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Design of a creep resistant iron-base superalloy for Herreshoff furnaces. Part I– Mechanical properties modelling and phase diagram simulation

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Abstract
The furnaces of the Nickel Plant Ernesto Che Guevara have been failing due to the low heat resistance of the alloy material of furnace arms. Neural network models have been applied as tools to create a new iron-base superalloy for Herreshoff furnaces. Thermofluency and creep resistance of the superalloy depending on its composition and processing parameters were modelled by using large databases on existing alloys. Simulations of stage and segregation diagrams were completed to foresee the formation of undesirable stages, calculate solidification levels and determine the practicality of heat treatment application based on the results of simulated stage diagrams. The potential for chemical segregation has also been estimated by applying Scheil's approximation models. These results were used in combination with metallurgical concepts and technological requirements as a basis to obtain a new Fe-Cr-Ni-C-Al superalloy with the desired properties. The strength was determined based on temperature values of up to 800°C for 100 000 h at a stress of 180 MPa. The resulting alloy is much more cost-effective compared to alloys with similar properties available in the market.

Keywords
Segregation simulation, superalloys, creep, mechanical properties modeling

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Diseño de una aleación termorresistente base hierro para hornos Herreshoff. Parte I- Modelación de propiedades mecánicas y simulación del diagrama de fase

Resumen

La baja termorresitencia de la aleación utilizada en los brazos de los hornos de reducción de la planta metalúrgica Ernesto Che Guevara ocasiona fallas prematuras en los mismos. Se utilizaron los modelos de redes neuronales como herramientas para diseñar una nueva superaleación base hierro para los hornos Herreshoff. Las propiedades de tracción y termofluencia de la superaleación en función de su composición y parámetros de procesamiento se modelaron haciendo uso de bases de datos de aleaciones ya existentes. Se simularon los diagramas de fases y de segregación para prever la formación de fases indeseables, calcular el rango de solidificación y predecir la viabilidad de aplicar tratamientos térmicos utilizando los resultados de los diagramas simulados; también se estimó el potencial para la segregación química siguiendo los modelos de aproximación de Scheil's. Estos resultados fueron utilizados, conjuntamente con conceptos metalúrgicos y requerimientos tecnológicos, como base del diseño de una nueva superaleación Fe-Cr-Ni-C-Al con las propiedades deseadas. Se estimó el valor de resistencia a la rotura a la termofluencia hasta a 800º C y 100 000 h a una tensión de 180 Mpa obteniéndose una aleación más económica respecto otras comerciales de propiedades similares.

Palabras clave

Simulación segregante, superaleación, fallas, modelación de propiedades mecánicas.

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INTRODUCTION

Austenitic stainless steels are commonly used in the power generation industry at temperatures greater than 650°C and stresses of 50 MPa or more, and are expected to remain in service for more than 100 000 h. Such time periods are seldom accessible experimentally and long-term properties are often extrapolated from shorter term tests conducted at high stresses. Therefore great care is needed in extrapolating the experimental data during design. A further difficulty in trying to predict the long term properties of austenitic steels is the strong influence of alloying elements and their numerous interactions. This explains why most of the empirical approaches are restricted to limited ranges of compositions (Sourmail et al, 2002).

Because the influence of the composition and processing parameters on the material properties is extremely complex and multivariate, designing an alloy "to measure" is not feasible using experience alone. Modern alloys contain many chemical elements added to achieve particular properties. The influence of individual alloying elements on mechanical properties can be measured and understood in isolated cases; simple interactions between two or three elements can be formulated, but describing all the interactions as a whole is generally impossible (Tancret et al, 2003). For this reason, various modelling techniques have been proposed and implemented to predict the mechanical properties of alloys, microstructural parameters, and high temperature phase stability. They include Gaussian processes, Neural Networks simulations (non-linear multidimensional statistical regression analyses) and phase diagram simulations.

The aim of this paper is to present the results concerning to the use of this tools to design and evaluate a new creep resistant iron-base superalloy for Herreshoff furnaces strengthened by γ' nanoparticles that provide a precipitation strengthening effect. The alloy should possess, as well, the required mechanical

properties and a stable microstructure that avoids the formation of undesirable phases such as σ. Part 1 of this series of papers deals with mechanical properties modelling, phase diagram and segregation simulation. Part 2 will deal with the experimental results.

REVIEW OF LITERATURE

Recent papers (Murugananth et al., 2002; Yescas-Gonzalez & Bhadeshia, 2002; Yescas-Gonzalez, 2003; Tancret et al., 2003; Bhadeshia, 1999; Guo & Sha, 2004; Bhadeshia, 2006 and Mandal et al., 2006) have demonstrated the possibility of using Neural Networks and Gaussian processes to model the properties of complex materials as a function of their composition and/or processing parameters. They perform a non-linear multidimensional regression of an output (a mechanical, physical, or microstructural property) as a function of many inputs (composition, thermomechanical treatments, temperature).

Ideally, the database on which the models are based must contain a large number of measurements, covering a wide range of alloy compositions and test conditions. However, neural networks or Gaussian processes models do not take into account any metallurgical or microstructural knowledge about phase formation and stability (Tancret & Bhadeshia, 2003). Thus, when used to predict the mechanical properties of a novel alloy, those models perform interpolations or limited extrapolations.

Even if the methodology has often proved successful, it may happen that a non-desired phase forms in the novel alloy, which could not be predicted by the mechanical property models, and could be detrimental to the mechanical properties. Also, the occurrence of microsegregation during solidification of a new alloy could have a major influence on its subsequent behaviour.

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For these reasons, use has been made of a phase diagram and microsegregation computer simulation approach in parallel with the neural network modelling of mechanical properties. For this purpose, the thermodynamic simulation softwares MT-DATA (Sourmail et al., 2002) and THERMO-CALC, with a special module to simulate microsegregation during solidification, based on Scheil's approximation (Tancret & Bhadeshia, 2003) have been widely used.

METHODOLOGY / ANALYSIS

Alloy design

The engineering requirements dictate a creep rupture life of 100 000 h at 800 °C under a maximum stress of 180 MPa. Other important design features must be satisfied simultaneously: the UTS to Y ratio should be as high as possible, and in any case in excess of 1.5 at room temperature.

The alloy must be able to cope with CO and CO_2 corrosive environments. An essential purpose of this work was price reduction with respect to existing alloys, which means that expensive elements such as Co, Mo, Ta, Nb, Hf and Re must be avoided. Consequently, the proposed alloy contains the following characteristics:

1. high chromium content, to achieve a good high temperature corrosion resistance;
2. high nickel content, to achieve an homogeneous austenitic that provides good high temperature corrosion resistance;
3. carbon, to precipitate grain boundary carbides, which limit grain boundary sliding;
4. aluminium, to form γ' precipitates that promote precipitation strengthening effect of the γ matrix. Its content must be adjusted to achieve a low γ/γ' lattice misfit but however, be small to ensure that the quantity

of γ' be less than ~25% by volume fraction after heat treatment in order to ensure ductility;

5. a usual commercial alloy level of silicon and manganese as deoxidants.

Ferrochrome, ferronickel and industrial scrap as cheap sources of Cr and Ni were considered to be used as row materials.

Table 1. Chemical composition (wt-%) of the proposed alloy

Cr	Ni	C	Al	Si	Mn	Fe
24	22	0.4	1.0-2.0	1.2	0.8	Bal.

These compositions have then been used as inputs in order to estimate the creep rupture life and the equilibrium compositions of γ and γ' phases at various temperatures. Having fixed the contents of Cr, Ni, C, Si and Mn, predictions were made with varying the amounts of Al. The latter were adjusted to find the necessary compromise between high creep rupture resistance with low γ' volume fraction, a low g/γ' lattice misfit and no undesirable phase formation at the maximum service temperature (800 °C).

The software capable of doing mechanical properties modelling can be obtained freely from http://www.msm.ac.uk./map/map.html. This model calculates the creep rupture life for a given stress and the creep rupture stress for a given life using a neural networks method within a Bayesian framework. The database used to create the model covers a large range of compositions and facilitated quantitative comparisons with the literature. In this case, the target was the stress and the life time until rupture.

Training and test of database

Neural networks represent a more general regression method, which ameliorates most of the problems encountered with linear regression. In the present study, neural network analysis was applied to a database covering a vast range of compositions of

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austenitic stainless steels to estimate the creep rupture life and the creep rupture stress as a function of many parameters. Because of the great flexibility of the functions used in the network, there is a possibility of overfitting data. For avoiding this, the training method was applied. The database was equally divided into a training set and a testing set. Training method involve finding the weights which minimise an objective function to build a model in the hidden units of the neural network. Once the models have been trained, it is necessary, before using them, to make predictions in order to test their validity, i.e. to check that they are able to make correct predictions in cases where the output in known, for example, for the points of the database or where the actual trends are known theoretically or experimentally.

A number of networks are created and trained with different numbers of hidden units and seeds, using the training set; they are then used to make predictions on the unseen testing set and are ranked by the results of the predicted error. When training a model, the choice of input variables is of great importance. Also, when a combination of these variables is believed to be of particular importance, the model can be improved by adding the combination as an explicit variable. The model was trained on the logarithm of the rupture life rather than the rupture life itself.

Phase diagram and segregation simulation

Because undesirable phases may form in this new alloy, a phase diagram and chemical segregation simulation method was used. As part of the recent design, THERMO-CALC Software AB V 2.0 was used for phase diagram and segregation simulation.

The program uses phase diagram calculations to extrapolate thermodynamic descriptions for use in an *n*-component system based on the assessment of binary, ternary, and higher order experimental data. It puts several models to work to minimise the Gibbs free energy of phases in the system, such as the

regular solution model and several extensions based on it, e.γ . the sublattice model. It can be used to predict the phases present as a function of temperature for a vast range of alloy compositions, and thus to check if undesirable phases, e.γ . σ and γ in superalloys, are to be expected or not. The expected equilibrium phases calculated using Thermo-Calc was made over a wide range of temperatures, from the liquid phase down to 500 °C, well below the normal service temperature of 800 °C.

γ / γ' Lattice misfit

The equilibrium compositions of γ and γ' phases at various temperatures have been estimated using the Thermo-Calc phase diagram simulation software. These compositions have then been used as inputs in the γ and γ' lattice parameter neural network models, in order to estimate the g/γ' lattice misfit in the material.

RESULTS AND DISCUSSION

Mechanical properties modelling

The results of the training are shown in Fig. 1 and 2. 118 networks were trained with up to 17 hidden units and 5 different seeds. According to figures 1 and 2, the model used showed its capacity to indicate uncertainty, including both an estimate of the perceived level of noise in the output, and an uncertainty associated with fitting the function in the local region of input space.

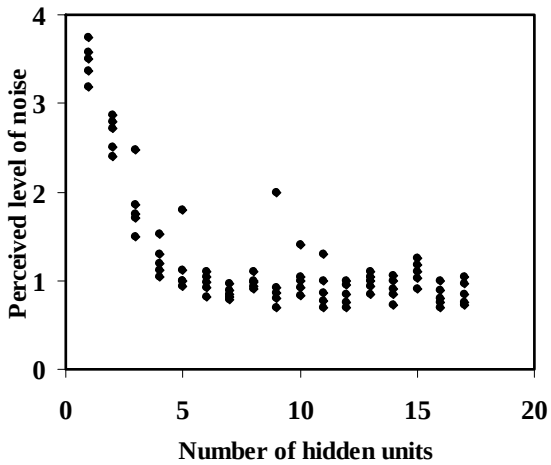

Figure 1. Perceived level of noise during predictions.

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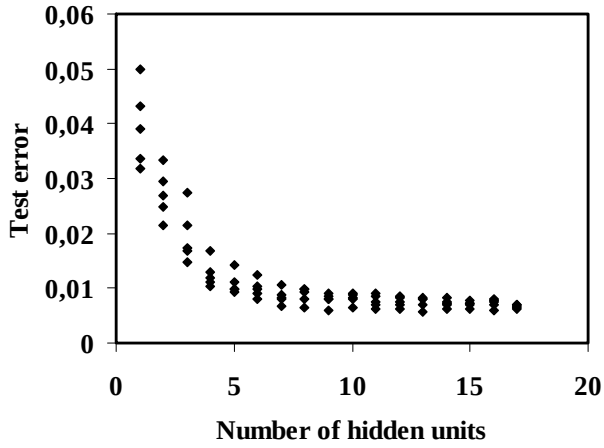

Figure 2. Test error of predictions.

The overall aspect of these graphs is satisfactory, and represents both a necessary step and a good first result. As expected, the perceived level of noise and the test error during training of data set decreased as the model became more complex, which indicates more accuracy of predicted values when the total number of hidden units was increased. The main mechanical properties of the proposed alloy (YS and UTS against the temperature and CRS against the logarithm of the rupture life) estimated using the neural networks models, are presented in Figs 3, 4 and 5.

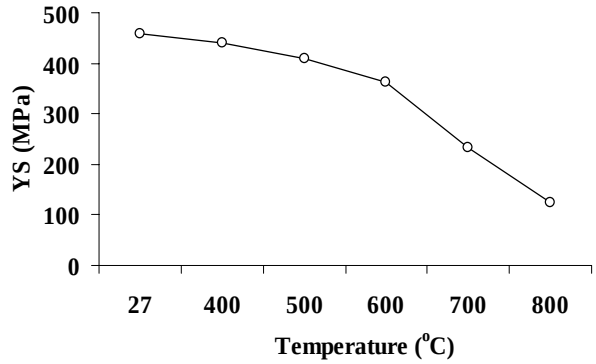

Figure 3. Predicted yield stress.

Predicted trends have been found to be consistent with those expected and the quantitative agreement seems to be satisfied. According with predicted values shown in Figs 3 and 4 this alloy

should have a YS s of about 125 MPa and UTS of 260 MPa at the maximum temperature service (800°C). The predicted UTS/ Y ratio at room temperature is about 1.6, which is consistent with the design criterion.

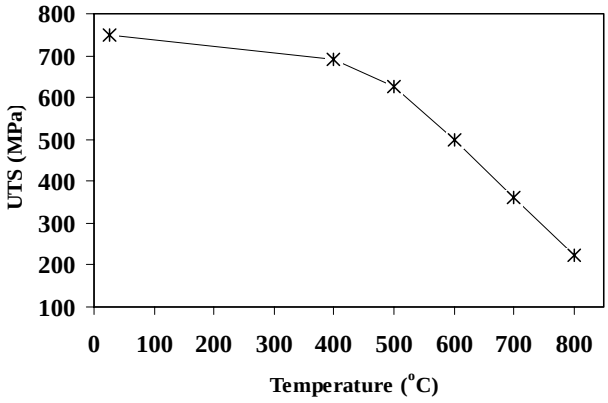

Figure 4. Predicted utimate tensile stress.

The predicted relations between creep rupture stress and lifetime at 500°C, 600°C, 700°C and 800°C are also presented in Fig. 5. The novel alloy should meet the main design target of 180 MPa for 100 000 h at 800°C, and be more creep resistant than the best performing steel presently available (ACI HK40). Predicted values of creep rupture life are 440, 387, 325 and 223 MPa at the respective temperatures of 500°C, 600°C, 700°C and 800°C, which satisfies also the design criterion.

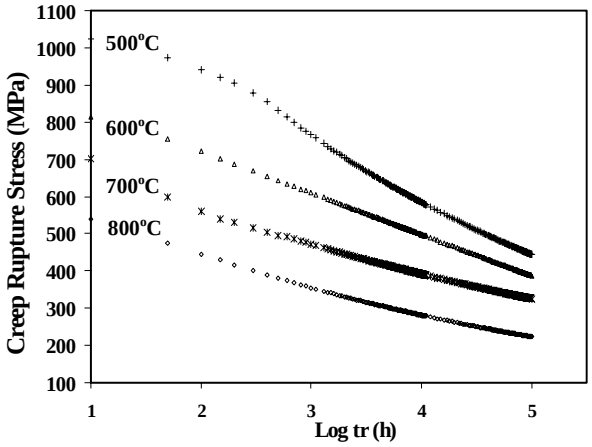

Figure 5. Predicted creep rupture stress.

Phase diagram and segregation simulation

The predictions of the equilibrium phase diagram are reported in Fig. 6 for simulations corresponding to 1.5 Al. This diagram reports the evolution of solid fractions (wt-%) of the prevailing phases: liquid, austenite "γ " and, in minor quantities, ferrite "α", corresponding to the metallic matrix. γ' and M_7C_3 - $M_{23}C_6$ complex carbides are reported to be appeared at higher temperatures in the free-γ' regions, which prevails down to low temperatures.

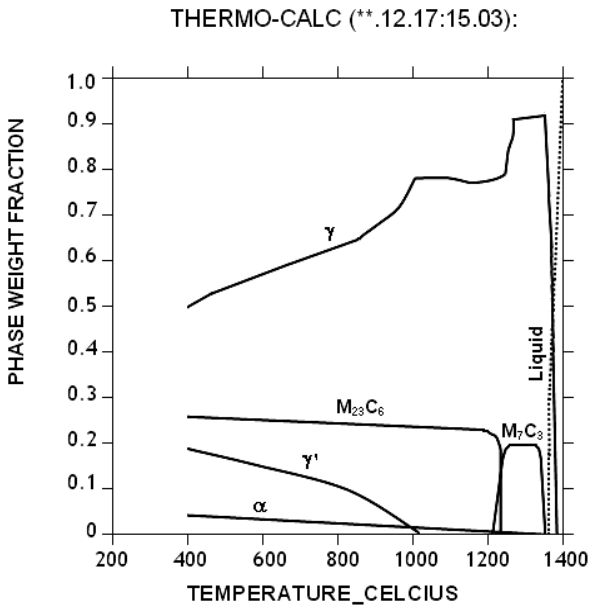

Figure 6. Predicted equilibrium phase formation in designed alloy as a function of temperature.

The presence of the expected γ' particles and M_7C_3 and $M_{23}C_6$ complex carbides is extremely important for the behaviour of the alloy at high temperatures due to the desired precipitation strengthening effect. The calculated liquidus, solidus, and γ' olvus temperatures are 1375°C, 1292°C, and 1021°C, respectively.

This graph also indicates the solution and aging heat treatments ranges, i.e. between 1021°C and 1292°C and below 1021°C, respectively. Finally, the expected γ' fraction at the temperatures of interest (500°C- 800°C)

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is kept in the range of 10-15 wt-%, which also matches the design criterion.

The evolution of solid phase fraction during solidification, studied using Thermo-Calc with both equilibrium data and Scheil's approximation, is presented on Fig. 7 as a function of temperature.

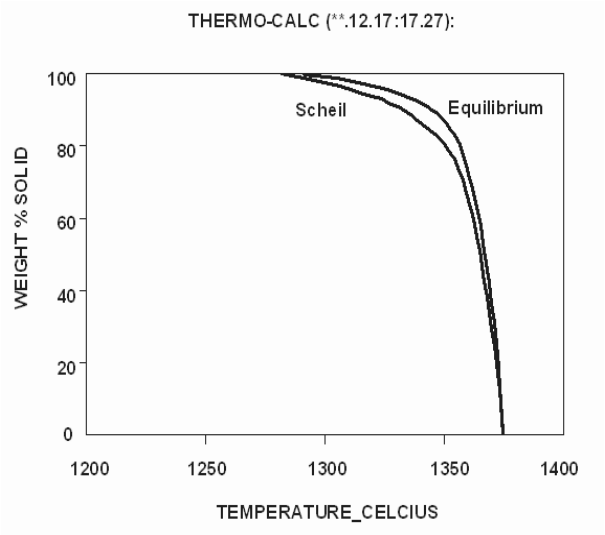

Figure 7. Predicted total solid fraction as a function of temperature during solidification calculated under equilibrium and Scheil's conditions.

Scheil's model assumes a perfectly homogeneous liquid, and that no diffusion occurs within the solid, which may not be true at such high temperatures. Consequently, because back diffusion reduces microsegregation, the actual concentration profile is likely to be between those predicted assuming equilibrium and by the Scheil method. Figures 8, 9, and 10 present the evolution of the concentration of various elements in the liquid as a function of the total solid fraction, normalised with respect to the nominal composition.

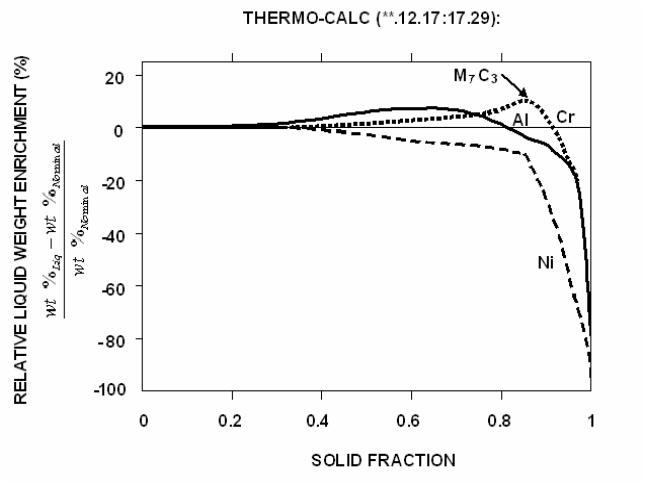

Figure 8. Evolution of Cr, Ni and Al relative concentrations in liquid as solidification progresses, calculated using Scheil's model.

Cr and Ni (Fig. 8) slightly segregate from the liquid until 40 % of solid fraction is reached. Both elements remain within +10% of the nominal composition until 87% of the material is solidified.

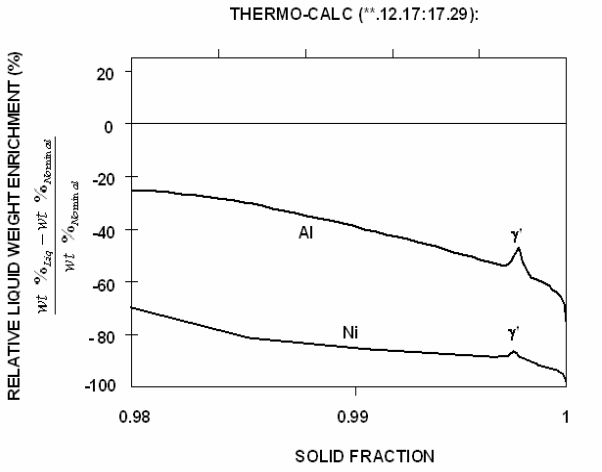

Figure 9. Zoom corresponding to the solidification window for Al and Ni.

Aluminium first slightly segregates in the liquid, and then starts to be removed from the liquid around ~70% solid, as its solubility becomes higher in γ than in the liquid. Then Cr and Ni are removed from the liquid to form M_7C_3 , which will constitute a form of desired segregation, as this carbide is expected in the equilibrium phase diagram of Fig. 6. "M" in M_7C_3 is mainly Cr, with also several per cent of Ni and Fe, varying throughout solidification.

As can be seen in Fig. 9, γ' precipitates from Al and Ni once ~99,75 % solid is reached. Fe (Fig.10) is slightly concentrated in the solid until 96 % of solidification is reached and then the nominal composition is reached.

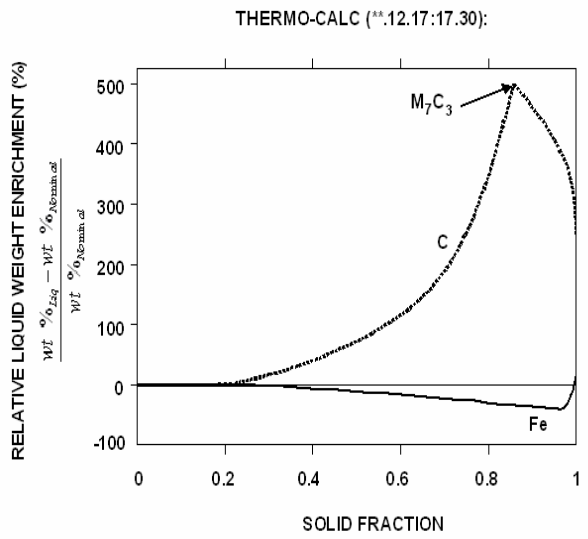

Figure 10. Evolution of Fe and C relative concentrations in liquid as solidification progresses, calcu-lated using Scheil's model.

Carbon does not segregate from the liquid until the formation of M_7C_3 carbides starts to precipitate. Following these concentrations during the solidification simulation allows one to predict which elements will segregate between dendrites; the program also predicts which phases will form as solidification progresses.

As reported from the previous diagrams, other undesirable phases do not form in this new alloy at the service temperature.

γ / γ' Lattice misfit

The predicted evolution of g/γ' lattice misfit with temperature of the proposed alloy with equilibrium compositions are presented in Fig.11.

Predicted lattice mismatch is small (between 0.25 and 0.5) at the service temperatures, which is beneficial to creep

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resistance, since it stabilises the g/γ' interface and prevents γ' growth at elevated temperatures and γ' rafting during creep.

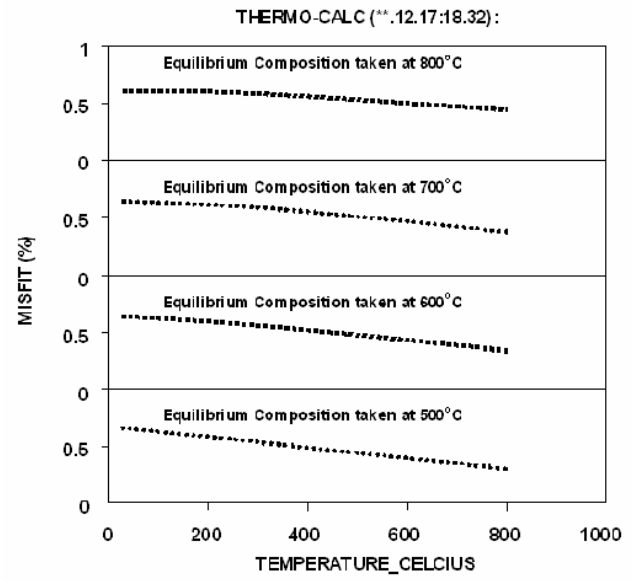

Figure 11. Predicted evolution of γ /_γ' lattice misfit.

CONCLUSIONS

Neural Network models have been used as quantitative tools to design a new and relatively cheap iron-base superalloy for Herreshoff furnaces applications. The main mechanical properties and the g/γ' lattice misfit of the new alloy as functions of its composition and test conditions have been predicted using general models.

The predicted UTS/Y ratio at room temperature is about 1.6 and the predicted values of creep rupture life are 440, 387, 325 and 223 MPa at the respective temperatures of 500°C, 600°C, 700°C and 800°C, which is consistent and satisfies the design criterion. So, the whole set of properties has been achieved using well balanced compositions excluding expensive elements such as Mo, Co, Ta, and Nb, consequently the elemental cost of the designed alloy should be less than some of the cheapest commercial superalloys having significantly poorer mechanical properties.

Phase diagram and chemical segregation simulation method has been used in parallel with the Neural Network modelling of mechanical properties, giving as result that undesirable phases may not form in this new alloy at the service temperature, which suggest the feasibility to produce this new creep resistant iron-base superalloy for Herreshoff furnaces applications, as described in Part 2 of this series.

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