SIMULATION OF DIFFUSIONAL PROCESSES DURING SOLIDIFICATION IN AUSTENITIC STEELS

D. Baldissin*, L. Battezzati, Dipartimento di Chimica IFM e Centro di Eccellenza NIS,
Università di Torino, Via P. Giuria 9, 10125 Torino, Italy
* corresponding Author: daniele.baldissin@unito.it

M. R. Ridolfi, O. Tassa, Centro Sviluppo Materiali, Via di Castel Romano 100, 00128 Roma, Italy

Abstract

The occurrence of microsegregation in steels is mainly a consequence of non-equilibrium solidification and results from incomplete diffusion in the solid or in the liquid causing compositionally inhomogenous phases. As this phenomenon influences the crystal morphology, the simulation of solidification is becoming a relevant tool for the prediction of such microstructural details assisting in the optimisation of industrial manufacturing of steels. In order to deal with complex systems, such as multicomponent steels, it is necessary to employ numerical simulations based upon finite difference or finite element methods. Several softwares are commercially available, e.g. IDS, DICTRA, dealing with the diffusion problem within domains of the material, named cells, which contain the moving solid-liquid interface. Each software makes specific assumptions on the geometry of the cell and the boundary conditions. In this study the DICTRA software is used, interfaced with the THERMOCALC software for the calculation of phase diagrams, in order to employ optimised thermodynamic data for the description of the transformation kinetics. The calculations have been performed at first for an AISI 304-type steel as a model system and compared with experimental data found in the literature. The procedure has then been extended to a high nitrogen and high manganese steel. A comparison between the results of DICTRA and IDS concerning solidification of the stainless steels are reported with attention to the differences in the database used by the two softwares.

Keywords: DICTRA, Austenitic stainless steels, Phase diagram, Solidification modelling, moving phase boundary calculations

INTRODUCTION

Solute redistribution during solidification of a steel can lead to compositional inhomogeneities that result in the formation of a second phase or porosity giving rise to cracking problems. Over many years numerical procedures have been developed to simulate microsegregation phenomena [1-4] in multicomponent alloys. The result of these efforts is the availability of many tools able to handle the various analytical and numerical models without limitation to binary alloys. Such models predict secondary dendrite arm spacing, distribution of elements within dendrite arms and the amount of non-equilibrium phases in dendritic solidification in multicomponent alloys. In this work, DICTRA (DIffusion Control TRAnsformations) has been choosen as a general software package for simulating diffusion controlled transformations in steels. Besides, the THERMOCALC software has been used in combination with DICTRA to solve the diffusion problem by means of a Newton-Raphson iteration technique so as to determine the migration rate of interfaces and the equilibrium at phase interfaces. DICTRA or THERMOCALC are based upon diffusivity and thermodynamic databases respectively. MOB2 has been the database used for the diffusivities while TCFE_2000 has been used for thermodynamic data.

MULTICOMPONENT DIFFUSION THEORY

The theoretical treatment of diffusion in alloys, involves the solution of the Stefan problem. The growth rate is calculated from a flux balance equation at the moving phase interface according to the relation:

$$v\ (c^{\gamma} - c^{\alpha}) = J^{\gamma} - J^{\alpha} \tag{1}$$

where v is the migration rate of interface, c^{γ}, c^{α} are the concentrations close to the interface on the γ and α side, respectively while J^{γ} and J^{α} are the corrisponding diffusional fluxes. These latter are calculated by means of the solution of a diffusion equation in the two phases. The difficulty of the problem is that the position of the interface is not known a priori but is a result of the solution of the problem itself.

Nevertheless, boundary conditions have to be formulated in order to solve the diffusion differential equation. This equation is dependent on time and its solution with generic boundary conditions can be obtained only with numerical methods by using the DICTRA software based upon the finite difference technique [5].

The numerical approach of DICTRA has been developed by taking the multicomponent diffusion theory into account. The interdiffusion coefficient is therefore calculated by using thermodynamic and kinetic parameters.

According to Onsanger's formalism [6] the diffusion equation is written by using the coefficients L'_{ki}:

$$J_k = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial x} \tag{2}$$

where μ_i is the chemical potential of the component i, J_k is the flux of the component k and n is the number of the components of the system. These equation can be rearranged by considering the concentration gradients instead of the chemical potentials:

$$J_k = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial x} \tag{3}$$

where D_{kj} are the interdiffusion coefficients. The concentrations are easier to measure than the chemical potentials. For this reason it is useful to express Fick's law by means of the coefficient D_{kj} defined as:

$$D_{kj} = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j} \tag{4}$$

In this equation the interdiffusion coefficients are expressed in terms of thermodynamic quantities $\partial\mu_i / \partial c_j$, called thermodynamic factors and in terms of phenomenological coefficients that are purely kinetic quantities. In order to obtain these parameters it is necessary to refer to a kinetic and thermodynamic database.

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DICTRA SIMULATION

The nominal composition of the austenitc stainless steel used for the first simulation of this work is Fe-18.2Cr-8.7Ni-1.2Mn-0.6Si-0.04C-0.03S-0.025P, expressed in weight percent. At first, calculation has been limited to the main components of the alloy (Fe, Cr, Ni), then, the effect of minority elements has been added by using the Schaeffler [7] equations for the Cr and Ni equivalent content.

$$Cr_{eq} = (\%Cr) + 1.5(\%Si) \quad (5)$$

$$Ni_{eq} = (\%Ni) + 0.5(\%Mn) + 30(\%C) \quad (6)$$

The simulation is performed from the middle of the interdendritic region to the middle of the dendrite itself. The extent of the area corrisponds to half of the interdendritic distance and its actual size is chosen according to the cooling rate in the following way for AISI 304-type steels [8]:

$$\lambda_{SDAS}\ [\mu m] = 63.91 \cdot [\text{cooling rate, K/s}]^{-0.347} \quad (7)$$

where λ_{SDAS} is the secondary dendrite arm spacing. The calculations have been performed for a cooling rate of 0.3 K/s that is the one used in experiments in [9] in a simulated area of 50 μm as the dendrites are assumed to be simmetric. In Fig.1. the simulation area is shown. The interface has been assumed to be planar.

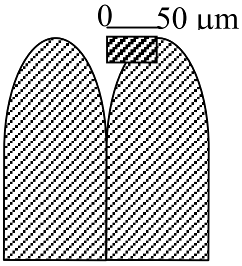

Fig. 1. Schematic rappresentation of the simulation area used in the calculation with the DICTRA software.

Initially, the system has been semplified by using ternary and quaternary equivalents as shown in table 1 according to equations (5) and (6). Then, the nominal composition has been employed.

Table 1. Composition sets used in the calculations with the DICTRA software

	Cr	Ni	C
Nominal composition	18.2	8.7	0.04
Ternary equivalent	19.1	10.5	
Quaternary equivalent	19.1	9.3	0.04

In Fig. 2 the equilibrium phase fraction of δ-ferrite as a function of temperature is shown for the composition sets of table 1. In Fig. 3 the fraction of δ-phase is shown as calculated with the DICTRA software by taking diffusion processes into account.

For both cases, no significant difference between the amount of δ-ferrite calculated using a quaternary equivalent composition and a nominal composition while there is a major difference when using the ternary composition since the carbon has been neglected.

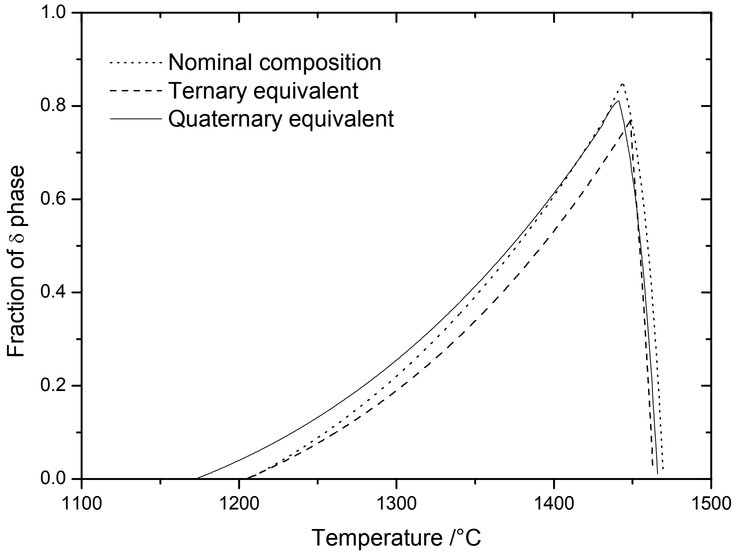

Fig.2. Equilibrium fraction of δ phase as a function of the temperature for a nominal composition alloy (dotted line), a ternary equivalent alloy (dashed line) and a quaternary equivalent alloy (full line) calculated with Thermocalc.

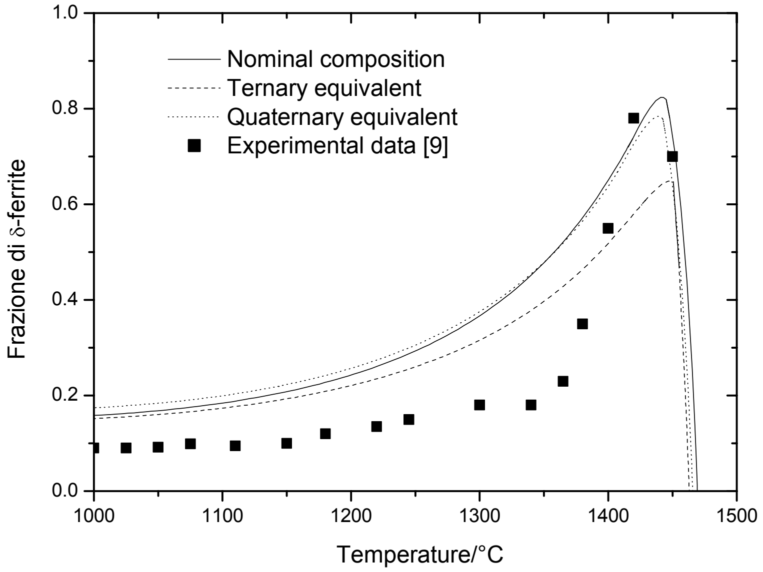

Fig.3. Non-equilibrium fraction of δ phase as a function of the temperature for a nominal composition alloy (dotted line), a ternary equivalent alloy (dashed line) and a quaternary equivalent alloy (full line) calculated with DICTRA. The three results are compared with experimental data [9].

A COMPARISON WITH IDS

IDS (InterDendritic Solidification) is a trade software specifically designed to simulate diffusional solidification processes of type-304 austenitic stainless steels. The results obtained with DICTRA have been compared with those obtained with IDS for the same quaternary equivalent composition as in table 1 continuously cooled at 0.3 K/s and with experimental results by Kim et al. [9].

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Calculations are shown in Fig.4. The difference between DICTRA and IDS can be due to the different database used. The liquidus temperature calculated with THERMOCALC is 1465 °C while that calculated with DICTRA is 1472 °C. IDS uses kinetic and thermodynamic databases based upon a work by Miettinen [10] different with respect to those used by DICTRA and THERMOCALC. Comparing with experimental results [9], IDS reproduces values of the fraction of δ- phase at low temperatures better than DICTRA, if a quaternary equivalent composition is used. In the range of temperature between 1400° C and 1500° C, instead, the results obtained with DICTRA are closer to the experiment.

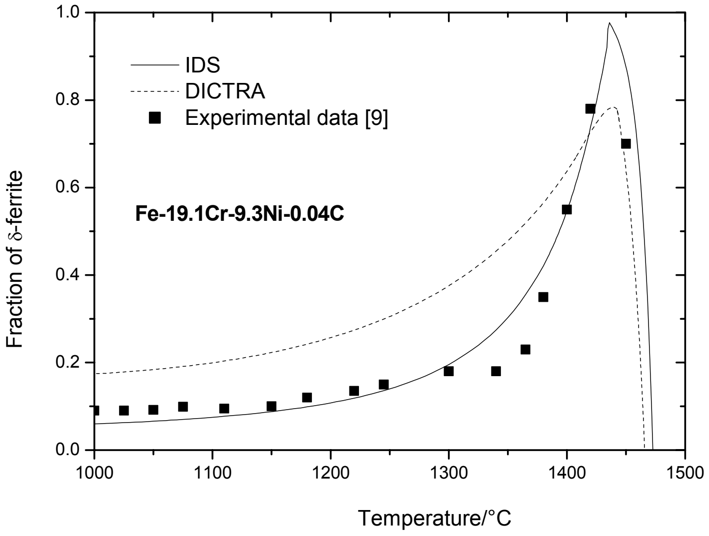

Fig.4. Comparison of the fraction of δ-phase for a quaternary equivalent composition performed with both DICTRA (dotted line) or IDS (full line). The cooling rate chosen for the calculation is 0.3 K/s

Nevertheless, if the calculation with DICTRA is repeated by abandoning the equivalents and taking all of the elements except the sulphur into account, the agreement with the experimental results becomes by far better at low temperatures as it is shown in Fig.5. The sulphur has never been considered for convergence problems probably due to lack of data in the database.

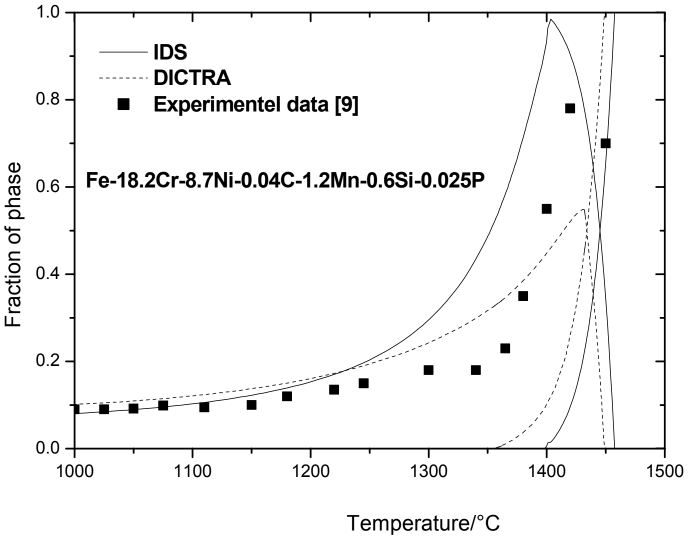

Fig.5. Comparison of the fraction of δ-phase and fraction of liquid with IDS (full line) and with DICTRA (dotted line) for a nominal composition without S element.

HIGH NITROGEN AND HIGH MANGANESE STEEL

The second type of steel analyzed in this work with the DICTRA software is a high nitrogen and high manganese steel of the following composition in weight percent: Fe-0.052C-0.43Si-0.002S-0.029P-8.01Mn-18.10Cr-4.02Ni-0.11Mo-1.3Cu-0.33N.

In Fig. 6 and in Fig.7 fractions of phases, calculated with THERMOCALC and IDS respectively, for the nominal composition of table 2 are shown. The liquid fraction calculated with the two simulation codes is similar and the liquidus temperature is 1411° C.

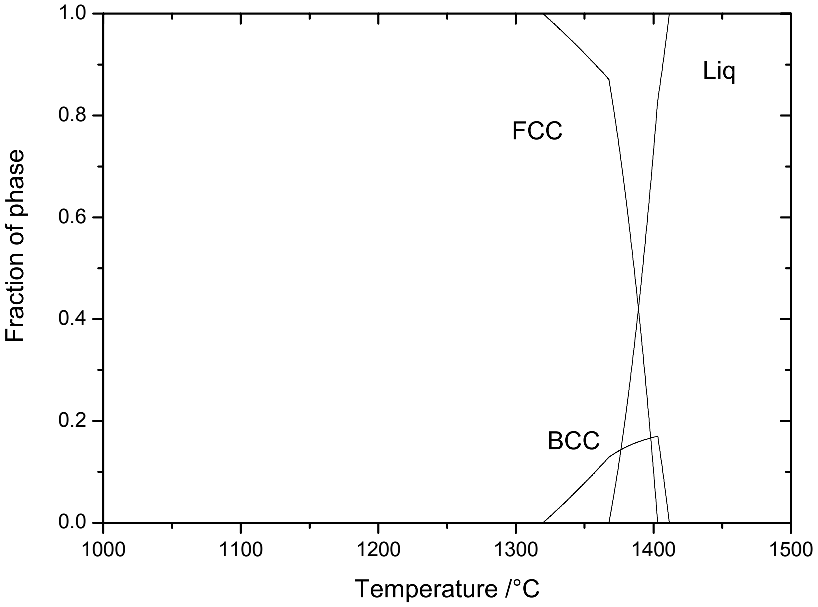

Fig 6. Fraction of equilibrium phase for the steel of composition Fe-18.1Cr-8.01Mn-4.02Ni-0.052C-0.33N-1.3Cu-0.11Mo-0.43Si calculated with THERMOCALC using TCFE database.

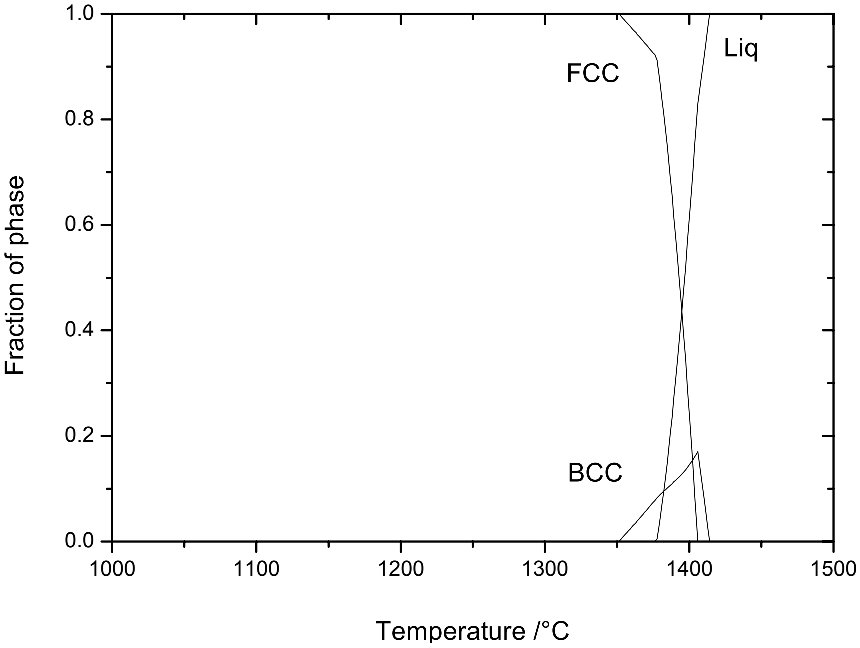

Fig 7. Fraction of equilibrium phase for the steel of composition Fe-18.1Cr-8.01Mn-4.02Ni-0.052C-0.33N-1.3Cu-0.11Mo-0.43Si calculated with IDS.

There are differences as regards the amount of fraction of austenite and ferrite, the latter being larger for the THERMOCALC calculation. Differently from database used by THERMOCALC, by examining in detail the database of IDS one can realize that the Mn and Cu contents of this steel do not fall into the range of compositions for which the database has deen designed. Therefore THERMOCALC results can be considered more reliable with respect to those predicted by IDS.
For this type of steel having high nitrogen content, Sanchez formula [11] have been used in order to calculate the Cr and Ni equivalent content.

$$Cr_{eq} = (\%Cr) + 1.25(\%Mo) + 0.7(\%Si) + 0.05(\%Mn) \tag{8}$$

$$Ni_{eq} = (\%Ni) + 0.35(\%Cu) + 27.4(\%C) + 22.7(\%N) \tag{9}$$

Sanchez equivalents take the nitrogen and manganese content into account, differently from Shaeffler equivalents. In these formula manganese is included as a ferrite stabilizer. For these steels, it usually is a weak austenite former up to 4% and a ferrite stabilizer for larger contents.
By using these equation the composition sets listed in table 2 have been employed in the calculations with the DICTRA software.

Table 2. Composition sets considered in the calculations performed with the DICTRA software.

	Cr	**Ni**	**N**	**Mn**	**Cu**
Ternary equivalent	18.94	13.39			
Quaternary equivalent	18.94	5.9	0.33		
Quinary equivalent	18.54	5.9	0.33	8.01	
Senary equivalent	18.54	5.45	0.33	8.01	1.3

The calculations show that δ is always the primary phase and γ is the secondary phase, except for the ternary equivalent composition. Usually, in this type of steels the mechanism of solidification is peritectic. It means that, once the primary δ-phase is formed, the peritectic γ-phase grows at the expenses of the liquid and the δ-phase.
As a consequence, the ternary equivalent composition cannot represent our system. In Fig. 8 the fraction of δ-phase calculated with DICTRA is shown as a function of the temperature for all composition sets in table 2. Passing from a ternary equivalent composition to the quaternary, it is evident that the accounting directly for nitrogen has the effect of lowering the equivalent nickel content of a large amount and to shift the phase equilibrium so that δ-phase is formed first. Besides, this causes the disappearance of the δ-phase below 1100°C and a major presence of δ-phase in the range of temperatures between 1350°C-1450°C.
If manganese is added to the quaternary equivalent composition, the δ-phase fraction decreases in the range of temperatures considered.
The addition of copper does not change the δ-phase fraction in a significant way. The liquidus temperature is closer and closer to the equilibrium one (1411°C).

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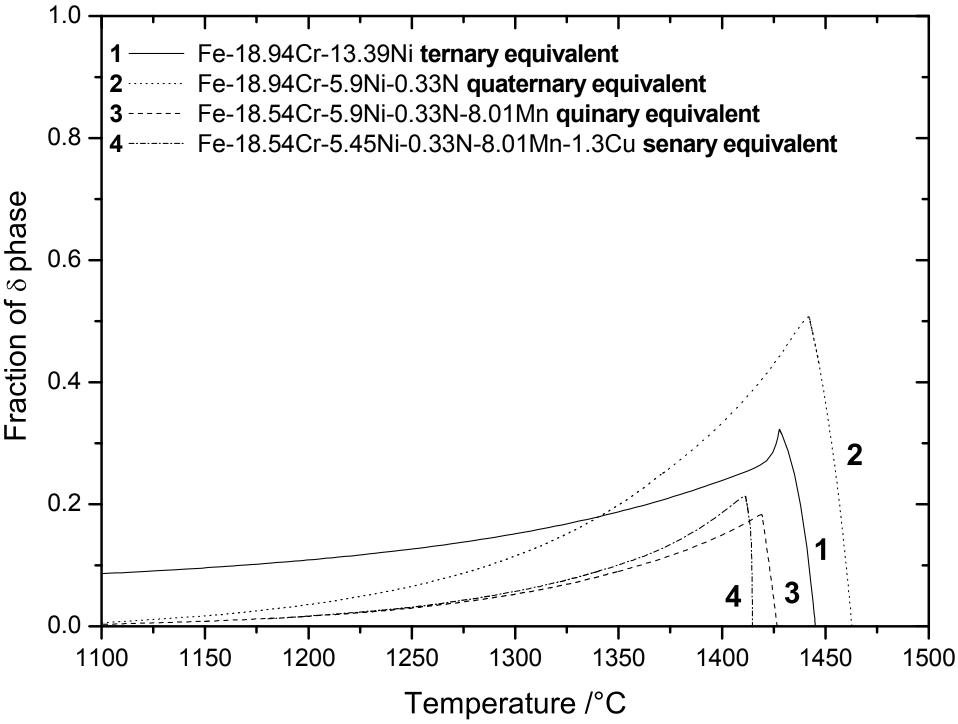

Fig. 8. Fraction of δ-phase for the different equivalent compositions listed in table 2 calculated with DICTRA at a cooling rate of 0.3 K/s.

In Fig.9 the calculation performed with IDS for a senary equivalent composition listed in table 2 is comparatively shown. IDS simulates a lower content of δ-phase fraction with respect to DICTRA. This can be due to the fact that content of copper and manganese of this steel fall out of the range of values of the database of IDS (from 0 to 2 wt% for Mn and from 0 to 0.5wt% for Cu).

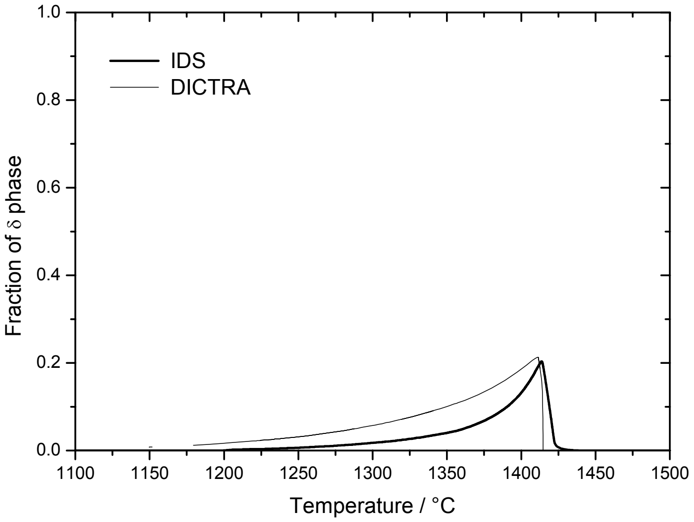

Fig. 9. Comparison among the fraction of δ-phase calculated with DICTRA and with IDS for a senary equivalent composition listed in table 2.

In Fig.10 and in Fig.11 concentration profiles calculated with DICTRA for Cr and Ni in the simulated area are shown at three different temperatures.

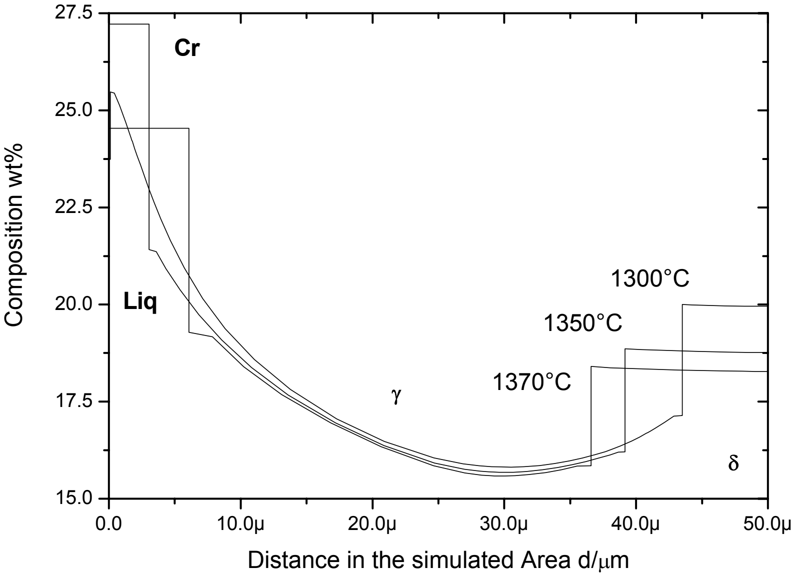

Fig. 10. Concentration profile of Cr as a function of the simulated area at three temperatures corrisponding to 1370°C, 1350°C e 1300°C.

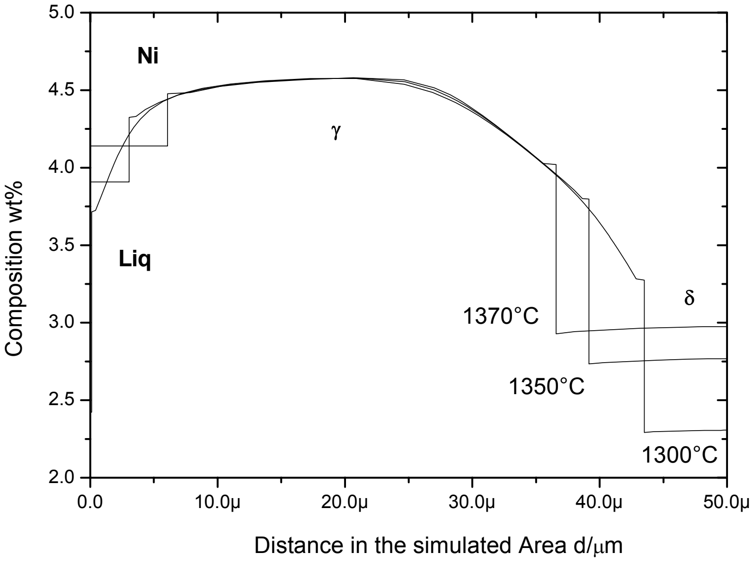

Fig. 11. Concentration profile of Ni as a function of the simulated area at three temperatures corrisponding to 1370°C, 1350°C e 1300°C.

Fig.10 and Fig.11 show that DICTRA predicts a movement of the γ/ δ interface from the left to the right of the simulation area when the temperature decreases. This means that the austenite is growing to the detriment of ferrite. At the same time the liq/ γ interface moves in the opposite direction. This means that the austenite is growing to the detriment of the liquid. The central region of the cell is enriched in Ni and depleted in Cr at all temperatures. On decreasing temperature the Cr concentration increases slightly and the content of Ni decreases very slowly. This variation of the concentration profiles shows the possible occurrence of phenomena of microsegregation at the end of the solidification.

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CONCLUSIONS

In this work, calculations of the solidification mode of two types of austenitic stainless steels are reported: one is a 304 steel for which experimental results are available in the literature, the other is a high nitrogen and manganese steel for which no experimental data are available.

Three softwares have been used in order to simulate a solidification process at a cooling rate of 0.3 K/s: DICTRA, IDS and THERMOCALC. To simplify the calculations the concept of equivalent composition has been used. The results have been improved by reducing the number of elements expressed as equivalents one at a time. IDS shows better results with respect to DICTRA owing to database designed for type-304 steels. DICTRA results become comparable when equivalents are abandoned and using data for all elements in the alloy. As regards the high nitrogen and manganese steel IDS does not provide reliable results because the steel composition is out of the range allowed by the database. In this case, the simulation performed with DICTRA results more reasonable. Convergence problems occur when the content of carbon and sulphur are treated separately without using equivalent compositions.

REFERENCES

[1] Roòsz A., Exner H.E. Acta Metall. Mater. 38, (1990), pp.375-80
[2] Rappaz M., Int. Mater. Rev. 34, (1989), pp.92-123
[3] Thomas P. Battle, Robert D. Pehlke, Metallurgical Transaction B, Vol.21, (1990), pp.357-375
[4] C. Beckermann, Int. Mater. Rev. 47, No.5, (2002), pp.243-261
[5] B. Sundman, B. Jonsson and J-O. Andersson: CALPHAD, 9, (1985), 153.
[6] J.A. Sarreal and G.J.Abbaschian, Metall.Trans. A, 1984, vol.17A, pp.2063-73
[7] A. Schaeffler, Met. Prog., 56 (1949), p.680
[8] T. W. Clyne, W. Kurz, Metall. Trans. A, 1981, vol.26, pp.1045-1051
[9] S. K. Kim, N. J. Kim, K. Shin, C. H. Lee, J. Korea Inst. Met. Mater., 33 (1995), 1144
[10] J. Miettinen, Report TKK-V-B112, Laboratory of Metallurgy, Helsinki, University of Technology, Espoo, (1995), Thermodynamic and diffusion data for modelling of solidification of steels
[11] R.Sanchez, T.Fernàndez, C.Del Campo, J.Botella, R. Gamboa, Proc. Stainless Int. Conf, KCI Publishing BV, 1999
[11] C.J.Long, W.T.De Long, Weld J.Res.Suppl., (1973), 52, 281S-297S
[12] R.H.Espy, Weld J.Res.Suppl., (1982), 61, 149S-156S

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