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Lattice parameter instabilities during multi-phase precipitation in Alloy 693

Shabana Khan [a, b], S.D. Kaushik [c], A. Verma [a], J.B. Singh [a, b, *], V. Siruguri [c], D. Srivastava [a]

[a] Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India
[b] Homi Bhabha National Institute, Anushakti Nagar, Mumbai, 400 094, India
[c] UGC-DAE Consortium for Scientific Research Mumbai Centre, Bhabha Atomic Research Centre, Mumbai, 400085, India

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ABSTRACT

Ni-base superalloy Alloy 693 exhibits mono-modal, bi-modal and tri-modal distribution of γ'-phase precipitates depending upon heat treatments and subsequent cooling rates employed. This multimodal distribution of γ'-phase particles is a consequence of their formation during isothermal and continuous cooling of the alloy. Further, γ' particles that form under isothermal and continuous cooling are known to exhibit varying phase chemistry. This difference in their chemistry is expected to alter their lattice parameters. Aim of the present work is to study the variation in lattice parameters of γ'- phase particles that form during isothermal and continuous cooling. These studies have been carried out on the basis of Rietveld refinement of neutron diffraction data in conjunction with scanning electron microscopy and energy dispersive spectroscopy. This work also brings out the effect of precipitation of a chromium rich phase on the lattice parameters of γ- and γ'- phases during prolonged annealing of the alloy.

1. Introduction

Ni superalloy Alloy 693 is based on Alloy 690 with additions of Al, Ti and Nb. The alloy is primarily strengthened by the precipitation of a coherent ordered phase of $Ni_3(Al,Ti)$ stoichiometry (having an ordered cubic $L1_2$ type crystal structure), termed as γ'-phase, within austenite γ-phase (face-centered cubic structure) matrix. In addition, the γ'-phase contains elements like Cr and Nb [1,2]. Sizes and size-distributions of the γ'-phase precipitates can be varied in a controlled manner by judiciously choosing heat treatments and cooling rates. In a recent paper, it has been shown that microstructure of Alloy 693 samples, subjected to water quenching after isothermal annealing treatments in the temperature range 800 °C to 950 °C, exhibit single size distribution of γ' precipitates [2]. However, bi-modal or tri-modal distribution of γ' particles can be induced in these samples by furnace cooling after the annealing treatment. The bi-modal and tri-modal particle morphologies appear as a consequence of their precipitation in second and third generations during cooling. This type of microstructure was consistent with earlier reports on the precipitation of γ'-phase in a few other Ni-base alloys (see, for example, [3–5]).

Size, size-distribution and morphology of γ' particles determine mechanical properties of these alloys. Morphology of particles has been found to evolve continuously from spherical to cuboidal during their growth and coarsening stage [6]. This morphological change is dictated by the misfit arising due to mismatch between lattice parameters of γ- and γ'-phases. Chemistry of the γ'-phase particles formed during continuous cooling has been found to be dependent upon temperatures of their formation as well as the cooling rates employed [5,7]. This implies that secondary and/or tertiary γ' precipitates that form during furnace cooling would have lattice parameters different from that formed during isothermal annealing (primary particles) [2]. In addition to multi-modal distribution of the γ' particles, Alloy 693 also exhibits a tendency to form needle shape particles of an α-phase during prolonged ageing at 800 °C and above temperatures, details of which have been presented elsewhere [8]. Development of such a complex microstructure is likely to affect lattice parameters of constituent phases due to selective partitioning of alloying elements during the evolution of γ'- and α- phases. The aim of the present manuscript is to study this effect on lattice parameters of γ-, γ'- and α- phases during the precipitation of latter two phases.

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* Corresponding author. Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India.
E-mail address: jbsingh@barc.gov.in (J.B. Singh).

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Various experimental techniques can be used to determine lattice parameter of a phase. These includes X-ray diffraction, see, e.g. Refs. [9–11], neutron diffraction, see, e.g. Refs. [12–15], and convergent-beam electron diffraction (CBED), see, e.g. Refs. [9,11,16,17]. Whereas CBED allows the detection of local variations in lattice parameters owing to misfit strain or local variation in chemical composition, X-ray diffraction and neutron diffraction techniques sample comparatively large volumes of the material, thereby providing statistically significant but an average information. Further, due to the limitation of X-ray diffraction in detecting superlattice peaks in Ni-base alloys owing to nearly similar atomic scattering factors of constituent species, neutron diffraction offer advantage as these peaks appear intense since their intensity is governed by nuclear scattering (neutron scattering lengths). In the present study, phase identification and lattice parameters of evolving phases under different microstructural states have been determined using the Rietveld refinement of the neutron diffraction data. These studies have been supplemented by microstructural investigations using scanning electron microscopy (SEM) in conjunction with energy dispersive spectroscopy (EDS). The present study has shown that, not only the γ' stabilizing solutes affected its lattice parameter but also chromium associated with the precipitation of α-phase.

2. Experimental techniques

Composition of the Alloy 693 studied in the present work is given in Table 1. Solution treated (1100 °C for 2 h) and water quenched samples of the alloy were subjected to isothermal annealing at 800 °C, 875 °C, 900 °C, and 950 °C temperatures for 100 h followed by furnace cooling (at a rate of about 1 °C/min). Samples furnace cooled after annealing at 875 °C and 900 °C exhibited bi-modal distribution of γ' precipitates while those cooled after annealing at 950 °C exhibited a tri-modal size distribution [2]. However, samples with same annealing treatments, when water quenched always exhibits a mono-modal distribution [2]. Neutron diffraction studies of annealed and furnace cooled samples were carried out at room temperature for phase identification and determination of lattice parameter. In addition, lattice parameter of the γ'-phase in the water quenched sample annealed at 950 °C was also studied to delineate the variation in its lattice parameter arising due to the precipitation of later generations of γ' particles during continuous cooling. Neutron diffraction studies were carried out on the PD-3 neutron diffractometer set-up by UGC-DAE CSR Mumbai Center at Dhruva reactor, Bhabha Atomic Research Center, Mumbai (India) using neutron beam of wavelength 1.48 Å. The neutron diffraction data was analyzed using Rietveld refinement procedure employing Le-Bail fitting method in the Fullprof Suite software package [18]. Microstructural examinations were carried out in a field-emission scanning electron microscope (Zeiss make SIGMA model) operated at 20 kV. Sample preparation procedure for microscopic studies are given elsewhere [2]. Chemical composition of needle shape α-phase particles that form during prolonged annealing was determined using EDS analysis of particles extracted from a bulk alloy sample by selective dissolution of the matrix phase in an electrochemical cell [19]. Reported chemical composition is an average of compositions of 10 particles analyzed using AZTEC microanalysis system (software version 3.1) manufactured by M/s Oxford Instruments Ltd, U.K. Internal library standards of the software were used to quantify the data.

Table 1
Chemical composition of Alloy 693 under study.

	Ni	Cr	Fe	Al	Ti	Nb	Mn	S	C
wt%	58.42	31.26	3.98	3.94	0.34	1.53	0.20	0.0064	0.0831
at%	53.81	32.51	3.86	7.90	0.38	0.89	0.20	0.011	0.373

3. Results

Fig. 1 shows an optical micrograph of a solution treated sample exhibiting a typical wrought microstructure of a nickel-base superalloy. The globular shaped particles observed corresponded to primary carbides, which are known to form during solidification of these alloys [1]. It has been shown earlier [20], that this alloy in solution treated condition contains fine particles of the γ'-phase distributed homogeneously within the γ matrix. These particles grow further during isothermal annealing to form a mono-modal distribution of precipitates (termed as primary particles). The alloy exhibits this mono-modal distribution in samples water quenched after annealing. However, during furnace cooling, the alloy precipitates out second and/or third generation of γ' precipitates (termed as secondary and tertiary, respectively) at temperatures below 950 °C exhibiting bi-modal and/or tri-modal distribution in samples annealed at temperatures from 875 °C to 950 °C. A detailed description of the development of such microstructures as a function of temperature and cooling rate has been reported recently [2]. Fig. 2 shows the sizes and distributions of γ' particles in samples aged for 100 h at 950 °C followed by: (a) furnace cooling, and (b) water quenching. This alloy also exhibited a tendency to form needle shape particles during prolonged annealing at temperatures above 800 °C. Fig. 3a shows a typical optical microstructure of the alloy aged for 100 h at 900 °C. SEM analysis of extracted out needle particles in conjunction with EDS analysis revealed that needle particles were primarily Cr rich containing about 95.1 at% Cr, 3.3 at% Ni and 1.6 at% Fe (Fig. 3b and c, Table 2). A detailed description of the evolution of these particles has been reported separately [8].

Neutron diffraction patterns of samples of the aged alloy exhibited additional peaks along with fundamental reflections of the γ-phase matrix (Fig. 4). Additional peaks could be indexed corresponding to the γ'-phase (shown by solid circle in Fig. 4) and an α-phase of chromium (shown by the # symbol in Fig. 4), having a body-centered cubic structure. This confirmed that needle shaped particles shown in Fig. 3 corresponded to the α-phase. Formation of γ'- and α- phases in the γ matrix at different temperatures was associated with shift in the positions of superlattice as well as fundamental peaks corresponding to these phases. This behaviour is illustrated by representative {110} peak of the γ'-phase, {310} peak of the α-phase and {400} peak of $\gamma + \gamma'$ -phases (Fig. 5). In the

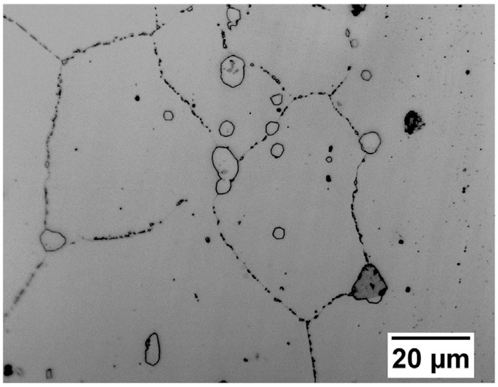

Fig. 1. Optical micrograph of solution treated Alloy 693.