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Time-resolved synchrotron diffractometry of phase transformations in high strength nickel-based superalloys

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Abstract—Phase transformations in prototype high strength polycrystalline nickel-based superalloys of varying Ti/Nb ratio are studied using time-resolved, high resolution X-ray synchrotron diffractometry. The dissolution kinetics of the ordered phase Ni_3(Al, Ti, Nb, Ta) upon heating to the solutioning temperature of ~1200 °C and its reprecipitation on cooling are deduced; effects of varying Nb and Ti alloy composition on the reaction kinetics are identified. Heating to 800 °C does not alter substantially the fraction of the strengthening phase Ni_3(Al, Ti, Nb, Ta) but further heating causes its rapid dissolution. At higher temperatures, evidence is provided for the formation of further ordered phases; Ni_3(Ti, Ta) is proposed and possibly $Ni_{0.45}Ta_{0.55}$; cooling causes their dissolution and reprecipitation of Ni_3(Al, Ti, Nb, Ta), so that it seems probable that the reactions are coupled. The unforeseen high temperature precipitation of further ordering by phases other than Ni_3(Al, Ti, Nb, Ta) implies the possibility of a contribution by them to the high temperature mechanical behaviour of these materials, which until now has been thought to be solely due to Ni_3(Al, Ti, Nb, Ta). The MC carbide, probably TiC, is stable even at the solution heat treatment temperature; no evidence of reactions involving other carbides such as $M_{23}C_6$ is found.

Keywords: Synchrotron radiation; X-ray diffraction (XRD); Ni-based superalloys; Lattice misfit; Alloy compositions

1. Introduction

Engineering alloys – for example those based upon Al, Fe, Ni and Ti – rely upon a phase transition to confer optimised properties. For the nickel-based superalloys one uses an ordering reaction involving long-range diffusion to transform the γ matrix phase to precipitates of compound Ni_3(Al, Ti, Nb, Ta), denoted as γ', with an $L1_2$ crystal structure. Dislocations cannot enter the precipitates easily; planar defects such as anti-phase boundaries and complex stacking faults of high energy arise if they do, resulting in considerable strengthening. This is the primary source of the excellent high temperature performance of these alloys [1].

The size, distribution and morphology of these γ' precipitates must be carefully controlled during processing heat treatments to optimise the mechanical performance of the nickel-based superalloy. To ensure this carefully tailored microstructure does not change when it is subjected to elevated temperatures in service, the lattice misfit between the γ and γ' phases must be minimised to retain interfacial coherency. The addition of refractory elements, primarily added to confer high temperature strength, heavily influences the lattice parameters of the γ or γ' phases which they partition to [2,3], directly affecting lattice misfit. This sensitivity of element partitioning to each phase is further influenced by processing heat treatments, and in particular, cooling rates from above the γ' solvus temperature [4,5]. Whilst it is clear that the optimal alloy performance is dependent on alloy composition and the conditions of thermo-mechanical processing, the kinetics of the $\gamma \rightarrow \gamma + \gamma'$ transformation have yet to be quantified in a meaningful manner. For example, time-dependent-transformation (TTT) or continuous cooling transformation (CCT) diagrams are not widely available, as they are for low alloy steels. Possibly this is because the transformation is rapid, with rather limited possibilities to quench-in partially-transformed configurations for study using analytical methods such as electron microscopy [6].

Using a classical approach to the nucleation and growth of precipitates [7], one may argue that with sufficient undercooling of the supersaturated γ matrix, nucleation of γ' precipitates will occur. These will grow at a rate depending on the time-dependent diffusion fields in the vicinity of each precipitate. If the cooling rate is sufficiently fast, the size of these diffusion fields will be restricted by the diffusional mobility of the elemental species, leading to channels in

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the γ matrix that will not interact with the γ' precipitates [8]. As the material is cooled further, another nucleation burst occurs in these channels, supersaturated in γ' forming elements [9]. The final microstructure, if cooled from a supersolvus temperature, will be composed of a bimodal distribution of secondary γ' and significantly smaller tertiary γ' precipitates. Such distributions will heavily influence the performance of the material and has thus been the subject of numerous experimental and modelling studies [6,9–13]. Understanding of superalloy microstructures is further complicated by the formation and evolution of second phases which, whilst present in only minor quantities, can have a substantial influence on the microstructure and hence the properties of these materials [14].

It follows that post-mortem analysis of the microstructure at ambient temperature is unlikely to provide the measurements needed for the reaction kinetics to be quantified in an accurate way. Instead, in situ time-resolved measurements are needed, ideally of very high spatial resolution. One can argue that this is a grand challenge in the field of superalloy metallurgy, which has yet to be addressed in a systematic and concerted way; if progress could be made, then it would represent a significant step in the search for optimised heat-treatments to confer the best properties. To date, X-ray synchrotron experiments have proved invaluable in gaining fundamental insights into the behaviour of nickel-based superalloys [15–17], as well as X-ray measurements of these materials made at elevated temperatures [5,18–20]. In this paper, synchrotron X-ray methods are used to measure the reaction kinetics of the ordering reaction. A number of different polycrystalline alloys are used, of composition comparable to that employed in engineering practice with a target operational temperature of 800 °C. This study reveals the kinetic response of these materials up to this temperature and beyond to determine the compositional sensitivity to service and processing temperatures.

2. Experimental procedures

Polycrystalline nickel-based superalloys were manufactured by ATI Powder Metals using a lab scaled version of a commercial powder metallurgy process. The three different alloys contained varying concentrations of Ti and Nb with Nb being substituted for Ti on a 1:1 basis. The measured composition of each alloy is listed in Table 1. For this study, disc-shaped samples measuring 3 mm in diameter by 1 mm thick were cut from the forgings using electro-discharge machining. Any surface oxide resulting from this process was removed using abrasive media.

Synchrotron experiments were conducted at Diamond Light Source using the I12 high energy beamline [21]. The beamline was equipped with a Thales Pixium RF4343 2D detector and a Linkam TS1500 furnace, permitting the acquisition of diffraction patterns in situ during heat treatment cycles. A flow of argon gas was supplied to the furnace to minimise oxidation of the alloy during the experiment. An illustration of the experimental setup is shown in Fig. 1.

For each experiment, X-ray diffraction patterns were obtained with the area detector located 1.6 m from the specimen. A thermal process typical of a super-solvus heat-treatment used on current generation turbine disc alloys was applied to each alloy tested. This comprised a controlled heating rate of 1 °C s^{-1} to approximately 30 °C above the γ' solvus temperature. During the diffraction experiments, each sample was held above its solvus temperature until the γ' superlattice reflections, associated with the presence of this phase, could no longer be observed. The specimens were subsequently cooled to 300 °C at 1 °C s^{-1}. The solution temperatures given to each material are listed in Table 2. The target heat treatment temperatures were chosen based upon γ' solvus temperatures previously measured using differential scanning calorimetry.

During the diffraction experiments, a beamline energy of 79.89 keV was used and calibrated, along with the sample to detector distance, using a NIST 674b CeO_2 standard. The beam size was fixed at 0.5 mm × 0.5 mm, which determined the data acquisition rate of 0.5 Hz. To account for measured temperature discrepancies between the beam position and the furnace thermocouple, the true furnace temperature was calibrated using a platinum foil of 99.9% purity. The foil was heated to 1250 °C at a rate of 0.5 °C s^{-1} whilst collecting diffraction patterns. With knowledge of the lattice parameter expansion as a function of temperature from the literature [22], temperature offsets were calculated from discrepancies between the expected and measured lattice parameters.

Micrographs of each material tested, before and after heat treatment, were obtained using a JEOL-6500F scanning electron microscopy (SEM), operating with an accelerating voltage of 10 kV and a beam current of 9 nA. Prior to this characterisation, the sample surfaces were ground and polished with increasingly fine media to a 1 μm finish. This was followed by chemical–mechanical polishing with 1:1 diluted colloidal silica prior to immersion etching with Kalling's waterless reagent (2 g $CuCl_2$, 50 ml ethanol & 50 ml HCl) to reveal the microstructure.

3. Data analysis method

A specially developed fitting procedure capable of providing the γ' volume fraction and the associated lattice misfit as a function of temperature and time has been used. Each Debye–Scherrer diffraction pattern was radially integrated using the open source software, DAWN [23]. All subsequent data analyses were performed using MATLAB. To monitor the evolution of the γ' phase, pseudo-Voigt line profiles were fitted to the superlattice and fundamental reflections. From the fitted line profiles, d-spacing and integrated peak intensity were extracted. These data were used to assist phase identification, γ'

Table 1. Measured compositions (at.%) of alloys used in this study.

Name	Cr	Co	W	Al	Ti	Ta	Nb	C	B	Zr
ABD-D2	18.91	18.49	1.00	7.89	4.31	0.66	0.00	0.132	0.046	0.039
ABD-D4	18.63	18.64	0.93	7.90	4.03	0.64	0.44	0.141	0.103	0.040
ABD-D6	18.94	18.83	0.94	8.07	2.90	0.63	1.24	0.119	0.103	0.043