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Age hardening behaviour of Alloy 693

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ABSTRACT

This paper reports the hardening behaviour of nickel base superalloy Alloy 693. The alloy is designed to derive its strength primarily from the precipitation of coherent γ' phase particles, induced by the addition of Al and Ti, in a face centered cubic matrix of Ni-Cr-Fe solid solution. The alloy possesses excellent combination of mechanical strength, corrosion and oxidation resistance properties at elevated temperatures. In the present work, uni-modal distribution of γ' particles is precipitated out during isothermal annealing of the alloy in the temperatures range 800 °C to 950 °C for time periods ranging from 0.5 h to 100 h. Variations in room temperature hardness and tensile properties of aged alloys have been correlated with precipitation behaviour of the γ' phase. These studies have been carried out in an Instron tensile testing machine in conjunction with microstructural characterization by electron microscopy. Mechanisms responsible for precipitation hardening of the alloy under different microstructural conditions have been identified on the basis of minimum critical resolved shear stress computed theoretically for competing mechanisms.

1. Introduction

Ni based superalloy Alloy 693 is designed to derive its strength primarily from the precipitation of coherent γ' phase particles, induced by the addition of Al and Ti, in a face centered cubic matrix of Ni-Cr-Fe solid solution. The γ' phase has an ordered $L1_2$ type crystal structure with Ni_3(Al,Ti) stoichiometry. The alloy offers an excellent combination of mechanical strength and corrosion/oxidation/sulfidation resistance properties at elevated temperatures [1]. It also exhibits good surface stability than that of its predecessor, Alloy 690, due to the addition of Al that enhances the stability of Cr_2O_3 scales and improves corrosion resistance under high temperature oxidizing and sulfidizing conditions [2]. The alloy finds applications in places, such as, management of high level nuclear waste [3] and petrochemical processing industry [1]. It is also a candidate material for high temperature waste and biomass incinerators and for high temperature fuel cells involved in synthesis gas production (e.g., fuel cells to power automobiles) and with potential to induce metal dusting [1].

Size, morphology, volume fraction and distribution of a second phase govern its hardening contributions in the alloy. To understand the effect of these parameters on mechanical properties of Alloy 693, an exhaustive study is being carried out on physical metallurgy and mechanical behaviour of the alloy in order to predict its behaviour under service and processing conditions. Parts of this study pertaining to precipitation behaviour of γ' and other phases in Alloy 693 at elevated temperatures have already been published recently [3–5]. In an earlier paper [6], it has been shown that it is difficult to suppress the formation of γ′ precipitates in Alloy 693 by solid solution treatment. This property has been exploited to induce multi-modal distribution of γ′ precipitates within the nickel matrix by tailoring heat treatment procedures. The alloy exhibits an uni-modal distribution of γ′ precipitates when water quenched after an isothermal annealing treatment at temperatures 800 °C and above [3].

Precipitation hardening at room temperature, in general, is governed by means of two mechanisms depending upon the size of precipitates and average spacing between them: (i) by shearing of particles by the movement of dislocations, and (ii) by Orowan looping or bypassing of particles. The former is usually active when particles are of small sizes and contributes to strengthening due to the involvement of chemical coherency, modulus mismatch and energy associated with their shearing. On the other hand, when particles are large and widely spaced, the latter is usually active where dislocations find it easy to loop around particles and strengthening arises due to additional stress required to make dislocations expand and bend between particles.

In a previous study, it has been shown that the γ′ phase particles in Alloy 693 precipitate out in a variety of sizes, volume fractions and distributions depending upon time and temperatures of ageing [3]. Aim of this work is to study the effect of the precipitation of γ′ particles on room temperature mechanical properties of Alloy 693 and delineate mechanisms responsible for precipitation hardening. This study has

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Table 1
Nominal composition (in wt%) of Alloy 693 and that of the alloy under study.

Elements	Nominal composition		Composition of the alloy under study
	Min	Max	
Ni	Balance		58.42
Cr	27.0	31.0	31.26
Fe	2.5	6.0	3.98
Al	2.5	4.0	3.94
Ti	–	1.0	0.34
Nb	0.5	2.5	1.53
Mn	–	1.0	0.20
S	–	0.01	0.0064
C	–	0.15	0.0831
Cu	–	0.5	–

been carried out in an Instron tensile testing machine in conjunction with microstructural characterization using a field emission scanning electron microscope.

2. Experimental techniques

Table 1 gives nominal composition of Alloy 693 and that of the alloy used in the present study. Chemical analysis of major alloying elements was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES) technique while C and S were analyzed using combustion analysis. Solution treated samples were aged isothermally at temperatures ranging from 800 °C to 950 °C for different periods of time (0.5 h–100 h) followed by water quenching to induce an unimodal distribution of γ′ precipitate within the disordered nickel matrix. Detailed descriptions of solution treatment and that of the isothermal heat treatment procedure have been given elsewhere [3]. Microhardness measurements were carried out using a Vicker's hardness tester with a load of 1 kgf for dwell time of 10 s. Reported microhardness values are averages of 10 independent readings for each measurement. Room temperature tensile properties were evaluated using M8 × 1.25 round tensile specimens of 4 mm diameter and about 20 mm gauge length as per ASTM E8 standard in an Instron (Model-1185) machine, using a constant strain rate of 0.98×10^{-4} per sec. Reported tensile properties are averages for two independent tensile tests for each sample. Microstructural characterization was carried out using a Carl Zeiss make SIGMA field-emission electron microscope operated at 20 kV. Preparation of samples for microstructural characterization was carried out by polishing samples on different grades of SiC papers (up to 2400 grit size) followed by a final surface polishing using collidal silica OPS. Polished surfaces were electrochemically etched at room temperature using a solution containing 8 g CrO_3 and 5 ml H_2SO_4 in 85 ml H_3PO_4 acid to reveal γ' phase particles. Sizes of particles were measured using the free ware image analysis software ImageJ [7]. Fine γ' particles in the solution treated samples were revealed by transmission electron microscopy, details of which are given in reference [3]. Lattice parameters of γ and γ' phases of samples were obtained by Rietveld refinement of x-ray data, obtained using a Cu K_α radiation source, utilizing the knowledge of lattice parameter of the γ' phase reported earlier [4].

3. Results

3.1. Microhardness studies

The solution treated alloy exhibited Vicker's hardness of about 253.8 ± 7.4 Hv. Aged alloy exhibited higher hardness values with respect to that of the solution treated alloy at all temperatures. Table 2 gives hardness values of samples aged for different periods of time. The alloy initially exhibited an increase in hardness with ageing up to 0.5 h at all temperatures studied. Further change in hardness values could be categorized into two broad categories with respect to ageing temperatures, namely, (i) a monotonous increase in hardness till it reached a plateau, as exhibited by samples aged at 800 °C and 850 °C temperatures; (ii) a monotonous decrease in hardness values after 30 min of ageing with a plateau during prolonged ageing, as exhibited by samples aged at temperatures above 850 °C. Fig. 1 shows variations in the hardness of aged alloys with ageing time at different temperatures studied.

3.2. Microstructural studies

3.2.1. Solution treated alloy

Scanning electron microscopy of solution treated sample showed single phase microstructure, though transmission electron microscopy exhibited the presence of fine particles (~10 nm size) of γ′ phase distributed homogeneously within the γ matrix (Fig. 2). Phase of precipitating particles was confirmed by superlattice reflections at positions characteristic of the γ′ phase (inset of Fig. 2). These particles have been reported to precipitate out during water quenching of the solution treated alloy [6].

3.2.2. Aged alloy

Aged samples exhibited a uniform distribution of γ′particles at all temperatures. Fig. 3 shows sizes and distributions of γ' precipitates in samples aged for 30 min, 2 h and 100 h at temperatures in the range 800 °C–950 °C. Since the solution treated alloy inherited fine particles of the γ' phase [6], isothermal annealing resulted in their further growth and/or coarsening depending upon annealing temperature. Samples aged at 800 °C exhibited the maximum density of particles at all annealing times (Fig. 3(a)–(c)). The γ' particles appeared to have grown continuously with time as their volume fractions and sizes increased monotonically (Tables 3 and 4). At higher temperatures, the alloy exhibited an increase in size of γ' particles and a decrease in their volume fractions with increasing aeging time. At 875 °C, the alloy exhibited almost constant volume fraction (within experimental errors) of particles though their sizes increased with time, due to faster coarsening kinetics at the higher temperature. Further increase of temperature decreased number density of γ' particles with concomitant increase their size. This suggested that, at temperatures above 875 °C, transformation was dominated by faster coarsening kinetics. Interestingly, at 900 °C and 950 °C temperatures, the alloy exhibited a larger volume fractions of the γ' phase during initial ageing times which reduced during prolonged ageing. This behaviour was attributed to under-saturated state of the γ matrix (with respect to γ′ forming solutes) at 900 °C and 950 °C temperatures. Due to the under-saturated state of the γ matrix dissolution of already formed γ′ phase particles would continue till composition of the γ matrix saturates at these temperatures. This was confirmed on the basis of variation in lattice parameter of γ matrix during isothermal annealing at 950 °C (Table 5). Lattice parameter values were estimated by Rietveld refinement of x-ray diffraction data (not presented here) corresponding to different heat treatments. Detailed description of this study is beyond the scope of present work and a part of it is published elsewhere [4]. From Table 5, it was clear that lattice parameter of the γ matrix in the sample aged for 30 min at 950 °C was more than that in the solution treated sample, indicating an increase in solute concentration in the matrix after 30 min of ageing. The observed decrease in the lattice parameter of the γ matrix after 100 h was due to the precipitation of a chromium-rich α phase, which has already been discussed earlier [4]. During prolonged ageing particles exhibited a tendency to transform from a spherical to cuboidal morphology. The γ' particles observed in the present study always remained coherent with the matrix during growth and coarsening. Evolution behaviour of these precipitates has already been discussed elsewhere [3].