Equilibrium characterization and thermodynamic calculations on highly alloyed refractory steels

Jean-Marc Joubert [a],*, Wisline St-Fleur [a], Julia Sarthou [a], Antonin Steckmeyer [b], Benjamin Fournier [b]

[a] Chimie Métallurgique des Terres Rares (CMTR), Institut de Chimie et des Matériaux Paris-Est (ICMPE), CNRS, Université Paris-Est Créteil, 2-8 rue Henri Dunant 94320 Thiais Cedex, France
[b] Manoir Industries, 12 rue des Ardennes, BP 8401 Pîtres, 27108 Val de Reuil Cedex, France

ARTICLE INFO

ABSTRACT

A comparison has been made between the phase equilibrium calculated within the Calphad method with different thermodynamic databases (TCFE7, TCNI5, TTNI7) and experimental data obtained on a Nb–Ti-modified industrial HP grade. The experimental measurements include phase equilibrium data at different temperatures and liquidus/solidus determination. The obtained agreement between experiments and calculations is generally good. Conclusions are made concerning the most suitable thermodynamic database to describe highly alloyed austenitic refractory steels.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Highly alloyed refractory steels are used as centrifugally cast tubes and sand cast junctions in the hot part of cracking and reforming furnaces for the petrochemical industry [1–3]. These alloys have high chromium content necessary to maintain high corrosion resistance while high nickel content allows to keep the austenitic structure necessary to insure good creep properties. The fine precipitation of primary (formed during solidification) and secondary (formed during ageing) carbides also contributes to provide good mechanical properties at high temperature [4,5]. For a complete review about creep resistant stainless steels, one may refer to Ref. [6].

The predictive results of theoretical or semi-empirical modeling tools are widely used in the development of low alloyed steels or nickel-based superalloys. However, up to now, the continuous development of highly alloyed refractory steels has been made mainly empirically. Given the particular service conditions in steam cracking and steam reforming facilities – where refractory alloys are maintained at high temperature during their whole lifetime – it can be considered that phase equilibrium is reached soon during service. Therefore thermodynamic equilibrium calculations may be particularly representative of the alloy state in service. This is the reason why, among various modeling tools that can be used in order to improve several characteristics of the alloys, the Calphad technique [7] was chosen for its ability to deal with complex multi-element systems. Before using it to develop new alloys, one has first to ensure their prediction as far as refractory alloys are concerned. This is the aim of the present work in which, calculations made with different thermodynamic databases (TCFE7, TCNI5, TTNI7) have been compared to one another and confronted to the experimental results obtained after equilibrating an industrial grade at various temperatures. Conclusions are made concerning:

- the ability of the Calphad method to reproduce the observed microstructure of these complex compositions far from the composition range for which the databases have been developed
- the best suited database to be used for these alloys that stand halfway between steels and Ni-based superalloys.

2. Thermodynamic calculations details

The Calphad (CALculation of PHase Diagrams) approach is an extensively used semi-empirical technique for phase diagram modeling and calculation. It consists in describing the Gibbs

* Corresponding author. Tel.: +33 1 49 78 13 44; fax: +33 1 49 78 12 03.
E-mail address: jean-marc.joubert@icmpe.cnrs.fr (J.-M. Joubert).

energies of the different phases present in a system by adjusting parameters to fit the known experimental data. The parameters are then collected for many different systems (generally related to a given element, *e.g.* Fe for the steel database) and gathered in large so-called thermodynamic databases allowing to make reliable predictions of phase equilibrium in multi-component systems.

In the present work, equilibrium calculations were performed using Thermo-Calc software (version S). Given the particular compositions of the alloys, with much lower Fe concentration than conventional steels, it seemed interesting to test databases developed for both steels and nickel-based superalloys. In principle, the industrial alloy composition does not stand in the validity range of any of these databases, which was the main reason for the benchmark. Equilibrium calculations were therefore performed with three thermodynamic databases (TCFE7, TCNI5, TTNI7). The calculations were made in general on the nominal composition of the alloy, while, for the comparison with the Differential Thermal Analysis (DTA), the real composition obtained by spectroscopy was used.

The composition under study corresponds to the Manaurite XM grade which is basically the commercial HP grade modified by Ti and Nb. The exact composition is very similar to that of HP-NbTi alloy in Ref. [5]. The typical nominal composition is given in Table 1 with the exact composition resulting from flame spectroscopy analysis.

The equilibrium calculations were done as a function of temperature using the STEP command of Thermo-Calc. The calculations with TCNI5 are done without Mn which is not included in the database.

3. Experimental details

For equilibrium measurement, a piece of material was cut in the outer diameter of a pipe cast industrially by centrifugal casting. The composition under study is alloy XM the nominal composition of which has been given in Table 1.

The alloy was studied as-cast, and after several thermal treatments at temperatures between 500 °C and 1300 °C. These treatments were done in order to reach or to approach equilibrium. They were done on massive samples in air. The slight oxidation layer was removed. Experimental measurements in equilibrated alloys may be representative of both the alloy state in service and the calculation performed with Thermo-Calc. The state after treatment was investigated using conventional powder X-ray diffraction (XRD, Philips X'Pert, Bragg-Brentano geometry, θ–θ set-up, Co Kα radiation, graphite monochromator in the diffracted beam) on polished sample and scanning electron microscopy (SEM, LEO1530) in order to evidence the nature and, to a certain extent, the proportion of the present phases as a function of temperature. One sample was also submitted to WDS measurement in an electron micro-probe analyzer (EPMA, CAMEBAX SX100).

Both Simple Thermal Analysis (STA) and DTA measurements were also performed in order to investigate the liquidus and solidus. For the STA, a thermocouple was introduced in the melt of an industrially cast alloy that was allowed to cool in air. The temperature was followed as a function of time and the thermal arrests were indicative of the liquidus. The DTA was performed on drill chips of the same heat ($\sim$100 mg) in a SETARAM Setsys-Evolution apparatus under flowing Ar atmosphere. Two measurements were performed on different samples in order to check the reproducibility. In each case two cycles were performed up to 1400 °C generally at 10 °C/min. For the second sample, the second cycle was done at 5 °C/min.

Table 1
Nominal and analyzed compositions of alloy XM (wt%).

Element	Nominal	Analyzed
C	0.40–0.45	0.44
Mn	0–1.5	1.23
Si	1.2–2.0	1.45
Ni	32.0–36.0	35.1
Cr	23.0–27.0	26.4
Nb	0.5–1.0	0.79
Ti	0.02–0.15	Add.
Fe	balance $\sim$40 wt%	34.1

The characteristic temperatures are taken from the heating run, supposed to be closer to equilibrium (*i.e.* not subject to undercooling) at the second cycle because of a better contact of the sample with the crucible. For the solidus, the onset is taken, while the liquidus has been identified at the end of the transformation.

4. Results

4.1. Calculation

Fig. 1 presents the results of the Thermo-Calc calculations done for the XM composition with the three tested databases.

Most features are reproduced by all databases:

- liquidus between 1340 °C and 1377 °C
- solidus between 1276 °C and 1296 °C
- primary precipitation of *fcc*
- eutectic co-precipitation of MC and M_7C_3
- transformation of M_7C_3 in $M_{23}C_6$ at lower temperature
- presence of *bcc* below 600–700 °C

Slight differences may however be noticed like, for example, the nature of the low temperature precipitation. G phase (a Nb (Ti)–Ni silicide) is predicted by TCFE7 and TTNI7 whereas the σ phase is predicted by TCNI5 despite the fact that all databases contain a thermodynamic description of both G and σ phase.

Tables 2 and 3 present a comparison of some of the phase composition results obtained for the different databases at two temperatures. Again, close results are obtained. All the compositions are equal to within approximately 1 at% except perhaps the Nb/Ti partition in MC carbide for TCFE7 which differs from the results obtained with TTNI7 and TCNI5. Another difference is found in the composition of the G phase, which strangely does not contain Nb in the TTNI7 calculation.

4.2. Experimental study

4.2.1. Equilibrium study at high temperature (750 °C–1200 °C)
Fig. 2 shows typical XRD patterns of the sample before and after heat treatment at 850 °C. It allows to evidence the changes of the nature of the carbides. Though in small quantity, these phases can, in most cases, be identified without resorting to phase extraction like is done, for example, in Ref. [8].

Fig. 3 shows the microstructure of the alloy after different thermal treatments. It evidences the precipitation of eutectic binary carbides in the as-cast sample (both MC in white and $M_7C_3/M_{23}C_6$ in black). After thermal treatment at temperatures 750–1000 °C, secondary precipitation of carbides may be noticed as fine intra-grain precipitation, while at 1200 °C, most carbides dissolve.

The EDS analysis was used in the SEM in a qualitative way, supporting the previous analysis on phase identification (*i.e.* MC