EXAFS studies of nickel superalloys

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Abstract. Seven Ni-superalloy foils have been studied using EXAFS together with X-ray diffraction and electron microprobe fluorescence mapping. The usefulness of EXAFS in characterising changes during heat treatment and in differences in the host phase of minor elements has been demonstrated, in addition to the ability of multiple-scattering RMC simulations to give reliable and accurate information on local lattice distortions in these alloys.

1. Introduction

Nickel superalloys are widely used in applications such as jet engine components due to their exceptional strength, creep-resistance and corrosion tolerance at temperatures approaching their melting point [1]. Modern alloys may have eleven or more intensional components in addition to impurities. They may contain several crystallographic phases either by design or through ageing. Early alloys such as Inconel 600 and Hastelloy C276 utilised solid-solution strengthening to achieve the desired properties but precipitation strengthened alloys are important today. These typically have a precipitate of an ordered phase containing a more covalent metal (Al,Ti,Nb) and Ni, (γ' or γ'' phase), which is coherent in one crystallographic plane with the disordered FCC austentite or γ phase. The structure and composition of these phases are presented in table 1 [2]. (Ni' implies low level substitution of other transition metals). Characterisation of the alloys is difficult, because coherency implies extensive diffraction peak overlap and strain, and phase composition may vary within individual crystals. Electron microscopy is often used in addition to X-ray diffraction, but these techniques cannot easily resolve detailed atomic level properties, such as clustering or partial ordering of atoms, and local distortions of the lattice associated with the various components of the solid solutions. For these reasons, we have embarked upon a feasibility study to determine the potential of EXAFS in evaluating these alloys. In addition to fluorescence EXAFS we have used X-ray powder diffraction (XRD) and electron microprobe X-ray fluorescence mapping. A distinct advantage of our method over electron microscopy is that it requires no significant specimen preparation and will work with unpolished foils, sheets or blocks of metal.

2. Experimental

Seven alloy foils (0.025-0.25 mm) representing 5 compositions (table 2). were purchased from Goodfellow.

2.1. X-ray diffraction
Patterns were recorded at room temperature (RT) with 22hr scans on a Siemens D5000 using Cu Kα₁ radiation. Data were analysed using the combined EXAFS/diffraction program P [3]. Strong preferred orientations were observed which required the use of arbitrary scaling factors for different crystallographic zones in order to extract cell parameters.

**Table 1.** The structure of major phases found in the Ni superalloys discussed here

| Phase | Site | Coordinates | Space Group | Strukturbericht Symbol | Type | Typical cell parameters | Characteristic 2θ values |
|-------|------|-------------|-------------|-------------------------|------|-------------------------|--------------------------|
| γ     | (NiCrFeMoW) | 0,0,0       | Fm-3m       | A₄₁        | Cu  | a=3.58 | 44*,51,75,91,96     |
| γ'    | Ni₃   | 1/2,1/2,0   | Pm-3m       | L₁₂        | AlCu₃| a=3.59 | 25,35,44*,51,57,64,75,80,86,91,96 |
| γ''   | Nb    | 0,0,1/2     | 1/2,0,1/4   | 0,0       | Al/Ti| a=3.61 | 28,43*,44,49,51,59,62,68,69,74,74,81, w,87,89,90,91w,94 |
| δ     | Ni₃   | 0,1/2,1/3   | 1/4,0,1/6   | 0,0,2/3   | Cu/Ti| a=5.11 | 26,28,34,40,41,43,45,46*,49,51,...60,73,80,84,88,93,97,99 |
| MC    | Nb    | 0,0,0       | Fm-3m       | B₁        | NaCl| a=4.47 | 35,40,58,70*,73,87,97 |

**Table 2.** Sample compositions in atomic%. Inc=Inconel, Has=Hastelloy. h=hard, a=annealed

| Name  | C   | Al  | Si  | P+S | Ti  | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Nb  | Mo  | Ta  | W   |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Inc 600h,a | .72 | 1.03 | .03 | .52 | .52 | .82 | .69 | .70 | .75 | .49 | .92 | .60 | .62 | .11 | .53 |
| Has c276h,a | .78 | .02 | .04 | 19.21 | .01 | 6.71 | .01 | 60.62 | 11.06 | 1.53 |
| Inc 625a | .48 | .54 | .04 | .30 | 24.54 | .01 | 5.19 | .01 | 60.28 | 1.97 | 5.44 | .16 |
| Inc 718a | .19 | 1.07 | .37 | .01 | 1.09 | .19 | 19.15 | .01 | 51.70 | .14 | 3.11 | 1.81 | .04 |
| Inc X750a | .19 | 1.46 | .50 | .01 | 2.93 | 16.74 | .51 | 7.04 | .01 | 69.84 | .22 | 0.54 | .02 |

2.2. Electron microprobe fluorescence mapping
Raster scans for eight elements over 512x512 microns were obtained from unpolished foils using a Cameca SX100 probe (15keV, 100nA beam current). These revealed relative element concentrations in terms of a colour scale and therefore element correlations which indicated the phase chemistry. (example, figure 1).

**Figure 1.** Photomicrograph of Inconel 718 foil (left) and 512x512 μm Nb Lα fluorescence map (right). High intensity areas to the top left are NbC surrounded by γ'' phase, within a γ matrix.
2.3. EXAFS
Fluorescence EXAFS spectra were obtained from the SRS for the Cr, Fe, Ni, and Mo K-edges, and W L3-edges, at 80+/−3K, for all relevant samples. RT scans were obtained for Inconel 600 and 625. Mo K-edge transmission EXAFS of 0.025mm foils were used to verify the self-absorption corrections, which could increase EXAFS amplitude by up to 100% close to an absorption edge [4]. Background subtraction and absorption correction used the authors program XMULT. Data were analysed using P both by fitting shells of atoms and by the previously described multiple scattering (MS) RMC method [5] using 864 atom clusters. The 80K EXAFS data was used because of the improved signal to noise, but this prevented simultaneous fitting of XRD data. Thus the cell parameters as well as the overall amplitude factors AFAC were rescaled slightly during simulations. Because multiple scattering is only treated approximately during simulations, the final results were obtained by a full MS EXAFS calculation within 6Å of every atom in the cluster. At this point, the effect of changing the energy zeros EF could be noted. Changes to EF required re-calculation of the tables used in the simulations.

3. Results and Conclusions

3.1. Inconel 600
The powder patterns reveal a pronounced broadening to the low 2θ side of all peaks in the hardened foil compared to the annealed (figure 2). By contrast there is almost no difference between the two sets of EXAFS data. This shows that heat treatment involves removal of strain and dislocations without substantial atomic rearrangement.

![Figure 2. 220 and 311 peaks of hardened and annealed Inconel 600 (left) and non-phaseshifted Fourier transforms of EXAFS spectra of the same samples (right)](image)

The 80K EXAFS data could be adequately modelled by a randomly occupied lattice (figure 3). The mean Ni-X distance was 2.5117, slightly greater than the inter-site distance of 2.5073 (which does not include the effects of motion normal to the lattice vector). Cr-X and Fe-X distances were 2.5024 and 2.5064 respectively. These represent an effective size difference compared to Ni of less than 1%, much less than the values of 5% and 6% respectively quoted by Reed [1] for FCC solid solutions. The overall lattice parameter of 3.5458 is however larger than that of Ni metal, which is 3.5132 after correcting for thermal expansion. The 2nd cumulants are 0.0058 for Ni-X, 0.0038 for Cr-X and 0.0041 for Fe-X, with Ni-X having the highest 3rd and 4th cumulants. This suggests a model in which minor components can adopt a more ideal site with strain taken up by the major component. Shell refinements actually gave Fe-X and Cr-X distances longer than Ni-X. This illustrates the danger of approximating a complex distribution by a single Gaussian shell, and shows the importance of using a valid structural model for the EXAFS data.
3.2. Hastelloy C276
This also showed marked changes in the diffraction between hardened and annealed samples but with few significant differences in the EXAFS. The structure was modelled using a five component MS RMC simulation. The results are currently not quite as good as for the Inconel 600 and the possibility of Cr clustering is being investigated. As expected Mo and W show much greater distortion of the lattice than Cr, Fe and Ni.

3.3. Inconel 625, 718 and X750 (annealed)
Inconel 625 has a single set of diffraction peaks, but microprobe results showed that $\gamma'$ was present in thin streaks. X750 was similar, but with an obvious shoulder to the main $\gamma$ peaks. Inconel 718 was much more complex with NbC and $\gamma''$ and possibly $\delta[6]$. This was revealed in the reduced long range order in the Nb K-edge EXAFS, showing it to be a useful indicator of the ordered phase in the sample.

We conclude that EXAFS is a useful tool in the evaluation of Ni superalloy structures, and in particular that the MS RMC method can lead to an essentially complete description of single phase alloys. Future work will address the more difficult problem of modelling two-phase systems.

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