SEGREGATION BEHAVIOR OF PHOSPHORUS AND ITS EFFECT ON MICROSTRUCTURE AND MECHANICAL PROPERTIES IN ALLOY SYSTEM Ni-Cr-Fe-Mo-Nb-Ti-Al*

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Abstract

Phosphorus is generally considered as a most common impurity and detrimental element in nickel-base superalloys. In contrary, the beneficial effect of P on 650 ℃ stress rupture life and creep behavior has been shown in this paper. For understanding the P behavior in Ni-Cr-Fe-Mo-Nb-Ti-Al system, the role of P has been studied in Ni-Cr-Fe and Ni-Cr-Fe-Mo system alloys and the beneficial effect of P on 650 ℃ stress rupture life and ductility has been also confirmed in INCONEL 718. Auger analysis has demonstrated the grain boundary segregation of P and its severe interaction with Mo. Experimental results suggest grain boundary strengthening effect of P. The detail mechanism and theoretical explanation is still undertaken in research.

* This project is supported by the Chinese National Natural Science Foundation and the Ministry of Metallurgical Industry.

Superalloys 718, 625, 706 and Various Derivatives
Edited by E.A. Loria
The Minerals, Metals & Materials Society, 1997

Introduction

Phosphorus is generally regarded as a common impurity and detrimental element in nickel-base superalloys and most specifications restrict P to a low levels (<0.015%). In some premium quality superalloys the content of P is controlled to a lower level. Recently Zhu et al.[1,2] suggested a new way to improve superalloys, that controlled P to an extreme low level (<0.001%). The effective results were shown in developing low segregation superalloys not only in cast but also in cast-wrought superalloys such as in INCONEL 718[3]. However, Cao et al.[4,5] and Xie et al.[6] have found on the contrary that phosphorus is beneficial for stress rupture lives at 650 ℃ in INCONEL 718.

Cleanliness is considered as a goal in developing premium quality superalloys. In fact, phosphorus and sulfur are non-metallic elements and generally considered as most common impurities in alloys. However, the effect of P and S on stress rupture lives at 650 ℃ are totally contrary[6]: Sulfur is to the detriment of stress rupture life but P is beneficial not only to stress rupture life but also ductility.

INCONEL 718 is a multi-component nickel-base superalloy with complicated structure i.e. γ'' and γ' strengthening phases precipitation in the grains and δ-phase precipitation at grain-boundaries. For systematical study on the role of P in Ni-Cr-Fe-Mo-Nb-Ti-Al system, the role of P (especially grain boundary segregation behavior) in INCONEL 718 has been studied in the first part of this paper. Because of the multi-element interaction and δ-phase precipitation at grain boundaries, the question has been raised that the beneficial effect on stress rupture properties in INCONEL 718 is considered as a special effect? In restriction of alloying elements interaction and grain boundary precipitation, the effect of P on mechanical properties has been studied in most simple alloy system Ni-Cr-Fe. In consideration of the important solid solution element Mo, the effect of P has been studied in Ni-Cr-Fe-Mo system also.

Experimental Procedure

Test Materials

Experimental materials were all vacuum melted, the chemical composition of tested alloys are divided in 3 groups as shown in Table 1 and Table 2. The effect of P on INCONEL 718 was studied in group I alloys in the range of 0.0010 to 0.0130%P. Five heats (see Tab.1 Alloys 11-15) of INCONEL 718 with different contents of P were melted in 25Kg VIM furnace and poured into 15Kg ingots, which were conducted with 2 steps homogenization treatment i.e., 1160 ℃/24hrs→1180 ℃/24hrs/A.C. Group II and group III (see Tab. 2) each contents 4 heats of Ni-Cr-Fe (Alloys 21-24) and 4 heats of Ni-Cr-Fe-Mo (Alloys31-34) with variation of P in the range of 0.0005 to 0.019%. These alloys were firstly melted in 70Kg VIM furnace and poured 2 master bars (Ni-Cr-Fe and Ni-Cr-Fe-Mo) with the lowest content of phosphorus. Each master bar was cut in 4 pieces, then separately remelted in 25Kg VIM furnace to add relevant P contents for producing Ni-Cr-Fe and Ni-Cr-Fe-Mo alloys with the gradient of P contents. Total 13 alloy ingots were forged down to 40mm square billets and finally hot rolled to 18mm round bars for this investigation.

Table I. Chemical Composition of Group I Test Alloys (wt%)

Group	Alloy	C	Mn	Si	S	P	Ni	Cr	Mo	Al	Ti	Nb	B	Fe
I	11	0.02	0.02	0.05	.001	.0010	52.52	18.69	3.01	0.52	1.01	5.20	.005	bal.
	12	0.03	0.02	0.05	.002	.0025	52.38	18.62	2.98	0.47	1.01	5.15	.005	bal.
	13	0.03	0.02	0.06	.003	.0033	52.79	18.56	3.01	0.52	1.00	5.24	.006	bal.
	14	0.02	0.02	0.05	.003	.0083	52.76	18.45	3.05	0.52	1.01	5.17	.006	bal.
	15	0.02	0.02	0.05	.003	.0130	52.90	18.76	3.01	0.50	1.01	5.17	.005	bal.

Table II. Chemical Compositions of Group II and III Test Alloys (wt%)

Group	Alloy	Ni	Cr	Fe	Mo	C	P	S
II	21	bal.	21.59	22.02	--	0.019	0.0005	0.0015
	22	bal.	21.58	21.59	--	0.017	0.003	0.0017
	23	bal.	21.59	21.85	--	0.019	0.010	0.002
	24	bal.	21.50	22.47	--	0.024	0.019	0.002
III	31	bal.	21.90	21.75	2.80	0.015	0.0005	0.001
	32	bal.	21.73	20.28	2.83	0.013	0.003	0.003
	33	bal.	21.90	21.23	2.72	0.018	0.008	0.001
	34	bal.	21.70	20.19	2.55	0.027	0.018	0.004

Heat Treatment

Specimens of Group I alloys for mechanical tests were subjected to standard heat treatment of INCONEL 718 as follows: 960 ℃/1hr/A.C.+720 ℃/8hrs/furnace cooling with the cooling rate of 50 ℃/hr to 620 ℃/8hrs/A.C.

Test alloys of group II and group III were treated as: solid solution treatment 1 hour at 960 ℃ and then air cooled.

Mechanical Tests

Stress rupture tests of group I alloys were performed in air at 650 ℃, 686MPa. Creep tests of some alloys were conducted at 650 ℃,725MPa. For group II and group III alloys, tensile tests at room temperature were taken and then stress rupture tests were conducted in air at 650 ℃,150MPa.

Microstructure and Fractography

Microstructures of Group I (INCONEL 718) alloys were analyzed by optical, scanning electron microscope (SEM) and transmission electron microscope (TEM). The grain elongation behavior was also quantitatively determined by means of optical microscopy.

The Fractography analysis of stress rupture tested specimens of Group I (INCONEL 718) alloys was done by SEM.

Auger Analyses

Auger analysis was directly conducted at fresh fracture surface(in situ) from the stress rupture tested specimens which were hydrogen charged to produce fracture separation at grain boundaries without altering the segregation behavior of the elements found there[7]

Results and Discussion

The content of P in the range less than 130ppm it has almost no effect on tensile strengths (UTS and YS) and ductilities (EL and R.A.) at 650 ℃ and ambient temperature both. However, phosphorus can remarkably increase 650 ℃ stress rupture life and mildly improve ductilities as shown in Figure 1. Figure 2 shows that P has pronounced improvement on creep behavior, especially to prolong secondary creep stage tremendously and results in a longer creep life. INCONEL 718 alloy with high content of P (130ppm) characterizes with unbelievable creep properties.

Microstructure observation on grain structure, δ-phase at grain boundaries, γ" and γ' precipitates in the grains by means of SEM and TEM can not reveal the effect of P on the grain size, morphology and amount of precipitates both.

Optical metalographic observation on the longitudinal sections of stress rupture failed specimens shows grain boundary cracks in the specimens with different contents of phosphorus. A pronounced grain elongation has been observed in INCONEL 718 with higher content of P (83ppm P in Alloy 14) in comparison with low phosphorus content INCONEL

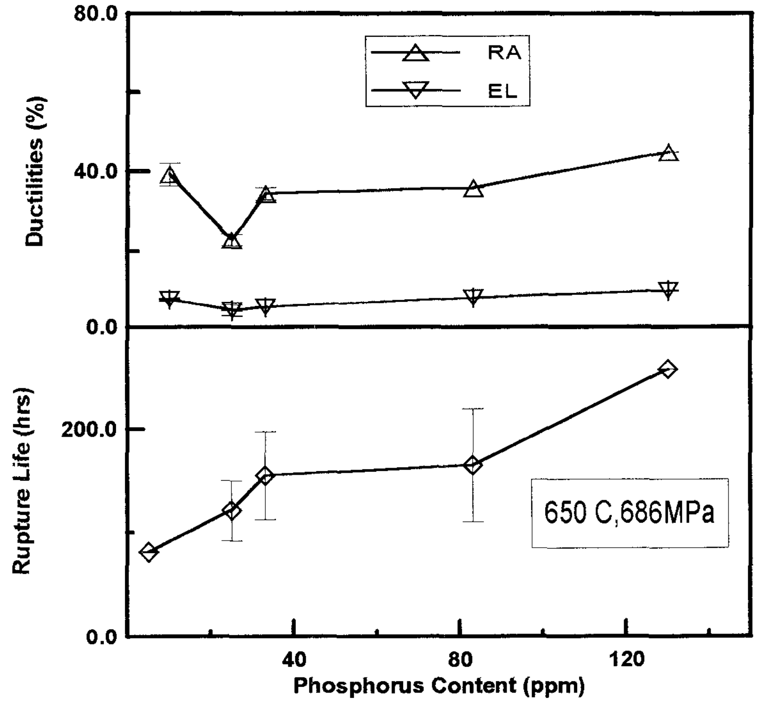


Figure 1- Effect of P on Stress Rupture Properties of IN718.

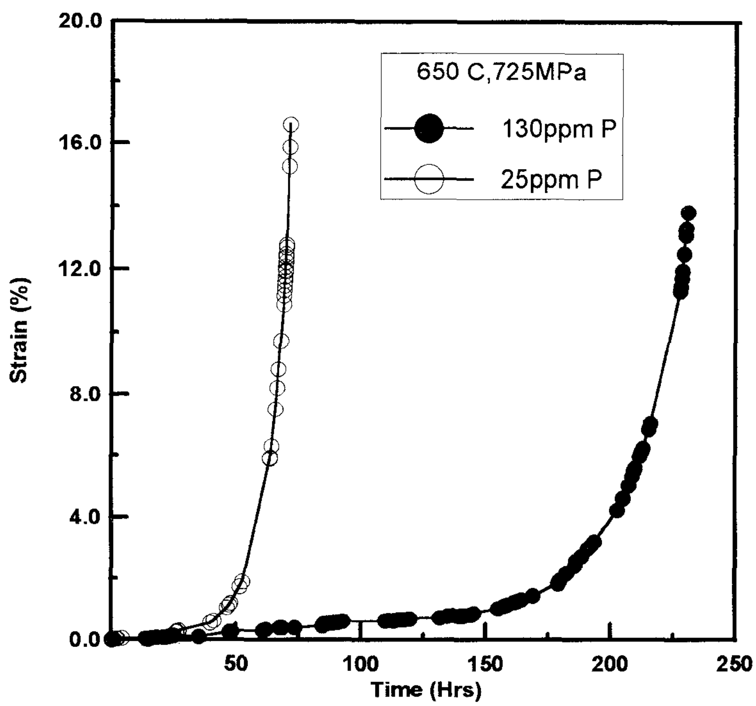


Figure 2- Effect of P on Creep Curves of IN718.

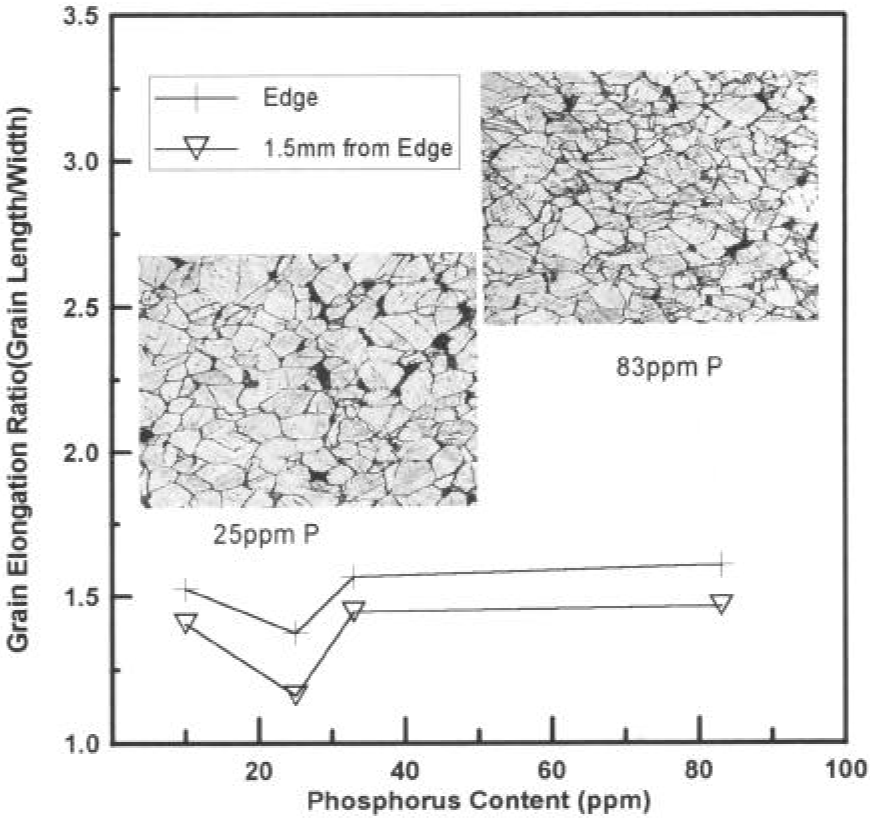


Figure 3 - Effect of P on Average Grain Elongation Ratio of IN718 after 650 C, 686MPa Stress Rupture Test.

718 (25ppm P in Alloy 12) and the average grain elongation ratio can almost reach 1.5 in higher P content INCONEL 718(Alloy 14), see Figure 3.

In similar to INCONEL 718 phosphorus has not pronounced effect on tensile properties as shown in Figure 4 and Figure 5 for Ni-Cr-Fe (Alloys 21-24) and Ni-Cr-Fe-Mo(Alloys 31-34) alloys in the range of phosphorus less than 0.019%. It is valuable to indicate, that P has pronounced effect to increase stress rupture lives in Ni-Cr-Fe and Ni-Cr-Fe-Mo alloys both (see Figures 6 and 7). Molybdenum addition (~3%) in Ni-Cr-Fe base alloys has tremendous effect to prolong stress rupture lives in comparison with Ni-Cr-Fe ternary alloys.

These mechanical test results in different system alloys have confirmed the beneficial effect of P on high temperature stress rupture properties and shown the strengthening and ductility improvement effect of phosphorus.

A pronounced grain elongation as the result of grain boundary strengthening effect of P during high temperature creep of alloys with higher content of P reminds us to study the grain boundary segregation behavior of P and relevant elements.

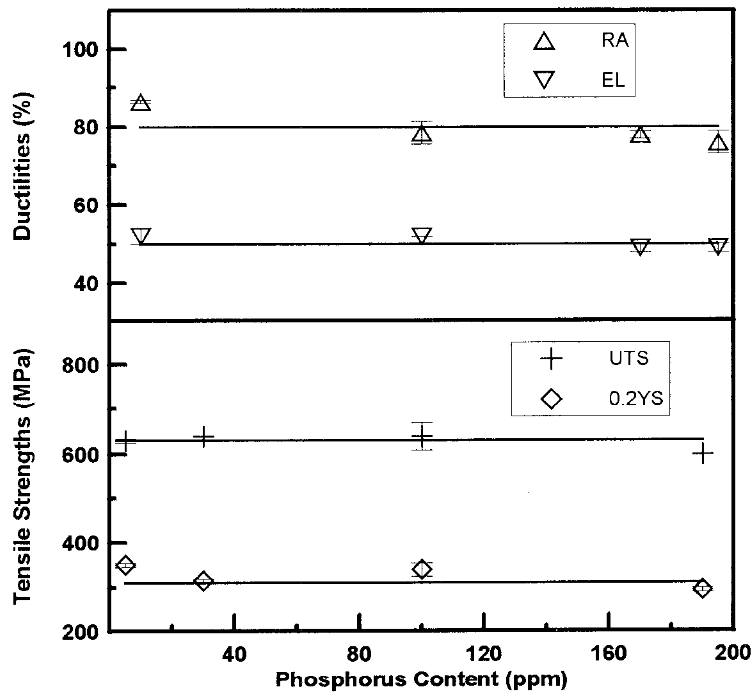


Figure 4 - Effect of P on Tensile Properties of Ni-Cr-Fe Alloys at Room Temeprature.

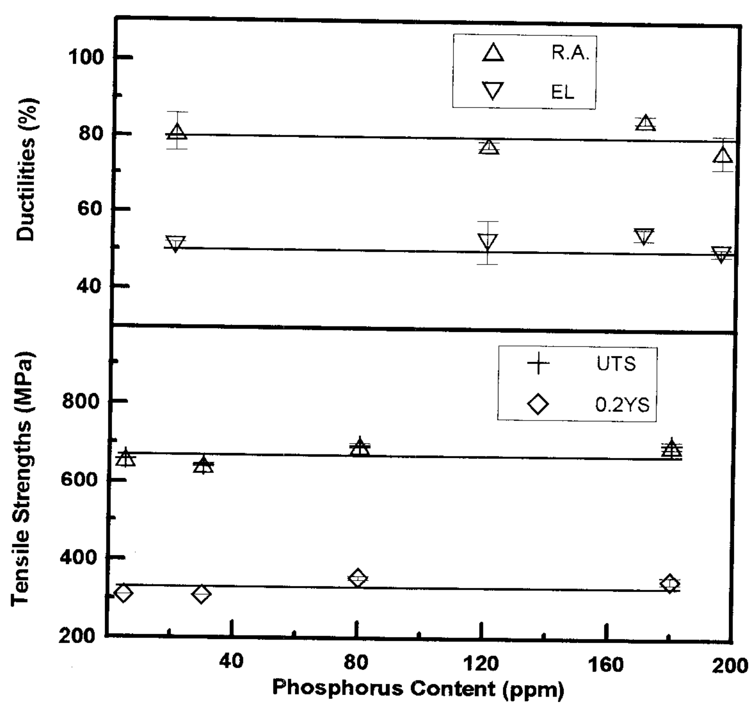


Figure 5- Effect of P on Tensile Properties of Ni-Cr-Fe-Mo Alloys at Room Temperature.

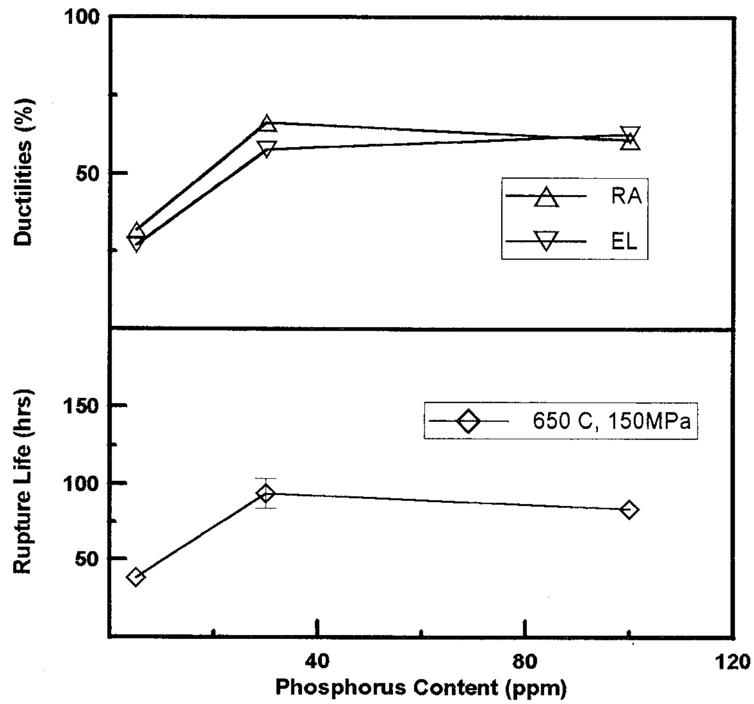


Figure 6 - Effect of P on Stress Rupture Properties of Ni-Cr-Fe Alloys.

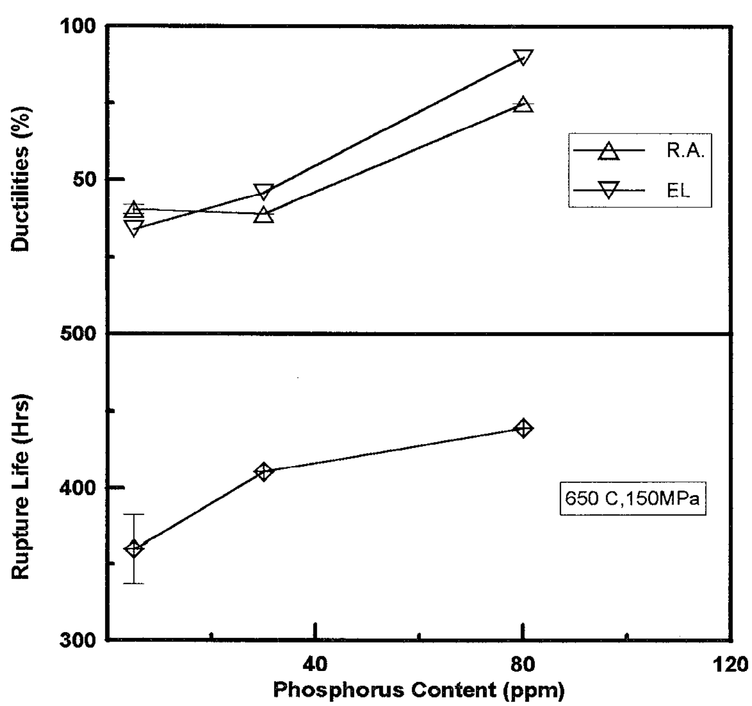
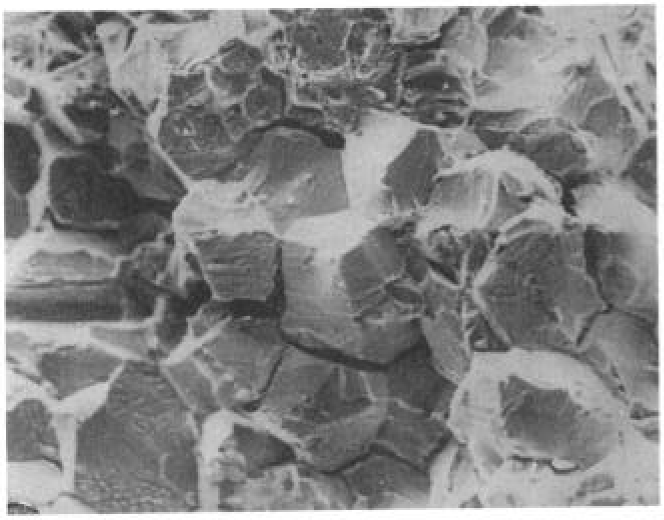
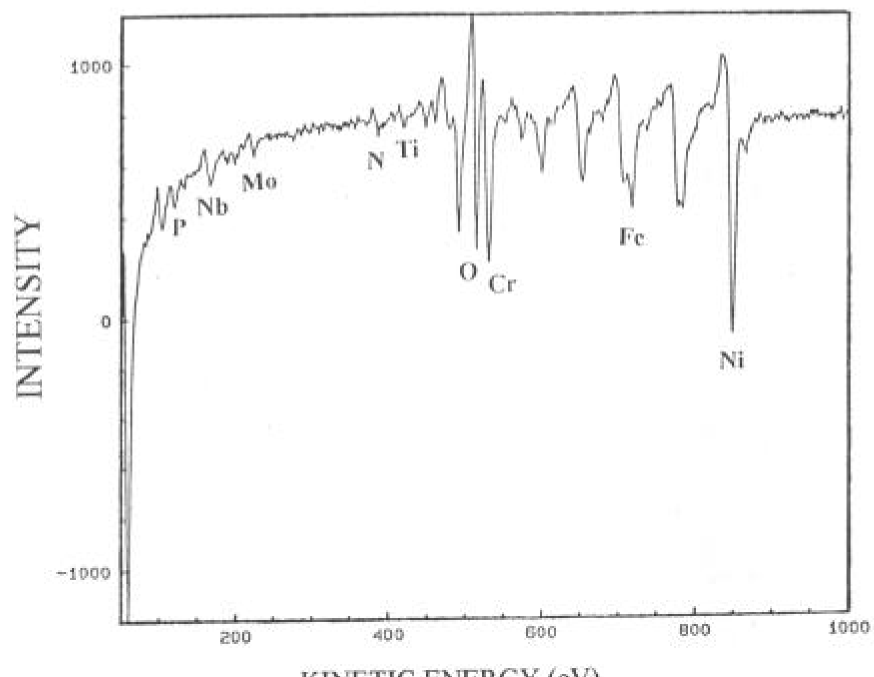


Figure 7- Effect of P on Stress Rupture Properties of Ni-Cr-Fe-Mo Alloys at 650 C, 686MPa.

Figure 8 is a typical Auger-spectrum at the intergranular failed surface which was in situ fractured in the specimen chamber of JAMP-30 Auger-Microprobe and reveals the concentration of Mo, Nb, Ti, Cr and P at grain boundaries.



(a) _______ 20μm



(b)

Figure 8- A Typical Auger Spectrum (b) at Intergranular Fracture (a) Surface of INCONEL 718 Specimen with 30ppm P.

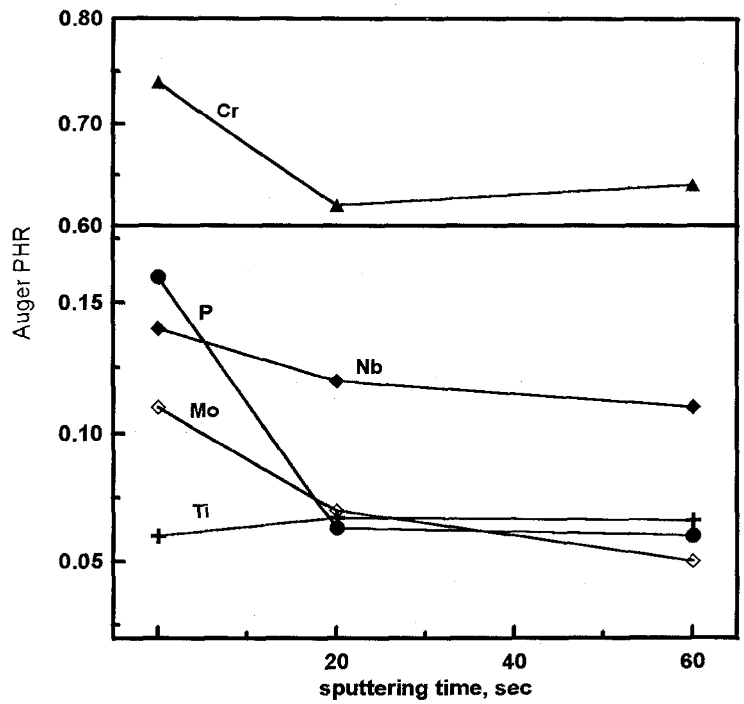


Figure 9 - The concentrations of various elements as a function of ion sputtering time from frature surface.

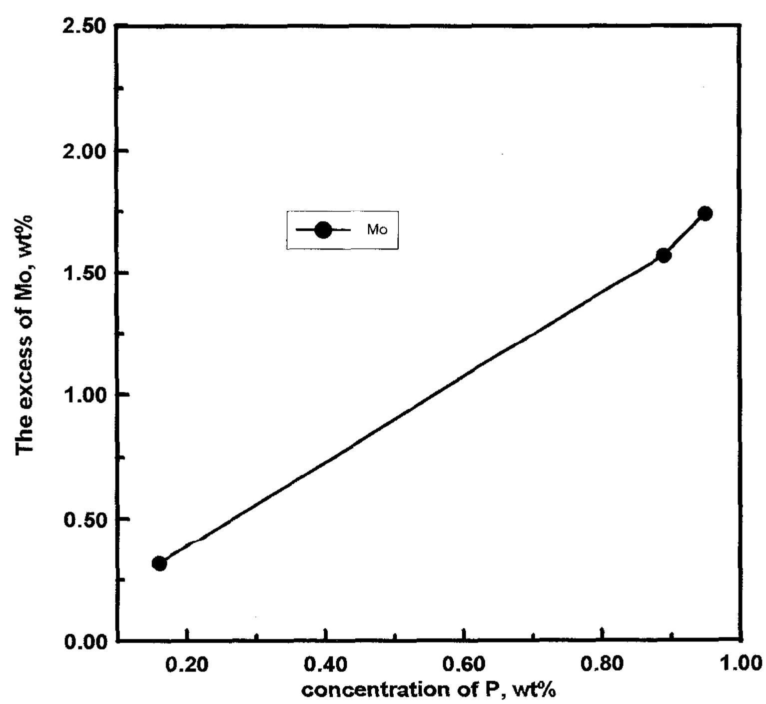


Figure 10 - The Relationship of Mo and P Concentration at Grain Boundary(Average).

Except the severe concentration of P at grain boundaries, the solid solution strengthening alloying elements Cr and Mo also tremendously concentrate there. However, the γ" and γ' forming elements Nb and Ti concentrate mildly at grain boundaries as shown in Figure 9. The highest content of P at grain boundaries can reach 1% as shown in Figure 10 and the excess of Mo at grain boundaries than in γ-matrix is also proportional to P segregation at grain boundaries. The fact of coexistence of high concentration of P and Mo at grain boundaries gives us the idea of atomic interaction of P and Mo. Stress rupture test results have also shown, that the beneficial effect of P is more effective in Ni-Cr-Fe-Mo system than in Ni-Cr-Fe alloys(see Figures 6 and 7). A few experimental results in the recent years show that P can be beneficial for high temperature creep and creep-fatigue properties in Ni-Cr-Fe[8] and 304L[9] austenitic steels as in our investigation.

A hypothesis is tried to suggest that grain boundary segregation of P and its interaction with different elements such as Mo may decrease grain boundary binding energy and increase grain boundary cohesive force. In result of these, phosphorus may effectively strengthen grain boundary and to retard grain boundary cracking at high temperature stress rupture and creep tests. A computer modeling of grain boundary structure is taking in consideration with the results of Auger-Microprobe analyses in further investigation.

Conclusions

1. Phosphorus has almost no influence on tensile strengths and ductilility properties in Ni-Cr-Fe, Ni-Cr-Fe-Mo and Ni-Cr-Fe-Mo-Nb-Ti-Al(INCONEL 718) alloys.

2. Phosphorus can prolong stress rupture lives in Ni-Cr-Fe, Ni-Cr-Fe-Mo and Ni-Cr-Fe-Mo-Nb-Ti-Al(INCONEL 718) alloys and characterizes with strengthening effect and ductility improvement at 650 ℃ stress rupture and creep tests.

3. Phosphorus severely concentrates at grain boundaries and may have intensive interaction with grain boundary segregated alloying elements (such as Mo) in Ni-Cr-Fe-Mo-Nb-Ti-Al (INCONEL 718) alloys.

4. In the view-point of industrial production special attention should be paid on phosphorus content control. However, the theoretical understanding on the phosphorus behavior in superalloys is still not clear yet.

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