A COMPARISON OF THE PRECIPITATION KINETICS OF γ'' PARTICLES IN VIRGIN AND RE-SOLUTIONED ALLOY 625

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Abstract

Alloy 625 is used as superheater tubes and ammonia cracker tubes in many ammonia plants and in chemical industries. The components, made of this alloy are expected to have a life of about 100,000 hours at an operating temperature in the range of 450 °C to 700 °C. Since the availability of nickel is scarce and the alloy is very expensive, attempts are being made to resolution the material which has seen its service life and use it again. The data about the ageing behaviour of the resolutionised material under service conditions is necessary to determine the expected life of the component. The results of a detailed investigation on the kinetics of precipitation of intermetallic phases in the resolutioned material as well as virgin alloy are reported in this paper. The ageing behaviour of virgin and resolutioned material was found to be quite different. The distribution of γ'' precipitates was non-uniform and the precipitation was found to occur heterogeneously on dislocations in the resolutioned specimens. These observations are discussed in the light of redistribution of different alloying elements during service and their effect on subsequent precipitation kinetics of resolutioned material.

Introduction

Alloy 625 is a nickel base superalloy which has found extensive use in the petrochemical, aerospace and many marine engineering applications because of its high strength and toughness from cryogenic temperatures up to 1100° C. The alloy is endowed with good fatigue strength, oxidation resistance and good resistance to chloride ion stress corrosion cracking [1]. Although the alloy was originally designed as a solid solution strengthened alloy, it has subsequently been shown that the precipitation of intermetallic phases occurs in it during ageing or service at intermediate temperatures [2]. The strengthening in this alloy is caused mainly by the precipitation of γ'' which has the ordered body centred tetragonal D0₂₂ structure with Ni₃(Nb,Al,Ti) stoichiometry[1, 3, 4] and the Ni₂(Cr,Mo) phase with orthorhombic unit cell and Pt₂Mo type crystal structure[5, 6]. The stability range of Ni₂(Cr,Mo) phase is from 350 °C to 600 ° C[5]. The γ'' phase forms on ageing at temperatures above 400° C. The equilibrium intermetallic phase, δ (with D0_a structure and Ni₃(Nb,Mo) composition), can form directly from the supersaturated solid solution on ageing at relatively high temperatures or by the replacement of the metastable γ'' phase on prolonged ageing at relatively low temperatures [7-9]. M₆C and M₂₃C₆ carbides have been observed to precipitate on grain boundaries during ageing [4, 10]. M₆C forms at relatively higher temperatures and they are stable up to 1080° C [4].

Alloy 625 is used as superheater tubes and ammonia cracker tubes in many ammonia plants and in chemical industries and the components, made of this alloy are expected to have a design life of about 100,000 hours at an operating temperature in the range of 450° C to 700° C. Since the availability of nickel is scarce and the alloy is very expensive, attempts are being made to extend the service life of components made of this alloy by different methods [11]. Tensile and creep properties of resolutioned Alloy 625 has been reported recently [12, 13]. One such option being considered is to resolution the material and use it again. In order to implement this option, the data about the ageing behaviour of the resolutionised material under service conditions vis a vis that of fresh material is necessary. The present paper reports the comparison of the results of ageing studies carried out on resolutionised and virgin Alloy 625 material. The results are rationalized on the basis of changes in matrix composition as a result of service exposure (ageing), the different phases that precipitate and also their stability.

Experimental Procedure

The chemical composition of the alloy used in this work is given in table I. Thin slices of 0.5 mm thickness were cut from the Alloy 625 material which has seen a service life of 100,000 hours at 650° C, designated as **S** alloy and the one obtained from the virgin material designated as **V** alloy respectively. Specimens from **S** and **V** alloys were solution treated at 1100° C for 2 hours to completely dissolve all intermetallic phase precipitates and then water quenched. The samples from both alloys were subsequently subjected to identical ageing treatments at temperatures between 600° C and 700° C for different periods of time up to 500 hours. By keeping one sample from each alloy together in the furnace, it was ensured that they have undergone identical heat treatment. The average γ'' particle size corresponding to different ageing treatments was determined from the dark field micrographs obtained by imaging with $\{100\}$ and $\{1\ 1/2\ 0\}$ type superlattice reflections with the foil oriented in $\langle 001 \rangle$ orientation. Sample preparation for TEM is described elsewhere [9].

Table I. Chemical Composition of Alloy 625

Element	Ni	Cr	Mo	Nb	Fe	Al	Ti	Co	Mn	Si	C
Conc.wt%	60.81	21.73	8.82	3.90	3.92	0.17	0.23	0.08	0.14	0.15	0.05

Results

Solution Treated Structure

The typical microstructure of **S** and **V** alloys after solution treatment is illustrated in figure 1. Except for some randomly distributed blocky precipitates which were identified by SAD to be predominantly M_6C type carbides, the microstructure was free of any intermetallic phase precipitates. Uniform distribution of dislocations was also noticed in the matrix.

Aged Microstructure

V Alloy Extensive precipitation of all three γ'' variants occurred during ageing in the temperature range from 600° C to 675° C. The γ'' variants could be identified from the presence of superlattice reflections corresponding to them in the SAD pattern and also from their orientations in dark field images. An illustrative example of the γ'' distribution in specimens subjected to heat treatment at different temperatures for maximum period of time employed in

Figure 1. Microstructure of solution treated (a) V and (b) S alloys.

Figure 2. γ' precipitation in solution treated V alloy aged at (a) 625° C, (b) 650° C, (c) 675° C and (d) 700° C. Ageing period for (a) to (c) is 500 h and for (d), it is 100 h.

this study is shown in figure 2. For the same ageing period, γ' particle size increased with increasing the heat treatment temperature. The γ' particles exhibited a lens shape morphology with $\{001\}$ habit plane. Evolution of γ' precipitates during ageing at 675° C as a function of ageing time is given in figure 3. The plot of γ' particle size as a function of cube root ageing time, for 650° C and 675° C ageing temperature obeyed a linear relationship (figure 4) indicating that these precipitates grew by volume diffusion in Alloy 625 [14]. It is interesting to note that shorter periods of ageing at 700° C resulted mainly in the heterogeneous precipitation of

Figure 3. . γ' precipitation in solution treated V alloy aged at 675° C. (a) and (b) are bright field and dark field micrographs respectively for specimen heat treated at 100 h. (c) 200 h and (d) 500 h.

γ' particles on dislocations (figure 5). Nucleation of all the three γ' variants on dislocations could be noticed. However, the nucleation density appears to be high for only two variants. Increasing the ageing period to 100 hours resulted in the homogeneous nucleation of γ' within the austenite matrix (figure 6). Heterogeneously nucleated γ' precipitates on dislocations could also be noticed (marked by arrows in figure 6a and 6b).

S Alloy γ' precipitation was not observed in solution treated S alloy specimens subjected to identical ageing treatments as the V alloy specimens for temperatures up to 700° C. An illustrative example of microstructures evolved after short time heat treatments at 650° C and 675° C are shown in figure 7. High density of perfect dislocations and stacking faults, often arranged in the planar arrays, could be seen in the matrix. Ageing for longer period resulted in the heterogeneous precipitation of γ' particles on dislocations (figure 8) with the nucleation density increasing with rise of ageing temperature.

Discussion

The present study clearly indicated that the ageing treatment in the temperature range 600° C and 700° C resulted in profuse precipitation of γ' particles in the virgin V alloy. Homogeneous precipitation of γ' phase occurred at lower temperatures of ageing while at 700° C, the γ' nucleation was initiated heterogeneously but on progressive ageing became homogeneous. The present observations are similar to that reported by earlier investigators in alloy 625 [3].

Figure 4. Plot of γ'' particle size as a function of ageing time, T , in solution treated V alloy.

Figure 5. Heterogeneous precipitation of γ'' on dislocations in solution treated V alloy aged at 700° C for 24 h. (a) BF, (b) $g = 010$, (c) $g = -100$ and (d) $g = -1-10$. (b), (c) and (d) represent (010), (100) and (001) variants of γ'' phase

These results have been explained on the basis of narrow overlap of TTT curves corresponding to the metastable γ'' and the equilibrium δ phase forming at high temperature [3, 4]. Because of the small overlap, it was possible to get an access to a temperature range where the super saturation with respect to γ'' phase was low and at the same time the competing process of δ precipitation could not operate, resulting in favoring heterogeneous nucleation. However, once all the heterogeneous sites are exhausted, further ageing would result in the homogeneous nucleation in the matrix. At lower temperatures, homogeneous nucleation is preferred over heterogeneous nucleation because of high density of sites for homogeneous nucleation, in spite of the fact that the free energy for the heterogeneous nucleation is always lower than that for homogeneous nucleation.

Figure 6. Homogeneous nucleation of γ'' on dislocations in solution treated V alloy aged at 700° C for 100 h. (a) and (b) are bright field and dark field images with (100) reflection.

Figure 7. Microstructure of solution treated S alloy aged at (a) 675° C for 100h and (b) 700° C for 24 h.

Another important result of the present study is the profuse precipitation of γ'' phase in V alloy and hardly any precipitation in the S alloy under identical conditions of ageing in the temperature range between 600° C and 700° C. It is well known that small variation in alloying elements can strongly influence the precipitation behavior. The effect of alloying elements on promoting or inhibiting the precipitation of γ'' phase in nickel base superalloy has been qualitatively rationalized on the basis of electron concentration models and also the lattice mismatch between the matrix and the precipitate governed by the preferential occupation of different sites in the unit cell by different atomic species[1]. The minor variation in the concentration of different alloying elements has also been reported to influence the temperature range of precipitation, the sequence of precipitation and also their volume fraction [15]. The addition of iron, cobalt, and aluminum to binary Ni-Nb and Ni-Ta alloys have been shown to strongly influence the formation as well as the relative stability of γ'' and γ' phases [16, 17]. These metastable phases do not generally precipitate in the binary alloy system. Garzarolli et al. [8] have noticed that the γ'' precipitation did not occur in alloy 625 in the absence of titanium and aluminum. The nominal concentration of aluminium and titanium normally added in Alloy 625 is the minimum amount required to initiate γ'' precipitation [8]. From this discussion, it is obvious that variation in alloying elements exert a strong influence in the precipitation of different intermetallic phases during ageing.

Figure 8. Microstructure of solution treated S alloy aged at different temperatures for longer periods (a) 650° C for 500 h and (b) 650° C for 500 h. (c) and (d) are BF and DF images in specimen heat treated at 700° C for 100 h.

In the S alloy, during prolonged service at temperatures similar to that employed in the present study, in addition to γ' and $\text{Ni}_2(\text{Cr},\text{Mo})$ phase, profuse precipitation of M_{23}C_6 and M_6C carbides has occurred predominantly at grain boundaries[5, 6]. All intermetallic phases like γ' , $\text{Ni}_2(\text{Cr},\text{Mo})$ and δ particles dissolve during the resolution treatment at 1100° C. However, this temperature is very close to the solvus temperature of 1080° C for M_6C carbides and slightly lower solvus temperature for M_{23}C_6 carbides. Still lot of carbides could be seen in the matrix after resolution treatment. On the contrary, Shankar et al [12] have noticed complete dissolution of M_{23}C_6 and M_6C in the S alloy after solution treatment at 1150°C for 30 minutes and observed profuse precipitation of γ' on subsequent ageing. The major difference in composition between

Table II. Relative Concentration of Major Alloying Elements Determined by EDS

Sample Identification	Elemental concentration (wt. %)				
	Ni	Cr	Fe	Mo	Nb
Solution treated V alloy	59.23	22.41	4.48	9.07	4.81
S alloy	61.83	20.76	4.20	8.32	4.89
Solution treated S alloy	62.54	20.96	4.02	8.45	4.03

the resolutioned S alloy in the present study and that employed by Shankar et al [12] could have arisen mainly due to dissolution of carbide phases in their sample. This dissolution is expected to bring about changes in concentration of carbide forming elements like chromium, molybdenum etc in the matrix of solution treated sample. The composition of the major alloying elements of the matrix determined using EDS in SEM for S and V alloys is given in table II. The small variation in the concentration of alloying elements between table I and II are expected when different analysis methods are used. In fact, the present study revealed higher amount of chromium and less of nickel in solution treated V alloy than in service exposed and solution treated S alloys (table II). This result corroborates with the microscopic observation that the carbides have not completely dissolved during solution treatment at 1100° C. As mentioned earlier from the work of Garzarolli et al [8], the composition of Alloy 625 is delicately balanced for γ'' precipitation. A small variation in matrix composition may change the minimum amount of aluminum and titanium required for γ'' precipitation. From the present study, it appears that the variation in the matrix composition due to retention of carbides precipitated during long time service might be responsible for the poor response to precipitation of γ'' phase in the solution treated S alloy. Further detailed investigations are necessary to understand this behaviour.

Conclusions

The following conclusions could be drawn on the basis of present investigation:

Uniform distribution of γ'' precipitates occurred in the austenite matrix in the virgin alloy after ageing treatment. Identical ageing treatment did not result in the precipitation of γ'' particles in the service exposed alloy resolutioned at 1100° C. This difference has been attributed to the changes in the austenite matrix composition brought about by the precipitation of $M_{23}C_6/M_6C$ carbides during service and their retention in the solution treated S alloy in the present study.

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