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A Pt-modified Ni-base superalloy with high temperature precipitate stability

Jason S. Van Sluytman [a,b,*], Charles J. Moceri [a], Tresa M. Pollock [a,b]

[a] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA
[b] Materials Department, University of California, Santa Barbara, CA 93106, USA

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ABSTRACT

Nickel-base alloys display exceptional mechanical properties to high fractions of their melting point due to the presence of $L1_2$ γ′ precipitates. However, above 1000 °C, the precipitates typically coarsen or rapidly undergo shape changes along with dissolution into the matrix, thereby degrading the mechanical performance of the alloy at higher temperatures. In this research, a Pt-modified Ni-base alloy with exceptional high temperature stability has been identified. Coarsening studies conducted in the temperature range from 1050–1200 °C reveal unusually high volume fractions of morphologically stable γ′ precipitates up to 1200 °C. Electron-probe micro-analysis demonstrates strong partitioning of Pt to the γ′ phase. The presence of a high volume fraction of slowly coarsening precipitates at 1200 °C suggests that the alloy would have excellent performance as a bond coat and/or single crystal blade.

1. Introduction

A common characteristic of commercial cast nickel (Ni)-base superalloys is the presence of a high volume of the gamma prime (γ′) precipitate phase at temperatures up to 1000 °C. The mechanical strength of the alloy is dependent on the volume fraction, size, and chemical composition of these precipitates. However, strength rapidly decreases above 1000 °C due to a decay in precipitate volume fractions, high diffusional rates and/or directional coarsening [1,2]. Consequently, the design of the next generation of superalloys that display impressive creep resistance and surpass current operating temperatures will be constrained by the γ′ phase stability. To this end, understanding the thermodynamic and morphological stability, partitioning of γ′-forming elements, and coarsening kinetics in new compositional domains is necessary.

Improving the morphological stability of the γ′ requires additional alloying elements beyond the binary Ni–Al system. Ni_3Al precipitates begin to coarsen at a significant rate at temperatures as low as 645 °C [3]. When refractory elements such as Ta, W, Mo, and Re are added, the γ′ microstructure is stabilized up to 850 °C [4–8]. Sudbrack et al. [5], as well as Nathal and Ebert [6], established that W partitioning to the γ′ phase slows coarsening considerably for aging temperatures of 800 and 871 °C, respectively. Giamei and Anton reported that Re additions stabilize cuboidal γ′ morphology up to 982 °C [7]. Unfortunately, when temperatures exceed 1000 °C, the γ′ precipitates become morphologically unstable, regardless of the refractory content [4–7], suggesting that the refractory additions are less effective at preserving precipitate stability in these high temperature regions.

Developing Ni-base alloys that maintain microstructural stability above current operating temperatures of approximately 1000 °C necessitates exploration of new compositional domains. To date, control of coarsening has been accomplished primarily via refractory additions [4–8] to γ-γ′ Ni-base alloys without the consideration of platinum group metal (PGM) additions. Limited investigations of Pt-modified Ni-base superalloys demonstrate impressive high temperature mechanical [9,10] and intrinsic oxidative [11,12] properties at temperatures of 1000 °C and 1150 °C, respectively. Heidloff et al. examined Ni-base alloys containing (at%) 15Al-*X*-5Cr-0.1Hf (X=2.5 Pt or Ir) aged at 1000 °C [13], and reported that Pt, which preferentially partitions to the γ′ phase [14,15], slows the coarsening kinetics. As such, a deeper understanding of the influence of PGMs on microstructural stability in alloys also containing high levels of refractory additions would be useful.

Carroll investigated precipitate stability in Ru-modified Ni-base superalloys containing moderate levels of Re, Ta, and W additions [16]. Stable precipitate morphology was reported at 950 °C, but irregular faceted precipitate morphologies were observed at 1100 °C, corresponding to a precipitous drop in the γ′ volume fraction (<0.40). A coarsening study conducted by Cui et al. at

* Correspondence to: 1355 Engineering II Bldg, Materials Department, University of California, Santa Barbara, CA 93106-5050, USA.
E-mail address: jason.vans@engr.ucsb.edu (J.S. Van Sluytman).

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850 °C on two UDIMET 720LI Ni-base superalloys, one containing Ru additions and another lacking the PGM, demonstrated that Ru suppressed precipitate coarsening [17]. However, it is uncertain whether Ru, or any other PGM for that matter, strongly influences precipitate coarsening at temperatures beyond 1000 °C.

This article examines the unique partitioning behavior of the PGM element Pt integrated into a refractory-containing Ni-base composition. High temperature coarsening studies have been conducted on an experimental alloy, designated PX5, in the temperature range of 1050–1200 °C. An exceptionally high volume fraction of γ′ precipitates in this alloy at temperatures above 1050 °C is reported. The results suggest new compositional domains for the development of highly creep resistant alloys and/or bond coatings.

2. Experimental

PX5 is a Ni-base alloy containing (at%): 13.5Al–2.5Pt–7.5Cr–1Re–2Ta–1W–0.5Ti–1Mo–0.5Si with 0.2Hf–0.014Zr–0.1C–0.087B as grain boundary strengthening additions. The composition is listed in Table 1, along with other Ni-base alloys for comparison [4,18,19]. Alloy PX5 was fabricated by vacuum arc melting at facilities located at Iowa State University [13]. Differential thermal analysis (DTA) was performed to measure solidus (T_S) and γ′ solvus (γ'_{Solvus}) temperatures. DTA samples weighing approximately 250–300 mg were machined to 3.0 mm in diameter using a wire electric discharge machine. A SETARAM SETSYS DTA unit, with a pure Pt standard, was utilized for thermal measurements with a heating rate of 5 °C / min.

Specimens for coarsening studies measuring $4\times4\times3$ mm^3 were heat-treated using a standard tube furnace. A type-R thermocouple monitored the temperature throughout the homogenization and aging sequences, verifying that samples were within ±2 °C of the prescribed temperature. Samples were homogenized in sealed quartz tubes back-filled with Ar. Homogenization was conducted at 1325 °C (6 h), after which tubes were quenched in ice water. Individual samples of alloy PX5 were aged in laboratory air at various time intervals: 0.5, 2, 4, 8, 16, and 24 h. After aging, the samples were immediately submerged into an ice water bath. Aging was carried out at 1050, 1100, 1150, and 1200 °C.

To observe microstructural features, samples were etched by two different techniques: (1) a standard etchant of 33% acetic acid ($C_2H_4O_2$), 33% deionized water, 33% nitric acid (HNO_3), and 1% hydrofluoric acid (HF). The second etch was an electrolytic etch, and consisted of 45% sulfuric (H_2SO_4), 43% nitric (HNO_3), and 12% phosphoric (H_3PO_4) acid. A DC power source supplied 10 V over 15 s intervals. Images were captured using a Phillips XL30 FEG in SE mode at 15 kV. The γ′ volume fractions (V_f) of precipitates were measured at each aging time for all tested temperatures. A minimum of 200 particles were analyzed for each aging treatment. The γ′ volume fraction measurements and edge length counts were acquired using both etching techniques with similar results. Subsequent processing and analysis of images was performed using *ImageJ* software [20].

The characterization of the γ′ shape utilized the method of two-dimensional (2D) moment invariants [21]. The absolute moment invariant, ω_2, permits shape classification *independent* of particle size and is expressed by a dimensionless parameter termed the shape parameter ratio, η. The shape parameter ratio quantifies the γ′ shape with a numerical value between 0–1, where $\eta=0$, and 1, indicate a geometrically perfect circle, and square (in 2-D), respectively. Shape parameter ratios have been recently measured for a series of experimental Ni-base alloy compositions with γ′ volume fractions ranging from $0.45 < V_f < 0.70$, with an optimum value of $\eta\cong0.75$ observed to maximize creep resistance [22]. The shape parameter ratio evolves during extended aging and provides a measure of the equilibrated shape a coherent γ′ particle achieves over time, termed the attractor shape, η_{Att}[21,22]. In this study, at least 75–100 precipitates were analyzed for each aging time and temperature in order to acquire η(T,t) where T and t correspond to temperature (°C) and time (h), respectively. All shapes were measured from secondary γ′ precipitates.

An extended aging treatment at 1250 °C for 720 h was performed on one homogenized sample so that particle diameters would reach approximately 4–5 μm in order to allow an accurate measurement of the precipitate composition. The sample was mounted in epoxy and finely polished. Electron-probe microanalysis utilized a CAMECA SX-100 microprobe mounted with five WDS detectors. A NiAl standard was used for Al peak determination. Spot scans were conducted with $I=10$ nA, $V=20$ kV, and a beam diameter approximately 2 μm. At least 25 spot scans were acquired on coarsened precipitates. Compositional analysis of the coarsened γ′ ($C_{\gamma'}$) was used to acquire the γ composition (C_γ) using the Lever Law:

$$C_\gamma = \frac{(C_n) - V_f(C_{\gamma'})}{1 - V_f} \tag{1}$$

with C_n being the nominal composition of PX5, and V_f measured at 1250 °C. Elemental partitioning coefficients, q_x, where x represents each individual element in alloy PX5, were calculated:

$$q_x = \frac{C_\gamma}{C_{\gamma'}} \tag{2}$$

Values greater, or less, than one indicate preferential partitioning to the matrix, and precipitate, respectively. Standard deviations, s, were measured for all values:

$$s = \sqrt{\frac{\sum (A_x - \bar{A}_x)^2}{(n-1)}} \tag{3}$$

where A_x and $\bar{A}_x$ are individual and average values for measured variables, respectively, and n is the number of measurements. All plots contain a 5% standard error, 5%*SE*:

$$5\%SE = \frac{s}{\sqrt{n}} \tag{4}$$

3. Results

Since coarsening requires diffusional redistribution of elements that strongly partition into the γ′ phase, it is important to determine whether Pt partitioning influences precipitate coarsening and stability. The following sections address microstructure, equilibrated fractions of γ′ precipitates, and coarsening kinetics in the temperature range from 1050 °C to 1200 °C.

3.1. Microstructure

The shape and size of the precipitates was characterized at each annealing temperature. The microstructure of alloy PX5 after homogenization above the γ′ solvus at 1325 °C for 6 h is shown in Fig. 1. A high density of precipitates, with a shape parameter ratio, η (1325°C, 6 h)=0.12, and γ′ volume fraction, V_f=0.61 (±0.04) is established immediately after quenching. In Fig. 2, the shape parameter, η, maps the evolution of the γ′ shape at $T=1050$ °C. SEM micrographs depict the microstructures from t=0.5–16 h. By 2 h, the shape parameter (though not the precipitate size) reaches a saturated value corresponding to a geometrical shape considered "semi-spherical". This value, termed the attractor shape, η_{Att}, is