Thermodynamic modelling of a 6w/o Al P/M processed Ni base superalloy

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Abstract

A thermodynamic java based software package (JMatPro) was used to predict the powder metallurgy (P/M) processing of a superalloy based on the composition of IN600. The effects of adding 6w/o Al to the alloy on sintering time and temperature were estimated and compared with results obtained experimentally from a combination of X-ray diffraction and metallography. Phases predicted by the modelling compared favourably with microstructural observations and phase identification of the P/M processed alloy in terms of prediction/microstructural observation of austenite, gamma prime and chromium rich carbides. Furthermore, both microstructural predictions for the alloy after solution treatment and hardness values generated were in agreement with metallographic observations and hardness measurements respectively. These results suggest that the software and predictions used in this study offer a reasonable way to simulate the characterisation of P/M processed nickel-based superalloys.

Keywords: superalloy, powder metallurgy, thermodynamic modelling, morphology.

1 Introduction

Superalloys are high temperature and high strength alloys. Among the large number of superalloys available is Inconel 600 which is a NiCrFe alloy. Some advantages of this alloy include: good mechanical properties at elevated temperatures, good workability and reasonable weldability. Because of these
advantages, this alloy has found usage in both cryogenic and elevated temperature environments, examples of which include: furnace components, chemical and food processing materials and nuclear applications [1].

The ternary NiCrFe alloy is strengthened via a solid solution mechanism and on addition of an element such as Al can also benefit from precipitation hardening [2]. This strengthening can be achieved through various fabrication techniques including processing through powder metallurgy (P/M).

Whereas it is important to determine the phase(s) present in an alloy, a prediction of alloy microstructure using modelling tools has to date been quite difficult [3], perhaps because of the chemically dynamic nature of superalloys and the inherent complexity of a P/M process. However a new Java-based material processing software, JMatPro, has recently been developed by Sente Software™ to address some of these modelling shortcomings [3, 4]. In the present study this thermodynamic modelling tool has been used to characterise the microstructure of the ternary alloy, with and without addition of 6w/o Al. Also, the results from the simulation are compared to similar alloys produced experimentally using P/M techniques previously developed by the authors.

2 Experimental

The powder used was a prealloyed NiCrFe alloy (particle size 45µm), fabricated by inert gas atomisation [5]. The optimum P/M processing parameters have been reported previously [6]. Briefly, the process involves compacting prealloyed NiCrFe alloy powders and adding 0.75w/o lubricant (microwax). Sintering regime included delubrication at 400ºC for 0.5h, heating to 1300ºC (10K/min.), holding for 2h at 1300ºC followed by furnace cooling, all under a vacuum of 6 millitorr. To enhance precipitation hardening via formation of intermetallics such as gamma prime, up to 12w/o Al (average particle size ~ 10µm) was added to the prealloyed alloy and subsequently sintered at the optimised conditions.

Samples were prepared for characterisation following standard metallographic techniques (samples ground through 1200µm SiC and polished through 0.1µm diamond). Etching was carried out electrolytically using 5V for 10s in a solution of 12ml H3PO4 + 40ml HNO3 + 48mlH2SO4. Microstructure was observed using a JEOL (JSM5900LV) scanning electron microscope (SEM) with EDS capability whereas the phase(s) present were identified using a Rikagu XRD with Cu, Kα radiation, a wavelength of λ = 1.54056nm, current of 40mA and voltage of 44kV. Vickers hardness and image analysis were used to measure the mechanical response (10kgf, 5s, average of 9 indentations) and to estimate the amount of pertinent phases present, respectively.

3 Results and discussion

Representative micrographs for the ternary alloy and the alloy with up to 12w/o Al addition are given in Figure 1(a)–(d). Because the 6w/o Al modified ternary alloy gave a reasonably high quantity of a second phase (determined to be Ni3Al-γ’) in the as-sintered compact and because 5 to 6w/o Al is traditionally added for oxidation resistance, this composition was selected for subsequent study.
Figure 1:  (a): SEM-BE image of the ternary NiCrFe alloy showing porosity and the ternary solid solution. (b): SEM-BE image of the 3w/o Al modified ternary NiCrFe alloy showing porosity and the solid solution. (c): SEM-SE image of the 6w/o Al modified ternary NiCrFe alloy showing porosity, primary and secondary gamma prime. (d): SEM-BE image of the 12w/o Al modified ternary NiCrFe alloy showing the presence of gamma prime and the ternary NiCrFe alloy rich in Al.
An equilibrium phase step calculation for the alloy (Ni - Cr: 11.3, Fe: 8.5: C: 0.045 [wax residual], Al: 6, all in w/o) is shown in Figure 2. Briefly, the phase identification was based on determination of the minimum free energy of the calculation based on CALPHAD analysis [3, 4] and simplified into eqn (1):

\[
\Delta G = \Delta G^0 + \Delta G_{mix}^{\text{ideal}} + \Delta G_{mix}^{\text{xs}}
\]  

(1)

where \( \Delta G \) = Gibbs free energy, \( \Delta G^0 \) is the Gibbs free energy due to contributions from pure components, \( \Delta G_{mix}^{\text{ideal}} \) is the ideal mixing term, and \( \Delta G_{mix}^{\text{xs}} \) is the excess free energy of mixing (J.mol\(^{-1}\)).
From Figure 2, five main phases were predicted to be present. These are gamma, gamma prime, M\textsubscript{7}C\textsubscript{3}, M\textsubscript{23}C\textsubscript{6} and liquid. Because their presence was based on equilibrium conditions without regarding kinetic considerations, not all phases may be present in the experimental samples. For example, gamma and gamma prime should predominate as temperature is increased from room temperature to the melting point (approximately 1425\textdegree C) whereas the carbides may be difficult to detect on the SEM if they are finely distributed. However, it should be noted that the presence of carbides in superalloys acts to reduce grain boundary sliding and therefore should enhance the creep resistance of the alloy.

\textit{Figure 2:} JMatPro step calculation for the 6w/o Al modified ternary NiCrFe alloy.

The continuous cooling transformation (CCT) curves were derived from the Johnson Mehl Avrami Kolmogorov model for various temperatures and times based on nucleation and growth principles. For nuclei that reach the critical nucleus, the model gives the following relationship [7].

\[
f(t) = 1 - \exp\left( -\frac{\gamma_0}{t^4} \right) NG^3 t^4
\]  

(2)

where \( t \) is the time for the fraction of phase(s)/or materials transformed (in seconds), \( f(t) \) is the fraction transformed in the time \( t \), \( N \) is the nucleation rate (number of nuclei/cm\textsuperscript{3}/seconds), \( G \) is the growth rate (cm/seconds). This was the basis for Figure 3.
Figure 3: JMatPro CCT simulation for the 6w/o Al modified NiCrFe ternary alloy.

Figure 3 shows the cooling regime superimposed onto the sintering profile. Whereas Figure 2 represents all the phases that are thermodynamically feasible, Figure 3 shows the JMatPro CCT simulation indicating the presence of the matrix gamma phase, and also the 20, 25 and 30% transformation curves for the gamma prime. From the curves it may be seen that the cooling profile after sintering at 1300°C for 2h cuts across the gamma prime transformation after 25% transformation but before 30% transformation. This suggests that if the alloy is fabricated in the as-sintered condition, the amount of gamma prime present in the compact should be in the range 25-30%.

To verify the simulation, compacts were fabricated with the optimum 6w/o Al and sintered at 1300°C. EDS analysis confirmed the presence of gamma prime in the compact. From the SEM micrograph, Figure 4, two main types of gamma prime precipitates were noticed. The first type is fine, well-distributed gamma prime phase (A), whereas the other is the gamma prime phase formed along the grain boundary, being larger and identified as (B). When cooling from 1300°C, gamma prime precipitates are initiated with preferential formation at the grain boundaries; as cooling continues, the grain boundary gamma prime grows as in (B) of Figure 4. The finer gamma prime precipitates are formed as a result of nucleation and growth at relatively lower temperatures being similar to the morphology previously reported by Johnson, and Donachie Jr. [8].
Figure 4: SEI-SEM image of the as sintered 6w/o Al modified NiCrFe ternary alloy, showing fine (A) and coarse (B) gamma prime precipitates.

Image analysis showed that the amount of gamma prime in Figure 4 is estimated to be 62±5%. It is suggested that the difference is related to the numerous micrograin boundaries present as a result of the powder fabrication route used. These tend to encourage nucleation of precipitates and therefore may lead to higher levels of gamma prime than might be expected for a similar alloy produced through ingot metallurgy.

X-ray diffraction (XRD) analysis was carried out on the as-sintered compact to identify all phases present, to estimate their lattice parameters and to also determine any lattice mismatch present between the gamma prime and gamma phase. Figure 5 shows an XRD spectrum for an as-sintered compact. Referring to the figure it is evident that the two main phases predicted by JMatPro, namely gamma and gamma prime, are present. In particular, (100) and (110) are specific to gamma prime whereas the remaining peaks are as a result of superimposition of both gamma prime and gamma phase. Using the Bravais lattice \( (h^2 + k^2 + l^2) \) sequential method [9] for FCC and Bragg’s law, the lattice parameter of gamma prime was calculated to be \( 3.5634 \pm 0.0005 \) \( \text{Å} \), whereas that of the gamma phase was estimate to be \( 3.5565 \pm 0.0005 \) \( \text{Å} \).

Using eqn (3) [10] the lattice parameter mismatch, \( \delta \), may be written as:

\[
\delta = \frac{2(a_\gamma' - a_\gamma)}{(a_\gamma' + a_\gamma)}
\]
where $a_\gamma$ is the lattice parameter for the gamma prime phase and $a_\gamma$ is the lattice parameter for the gamma phase, the lattice parameter mismatch, $\delta$, which can be used as an indication of strength (resistance to dislocation movement), was estimated to be 0.0019. According to Decker [11], a lattice mismatch as much as 0.8% could double the peak-aged hardness of some materials. Although this amount of lattice mismatch was not achieved in this study, it should still be noted that the effect of coherency strains introduced into the crystal structure due to the formation of gamma prime would enhance the strength of the sintered compact.

Figure 5: XRD spectrum for the 6w/o Al modified NiCrFe ternary alloy.

Vickers hardness values for the 6w/o Al modified NiCrFe alloy were 183±5 as measured and 192 as predicted from JMatPro. Although the predicted value was slightly higher than experimental it is within experimental error; also, a slightly lower value would be expected for the experimental samples due to the presence of minor residual porosity.

4 Conclusions

From the results, the following conclusions may be drawn:

1. Despite various problems reported in P/M processing for a typical superalloy, some of which include porosity and prior particle boundaries,
the experimental methodology used provides a sample compact with a microstructure that should be comparable to a wrought product.

(2) The main phases expected from thermodynamic calculations using JMatPro, $\gamma$ and $\gamma'\) were successfully predicted and their presence confirmed experimentally.

(3) Predicted hardness values were in reasonable agreement with experiment.

(4) The software may be used as a guide to design and model this alloy system.

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References


