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► **To cite this version:**

Patrice Berthod, Thierry Schweitzer, Lionel Aranda. Behavior at elevated temperature of cobalt-based superalloys strengthened by ZrC carbides. Pacific Operational Science and Technology conference (POST 2018), Mar 2018, Honolulu (Hawai'i), United States. hal-03251169

HAL Id: hal-03251169

<https://hal.science/hal-03251169>

Submitted on 6 Jun 2021

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Behavior at elevated temperature of cobalt-based superalloys strengthened by ZrC carbides

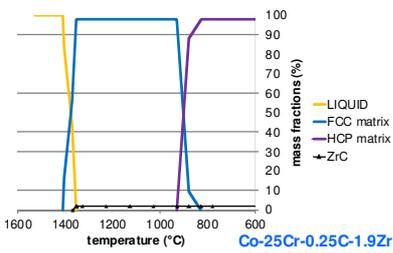
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Cobalt-based superalloys exploiting MC-carbides can be of great interest for some of the hottest components of aero-engines. In the specific case of military aircrafts ZrC carbides may allow high mechanical strength at elevated temperatures for resisting sudden increases in temperature and stresses such as in fighting conditions.

Zirconium is an element which is commonly used for trapping the impurities (e.g. sulfur) during the casting of metallic alloys to prevent any detrimental effect on their mechanical properties. Zr is also a possible base element for some alloys used in the nuclear industry (e.g. Zircaloy-4). In addition, zirconium is also a MC carbide-former element which may bring superalloys potential high strength at high temperature. As many MC carbides, eutectic ZrC may precipitate at solidification with high imbrication with the matrix. They are also very stable at elevated temperatures, in term of morphology and volume fraction. ZrC are thus possibly very efficient for the strengthening of alloys needing high resistance to creep deformation at high temperature. Despite these advantages, ZrC are curiously rarely used for this purpose and this study aims to test this alternative strengthening solution in refractory cobalt-based alloys.

Two Co-based alloys, Co-25Cr-0.25C-1.9Zr and Co-25Cr-0.50C-3.8Zr, were elaborated by casting to investigate their high temperature microstructures and properties. SEM/BSE examinations were carried out to verify if the expected microstructures (matrix with dendritic development, single MC nature and script-like morphology of carbides) were well obtained. Differential Thermal Analysis, flexural 3-points creep and thermogravimetric oxidation were performed to explore the potentials of high temperature properties and to identify the eventual problems to solve before benefiting of such new high performance refractory alloys.

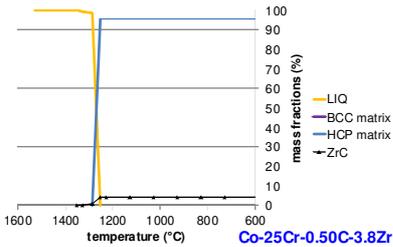
Preliminary exploration: thermodynamic calculations



Both alloys are really refractory (confirmed by the DTA measurements carried out later on real alloys):

Solidification should start with the crystallization of:

- The matrix for the {0.25C; 1.9Zr} alloy
- Pre-eutectic ZrC carbides for the {0.50C; 3.8Zr} alloy



- About 2 mass.% ZrC is expected for the {0.25C; 1.9Zr} alloy
- About 4 mass.% ZrC is expected for the {0.50C; 3.8Zr} alloy

As-cast microstructures (SEM/BSE) and melting temperature ranges (DTA)

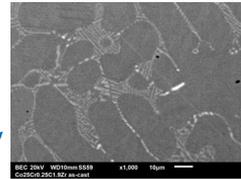
The {0.25C; 1.9Zr} alloy is composed of:

- A dendritic matrix
- Interdendritic script-like eutectic ZrC carbides



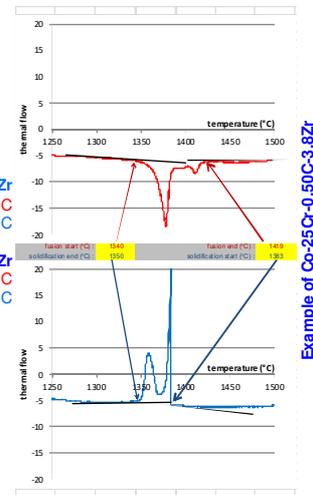
The {0.50C; 3.8Zr} alloy is composed of:

- A dendritic matrix
- Only ZrC carbides: rare blocky pre-eutectic ones and numerous eutectic ones

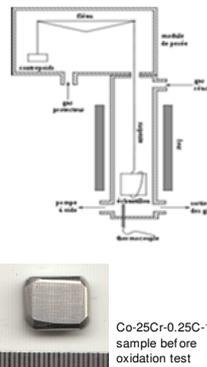
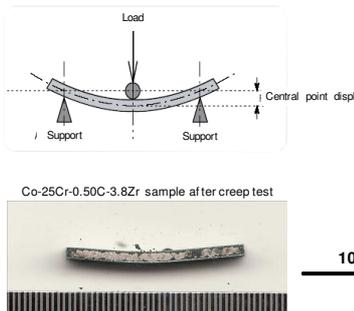
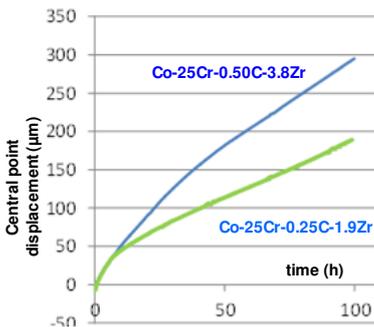


Co-25Cr-0.25C-1.9Zr
 Fusion over: 1330 → 1445°C
 Solidification over: 1350 ← 1400°C

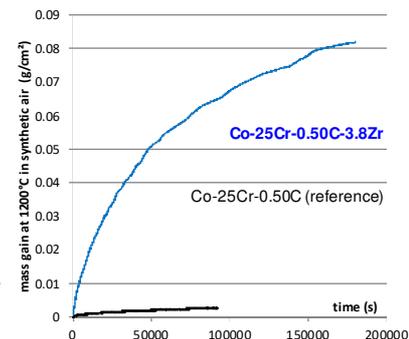
Co-25Cr-0.50C-3.8Zr
 Fusion over: 1340 → 1420°C
 Solidification over: 1350 ← 1385°C



Centered 3-points flexural creep at 1200°C, for 20 MPa just below the central point



Thermogravimetry tests at 1200°C in dry synthetic air



As preliminarily suggested by Thermo-Calc calculations, the two studied compositions appeared to be suitable to foundry process (not too high liquidus) and candidate to high temperature uses (solidus high enough). Both alloys were successfully synthesized by high frequency induction melting under 300 mbars of pure argon. Solidification led to the development of dendrites of Co(Cr) solid solution and to zirconium monocarbides: only eutectic ZrC for 0.25C-1.9Zr and both pre-eutectic and eutectic ZrC for 0.50C-3.8Zr. With the carbon and zirconium weight contents rated to respect their atomic equivalence, the ZrC carbides were thus exclusively obtained (no chromium carbides).

The totality (0.25C-1.9Zr) or the major part (0.50C-3.8Zr) of the ZrC are located in the interdendritic spaces and present a Chinese-script morphology allowing good imbrication with the matrix (the other part of the eutectic compound). Added with the rather high intrinsic strength of a Co-based matrix, very interesting results were obtained in high temperature creep-test, which cannot be really expected for equi-axed superalloys at temperature as high as 1200°C.

Unfortunately the behavior of these alloys in oxidation at 1200°C was catastrophic. The mass gain kinetic is parabolic but irregular and fast. With almost 100mg/cm² after 50 hours 25wt.%Cr is obviously not high enough to allow oxidation resistant at so high temperature. Ways of improvement may be enriching the bulk in chromium (e.g. increase of the Cr content beyond 30wt.%), enriching the subsurface in the same element (e.g. pack-cementation) or depositing another protective coating.

Acknowledgments: the authors wish to thanking Jérémy Peultier and Valentin Kuhn, Master students, for their participation to this work in their laboratory project