MULT-COMPONENT INTERGRANULAR AND INTERFACIAL SEGREGATION IN ALLOY 718 WITH CORRELATIONS TO STRESS RUPTURE BEHAVIOR

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Abstract

The effects of sulfur in the range of 15ppm to 175ppm on the stress rupture fracture and tensile properties of Alloy 718 were investigated. Stress rupture life dramatically decreased with increasing sulfur content. Auger analyses provided direct evidence of sulfur segregation to grain boundaries and carbide/matrix interfaces, and further indicated that stress rupture fracture was mainly controlled by the segregation of sulfur at grain boundaries. However, almost no sulfur segregation was found when the sulfur content was lower than 15ppm. Phosphorous was also found segregated on the grain boundaries. The experimental results suggested that there existed attractive segregation interactions between P and the metal elements Mo, Nb and Cr at grain boundary. The influence of the addition of Mg on mechanical properties was also investigated. Auger results showed that no Mg segregation was found at grain boundaries or carbide/matrix interfaces. However, small particles of Mg sulfide and MgO were found. This may have been associated with the negative effect of Mg on stress rupture life.

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Introduction

Surface and interfacial segregation is currently a very active area of research. This phenomenon is an important problem in materials. The most extensive work has been done on the segregation behavior in binary and ternary alloys[1-4]. Commercial steels and superalloys, such as Alloy 718, are complex systems with many elemental species. Interactions between these elements can powerfully modify their segregation to interfacial surfaces[5]. It is also well known that the process of ductile fracture in steels comprises the growth and coalescence of microvoids which nucleate initially on second phase particles, i.e. non-metallic inclusions and carbides with an intrinsically low interfacial strength[6,7]. Void or cavity formation can be affected by the presence of impurities in solution. Sulfur and phosphorus are generally regarded as the most common impurities and detrimental elements in Nickel-base superalloys. However, the effect of impurity elements on creep and stress rupture fracture is difficult to evaluate from the existing literature. Some studies show no effect[8], others show that impurities are deleterious[9], and others show that impurities can be beneficial[10,11]. Thus, a study of how impurities affect stress rupture fracture in nickel base superalloys is important.

This paper will focus on the influence of interfacial segregation, at grain boundaries and carbide/matrix interfaces, on stress rupture fracture. The influence of Mg at low sulfur levels on mechanical properties will also be investigated. The attractive segregation interaction of P with Mo, Nb, and Cr at grain boundaries is also examined.

Materials and Experimental Procedure

Six experimental heats of IN718 were melted in a 25kg VIM furnace and poured in 15kg ingots for this study. The compositions were developed along two routes. The first route consisted of four alloys with sulfur from a low of 15ppm to a high of 175ppm. The second route included two alloys with the addition of Mg. The chemical compositions of these alloys are listed in Table 1.

Table 1 Chemical Compositions of Alloys

Heat	C	P	S	Ni	Cr	Mo	Al	Ti	Nb	Mg
6	0.040	0.004	0.0015	52.52	18.58	2.98	0.54	1.02	5.18	-
7	0.036	0.004	0.0050	52.52	18.56	2.95	0.49	1.01	5.22	-
10	0.019	0.001	0.0145	52.44	18.52	2.95	0.54	1.05	5.15	-
11	0.019	0.001	0.0175	52.64	18.45	2.97	0.55	1.01	5.11	-
8	0.025	0.003	0.0015	52.70	18.62	2.95	0.50	1.01	5.22	0.0094
9	0.017	0.001	0.0015	52.64	18.56	2.99	0.51	0.99	5.11	0.0076

Mn=0.02, B=0.005, Fe=Bal.

The six ingots were given a two step homogenization treatment (1140°C for 24 hrs plus 1180°C for 24 hrs and air cool). All ingots were forged to 40mm square bars and hot rolled to 18mm round bars. Tensile tests were conducted at room temperature and 650°C and stress rupture tests were conducted at 650°C and 686MPa. Fractographic analysis after stress rupture tests was performed using a Scanning Electron Microscope(SEM). Samples for Auger analysis were cut from the stress rupture test specimen. Grain boundary surfaces were prepared for intergranular fracture by electrolytic hydrogen charging in 0.5M sulfuric acid with 50 mg of $NaAsO_2$/L at room temperature and a current of 400 mA/cm^2. After hydrogen charging for 15 to 20 days, the samples were immediately loaded into a Scanning Auger Microprobe(SAM). The samples were fractured in the hard vacuum of the SAM using a slow strain rate. A 10 kv electron beam with a 1 to 2 micron diameter was used to gather dN(E)/dE Auger spectra from exposed grain boundaries, cleaved matrix areas and carbide/matrix interfaces. For this study, concentrations were reported as peak height ratios(PHR) for the following elements: S 152eV, P 120eV, Ni 848eV, Mo 222eV, Nb 168eV, Cr 529eV, Ti 418eV. Estimates of the interfacial segregation levels were made using sensitivity factors in the *Handbook of Auger Electron Spectroscopy*[12].

Results and Discussion

Mechanical Properties

The tensile properties at room temperature and 650°C as well as stress rupture properties without Mg are illustrated as a function of sulfur contents in Figs.1 and 2. It is apparent that tensile strength, including both ultimate and yield strengths, are not significantly changed with increasing sulfur content. However, sulfur has an obviously detrimental effect on the 650°C tensile properties. It can also be seen that sulfur has a strong detrimental effect on stress rupture life, especially ductility loss. Figs.3 and 4 compare the influence of Mg on tensile properties and stress rupture life at a sulfur level of 15ppm. It should be noted that the addition of Mg did not significantly change the tensile strength either at 650°C or room temperature. Although the ductility at 650°C decreased slightly, the stress rupture life decreased dramatically with the addition of Mg.

Fractography

SEM fractograpy observations of the 650°C stress rupture specimens showed that Alloy 6, with a low sulfur content, was characterized by a microvoid coalescence fracture mode (Fig.5(a)). Alloy 11, with a high sulfur content, had microvoid coalescence within a network of secondary cracks along grain boundaries (Fig.5b). This was taken as an indication of grain boundary embrittlement when the sulfur content was increased to 175ppm. It was also found that the stress rupture life was reduced from 260hrs to 81.2 hrs with the increase in sulfur content (Fig. 14).

Grain Boundary Segregation and Cosegregation

Fig.6(a) shows the fracture surface along multiple grain boundaries produced in the SAM after hydrogen embrittlement. The corresponding Auger spectrum collected from a typical grain boundary in Alloy 7 is shown in Fig.6(b). The grain boundary showed the presence of both phosphorus and sulfur with a characteristic signature of Mo, Cr, Nb, C and N. In order to illustrate the depth profiles of segregated elements at the grain boundary surface, inert ion sputtering was used. The concentration variation of impurity elements P and S and metal elements Mo, Nb, Ti and Cr with sputtering time is shown in Fig.6(c). It was seen that the intergranular concentrations of phosphorus and sulfur decreased with increasing sputtering time. The concentrations of metal elements such as Mo, Nb and Cr also deceased with increasing sputtering time. This excess of elements such as Mo and Nb suggests they may also be segregated to grain boundaries.

Auger measurements were made at more than 20 different grain boundary in each Auger sample.

Fig.7 illustrates the scatter of the cumulative average of S, P, Mo, Nb and Zr as a function of the number of SAM measurements. Alloys 6 and 7 with 40ppm of phosphorus showed average segregated concentrations of phosphorus up to 0.89wt% and 0.95wt%, respectively. The segregation of sulfur was found to be lower than that of phosphorus on grain boundaries. When the sulfur content was reduced to 15ppm as in Alloy 6, the intergranular sulfur content tended to zero. However, as seen from Fig.7(c), a high level of sulfur was detected at grain boundaries in Alloy 11 where the bulk sulfur level was higher(175ppm S). Although Alloy 11 contained only 10ppm of phosphorus, it was still detected on grain boundaries. It appears that phosphorus segregates more strongly to grain boundaries than sulfur.

In addition to the segregation of the impurity elements P and S to the grain boundary, metal elements were also found to segregate to grain boundaries. Fig.8 shows the difference in concentrations of Mo and Nb at grain boundaries and matrix regions. It is obvious that the content of Mo and Nb at the grain boundary is higher than at the matrix.

Alloy 718 is a complex system with many elemental species. Interactions between these elements could modify their segregation to interfacial surfaces. The excess concentration of Mo and Nb at grain boundaries may be due to interactions with other elements. Auger measurements on a large number of grain boundaries supports the contention that Mo and Nb cosegregate to grain boundaries with P. This is shown in Fig.9. Each point in Fig. 9 represents an individual grain boundary. Since Mo and Nb are not normally surface active, they would not be expected to exist in excess on the grain boundaries. One explanation for their behavior is an attractive interaction with P. The distributions of P, Mo, Nb and Cr among individual grain boundaries in three alloys is shown in Fig.10. The Auger PHR distributions of Mo and Nb appear to correlate with that of P while the bulk contents of Mo and Nb in the three alloys is almost constant. However, no correlation was found for S with any of the metal elements. Cr was not found to correlate strongly with the P segregation.

Carbide/Matrix Interface Segregation

Fig.11(a) shows the secondary electron image of a freshly fractured carbide from Alloy 6. The corresponding Auger spectra of the carbide surface before and after ion sputtering is shown in Fig.11(b). This spectra shows a high S peak and a low P peak along with a characteristic signature of C, Nb, N. Fig.12 compares the segregation of sulfur and phosphorus at grain boundaries and carbide/matrix interfaces. Contrary to the grain boundary which exhibits greater P segregation, the carbide/matrix interfaces showed greater segregation of S.

In addition to the sulfur segregation found at grain boundaries and carbide/matrix interfaces, sulfur was also found as sulfide in IN718. Fig.13 shows the SAM photograph of a freshly fractured sulfide morphology and the corresponding Auger spectra before and after ion sputtering. Sulfides were generally smaller than the lateral resolution of the electron beam. This meant that the surrounding matrix was usually present in the spectra from these particles. But it still can be determined that these are iron sulfide in Alloy 6.

The Role of Sulfur Segregation on Stress Rupture Fracture

Fig.14 shows the correlation of stress rupture life and intergranular sulfur segregation with bulk sulfur concentration. Stress rupture life decreased as intergranular sulfur content increased. That suggests that the observed reduction of stress rupture life in this study was due to sulfur segregation at the grain boundaries. There was also evidence for this behavior in the transgranular fracture mode seen in Alloy 6 (low sulfur) compared to the partial intergranular fracture in Alloy 11(high sulfur) (Fig.5a and b). It was found that stress rupture fracture was more sensitive to grain boundary segregation of sulfur than to the much greater concentration of sulfur found at the carbide interface. Thus, sulfur must be kept low to control intergranular sulfur segregation. A threshold in stress rupture improvement appears to be reached at about 50ppm. Below this level the stress rupture life appears not to be controlled by intergranular sulfur concentration(Fig. 14). The next barrier may be the sulfur concentration at the carbide/matrix interface. To strengthen this interface would take the elimination of most sulfur from the system, ie., below 10ppm.

The Distribution of Mg

Several investigators have reported the beneficial effect of Mg on mechanical properties. However, most of these studies were based on alloys that had high sulfur concentrations. In this study no improvement in stress rupture life or tensile properties were found by adding Mg to a low sulfur alloy(Figs.3,4). Fig.15 illustrates the typical SAM spectra from a freshly fractured grain boundary(Fig.14a) and carbide/matrix interface(Fig.15b). The Auger analyses revealed that no Mg segregation was detected on either grain boundaries or carbide/matrix interfaces. Fig.16 shows the SAM photograph and Auger spectrum indicating the probable existence of Mg-rich particles with high sulfur contents. Fig.17 shows another SAM photograph and the Auger spectra before and after ion sputtering. These results suggest that Mg getters sulfur. The formation of Mg sulfide reduces sulfur segregation and promotes beneficial mechanical properties. However, the Mg sulfide and MgO particles have a negative influence on mechanical properties. This is a possible reason for the opposite effects on mechanical properties observed for Mg additions in high and low sulfur alloys.

Conclusions

1. Sulfur has almost no influence on strengths and ductilities of room temperature tensile tests. However, sulfur significantly reduces the 650°C tensile elongation. It also has a strong detrimental effect on stress rupture life and especially on ductility loss at 650°C. The addition of Mg did not significantly affect the tensile properties but decreased the stress rupture life in the low sulfur alloy.
2. Auger analysis provided direct evidence of sulfur segregation to grain boundaries and carbide/matrix interfaces. The segregation was shown to correlate with significant loss in stress rupture life. Even though P also preferentially segregated to grain boundaries, its presence did not correlate with observed changes in mechanical properties.
3. Grain boundary segregation showed the tendency toward attractive interactions of P with Mo and Nb.
4. No Mg segregation was detected at grain boundaries or carbide/matrix interfaces. However, various small particles of Mg sulfide and MgO were observed. It is suggested that these small particles increase void nucleation and lead to a negative influence on stress rupture life when the sulfur content falls below 15ppm.

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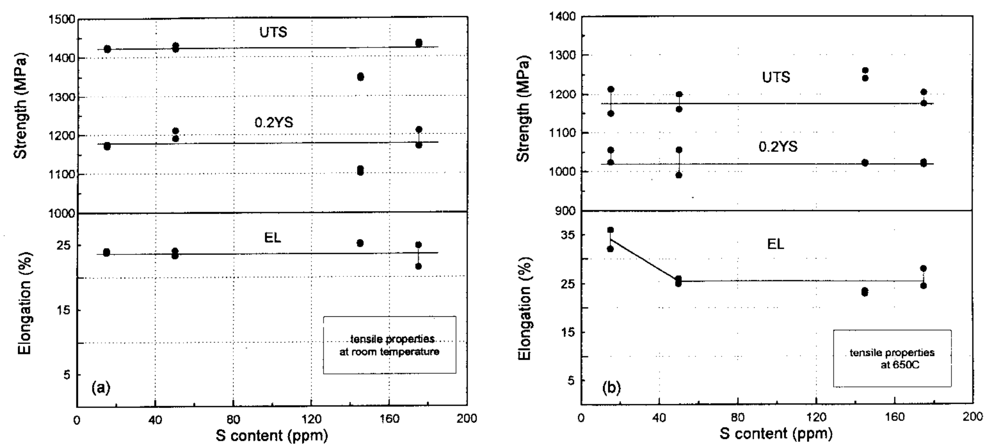

Fig.1 Effect of sulfur on tensile properties at room temperature (a) and 650C (b)

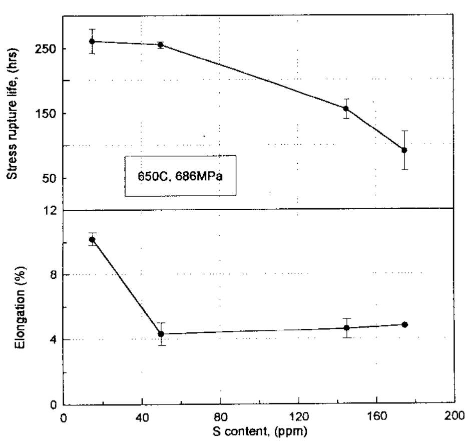

Fig.2 Effect of sulfur on 650C/686MPa stress rupture life and ductility

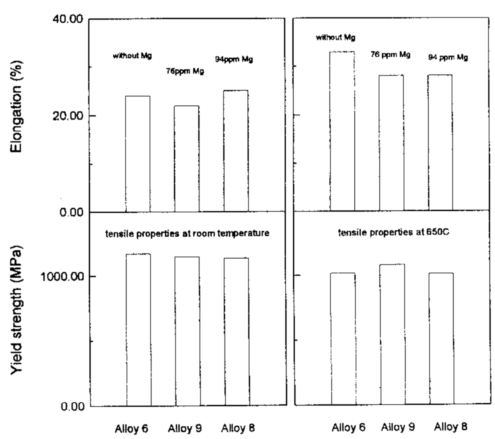

Fig.3 Effect of Mg on tensile properties at room temperature and 650C with the same sulfur level of 15ppm

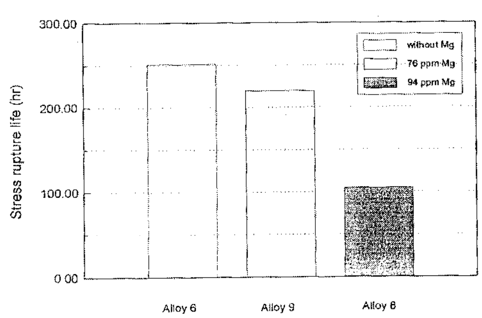

Fig.4 Comparison of stress rupture life with and without Mg during low sulfur level of 15ppm

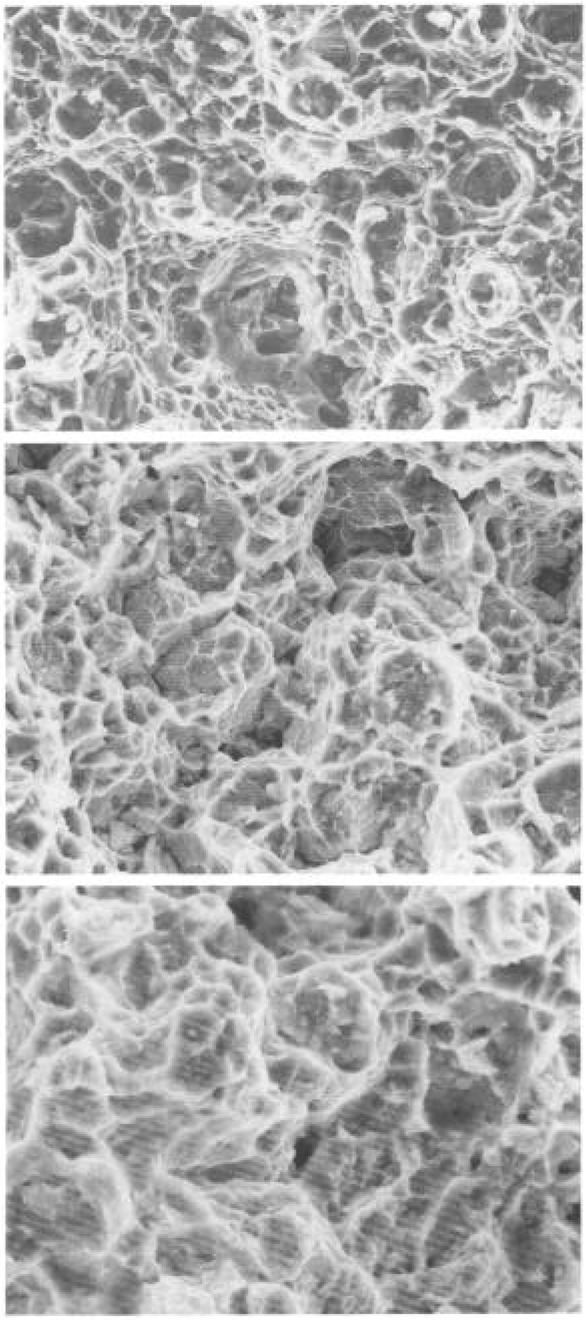

Fig.5 Fractography observations of Alloy 6 with 15ppm S(a), Alloy 11 with 175ppm S(b) and Alloy 9 with addition Mg(c)

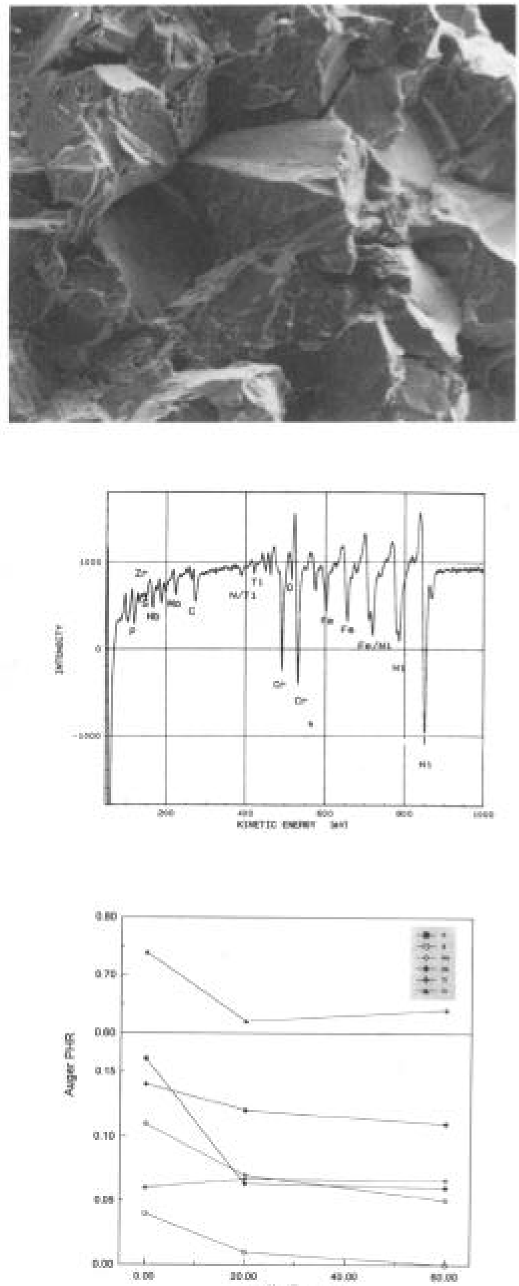

Fig.6 Fractured grain boundary surfaces(a), Auger spectrum(b) and the concentrations as a function of sputter time(c)

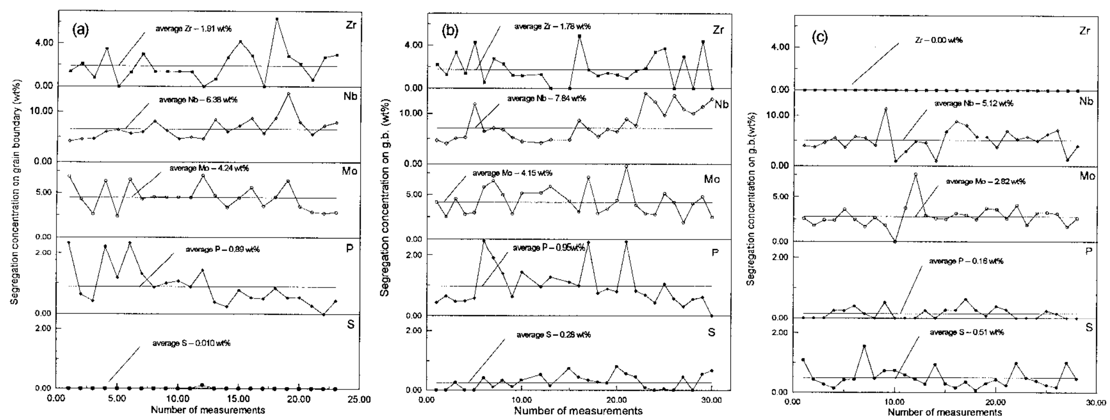

Fig.7 The scatter of the cumulative average of S, P, Mo, Nb and Zr as a function of a number of AES measurements
(a) Alloy 6 (b) Alloy 7 (c) Alloy 11

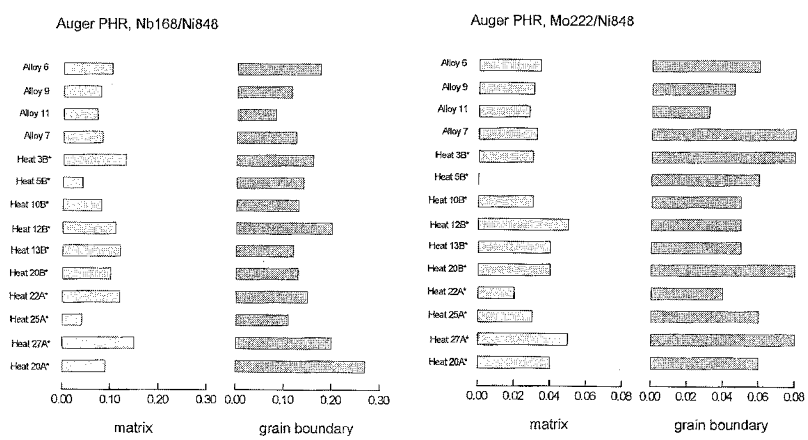

Fig.8 The difference of the average concentrations of Mo and Nb at grain boundaries and matrix regions
(* data from R.G. Thompson, M.C. Koopman and B.H. King, Superalloys 718, 625 and Varivatives, 1991,pp53)

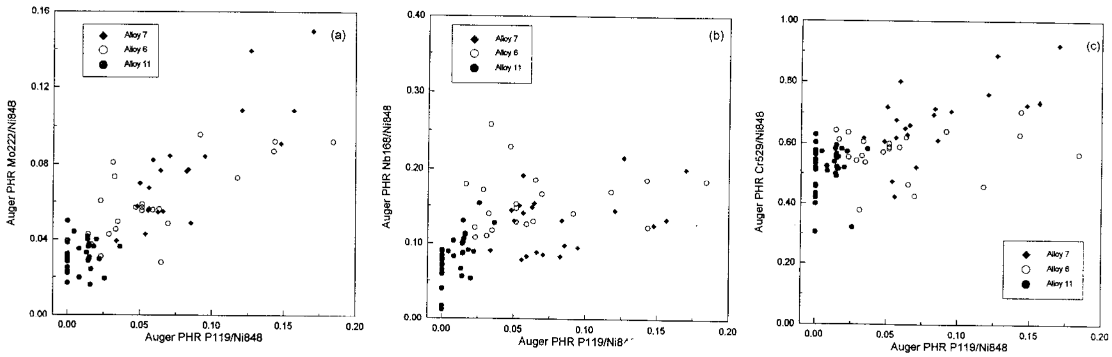

Fig.9 Relationship between the Auger peak ratio of P with Mo (a), P with Nb(b), and P with Cr(c)

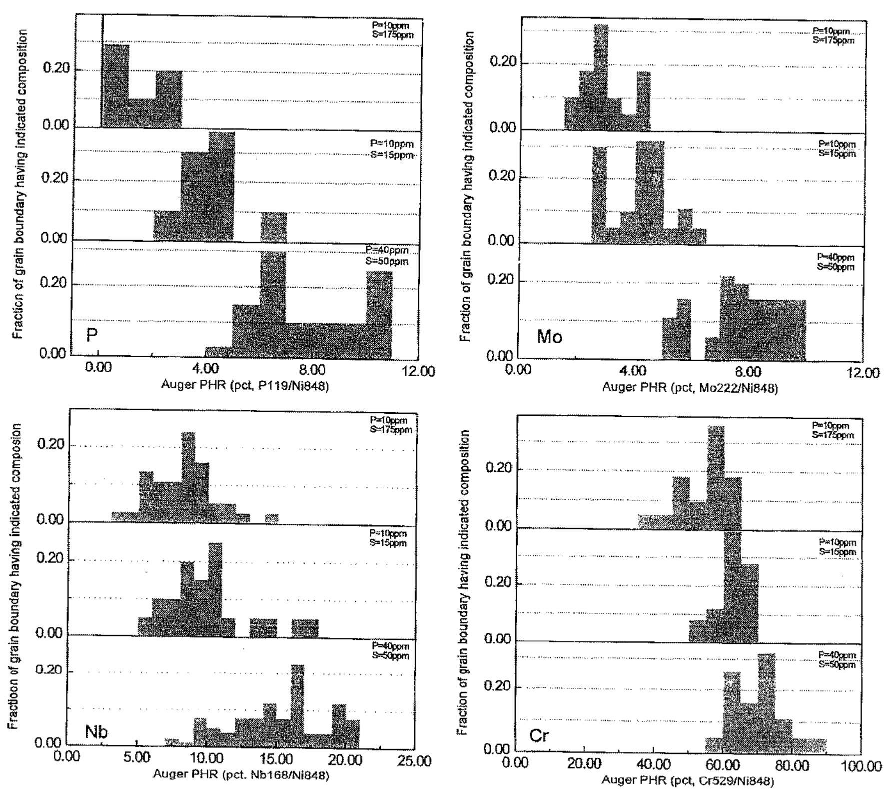

Fig.10 Distributions of P, Mo, Nb and Cr among individual grain boundaries

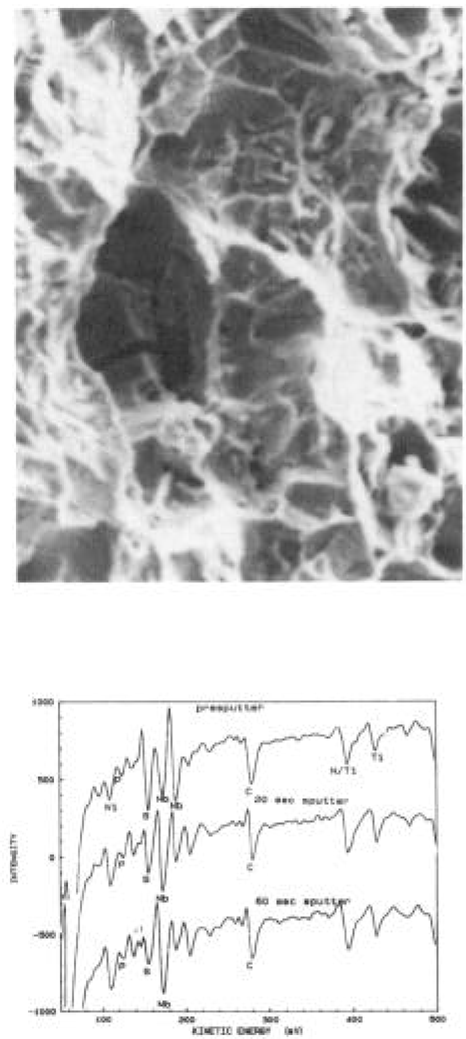

Fig.11 Freshly fractured carbide/matrix surface (a) and Auger chemical spectrum (b) from Alloy 6

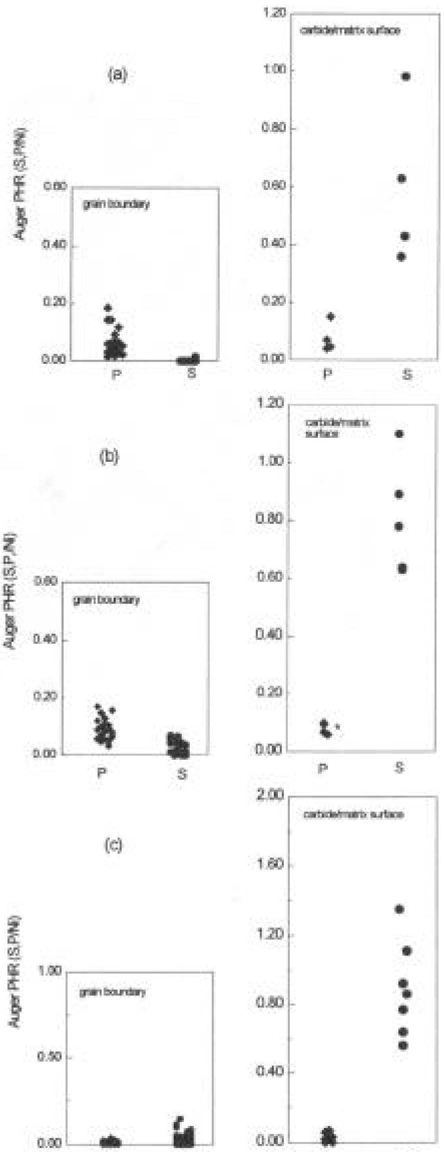

Fig.12 The scatter of the cumulation situation of P and S as a plot of a number of AES measurements at grain boundaries and carbide/matrix surfaces in Alloy 6(a), Alloy 7(b) and Alloy 11(c)

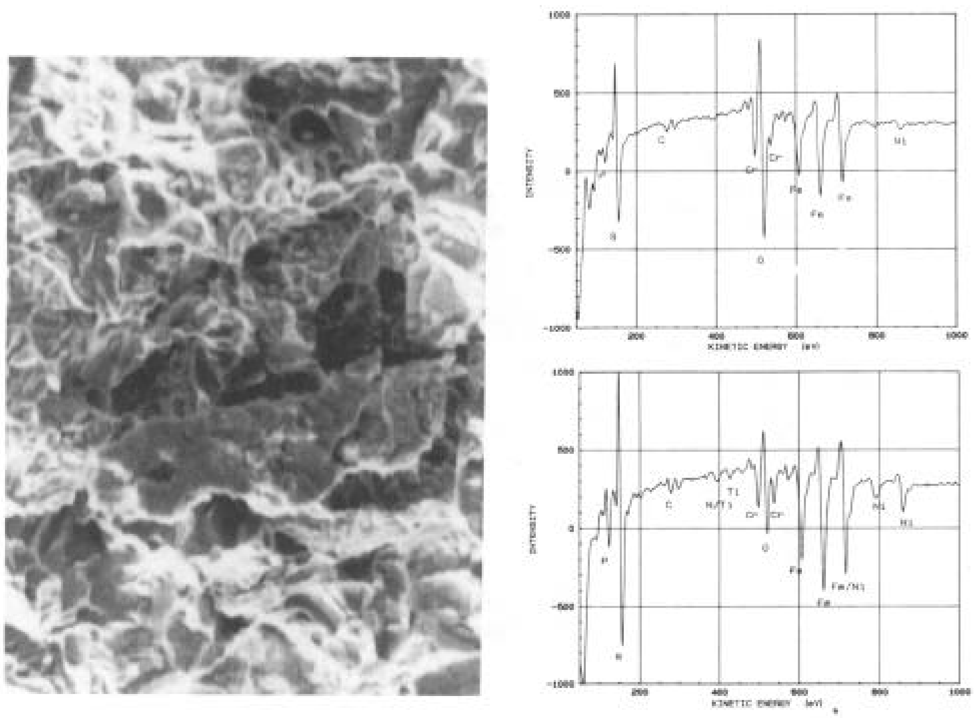

Fig.13 SAM freshly fractured sulfide(a) and Auger chemical spectra of in situ sulfide surface before(b) and after(c) ion sputter in Alloy 6

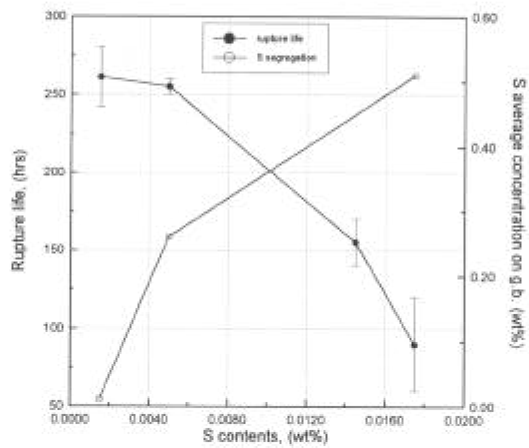

Fig.14 The relationship of stress rupture life with the average segregation concentrations of sulfur with increasing the sulfur content

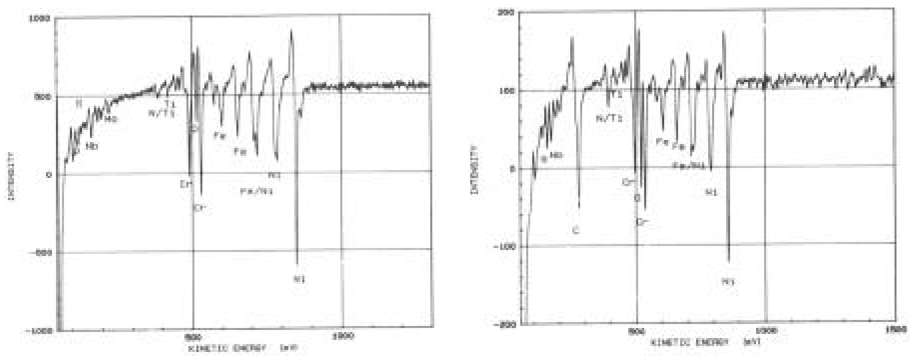

Fig.15 Auger chemical spectra from Alloy 9 showing no Mg segregation at grain boundary(a) and carbide/matrix surface

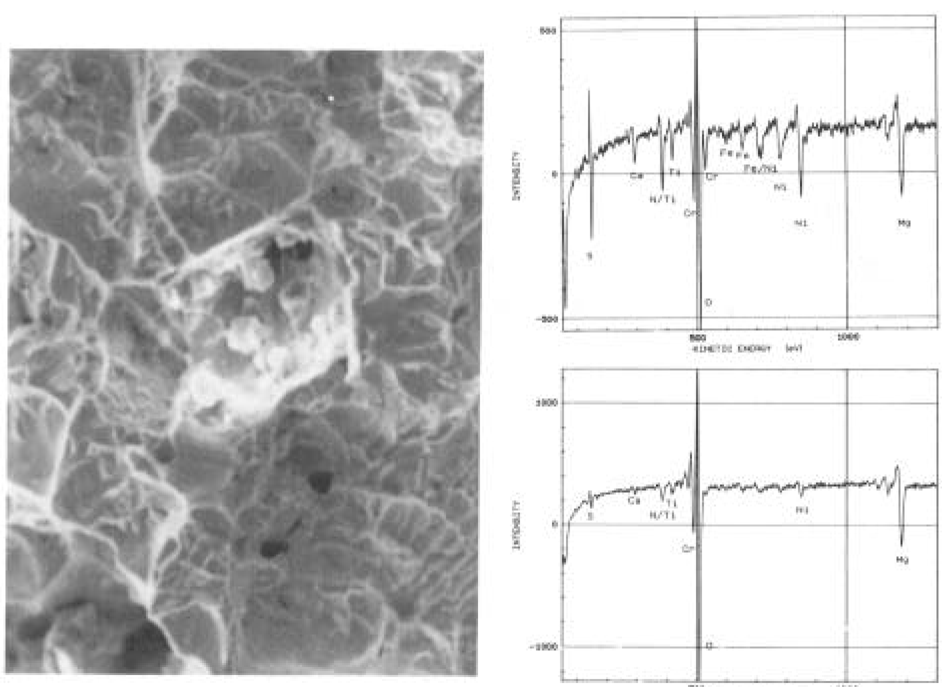

Fig.16 SAM images of small particles(a) and Auger spectra before(b) and after(c) sputter

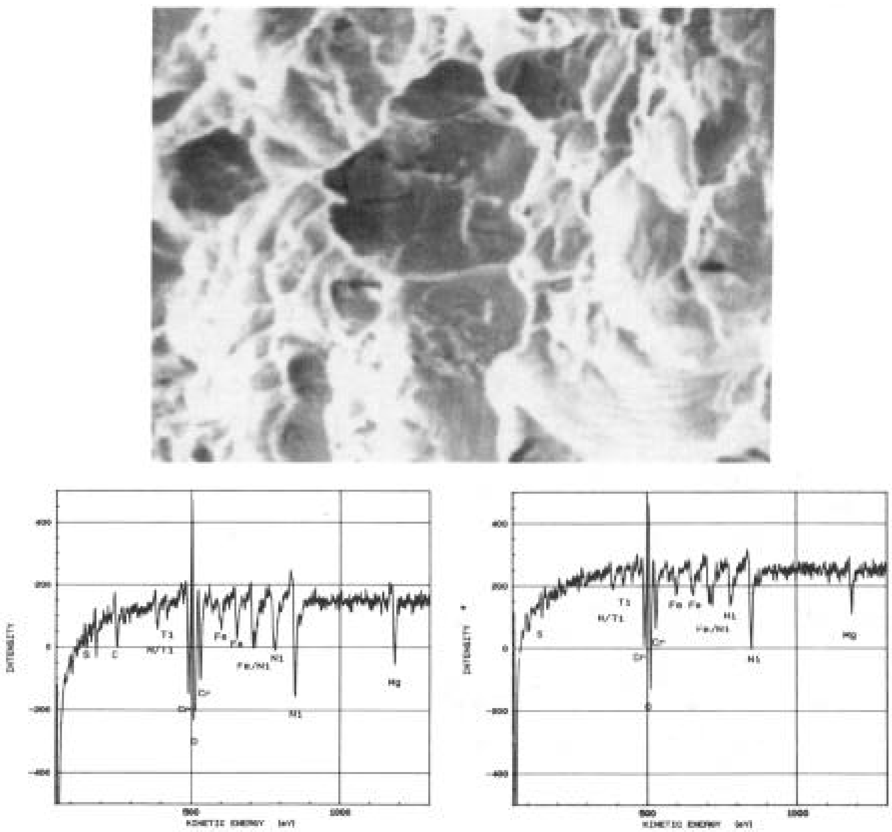

Fig.17 The SAM observation and Auger detection indicating the small particles may be Mg sulfide
(a) SAM image (b) pre-sputter (c) sputter