COMPUTATIONAL THERMODYNAMICS AS A TOOL TO UNDERSTANDING AND DESIGNING INTERCRITICAL HEAT TREATMENT OF STEELS*

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Abstract
Intercritical heat treatments are used during the processing of many steels. The possibilities associated with the partitioning of carbon between ferrite and austenite and the formation of different austenite decomposition products on cooling has been the reason for the wide acceptance of these treatments. However, the result of the intercritical treatments may deviate from equilibrium predictions. Treatment temperature, heating (or cooling rate) to the treatment temperature, and holding time at temperature are known to have significant effects on the resulting microstructure at the end of the intercritical treatment. Different approaches have been used to model these transformations and better understand the related phenonema. Equilibrium and para-equilibrium calculations have been used, diffusion model with different degrees of complexity have been applied and phase field modeling has also been used. In this work we compare the results of intercritical treatments performed at different temperatures to the predictions that can be obtained using common computational thermodynamic tools: equilibrium, para-equilibrium and diffusion controlled transformation. As a result of this comparisons we highlight how computational thermodynamics can help in understanding and design intercritical heat treatment of steels and, to some extent, alloy design of these steels. Furthermore, the current limitations of the technique are discussed and further work to improve it, where justified, is suggested.

Keywords: Complex Phase; Intercritical treatment; Computational thermodynamic.

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1 INTRODUCTION

Many steels rely on intercritical heat treatments to obtain their optimum properties. The automotive industry, for instance, relies on multiphase steels to achieve interesting combinations of high strength, formability and toughness [1]
Complex phase steels usually have a ferritic/bainitic matrix coupled with adequate volume fractions of martensite, bainite and retained austenite. [2]
The industrial production of multiphase steels involves heat treatment in the intercritical austenite-ferrite region of hot or cold rolled steels. Adequate cooling is required and frequently a slower cooling rate in the bainitic range is performed [3]
The intercritical treatment is of paramount importance to define the volume fraction of ferrite as well as the volume fraction and carbon content of the austenite that will give rise to the complex microstructure after cooling. Defining the conditions for the intercritical treatment as well as the cooling program is a complex challenge. The search for a chemical composition that will retard carbide precipitation, promote bainite transformation, the proper amount of MA constituent and of martensite has to be coupled to the processing cycle design. Computational thermodynamics make possible forecasting equilibrium, and para-equilibrium conditions as well as describing the diffusional formation of austenite during the intercritical cycle. The use of computational thermodynamics can, then, substantially enhance the alloy-process design cycle, by limiting the range of compositions and cycles to be experimentally tested. However, these techniques have some limitations and must be understood to be correctly applied and for the user to benefit from the results. In this work we compare the results of intercritical treatments performed in different steels to the predictions that can be obtained using common computational thermodynamic tools: equilibrium, para-equilibrium and diffusion controlled transformation. As a result of this comparisons we highlight how computational thermodynamics can help in understanding and design intercritical heat treatment of steels and, to some extent, alloy design of these steels. Furthermore, the current limitations of the technique are discussed and further work to improve it, where justified, is suggested.

2 BACKGROUND

2.1 EQUILIBRIUM CALCULATIONS

Softwares such as Thermo-calc use free energy minimization to calculate stable and metastable equilibria [4]. Equilibrium calculations are very useful in exploring the limiting conditions for treatments that approach this conditions (in general, long times and/or moderate heating and cooling rates) as well to exclude impossible transformations from the exploratory studies. However, it has been observed that, in some cases austenite can decompose with carbon partitioning but without partitioning of the substitutional elements between the formed phases. This is frequently the case when time and temperature processing conditions are not adequate to achieve equilibrium [5]. Hultgren identified this possibility and introduced the concept of para- equilibrium [6]. Recently Agren and Hillert [7] summarized the thermodynamic conditions for para-equilibrium as the occurrence of the following three constraining conditions at the phase interface: “[4] same ratio of the alloying elements to iron in both phases, [5] equal chemical potential of carbon as well as [6] of the weighted average of iron and the alloying elements.”. Thermo-calc can also calculate para-equilibrium.[8], i.e., the conditions that would prevail if only carbon (or interstitials, in general) could partition between the product phases of a transformation. Both equilibrium and para-equilibrium define limiting cases of phase transformations. When diffusion rates play an important role in the search for equilibrium they cannot be overlooked. The computational

thermodynamics (CALPHAD) approach has been extended to model mobilities and diffusion in DICTRA [9] DICTRA uses mobilities and chemical potential gradients to solve one-dimensional diffusion problems in multi-component systems. [10].

As discussed above, the processing of multiphase steels is defined by phase transformations during two stages: the intercritical annealing and the posterior cooling. The concepts involved are not new. Speich, for instance, [5] has discussed in depth the importance of intercritical treatment for dual phase steels and how diffusion and thermodynamics play an important role in these transformations. Other authors have studied these transformations experimentally of by computational thermodynamic modeling or by combining these techniques (e.g.[11][12][13][14][15]).

The decomposition of the austenite formed during the intercritical annealing has also been extensively investigated, normally in a more classical way, using dilatometry and other experimental techniques. Nonetheless, interesting phenomena related in special to the extent of solute partitioning during cooling have been identified (e.g. [16]) and gave birth to new treatments such as Q&P as reviewed by Matlock and Speer [17].

Diffusion modelling using the CALPHAD approach has been helpful in the development of advanced high strength steels (AHSS) as discussed above. The development of multicomponent thermodynamic and kinetic databases has made possible modeling closer to real situations than ever. However, some of the limitations of the technique cannot be ignored: (a) only one-dimensional simple geometry problems can be treated (b) if nucleation is to be considered, arbitrary barriers must be introduced and (c) the geometry constrains limit the modeling of some multiphase problems and enhanced diffusion paths that are certainly important in the development of AHSS steels.

In the present work we focus on the intercritical annealing of a complex phase steel and compare experimental measurements performed under controlled conditions to various predictions that can be performed using equilibrium, para-equilibrium and diffusion modeling through computational thermodynamics (CALPHAD). We aim at highlighting the agreements and discrepancies observed and at pointing to useful applications of the techniques as well as to desired developments.

3 MATERIAL AND METHODS

3.1 MATERIAL

A low carbon steel produced by CSN with the composition given in Table 1 was used in all tests.

Table 1. Main elements in the chemical composition of steel used in this study (mass percent)

C	Mn	Si	Cr + Mo
0,18 máx.	1,6 mín.	0,3	1,0

3.2 METHODS

3.2.1 Computational Thermodynamics

Thermo-calc 2019a with the DICTRA module [4][9] was used with TCFE9 [18] and MOBFE4 [19] databases.

3.2.2 HEAT TREATMENTS

All heat treatments were performed in a laboratory furnace with calibrated thermocouples. All samples were previously rolled by CSN. Intercritical treatments were performed at different temperatures in the ferrite+austenite region for 4 minutes holding time. After a sufficient time at temperature the specimens were removed from the furnace and quenched in water. Specimens for metallography were cut, removed from interfaces polished and etched. Image analysis was performed with the Image J software.

4. RESULTS AND DISCUSSION

4.1 PRELIMINARY CALCULATIONS

In order to define the heat treatment temperatures, equilibrium and para-equilibrium calculations were performed with Thermo-calc, as indicated in Figure 1.

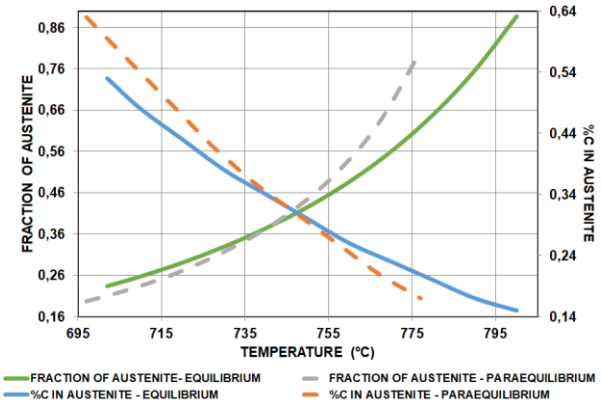

Figure 1. Austenite carbon content and volume fraction calculated for the steel used in study under equilibrium and para-equilibrium**.**

4.2 OBSERVED MICROSTRUCTURE

Specimens treated at 760ºC, 780ºC e 800ºC for 4 min holding time were examined. Figure 1 and 2 present some examples of the observed microstructure after the intercritical treatment followed by quenching. The microstructures are very fine and quite complex. Phase identification in these systems is quite difficult (e.g. [20][21]).

Figura 2. Optical Micrograph of sample subjected to Intercitical heat treatment at **760ºC – Etched with 3% Nital original magnification 500x.**

Figura 3. Optical Micrograph of sample subjected to Intercritical heat treatment at 800ºC – Etched with 3% Nital original magnification 500x.

Table 2 presents the volume fraction of austenite formed during the intercritical treatments determined from the measured volume fraction of undissolved ferrite in each sample.

Temperature (ºC)	UNDISSOLVED FERRITE	AUSTENITE
760	0,654	0,346
780	0,572	0,428
800	0,516	0,484

4.3 EQUILIBRIUM CALCULATIONS

Figure 4 compares the measured volume fraction of austenite with that calculated assuming equilibrium and para-equilibrium.

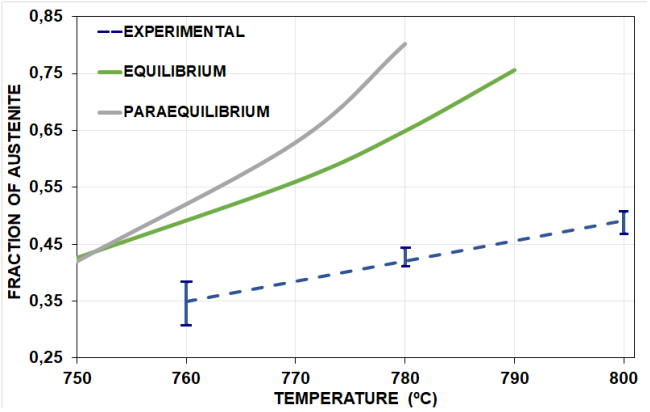

Figura 4. Fraction of austenite formed at different temperatures. Calculated by two equilibrium criteria compared with experimentally determined (see text for discussion).

These results indicate a significant over estimation of the austenite fraction when

one consider the assumption of equilibrium or para-equilibrium. For the composition studied, this does not seem to give a precise estimate of the austenite formed in the intercritical annealing.

4.4 DIFFUSION CALCULATION

In the case of diffusion calculation, two aspects must be considered to properly formulate the model. First, one must consider how the austenite nucleate and grows in an complex microstructure such as the one existing in hot rolled strips of this steel. In some cases, it has been assumed that carbide-ferrite aggregates (such as pearlite, bainite and even tempered martensite) will austenitized in short times, since the diffusion distances are relatively smaller [20][12]. The growth of austenite would then be controlled by the rate at which equiaxial ferrite is consumed.

This was the assumption in this model. Equilibrium at the lowest temperature in which austenite and ferrite co-exist (around 700C for this steel) was calculated. The volume fraction and composition of these phases were considered the starting point for the diffusion model.

Furthermore, distances are importance in the formulation of diffusion problems. Based on previous published modeling [12] and on observation of the quenched structure, two geometries were proposed, as indicated in Figure 5.

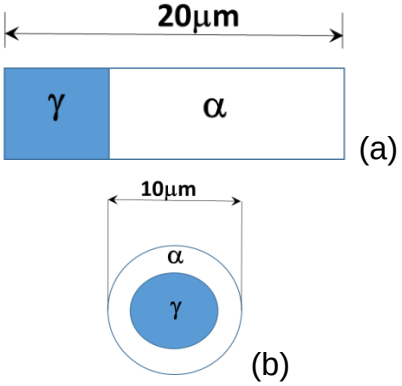

Figure 5. Geometries adopted for DICTRA modeling. (a) Linear (12) (b) Spherical. See text for discussion.

In the linear geometry, it is assumed that the carbide+ferrite aggregate transforms into a volume of austenite that is juxtaposed to the ferrite volume (in the calculated proportion of volume fractions). Then the interface will migrate to the right, in the Figure. The scale of the idealized structure is defined by the cell length. Based on the microstructure observation, it was proposed that once the carbide+ferrite aggregate transforms into austenite it is surrounded by ferrite, in the scale indicated in Figure 5b. As the geometry is spherical, radial directions are not directly proportional to volume fractions, evidently.

Some results obtained with DICTRA for the spherical geometry are presented in Figure 6.

Figure 7 compares the DICTRA calculations using both geometries with the experimental results. It is evident that there is a better agreement than with the simple equilibrium calculations. Furthermore, the spherical geometry model seem to have a better agreement with the experimental results.

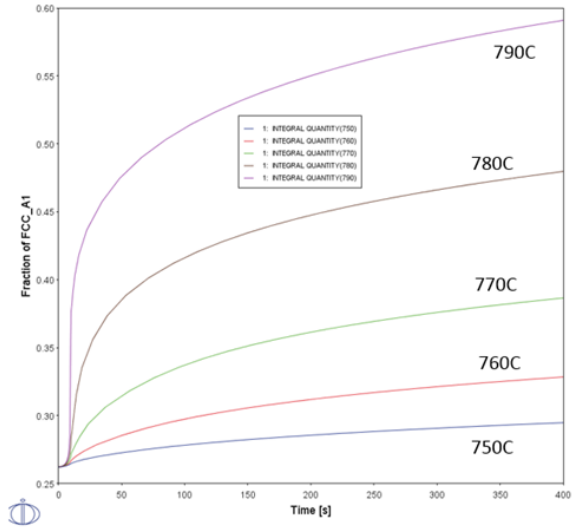

Figure 6. Austenite volume fraction calculated for different intercritical treatments with the spherical geometry described in Figure 5b.

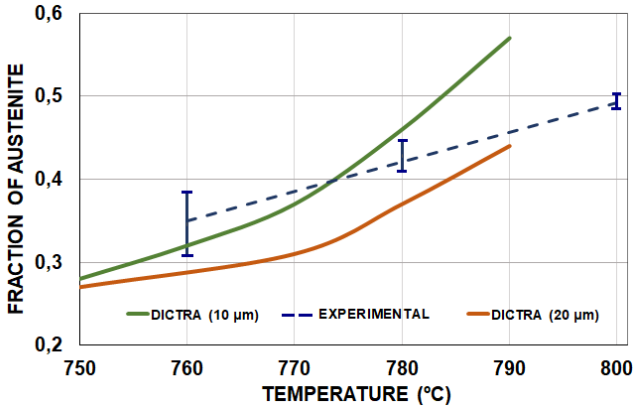

Figure 7. Results calculated with two DICTRA geometries compared to the experimental results.

5. CONCLUSIONS

Computational thermodynamics tools offer interesting insights in the design of intercritical treatment of complex phase steels. Equilibrium and para-equilibrium results are useful for preliminary design and estimation of austenite carbon content. Diffusion modeling is effective to perform more accurate estimates of partition of solutes during the intercritical annealing treatment. indeed effective and auxiliary in
The choice of the model geometry influences significantly the diffusion calculation results. The geometry should be selected with due consideration of the actual microstructure..
The knowledge of thermodynamics coupled with kinetics and phase transformation shows that software such as ThermoCalc and Dictra used together can be quite useful.
On the empirical side, it should be noted that , for the steel used in these, a linear correlation was observed between the austenite fraction and the intercritical treatment temperature. This will be further investigated.

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