FORMATION OF A Pt_2Mo TYPE PHASE IN LONG-TERM AGED INCONEL® ALLOY 686

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Abstract

INCONEL[1] alloy 686 is a newly developed highly corrosion-resistant Ni-Cr-Mo superalloy, intended for usage at moderate temperatures. The alloy is ordinarily single-phase austenitic in the as-fabricated, i.e., mill-annealed condition. The metallurgical stability of this alloy upon extended aging at two different temperatures of 450 °C (842 °F) and 500 °C (932 °F) for times up to 5,000 hours was investigated. The material originated from a commercial heat. Samples were aged in both the mill-annealed and mill-annealed plus 15 % cold worked conditions, and subsequently examined by differential thermal analysis, optical and electron microscopy. Evidence for the formation of a low-temperature intermetallic Pt_2Mo type phase is provided. The implications of this metallurgical reaction for ductility and corrosion resistance are discussed.

Introduction

INCONEL alloy 686 is a newly developed Ni-Cr-Mo superalloy designed to be highly corrosion resistant to both oxidizing and reducing acids [1]. In the as-fabricated, i.e., mill-annealed condition the alloy is ordinarily single-phase austenitic. Due to heavy alloying with Cr and, in particular, Mo, it is not surprising that this alloy is prone to μ / P phase formation at temperatures exceeding approximately 760 °C (1500 °F) [2]. Such exposure temperatures are, however, well above the intended rather moderate usage temperatures.

Despite the relatively low usage temperatures of 550 °C (1000 °F) or less, the excessive lifetimes required from the material in some applications warranted a study of its metallurgical stability. At the same time, the retention of the corrosion resistance and selected mechanical properties such as tensile ductility upon extended aging were investigated and correlated with any microstructural changes observed.

Experiment

For this study material was available from a commercial heat of INCONEL alloy 686 whose composition is shown in Table I. Note the very low C and Si contents typical of this family of highly corrosion-resistant alloys.

Table I : Chemical composition (in wt.%) of the INCONEL alloy 686 material studied.

Ni	Cr	Mo	W	Fe	Mn	Si	Co	Al	C
bal	20.4	16.3	3.9	0.4	0.2	0.01	0.04	0.2	0.002

The sample blanks originated from mill-annealed, approximately 25 mm (1") thick hot rolled plate (ASTM grain size # 1 1/2). A portion of this plate was cold rolled (15% reduction in thickness) prior to aging. Both, blanks from the mill-annealed and mill-annealed plus cold worked material were exposed to temperatures of 450 °C (842 °F) and 500 °C (932 °F), respectively, for times up to 5,000 hours in air. Samples were pulled after 200 h, 2,000 h, and 5,000 h.

Differential thermal analyses (DTA) were performed on 200 mg specimens prepared from the aged samples. The dynamic atmosphere was He, and alumina powder was used as a reference sample. The heating rate was set to 40 °C /min, and the cooling rate upon reaching 1200 °C to 20 °C /min. From a few selected aged conditions specimens were prepared for transmission electron microscopy following standard procedures, i.e., jet polishing in a solution of 10% perchloric acid in methanol at – 45 °C. A Philips EM 400 operated at 100 kV was employed for the microscopy.

Tensile and corrosion testing were performed on the aged material in conformance with ASTM standards E-8 and G28 practice A (sulfuric acid + ferric sulfate).

[1] INCONEL is a registered trademark of the Special Metals Corporation family of companies

Superalloys 2000
Edited by T.M. Pollock, R.D.,Kissinger, R.R. Bowman,
K.A. Green, M. McLean, S. Olson, and J.J. Schirra
TMS (The Minerals, Metals & Materials Society), 2000

Results

Thermal Analysis

Typical DTA traces of the as-fabricated and long-term aged material are shown in Figs. 1 a and 1b, respectively. Note the strong endothermic reaction that took place at around 700 °C (1300 °F) in the aged sample upon heating. This reaction is virtually non-existent in the mill-annealed condition.

No complementary exothermic reaction was detected upon cooling, nor was the endothermic reaction present upon second heating. This is indicative of the dissolution of a low-enthalpy phase upon first heating, which does not re-form in any appreciable amounts upon cooling at the cooling rates employed in this study.

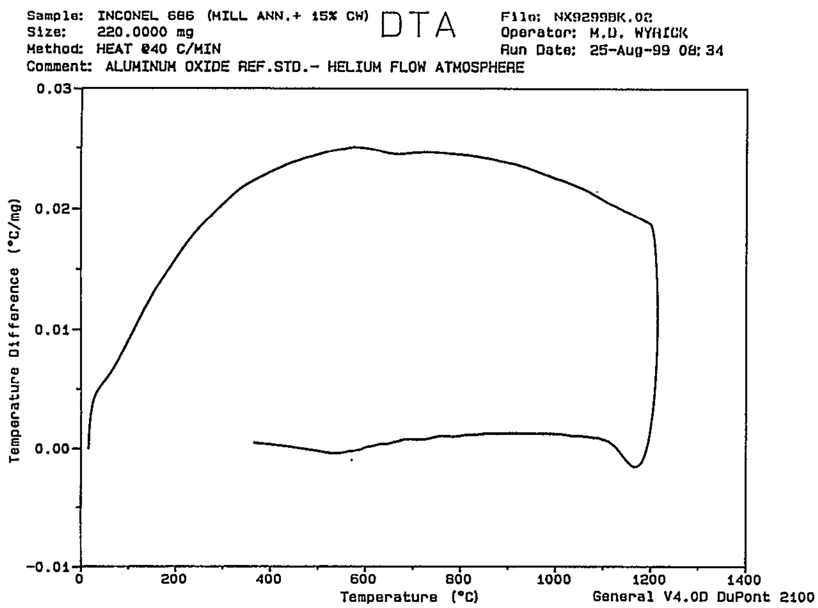

Fig. 1 a : Typical DTA trace of mill-annealed samples of INCONEL alloy 686.

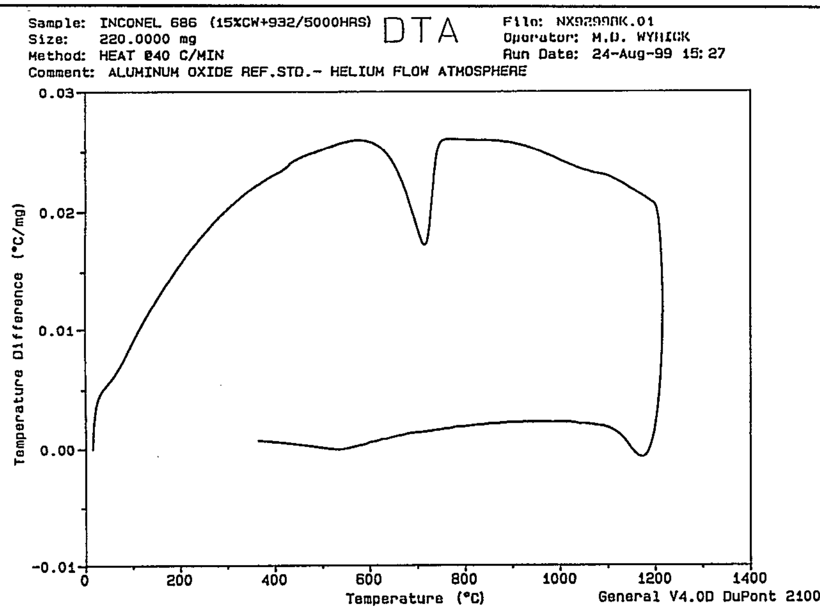

Fig. 1 b : DTA trace of a sample of INCONEL alloy 686, mill-annealed plus 15% cold worked, and aged for 5,000 hours at 500 °C (932 °F).

A strong dependence of the magnitude of the endothermic reaction on the aging conditions was observed. This relationship is semi-quantitatively reflected in Fig. 2, in which the latent heat of dissolution of that phase was expressed by the area under the respective DTA master curve. The reproducibility of the quoted numbers is about ± 1 unit. Although not necessarily accurate in absolute terms, this parameter does reflect trends since the same conditions (heating rate, gas flow etc.) were employed in the thermal analysis.

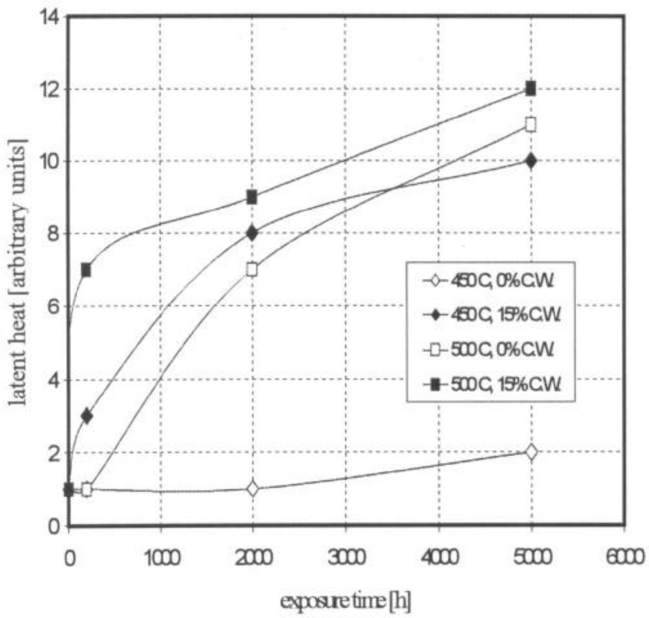

Figure 2 : The latent heat of dissolution (in arbitrary units) of the phase(s) formed upon long-term aging in samples of INCONEL alloy 686 is plotted as a function of aging time. Curve parameters are the aging temperature and the amount of cold work prior to aging.

The magnitude of the effect increases continuously with aging time and temperature, indicative of a diffusion-controlled phase transformation. For longer aging times the effect seems to saturate. Evidently, prior cold work greatly enhances the kinetics of formation of the phase(s) as most compelling for the 450 °C exposures.

Aged Microstructure

TEM selected area diffraction patterns (Fig. 3) of the long-term aged samples revealed consistently well-resolved superlattice reflections at every 1/3 <220>, 1/3 <420>, and 1/3 <311> type reciprocal lattice vectors for various beam directions. This was true regardless of the amount of prior cold work and the actual aging temperature.

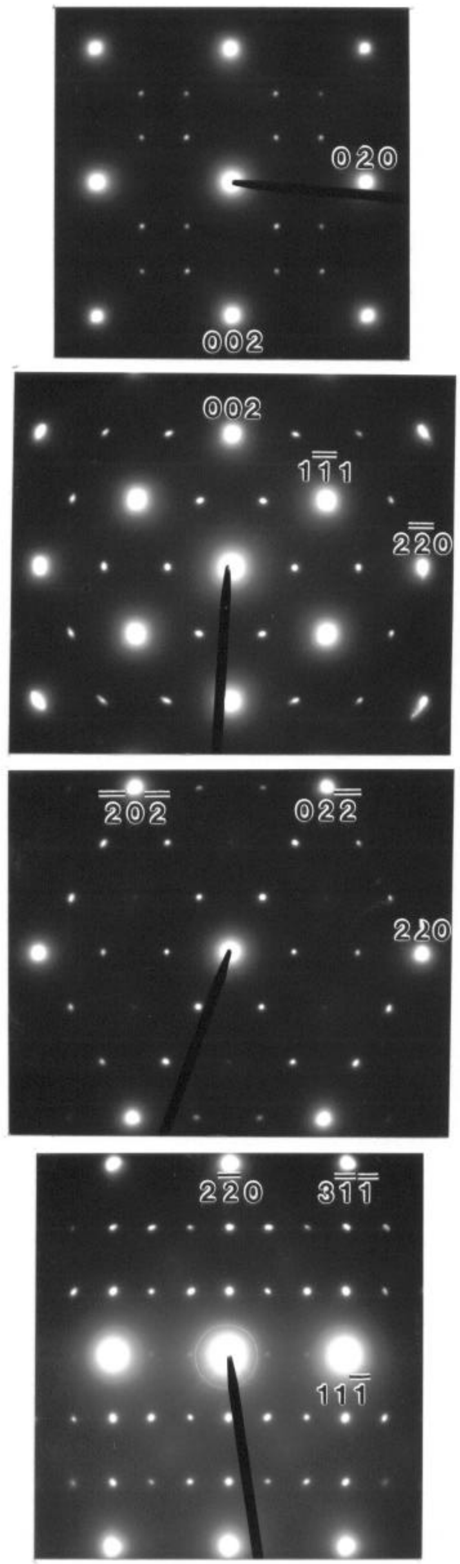

Figure 3 : TEM selected area diffraction patterns (750 mm camera length) obtained from long-term aged samples of INCONEL alloy 686 for various zone axes : (a) [100], (b) [110], (c) [111], and (d) [112]. The fundamental reflections were indexed in terms of fcc notations.

to the fundamental reflections (the location of the fundamental diffraction spots agreed well with the location of the diffraction spots of the matrix in the mill-annealed condition) indicate the presence of a second phase whose structure is derived from the matrix phase by some ordering reaction. The ordered phase was subsequently examined using dark-field techniques employing the various superlattice reflections for imaging.

Fig. 4 shows the typical intragranular precipitation of the ordered phase. Note the uniformity of the dispersion and the extremely fine length scale involved : the precipitate size is of the order of 10 nm. Such features cannot be resolved with a light microscope nor a scanning electron microscope. Also note the large apparent volume fraction of the ordered phase.

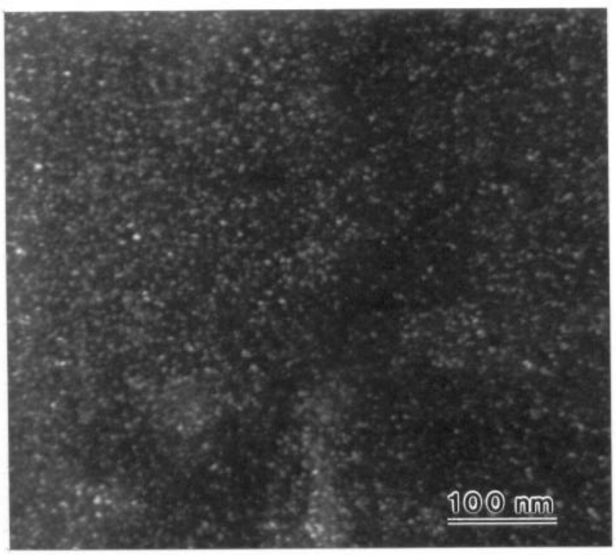

Figure 4 : Typical dark-field image ($\mathbf{g}$ = 1/3 <311>) of the microstructure obtained after long-term aging of samples of INCONEL alloy 686 at 450 °C (magnification 135,000x). The beam direction is close to a <114> zone axis.

At even higher magnifications the morphology of the ordered precipitates (Fig. 5) becomes more apparent : their shape is predominantly disk-like for both aging temperatures studied.

The size of the ordered features appears to be markedly bigger in the sample aged at 500 °C in comparison with the sample aged at 450 °C for the same aging time of 5,000 hours (Fig. 5). A comparison of the volume fractions is problematic due to the generally low-contrast images and their sensitivity to foil bending. Moreover, different type **g** vectors were employed for imaging in the micrographs of Fig. 5.

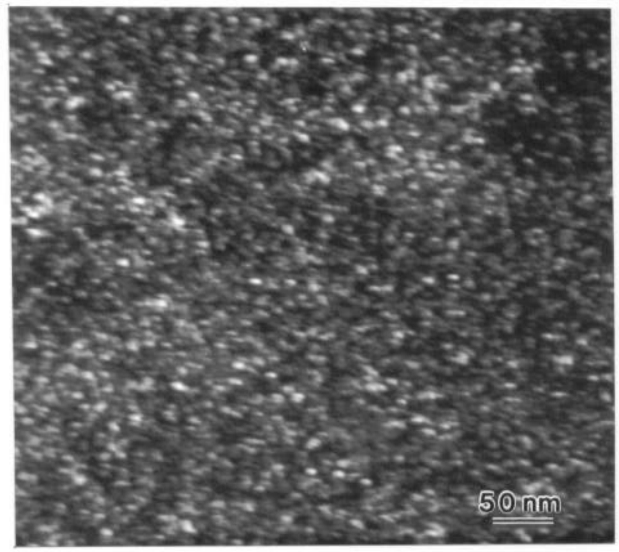

Fig. 5 a : Dark-field image ($\mathbf{g}$ = 1/3<311>) of the microstructure obtained after aging mill-annealed plus 15% cold worked samples of INCONEL alloy 686 for 5,000 hours at 450 °C (magnification 170,000x). The beam direction is close to a <114> zone axis.

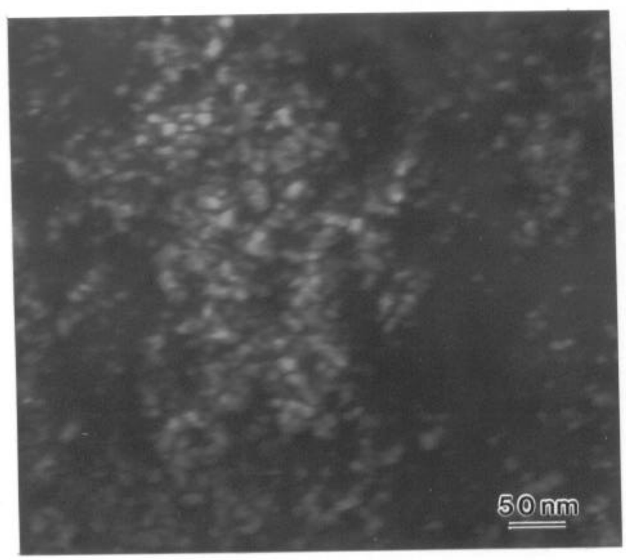

Fig. 5 b : Dark-field image ($\mathbf{g}$ = 1/3<220>) of the microstructure obtained after aging mill-annealed plus 15% cold worked samples of INCONEL alloy 686 for 5,000 hours at 500 °C (magnification 170,000x). The beam direction is close to a <114> zone axis.

Surprisingly, a relatively low dislocation density was observed in all TEM specimens prepared from the 15% cold worked material even though the data in Fig. 2 suggests a marked effect of prior cold work on the kinetics of formation of the ordered phase. In fact, fairly large areas where the ordered phase had apparently homogeneously nucleated were found to be devoid of dislocations (Fig. 6).

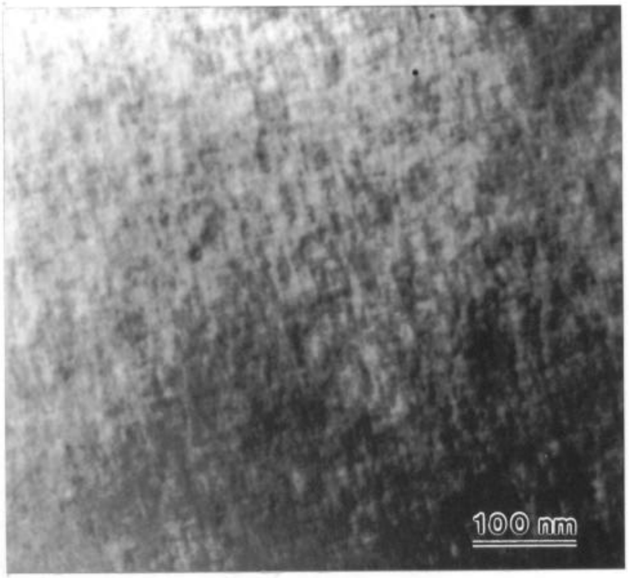

Fig. 6 : Bright-field image (two-beam condition, **g** = <220>) of the microstructure obtained after aging mill-annealed plus 15% cold worked samples of INCONEL alloy 686 for 5,000 hours at 450 °C (magnification 135,000x).

The grain boundary microstructure is usually of great concern when retention of ductility and corrosion resistance (in particular, susceptibility to intergranular attack) upon aging are required.

Examination on both the light microscopy and scanning electron microscopy (SEM) levels did not reveal any marked precipitation in the grain boundaries of the aged samples in comparison with the mill-annealed samples (Fig. 7).

Examination of a TEM specimen which happened to contain a grain or twin boundary (the exact nature of this boundary was not elucidated) confirmed these findings : the boundary appears to be devoid of any gross precipitation (Fig. 8). The ordered phase nucleated homogeneously even in very close proximity to the boundary, and no denuded zones were observed (Fig. 9).

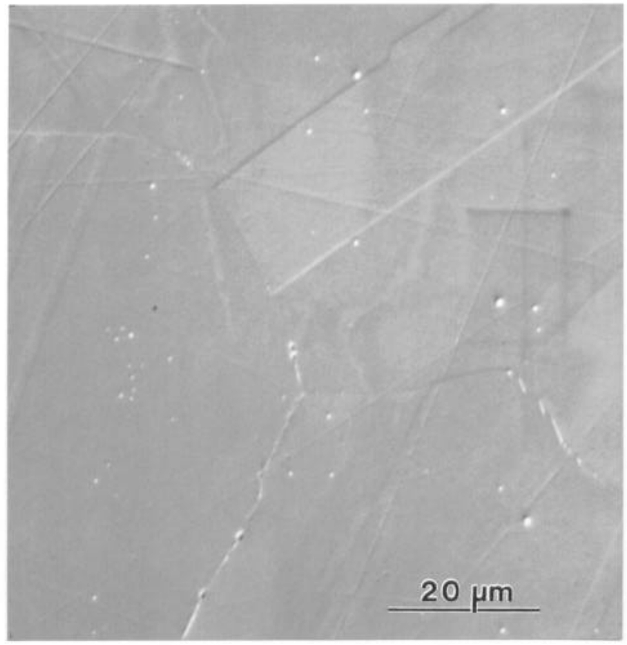

Fig. 7 a : SEM image of the typical microstructure of INCONEL alloy 686 in the mill-annealed plus 15% cold worked condition. The sample was etched electrolytically in 10 % chromic acid.

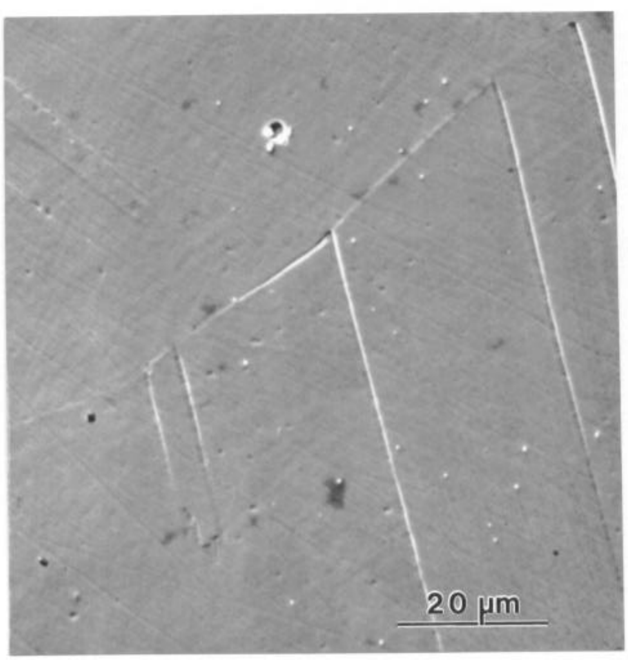

Fig. 7 b : SEM image of the microstructure obtained after aging mill-annealed plus 15% cold worked samples of INCONEL alloy 686 for 5,000 hours at 500 °C. The sample was etched electrolytically in 10 % chromic acid.

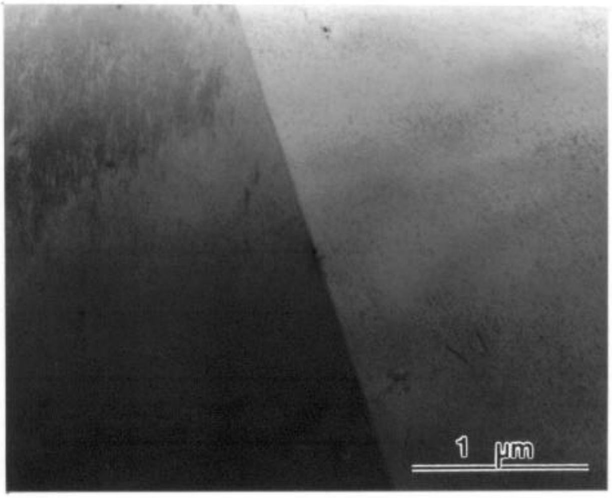

Fig. 8 : Bright-field image of a grain or twin boundary after aging mill-annealed plus 15% cold worked samples of INCONEL alloy 686 for 5,000 hours at 450 °C (magnification 22,000x).

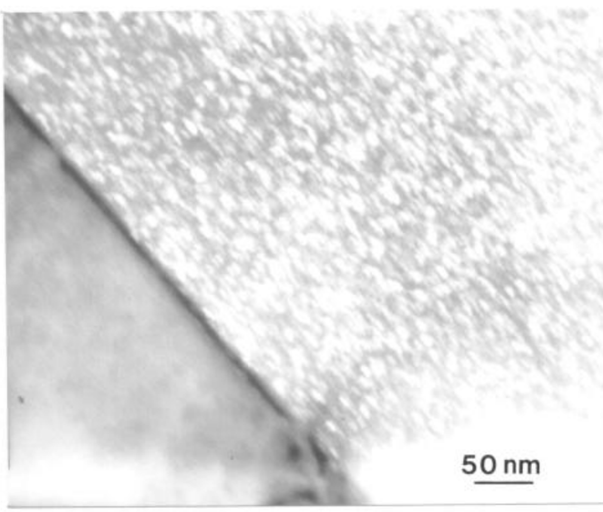

Fig. 9 : Dark-field image (**g** = 1/3<220>) of the microstructure in the vicinity of the boundary shown in Fig. 8 (magnification 170,000x). The beam direction is close to a <112> zone axis.

Retention of tensile ductility and corrosion resistance upon aging is shown in Figs. 10 and 11, respectively. Except for the expected drop in ductility due to cold work, aging by itself did not lead to any significant ductility losses for the times and temperatures studied. The same is true for the corrosion resistance : within the scatter of the individual tests no significant deterioration of corrosion resistance was observed in this particular environment.

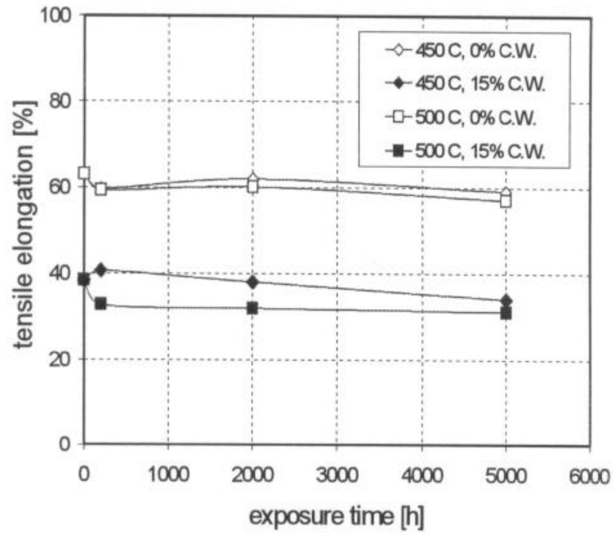

Fig. 10 : The tensile ductility of aged samples of INCONEL alloy 686 is plotted as a function of aging time. Curve parameters are the aging temperature and the amount of prior cold work.

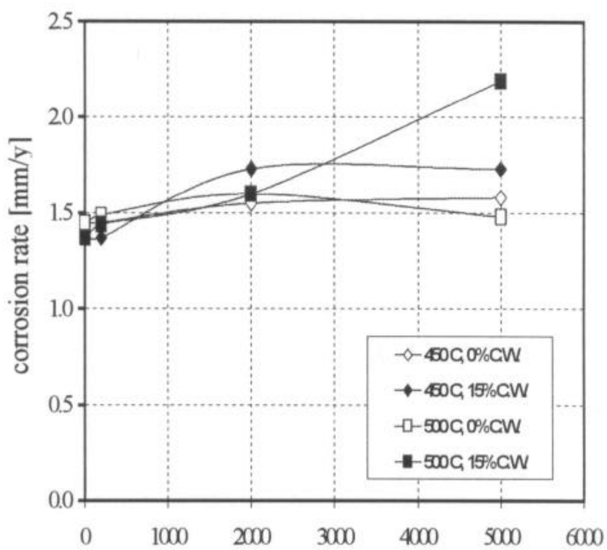

Fig. 11 : The corrosion rate per ASTM G28A of aged samples of INCONEL alloy 686 is plotted as a function of aging time. Curve parameters are the aging temperature and the amount of prior cold work.

Discussion

The combination of thermal analysis and electron diffraction provides compelling evidence for the formation of an ordered, low-enthalpy phase in mill-annealed INCONEL alloy 686 upon aging at moderately elevated temperatures.

The observed diffraction patterns are identical with those reported for Ni_2Cr and (metastable) Ni_2Mo in the respective binary systems [3,4], and a presumed $Ni_2(Cr,Mo)$ phase in HASTELLOY[2] alloys S, C-4, and C-276 [5,6]. The patterns are typical of the Pt_2Mo structure type (orthorhombic crystal lattice) which can be derived from the A1 matrix structure by a peculiar stacking of the {220} planes, i.e., the alternation of two planes of predominantly Ni atoms followed by one plane of predominantly Cr / Mo atoms [4]. The length scale of the extremely fine and uniform intragranular distribution of the low-temperature phase found in this study (Fig. 5) is very similar to that observed in other Ni-Cr-Mo alloys aged at comparable temperatures [5,6].

The combined atomic fraction of Cr and Mo in INCONEL alloy 686, equaling roughly 30 at.%, leads one to believe that an ordering mechanism was active (the composition range for Ni_2Cr is quoted to be 25 to 36 at.% [3]). Such ordering only requires short-range lattice diffusion (characteristic diffusion length of the size of the unit cell) and can, thus, proceed at a reasonable pace even at temperatures as low as 450 °C. Moreover, it would promote a uniform dispersion since no nucleation event in the classical sense is needed.

Following this line of reasoning one would expect the long-term aged material to consist of 100 % ordered phase. This seems to be in contradiction to the apparent volume (area) fraction displayed in the dark-field images in Fig. 5. It has to be recalled, however, that, depending on the particular g vector selected, only a fraction of the six possible orientational variants [4] will be in contrast. For instance, when employing g = 1/3 [220], only one variant will be in contrast. Hence, the actual volume fraction of the ordered phase will be quite high after 5,000 hours of aging, and the reaction kinetics will have slowed down already considerably at this point as suggested by Fig. 2.

A poorly understood aspect of the ordering reaction concerns the accelerating effect of prior cold work on the kinetics of formation of this phase. Although well documented in Fig. 2, no direct microscopic evidence could be obtained. It is speculated that the generally higher vacancy concentration resulting from cold work might have enhanced the kinetics.

Notwithstanding the detailed nature of the mechanism, the extremely small size and, more importantly, uniform distribution of the ordered phase up to grain boundaries (Fig. 9) are thought to be primarily responsible for the retention of corrosion resistance. This reasoning is based on the apparent absence of zones deprived of the alloying elements, in particular Cr and Mo, that made the aged material virtually immune to intergranular attack. In contrast, "sensitized" microstructures, i.e., microstructures exhibiting heavy precipitation of μ /P phases in the grain boundaries [2], are generally susceptible to massive intergranular corrosive attack. At the same time, the "clean" grain boundaries (being devoid of gross precipitation of continuous films like the ones reported for HASTELLOY alloy C-276 [6] after long-term aging at 537 °C) are believed to have been instrumental in retaining tensile ductility.

It is interesting to note that the magnitude of the endothermic DTA peak associated with the dissolution of the ordered phase (Fig. 2) upon heating is much greater than the magnitude of the endothermic DTA peak associated with the dissolution of μ / P phase in a sample exhibiting massive precipitation thereof. Hence, in addition to facilitating kinetics, the ordered phase also seems to be favored thermodynamically at the temperatures studied.

Summary

The microstructural stability of INCONEL alloy 686, a newly developed highly corrosion-resistant Ni-Cr-Mo superalloy, was studied at two temperatures of 450 °C (842 °F) and 500 °C (932 °F) for aging times up to 5,000 hours.

Employing differential thermal analysis and electron microscopy, it was found that the austenitic matrix undergoes an ordering reaction at these rather moderate temperatures, resulting in the formation of a phase isomorph to Pt_2Mo. Cold working prior to aging greatly enhanced its kinetics of formation.

The extremely fine-scale and, more importantly, apparently uniform dispersion of this phase are believed to be the main cause for the excellent retention of resistance against intergranular corrosion and the retention of tensile ductility upon aging.

Acknowledgments

Helpful discussions with T. Summers (Lawrence Livermoore National Laboratories) are acknowledged.

[2] HASTELLOY is a registered trademark of HAYNES INTERNATIONAL

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