Effect of Phosphorus on the Microstructure and Stress Rupture Properties in an Fe-Ni-Cr Base Superalloy

W.R. SUN, S.R. GUO, D.Z. LU, and Z.Q. HU

This article describes the effect of phosphorus on the microstructure and stress rupture property at 650 °C in an Fe-Ni-Cr base superalloy. The results showed that phosphorus markedly improved the intergranular precipitation in the range of 0.0005 to 0.016 wt pct, which facilitated $M_{23}C_6$ and M_3B_2 precipitation but inhibited the formation of MC carbide. A too high phosphorus addition (0.051 wt pct P) resulted in an excessive precipitation at grain boundaries, while a too low phosphorus content (0.0005 wt pct P) led to many precipitate-free grain boundaries. Phosphorus also enlarged the size of the γ' particles and lowered its stability, that η-Ni_3Ti preferred to form in the alloy with 0.051 wt pct P. Due to the improvement of the microstructure, appropriate amount of P content significantly prolonged the rupture life of the alloys in the range of 0.0005 to 0.016 wt pct. The peak value was 660 hours at 0.016 wt pct, more than 4 times that of the alloy with 0.0005 wt pct phosphorus, but phosphorus reduced the fracture elongation. The mechanism by which phosphorus influenced the alloy is discussed.

I. INTRODUCTION

PHOSPHORUS is always classified as a detrimental impurity in superalloys,[1] whereas relatively little is known about its effects, and the research about it is not systematic. Recent studies[2–5] showed that phosphorus greatly influences the solidification path, lowers the final solidification temperature, and aggravates the solidification segregation of elements in superalloys. Based on these studies, there has been a proposition that phosphorus should be controlled as low as possible to get supreme quality superalloys. However, to control the phosphorus content to an extremely low level will make the production complicated and uneconomical, because phosphorus cannot be removed by vacuum melting.[1] And, in addition, it is now uncertain what the condition is when the materials are pure of phosphorus. Except for the effect of phosphorus on the nonequilibrium segregation formed during solidification, the equilibrium segregation, which is generally constricted in a very small thickness and forms highly concentrated thin zones along grain boundaries, will also take place and play an important role in the microstructure and mechanical properties in the application. It can influence the grain boundary properties, such as intergranular diffusion, precipitation, and cohesion, as well as the microstructure and strength of the materials. Therefore, more work should be carried out on these aspects to evaluate the comprehensive effects of phosphorus.

An Fe-Ni-Cr base superalloy, GH761 wrought alloy, is designed to provide high room and elevated temperature strength. The alloy is mainly strengthened by γ'-$Ni_3(Al,Ti)$ phase. Because of the high addition of titanium (3.5 wt pct), the segregation of this alloy is relatively high, that is, prone to form the η-Ni_3Ti phase. In this article, GH761 alloy is selected and studied for the preceding results and to reveal the mechanism by which phosphorus influences the superalloys.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The materials were prepared in a vacuum induction furnace using high-purity raw materials. To minimize the compositional variations among the heats, the master alloy was prepared, and its composition (wt pct) was C0.011, Cr12.89, Ni43.54, W3.12, Mo1.59, Al1.71, Ti3.64, B0.003, Si0.059, and S0.003. Then the master alloy was remelted to give four 10-kg ingots, which were added into different contents of phosphorus with the same content of carbon and boron. The remelting also makes the alloy much more homogeneous. The levels of carbon, boron, and phosphorus were analyzed and are listed in Table I.

The ingots were forged into bars of 45-mm-square sections at 1120 °C and rolled at the same temperature into round rods 18 mm in diameter. These materials were then given a standard heat treatment of 1120 °C/2h, water cooled; 850 °C/4h, air cooled; and 750 °C/24h, air cooled.

The microstructure was observed by using optical microscopy and transmission electron microscopy (TEM). Phase identification was mainly carried out using selected area diffraction. The weight percent of precipitates was measured after anodic matrix dissolution, and the extractions were analyzed by X-ray diffraction (XRD). An electron microprobe was used to measure the composition of precipitate.

The stress rupture lives and elongations of the alloys were measured at 650 °C under a constant load of 637 MPa, and the fracture surfaces of the testpieces were examined by scanning electron microscopy.

III. RESULTS

Phosphorus has no effect on the grain size of the alloys. However, it increases the intergranular precipitation. The precipitates on the grain boundaries are MC and $M_{23}C_6$ carbides, as well as M_3B_2 boride.

Two kinds of $M_{23}C_6$ were observed: one in a form with a sharp angle, as shown in Figure 1. The no. 1 alloy with

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Table I. Contents of Carbon, Boron, and Phosphorus of the Alloys (Weight Percent)

Alloy	Carbon	Boron	Phosphorus
1	0.038	0.0049	0.0005
2	0.039	0.0044	0.0009
3	0.041	0.0045	0.016
4	0.036	0.0047	0.051

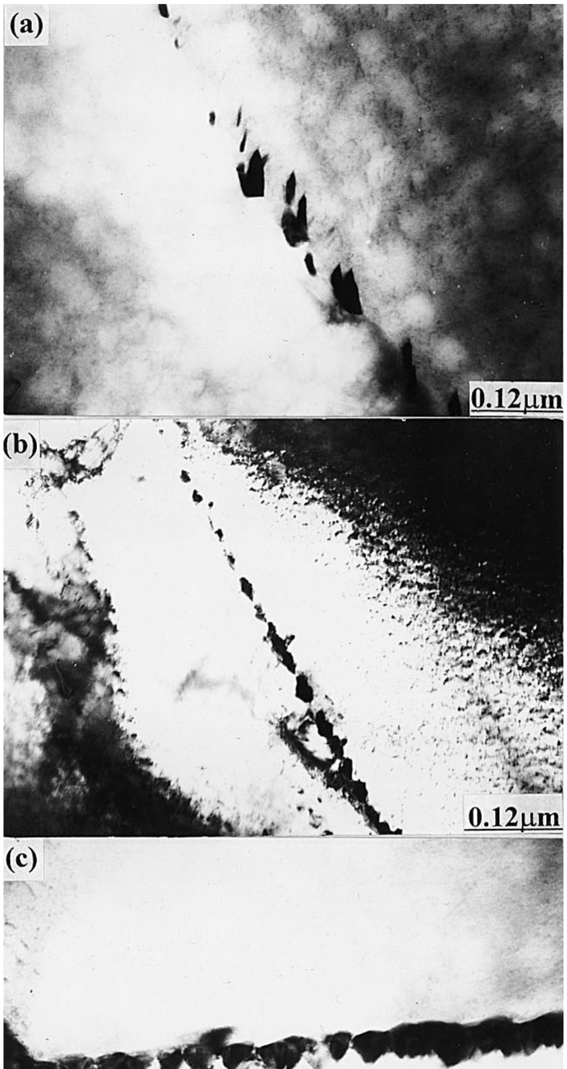

Fig. 1—Blocky $M_{23}C_6$ on grain boundary: (*a*) no. 1 alloy, (*b*) no. 3 alloy, and (*c*) no. 4 alloy.

the lowest phosphorus content has a relatively small amount of this phase, and the size of the particles and the distance between them are relatively large (Figure 1(a)). The particles in the no. 3 alloy are the finest (Figure 1(b)). Some of the precipitates in the no. 4 alloy are in large blocks. The other kind of $M_{23}C_6$ phase takes the form of an ellipsoid. As shown in Figure 2, the size and shape of these kinds of particles in the no. 1 and no. 3 alloys show no difference (Figures 2(a) and (b)), but in the no. 4 alloy, some of them grow into long pieces (Figure 2(c)). As shown in Figures 1 and 2, the intergranular precipitation of the $M_{23}C_6$ phase is enhanced by the increasing phosphorus content.

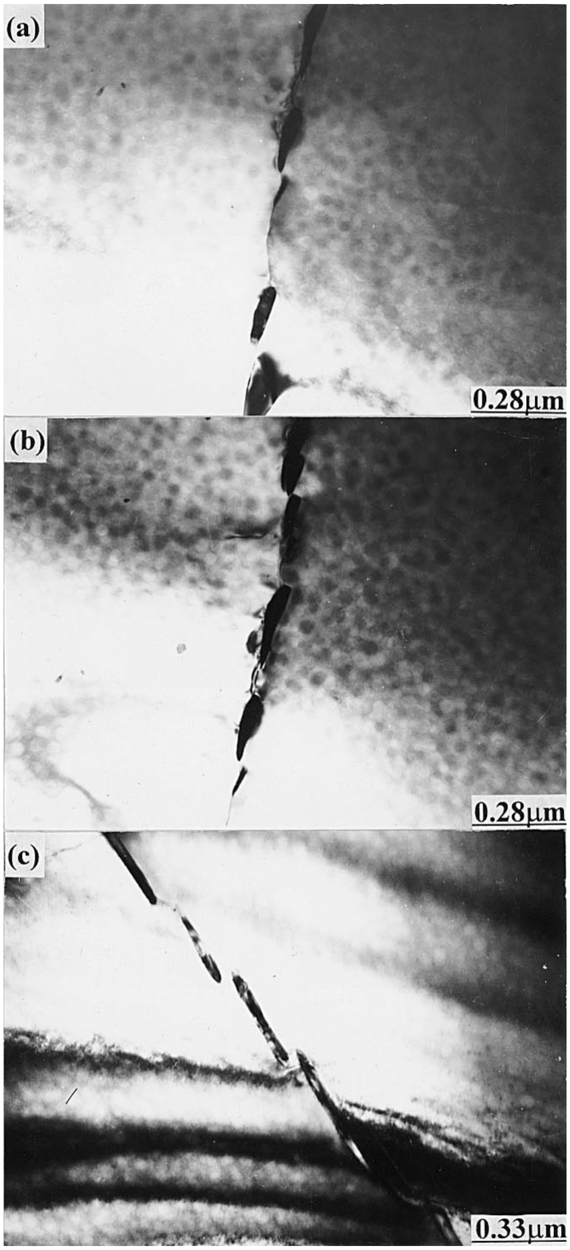

Fig. 2—Ellipsoidal $M_{23}C_6$ on grain boundary: (*a*) no. 1 alloy, (*b*) no. 3 alloy, and (*c*) no. 4 alloy.

The MC carbide usually appears as large blocks on the grain boundaries, as shown in Figure 3. With the increase of phosphorus content, the amount decreases.

Compared with $M_{23}C_6$, M_3B_2 particles are small precipitates with a curved outline (Figure 4). It is similar to $M_{23}C_6$ with relatively large M_3B_2 particles scattered on the grain boundaries in the no. 1 alloy (Figure 4(a)). Small and separate M_3B_2 particles usually form in a line on the grain boundaries in the no. 3 alloy (Figure 4(b)). However, different from $M_{23}C_6$, when the phosphorus content rises to 0.05 wt pct, (although most of the particles grow into large pieces), some of them form clusters of very small precipitates along the grain boundaries (Figure 4(c)).

The amounts of the trace phases are 0.029 wt pct (no. 1 alloy), 0.031 wt pct (no. 3 alloy), and 0.036 wt pct (no. 4 alloy). The average phosphorus content of the extracted trace phases were chemically analyzed as 0.018 wt pct (no. 1 alloy), 0.33 wt pct (no. 3 alloy), and 4.13 wt pct (no. 4 alloy). By using XRD, MC carbide and M_3B_2 boride were found in all of the alloys. The $M_{23}C_6$ carbide was found in the no. 3 and no. 4 alloys—perhaps the amount of $M_{23}C_6$ in the no. 1 alloy with the lowest phosphorus content is too low to be detected by XRD. The MC carbide, both within the γ matrix and on the grain boundaries, is the main constituent of the trace phases. The trace phase within the γ matrix is mainly the primary MC blocks aligned in the rolling direction. Some of the large MC blocks were analyzed by means of electron microprobe. It was found that phosphorus is extremely depleted in the MC carbide, and the phosphorus concentration in MC carbide is lower than that in the matrix. In this case, it is determined that the phosphorus in the extractions is mainly dissolved in the intergranular precipitates: $M_{23}C_6$, M_3B_2, or both. The rejection of phosphorus into MC crystal means that phosphorus may have an effect that retards the MC precipitation. Combined with the result of the trace phases amount, it is confirmed that phosphorus increases the intergranular precipitation, *i.e.*, increases the precipitation of $M_{23}C_6$ and M_3B_2. These are well in agreement with the results of the observation on the grain boundary microstructure by TEM.

The matrix-austenite of this alloy is primarily strengthened by γ' phase precipitated during the aging treatment. Of course, the amount and morphology of this phase play an important role in the mechanical properties. The weight percentages of the γ' particles electrolytically extracted out are 19.0 (no. 1 alloy), 18.7 (no. 3 alloy), and 19.8 (no. 4 alloy). Apparently, the change is not much and has no relation with the phosphorus content. The mean diameters of extracted γ' particles are 35 nm (no. 1 alloy), 39 nm (no. 3 alloy), and 40 nm (no. 4 alloy). Phosphorus has little effect in extending the size of the γ' particles. The η-Ni_3Ti phase could only be found in the no. 4 alloy, which is distributed within the γ matrix as a Widmanstätten type (Figure 5(a)). Only a few η-Ni_3Ti particles were found on the grain boundary (Figure 5(b)).

Rupture lives and elongations were tested at 650 °C under a stress of 637 MPa. The result is plotted in Figure 6. It is observed that phosphorus significantly enhances the stress rupture life in a wide range of 0.0005 to 0.016 wt pct. The curve reaches a peak value at 0.016 wt pct. The life of the no. 3 alloy (0.016 wt pct) is 660 hours, 4 times more than that of the no. 1 alloy (0.0005 wt pct) at 136 hours. Rupture life begins to reduce in the range of 0.016 to 0.051 wt pct, but the life of the no. 4 alloy (170.8 hours) is still longer than that of the no. 1 alloy.

IV. DISCUSSION

A. *Effect on Intergranular Precipitation*

The equilibrium segregation of trace elements has emerged as a major cause of alteration of grain boundary properties. It has been proposed that the driving force of equilibrium segregation involves the relief of lattice strain that occurs when a solute atom diffuses from the lattice interior to a solid-solid interface or a free surface.[6] After thermomechanical processing and heat treatment, the trace elements, mainly carbon, boron, and phosphorus in this alloy, diffuse to the grain boundaries and reach a concentration that is in equilibrium with that of the grain interior. In this test, the only difference among the alloys is the phosphorus content. Logically, the equilibrium concentration of phosphorus, both on the grain boundaries and within the γ grains, increases with the average content of phosphorus. Subsequently, on one hand, the increasing phosphorus dissolution in the γ matrix brings about more severe lattice strain and results in a large driving force for the trace elements, such as carbon, boron, and phosphorus, to diffuse to the grain boundaries. On the other hand, the segregated phosphorus atoms also have site competition with carbon and boron atoms at the grain boundary. However, when carbide and boride begin to precipitate, carbon, boron, and phosphorus will be trapped in the carbide and boride, giving rise to the reduction of trace element concentration at the grain boundaries. As a result, phosphorus, carbon, and boron will move from the grain interior to the boundaries to reach a new equilibrium. As discussed earlier for the relief of the lattice strain, more trace element atoms will diffuse toward the grain boundaries in the alloy with an increasing phosphorus addition, which provides more carbon, boron, and phosphorus atoms for the growth of the precipitates.

Fig. 3—MC carbide on the grain boundary of no. 1 alloy.

If a certain phase precipitates on the grain boundary, let r_c be the critical radius, of which the embryo is thermodynamically stable, we can obtain r_c by letting $\frac{\partial_G}{\partial_r}$ be equal to zero:

$$r_c = \frac{1}{\cos\theta}\,\frac{\sigma_{gb}}{\Delta G_V} \qquad [1]$$

Because the solubility limit of phosphorus in bulk is always low in nickel metal, the variation of ΔG_v can be neglected in the discussion. If the value of θ remains the same, then r_c decreases with the reduction of σ_{gb}, and the embryo can nucleate easily on the grain boundaries. It is well known that phosphorus is a surface active element, for it can lower the surface free energy of the boundaries it concentrates on. Study[7] shows that phosphorus can markedly reduce the surface tension of the liquid Ni-P alloy in a large range of

0.001 to 2 wt pct. Especially when the phosphorus content is below 0.01 wt pct, the surface tension decreases drastically. The mechanism for impurities to segregate on grain boundaries is the same as it concentrates on the free surface of the metal. It is rational to confirm that phosphorus also decreases the grain boundary free energy in pure nickel. In superalloys, the lattice strain is more severe because of the solution hardening effect, and, hence, the driving force for phosphorus to diffuse toward and accommodate at the grain boundaries is greater. As a result, the grain boundary free energy, σ_{gb}, decreases due to the segregation of phosphorus, and, from Eq. [1], the rate of the nucleation of the grain boundary precipitation is enhanced. If the value of σ_{gb} decreases, then θ can choose a higher degree. This means that the shape of the grain boundary particles becomes much more spheroidal.

In brief, phosphorus has effects to increase the precipitation and the rate of nucleation of the intergranular precipitates. As shown in Figures 1 through 3, the results of the observation conform well to this analysis. The particles on the grain boundaries in the no. 1 alloy are scarce, where there are many precipitate-free grain boundaries. The size of the particles is relatively large, because the rate of nucleation in the no. 1 alloy is small. Whereas, because the driving force for carbon, boron, and phosphorus to diffuse to the precipitates is also relatively small, the grain boundary carbide and boride in this alloy cannot grow excessively. In the no. 4 alloy, the high content of phosphorus leads to overprecipitation on the grain boundaries; some of the $M_{23}C_6$ carbide has grown into large pieces and forms a continuous sheet along the grain boundaries. The amount of M_3B_2 phase also rises. Because the average content of boron is lower than that of carbon, and the nucleation rate is largely enhanced, the clusters of the small M_3B_2 particles are, therefore, formed (Figure 4(c)). Comparatively, the no. 3 alloy exhibits an optimal configuration of the grain boundary precipitates.

B. *Effect on the γ' Phase*

Different from the grain boundaries, the interface of the γ and γ' phases is coherent. Strain energy plays an important role in the stability of γ' phase.[8] When two more atoms of impurities are placed on the ordered interface, the strain energy of the interface will increase; of course, the surface free energy of the interface will also increase. According to the Eq. [2]:[9]

$$[\ln C_r]/[\ln C_\infty] = [2VE]/[rRT] \qquad [2]$$

where

C_r = the solubility of the solid near the particle with r diameter;
C_∞ = the solubility of the solid near the particle with infinite diameter;
V = the volume of one gram molecule phase precipitated;
E = the surface free energy of the boundary between the precipitate and the matrix;
r = the diameter of the precipitated particle;
R = the gas constant; and
T = the absolute temperature.

The size of the particles will increase with the surface free energy. In this research, the diameter of γ' particles increases with the phosphorus content. This implies that phosphorus has an effect to lower the stability of the γ' phase. When the phosphorus content reaches 0.051 wt pct, perhaps the strain energy cannot be relieved by the growth of γ' particles, and the η-Ni_3Ti phase begins to precipitate. This phase has no coherent relationship with the γ matrix and is much more stable than the γ' phase. And, for this reason, the η phase was mainly found in the γ matrix.

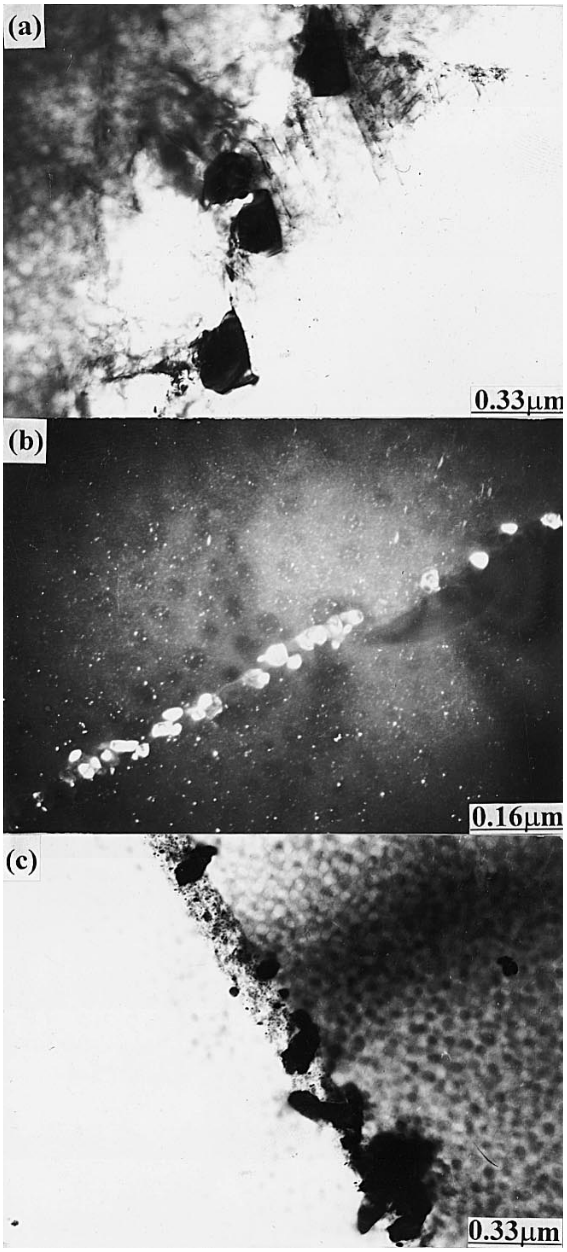

Fig. 4—M_3B_2 on grain boundary: (*a*) no. 1 alloy, (*b*) no. 3 alloy, and (*c*) no. 4 alloy.

C. *Effect on the Stress Rupture Properties*

The fractographs of the alloys are shown in Figure 7; all of the alloys exhibit an intergranular fracture mode. Relatively, the fracture surfaces of the no. 1 and no. 4 alloys are both very smooth (Figures 7(a) and 7(c)), indicating a weak cohesion of the grain boundaries. It has been proposed that phosphorus segregated at the interfaces would

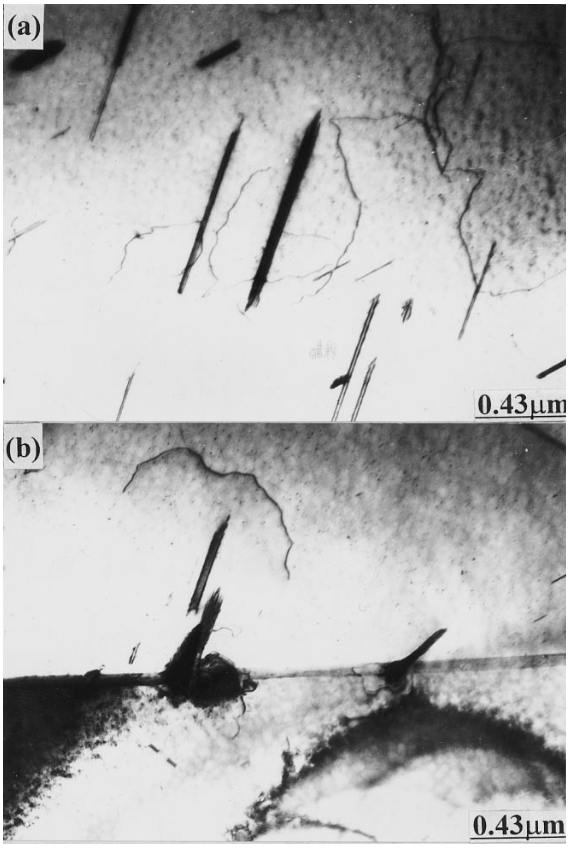

Fig. 5—(*a*) and (*b*) η-Ni_3Ti phase in no. 4 alloy.

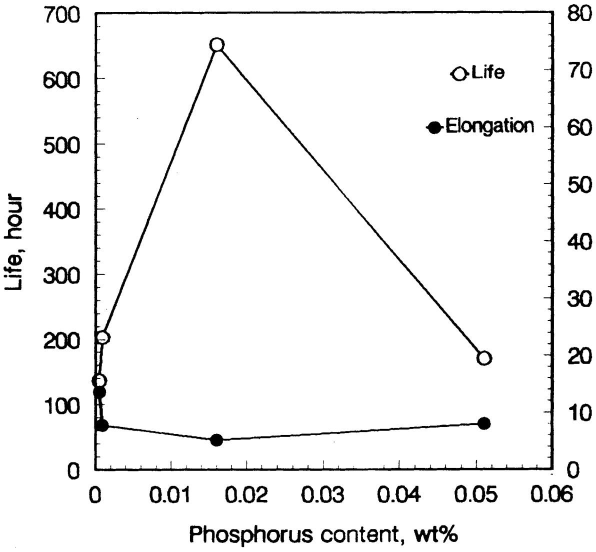

Fig. 6—Effect of phosphorus on the stress rupture properties.

inhibit the diffusion of the embrittling surface elements toward boundaries and, hence, prevent the decohesion.[10,11] If this is the only reason for phosphorus to improve the stress rupture properties, then the no. 4 alloy should have the longest life. But, in fact, the result is just the opposite. Besides, because phosphorus is dissolved into the intergranular precipitates, its function as a boundary scavenger is, therefore, relieved to some extent, although this effect cannot be wholly excluded. So, it is certain that there must be another mechanism for phosphorus to affect the stress rupture properties.

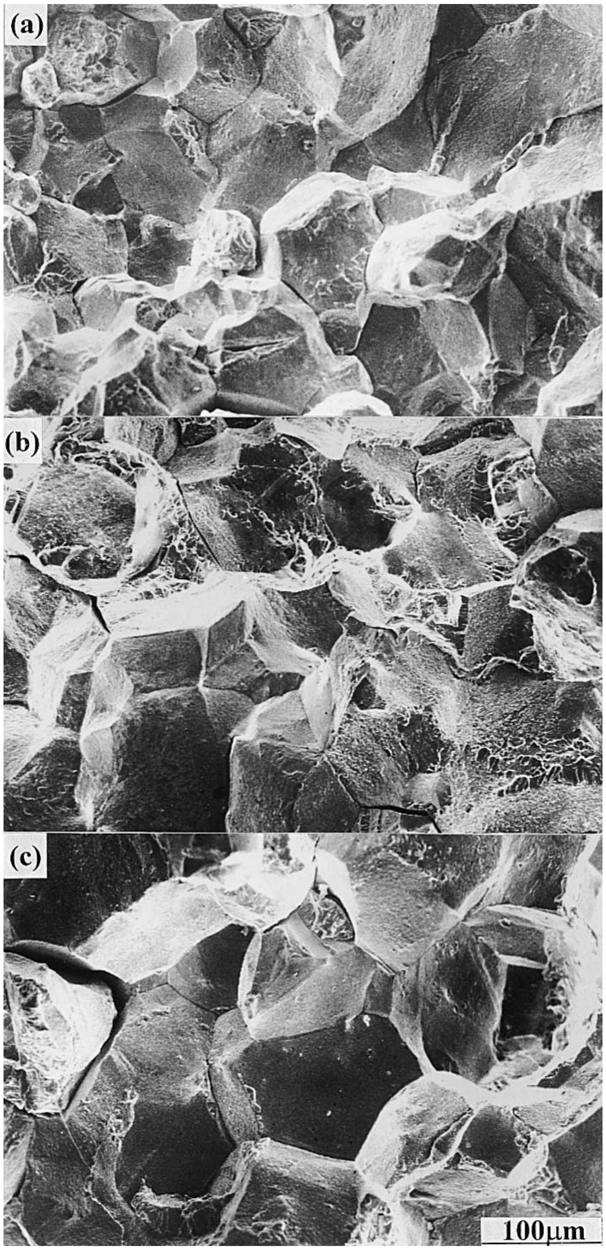

Fig. 7—Scanning electron micrographs of the fracture surfaces of the alloys: (*a*) no. 1 alloy, (*b*) no. 3 alloy, and (*c*) no. 4 alloy.

Grain boundary precipitation takes a great role in the properties, such as creep or stress rupture life.[12,13] The precipitates can inhibit grain boundary sliding and prevent cracking. Conversely, they can also act as the nucleation site of the crack. What role the precipitates takes is determined by the morphology and distribution on the grain boundaries. The no. 1 alloy has many precipitate-free grain boundaries. Although the γ' phase can form on these grain boundaries, as shown in Figure 8, it can only grow into one side of the grain with a not fully developed morphology, due to the coherent relationship with the γ matrix. Apparently, these γ' particles have no ability to prevent the grain boundaries from sliding. Of course, there is a great tendency for the embrittling surface elements to diffuse to the

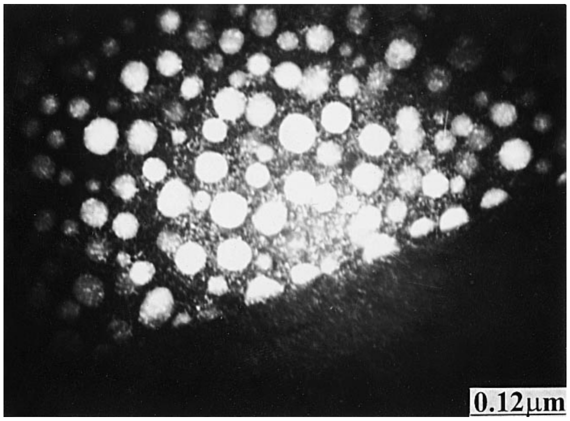

Fig. 8—γ'-$Ni_3(Al,Ti)$ on the grain boundary of no. 1 alloy.

grain boundaries in the no. 1 alloy and cause decohesion. But the most possible candidate, sulfur, may not take this effect. Because sulfur has a strong affinity with titanium and forms the Ti_2SC phase at an elevated temperature in this alloy, phosphorus has no effect on the formation of this phase.[14] So, sulfur segregation at the grain boundaries is slight, and the resulting decohesion effect can be neglected. Although the effect of other surface embrittlers has not been verified, it may be partly determined here that the scarce intergranular precipitation is an important reason for the premature failure of the no. 1 alloy.

In the no. 3 alloy, the intergranular precipitation is optimal. If there is a surplus of phosphorus segregated at the grain boundaries as free atoms, they will also do an additional beneficial effect to resist the surface embrittlers. The fractograph of the no. 3 alloy is shown in Figure 7(b). Many traces of plastic tearing are present on the exposed grain boundaries, indicating that the grain boundaries are bounded together strongly. So, the no. 3 alloy has the longest rupture life.

In the no. 4 alloy, many of the grain boundary particles have grown into large blocks, some have even developed into continuous sheets at many places. This configuration of grain boundary precipitates can easily become the originating site of the cavity and a favoring path for the cracks to propagate. Because the phosphorus segregation has no serious influence on the rupture life, it is confirmed, in this case, that the excessive intergranular precipitation does dominant the fracture process of the no. 4 alloy and makes a drop on the life curve.

V. CONCLUSIONS

1. Phosphorus promotes nucleation and precipitation at the grain boundary. Too low phosphorus content produces many precipitate-free grain boundaries, and too high phosphorus content leads to excessive intergranular precipitation.
2. Phosphorus markedly enhances the rupture life of this alloy in the range of 0.0005 to 0.016 wt pct due to its effect on the improvement of the intergranular microstructure. The optimal content of phosphorus is around 0.016 wt pct in this experiment.
3. Phosphorus increases the size of the γ' particles. When the phosphorus content is high, the η-Ni_3Ti phase inclines to precipitate.

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