2 (low temperature) calculated mass fractions of graphite to compare to 2.4 mass.% of graphite in real alloy,

17.5 (high temperature) to 13.9 (low temperature) calculated mass fractions of carbide to compare to 22.2 mass.% of carbide in real alloy,

Co40 with 15.5wt.%Cr

2.1 (high temperature) to 1.6 (low temperature) calculated mass fractions of graphite to compare to 1.9 mass.% of graphite in real alloy,

22.5 (high temperature) to 17.9 (low temperature) calculated mass fractions of carbide to compare to 27.9 mass.% of carbide in real alloy,

Co50 with 23wt.%Cr

2.0 (high temperature) to 1.5 (low temperature) cal-

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culated mass fractions of graphite to compare to 1.7 mass.% of graphite in real alloy,

34.2 (high temperature) to 26.5 (low temperature) calculated mass fractions of carbide to compare to 47.6 mass.% of carbide in real alloy.

CONCLUSIONS

The reduction of chromium content in the Co-30Cr-3.0C, Co-30Cr-4.0C and Co-30Cr-5.0C induces the appearance of lamellar graphite issued from solidification, with a shape more or less in rosette analogous to the lamellar graphite which can be observed in classical cast irons. Such graphite is useful to enhance the thermal conductivity as well as the lubrication of these materials for limiting their heating in case of friction or wear applications. Even if they have not really developed in conditions of thermodynamic equilibrium, these very interesting as-cast microstructures can be qualitatively predicted, and also quantatively in terms of mass fractions then volume fractions, by using thermodynamic calculations but by restricting the appearance of the cementite in the initial conditions. However some improvements of the database are required to obtain a better accuracy the predictions about for the phase quantities.

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REFERENCES

- [1] D.A.Bridgeport, W.A.Brandtley, P.F.Herman; Journal of Prosthodontics, 2, 144 (1993).
- [2] C.T.Sims, W.C.Hagel; "The Superalloys", John Wiley & Sons, New York (1972).
- [3] M.J.Donachie, S.J.Donachie; 'Superalloys: A Technical Guide - 2nd Edition', ASM International, Materials Park, (2002).
- [4] J.L.Bernard, P.Berthod, L.Hericher, C.Liebaut, S.Michon; Patent WO2009/071847.
- [5] B.Roebuck, E.A.Almond; Int.Mater.Rev., 33, 90 (1988).
- [6] A.Klimpel, L.A.Dobrzanski, A.Lisiecki, D.Janicki; J.Mater.Process.Tech., 164-165, 1068 (2005).

- [7] G.V.Samsonov; "Handbooks of High-Temperature Materials N°2. Properties Index", Plenum Press, New York, (1964).
- [8] P.Berthod, O.Hestin, E.Souaillat; Materials Science: An Indian Journal, 7(1), 59 (2011).
- [9] Thermo-Calc Version N: "Foundation for Computational Thermodynamics" Stockholm, Sweden, Copyright (1993), (2000).
- [10] A.Fernandez Guillermet; Int.J.Thermophys., 8, 481 (1987).

- [11] J.O.Andersson; Int.J.Thermophys., 6, 411 (1985).
- [12] P.Gustafson; Carbon, 24, 169 (1986).
- [13] A.Fernandez Guillermet; Z.Metallkde, 78, 700 (1987).
- [14] J.O.Andersson; Calphad., 11, 271 (1987).
- [15] A.Fernandez Guillermet; Z.Metallkde., 79, 317 (1988).