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Design of new creep-resistant nickel-base superalloys for power-plant applications.

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Keywords: nickel-base superalloys, creep, modelling, Gaussian processes.

Abstract: A Gaussian processes computer program has been used to model the mechanical properties of polycrystalline nickel-base superalloys as a function of their chemical composition and heat treatment. The models are able to reproduce well-known metallurgical trends, and to estimate the behaviour of new alloys. On this basis, several new creep-resistant alloys for power plant applications have been proposed. The candidate alloys have been scrutinised further using phase diagram calculations to reveal their equilibrium phase constitutions. This design process has led to a shortlist of alloys on the basis of their expected properties, microstructural stability and cost.

INTRODUCTION

In future, power plant for electricity generation will, for thermodynamic efficiency and ecological reasons, operate with steam temperatures as high as 750 °C. The best steels are currently limited to about 620 °C for such applications and are unlikely to extend in their application to temperatures beyond about 650 °C. On the other hand, many existing polycrystalline nickel-base superalloys of the kind used in the aerospace industry could easily serve the purpose, but they are far too expensive to be used in large scale power plant. The purpose of the present work was to develop novel nickel-base superalloys with good mechanical properties but with greatly reduced cost. The typical design requirements are a creep rupture stress of 100 MPa at 750 °C over 100000 h. To minimise experimental work, we have used a Gaussian processes computer modelling technique [1, 2]. It is an empirical method of representing complex, multidimensional patterns in experimental data in a reliable manner, which is useful in the design of new alloys [3, 4]. This approach has been augmented with phase diagram modelling [5] to help formulate heat treatments and to check the expected long-term microstructure.

MECHANICAL PROPERTY MODELLING ("Tpros" [6])

Modern metallic alloys generally have complex microstructures and may contain a large number of alloying elements. Even if the basic metallurgy is understood, the human brain is unable to explicitly visualise the role of the many interacting variables that contribute to the characteristics of the alloy.

Gaussian processes are statistical tools able to perform, on a database, a multidimensional non-linear regression of an output (in our case a mechanical property) as a function of many different inputs. It can then be used to make predictions on a set of previously unknown inputs. The general theory about Gaussian processes, and examples of their use in metallurgy, can be found in references [1, 2], and [3, 4], respectively. Basically, to make a prediction on a set of inputs, the model calculates the most probable value of the output and its corresponding distribution (through error bars) given the whole data and a set of so-called hyperparameters. These hyperparameters are optimised during the creation of the model, and express the level of noise in the database and the lengthscales on which the output is likely to vary with each input. They allow the definition of smooth-varying models that do not "fit" the noise. The details of the method have been described elsewhere [1 - 4, 6].

The databases we used concerned the yield stress, Y, and the creep rupture stress, CRS, of several tens of different commercial and experimental polycrystalline nickel-base superalloys. Table 1 presents the inputs, as well as the ranges, of the data used.

Input	Range in Y database	Range in CRS database
Cr (wt. %)	5.7 - 30	5.7 - 30
Co (wt. %)	0 - 20	0 - 20.1
Mo (wt. %)	0 - 14.5	0 - 14.5
W (wt. %)	0 - 12	0 - 12
Ta (wt. %)	0 - 9	0 - 9
Nb (wt. %)	0 - 6.5	0 - 6
Al (wt. %)	0 - 6.5	0 - 6.5
Ti (wt. %)	0 - 5	0 - 5
Fe (wt. %)	0 - 57.79	0 - 57.79
Mn (wt. %)	0 - 1.24	0 - 1.25
Si (wt. %)	0 - 2.35	0 - 2.35
C (wt. %)	0.02 - 0.35	0.02 - 0.35
B (wt. %)	0 - 0.16	0 - 0.16
Zr (wt. %)	0 - 0.6	0 - 1
Cu (wt. %)	0 - 0.21	0 - 0.56
N (wt. %)	0 - 0.017	0 - 0.04
S (wt. %)	0 - 0.009	0 - 0.05
P (wt. %)	0 - 0.006	0 - 0.011
V (wt. %)	0 - 1	0 - 1
Forged	0 (no) - 1 (yes)	0 (no) - 1 (yes)
Cold deformed	-	0 (no) - 1 (yes)
t1 (h)	0 - 8	0 - 8
T1 (°C)	0 - 1235	0 - 1235
t2 (h)	0 - 16	0 - 16
T2 (°C)	0 - 1100	0 - 1100
t3 (h)	0 - 50	0 - 50
T3 (°C)	0 - 870	0 - 925
t4 (h)	0 - 24	0 - 24
T4 (°C)	0 - 760	0 - 760
T (°C)	20 - 1093	500 - 1149
log t_r (h)	-	0.6721 - 4.7659
Output	28 - 1310 (Y, MPa)	0.30103 - 3.0149 (log CRS, MPa)

Table 1 : Inputs and outputs ranges in the yield stress and in the creep rupture stress databases.

In Table 1, the heat treatment 1, defined by its duration, t1, and temperature, T1, is the solutionising heat treatment. The heat treatment 2 refers to the new kind of "high temperature" precipitation of coarse cuboidal γ' inclusions (typically around 1000-1100 °C). Heat treatments 3 and 4 refer to a first and second classical "low temperature" γ' precipitation stages (fine and hyperfine inclusions). The inputs "ti" and "Ti" are set to 0 if the heat treatment "i" has not been performed. The cooling conditions following heat treatment have not been included in the analysis because a previous investigation revealed that they are not relevant, largely because they have not been quantitatively reported in the published literature. The yield stress database contained 642 experiments and the creep rupture stress database 1816.

Figure 1 shows that for both the yield stress and the creep rupture stress there is a narrow dispersion of the points around the "x=y" line in the graph reporting the predicted *versus* the measured output for the inputs of the databases. This is a necessary -but not sufficient- indicator of a good model.

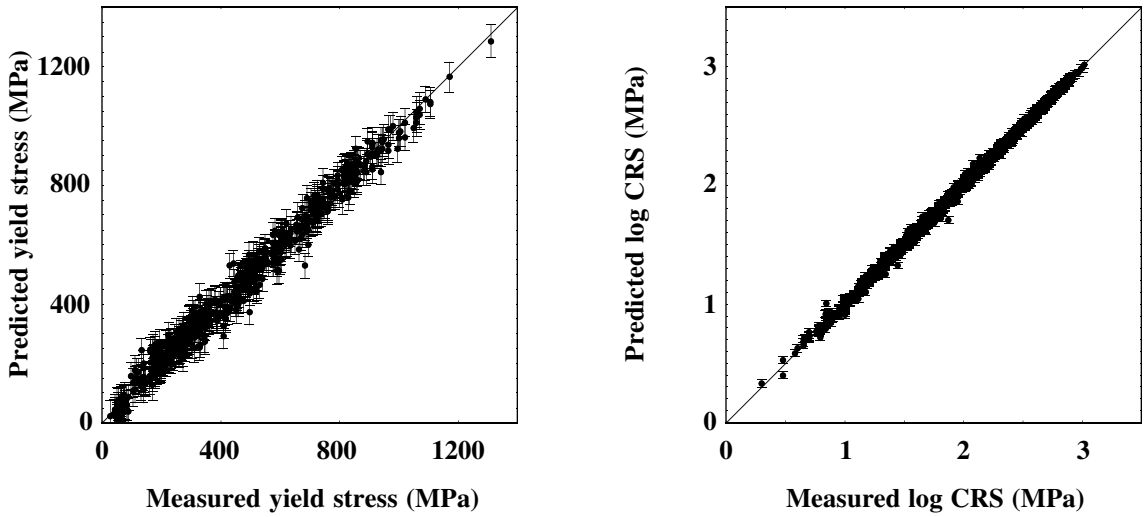

Figure 1: Predicted *versus* measured yield stress and logarithm of creep rupture stress for the inputs of the databases.

The ability of the models to predict and reproduce well-known metallurgical trends in cases *not present* in the databases can be revealing. For this purpose, the predicted influence of solute elements on the mechanical properties has been examined, as illustrated in figure 2.
The 10^5 h creep rupture stress predictions are associated with large error bars because very few measurements of the database exceed 10^4 h. These predictions are consequently extrapolations outside the known domain. Aluminium and titanium strengthen nickel alloys at all temperatures through the precipitation of γ' particles [7, 8]. The larger titanium atom (4% bigger than Al) is found to have a greater effect on the yield strength. This is also consistent with the fact that titanium increases the anti-phase boundary energy of the γ' phase, which makes it more difficult for dislocations to cut into the precipitates [9, 10]. The relative importance of Al and Ti is reversed for the CRS, probably because titanium increases the γ/γ' misfit, which has been reported to be harmful to the creep resistance [11]. However, it is important to note the large error bars associated to the predictions in this domain.

Tungsten partitions in both the γ matrix and the γ' precipitates, and acts as a solid solution strengthener for both phases [12, 13]. It is also known to form carbides that strengthen grain boundaries. It is not surprising that it enhances both the yield stress and the creep rupture stress.

An example where the model is able to predict trends in data that have not been included in its creation are presented on figure 3. The creep model is able to reproduce correctly the experimental data for an Inconel 939 alloy tested at 870 °C (data from [15]). Other trends have been tested (influence of alloying elements, prediction of other published results...), but cannot be all presented here. Most of the expected trends have been confirmed, especially the role of individual solute elements. However, almost all the alloys of the databases are commercial materials for which the heat treatments have already been "optimised". This means that there is a very limited range of heat treatments in the experimental dataset. Thus, the models are not able extrapolate with sufficient certainty to be useful in the study of novel heat treatments. Nevertheless, it has been noticed that including heat treatments as inputs produces better predictions than without them.

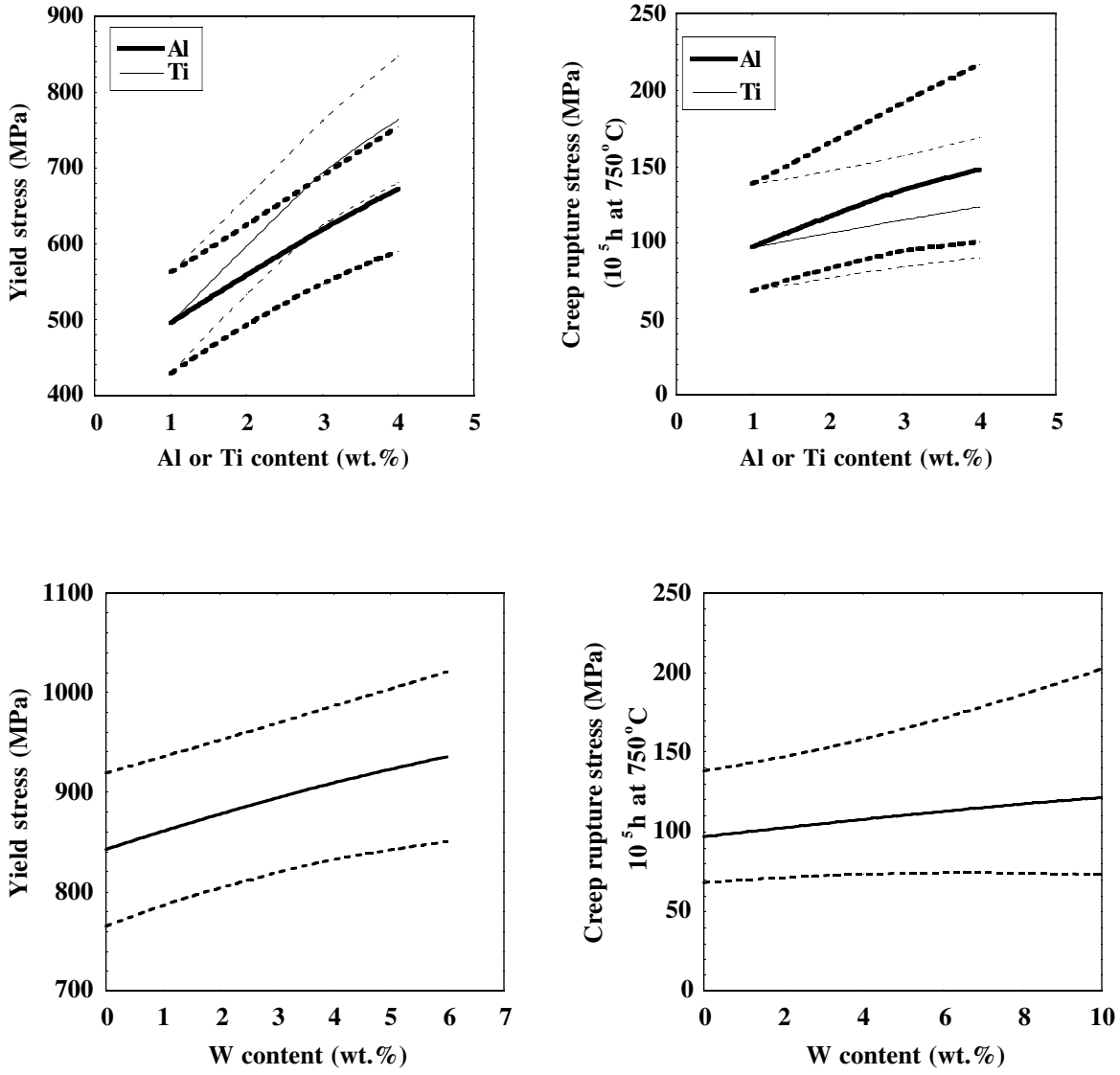

Figure 2: Predicted influence of Al, Ti and W on the room-temperature yield stress and creep rupture stress of a Ni-20Cr-10Co-1Al-1Ti-0.03C wt.% alloy heat-treated 1h at 1175 °C + 8h at 800 °C. Error bounds are indicated by the dotted lines.

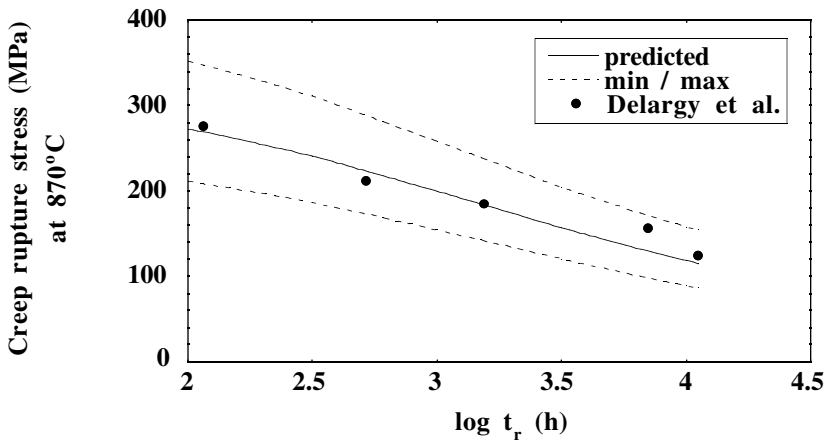

Figure 3: Predicted relation between the creep rupture stress and the lifetime of an Inconel 939 alloy at 870°C. Experimental points from [15].

DESIGN OF NEW ALLOYS

The above models, in combination with a knowledge of physical metallurgy and pricing considerations, have been used to design new creep-resistant nickel-base alloys for power-plant applications. A base alloy containing 15 to 20 wt% Cr is necessary to cope with the corrosive steam atmosphere, cobalt being avoided because of its high price. The main reinforcing elements in nickel-base alloys are Al and Ti (γ' formers)[7, 8], W, Mo, Ta and Nb (γ and γ' strengtheners) [12 - 14]. However, only Al, Ti and W have been chosen, first because of their relatively low price compared to Mo, Ta and Nb, but also because the Gaussian process model didn't infer a positive influence of the latter on the long-term creep rupture stress at 750 °C. Carbon must be included to form carbides which limit grain boundary sliding.
The candidates alloys have been selected on the basis of their predicted mechanical properties, and of their expected microstructure and thermodynamic stability.

1) Mechanical properties

The 750 °C, 10^5 h creep rupture stress of about 2000 alloys with different combinations of Cr, Al, Ti, W and C contents has been predicted. Selection has been made on successive criteria: a predicted minimum CRS above the design requirement of 100 MPa, an error bar smaller than 100 MPa and a relative error bar smaller than 35%. Amongst the remaining alloys, only the ones with the highest CRS/price ratio have been kept, the "price" estimation being based on a list of the relative cost of industrially used raw elements provided by INCO Alloys Ltd..
The predicted relation between the creep rupture stress at 750 °C and the lifetime of one of these alloys* is presented in figure 4.

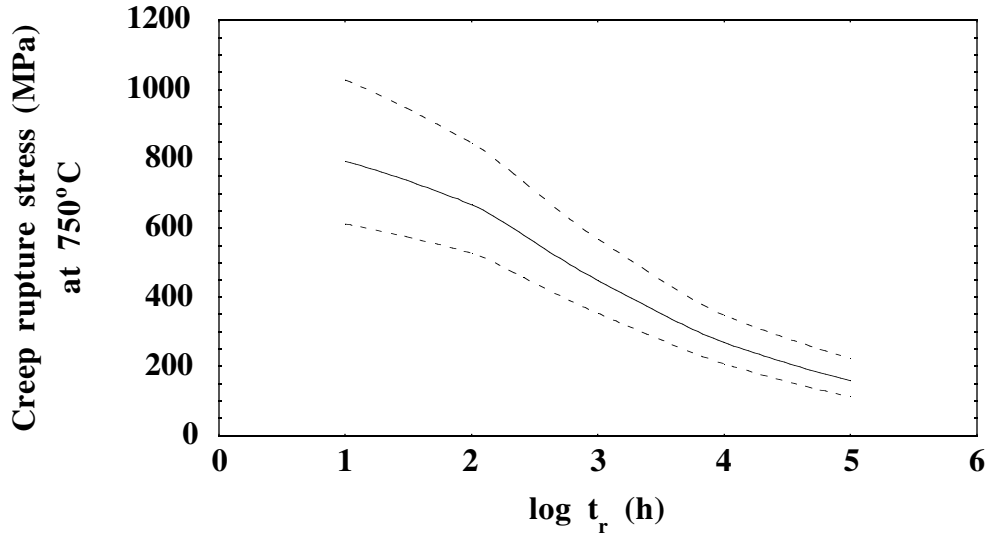

Figure 4: Predicted stress-lifetime relation for one of the candidate alloys at 750 °C.

The evolution of the yield stress of this alloy with temperature has also been predicted, and is presented in figure 5. The shape of this curve is typical of a γ'-strengthened γ matrix. The peak

* This work being part of an industrial project, the exact compositions of the candidate alloys are confidential.

effect results from the competition between the increasing strength of the γ' inclusions up to about 900 °C [16] and the softening of the γ matrix with increasing temperature.

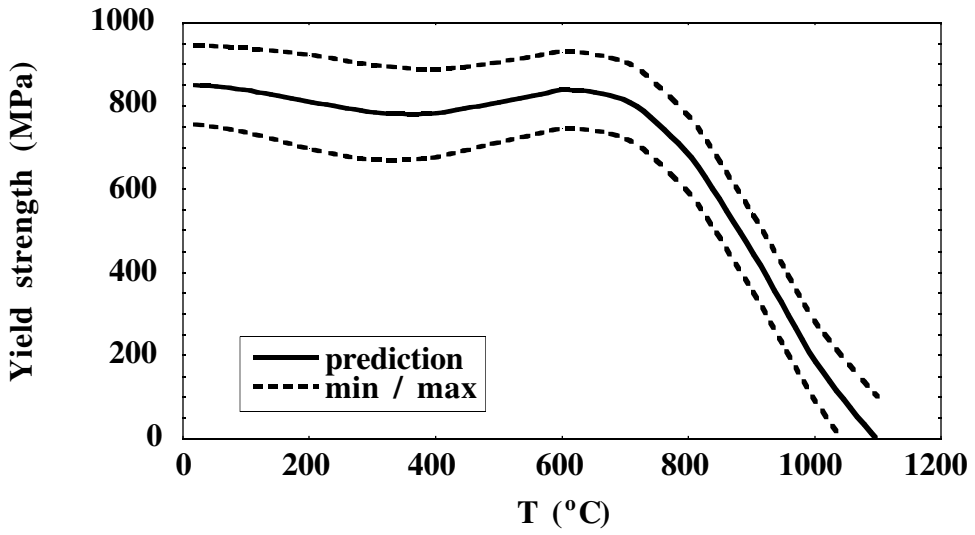

Figure 5: Predicted yield strength of one of the selected alloys as a function of temperature.

2) Thermodynamic simulation ("Thermocalc" [5])

Figure 5 shows the calculated relative amounts of all the phases expected in the temperature range 750 - 1400 °C, for the previously selected alloy (Ni-Cr-W-Al-Ti-C). It can be noted that only γ, γ' and $M_{23}C_6$ carbides are expected at service temperature (750 °C). In particular, no σ, μ, η nor Laves phases, which can be harmful to the creep resistance, are expected.
This graph also gives useful information for the processing of this alloy: it should be melted above 1360 °C, solidified in the range 1360 - 1330 °C, and forged in the range 1330 - 1070 °C, in the γ'-free region, to avoid cracking and a too high flow stress. Then, heat treatment could consist of a solutionising above 1070 °C, and of one or two γ' precipitation ageings below 1070 °C.

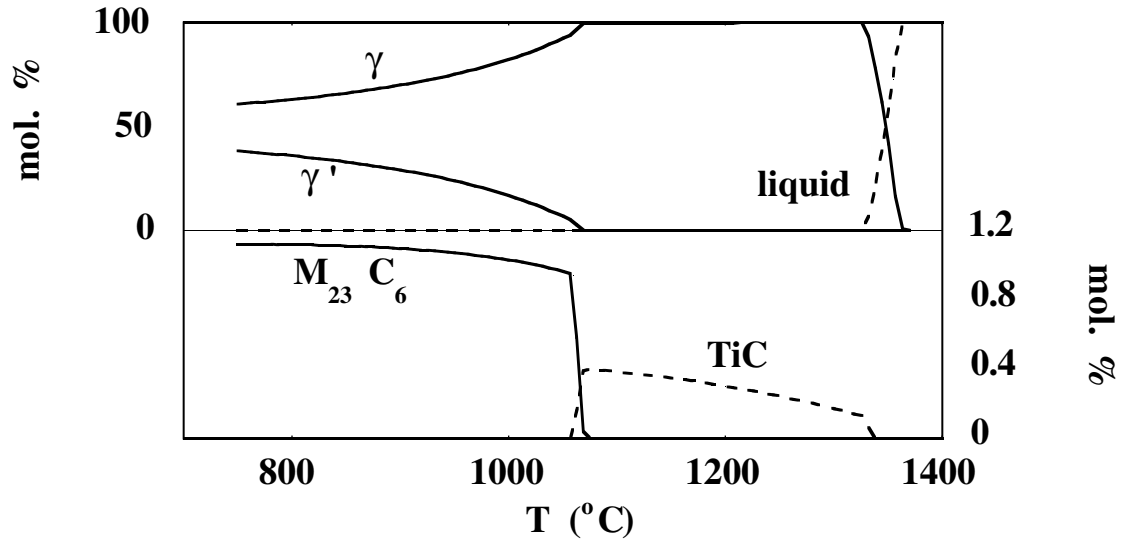

Figure 5: Calculated relative amounts of the phases expected in the selected alloy in the range 750 - 1400 °C.

CONCLUSIONS

A Gaussian processes computer modelling technique has been used to predict the yield strength and the creep rupture stress of novel nickel-base superalloys for high-temperature power-plant applications. A number of candidate alloys have been selected on the basis of their expected mechanical properties, and of their equilibrium phase diagrams at high temperatures. Promising results have been obtained.

However, further modelling is necessary, and the composition of the alloys should be refined, taking into account both metallurgical concepts and industrial requirements. For example, the alloys should not contain too much Al and Ti, since they are likely to increase the flow stress through γ' precipitation, and consequently to reduce the high temperature formability. Small amounts of boron and silicon should be added to ensure a good grain boundary quality and weldability, respectively. Finally, it will be necessary to predict the influence of other elements on both the mechanical properties and the phase equilibria, such as impurities (P, S...), or elements (Fe) whose presence can be due to the use of industrial scrap instead of pure raw materials.

ACKNOWLEDGMENTS

We are grateful to the Engineering and Physical Sciences Research Council for funding this work, and to Alstom Energy Ltd., British Steel plc., INCO Alloys Ltd., Mitsui Babcock Energy Ltd., Rolls-Royce Allen Steam Turines and the University of Wales, Swansea for partnership. The authors thank Dr Roger Reed for access to the Rolls-Royce UTC thermodynamic database on nickel-base superalloys. It is a pleasure to acknowledge all the help and support provided by Professor Colin Humphreys in the Technology Foresight Programme.

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