THE STRENGTHENING EFFECT OF TANTALUM

IN NICKEL-BASE SUPERALLOYS

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Summary

The strengthening effect of tantalum in nickel-base superalloy (B1900) has been systematically investigated. Tantalum not only raises high temperature tensile strength and creep resistance but also obviously improves ductility in high temperature tensile and stress rupture tests. About 70-80% of the tantalum in the alloy enters the γ' phase, about 15% Ta forms MC type tantalum-containing carbide, the remainder is dissolved in the γ matrix. The beneficial effect of tantalum not only results from enhanced γ' strengthening, but also by solid solution strengthening, and simultaneously the improvement of structural stability at high temperature during long time exposure. Tantalum can also improve thermal fatigue and marine-gas corrosion resistances. Considering strength effects, it may be possible to substitute Nb for Ta.

Introduction

Tantalum has beneficial effect on increasing high temperature strength and hot corrosion resistance in nickel-base superalloys (1,2). Up to date, a number of high performance nickel-base superalloys contain less or more tantalum (sometimes up to 10% Ta). However in recent year literature exist only a few papers dealing with the mechanism of Ta effect (1,2,3), and systematic research work has not been published yet. Tantalum is not only an important strategic metal but also has supply shortage in the world, so its price is very expensive (4). We have investigated the role of Ta in superalloys as a long-term research project and have published some informative papers (5,6). On the basis of systematic research the purpose of this paper is to clarify the role of Ta in nickel-base superalloys and from the viewpoint of alloy strengthening mechanisms this paper describes the possibility of partial or complete substituion of Nb for Ta.

Materials and Experimental Procedure

Vacuum melted experimental cast nickel-base superalloys on 8Cr-10Co-6Mo-6Al-1Ti base alloys with various additions (0-6.4% Ta) of tantalum (modified B1900 alloys) are listed in Table I (see T1-T7). For individual study the role of Ta in γ solid solution phase of these alloys with complicated chemical compositions, two special solid solution strengthened nickel-base alloys with and without Ta, based on results obtained by chemical phase analyses, were melted (see Table I, S1 and S2 alloys). For tentative study the substitution of Nb for Ta, several experimental alloys with 0-4.3% Nb were prepared (see Table I, N1 and N2 alloys).

Table I. Nominal Alloy Compositions(wt%)

Alloy	C	Cr	Co	Mo	Al	Ti	B	Zr	Ta	Nb	Ni
T1	0.13	8	10	6	6	1	0.013	0.08	0	0	Bal
T2	0.13	8	10	6	6	1	0.013	0.08	0.8	0	Bal
T3	0.13	8	10	6	6	1	0.013	0.08	1.5	0	Bal
T4	0.13	8	10	6	6	1	0.013	0.08	2.3	0	Bal
T5	0.13	8	10	6	6	1	0.013	0.08	3.0	0	Bal
T6	0.13	8	10	6	6	1	0.013	0.08	4.3	0	Bal
T7	0.13	8	10	6	6	1	0.013	0.08	6.4	0	Bal
N1	0.13	8	10	6	6	1	0.013	0.08	0	2.15	Bal
N2	0.13	8	10	6	6	1	0.013	0.08	0	4.3	Bal
S1	-	14	16	8.5	-	-	-	-	1	-	Bal
S2	-	10	13	7	-	-	-	-	0	-	Bal

Heat Treatment: 1080°C/4h/A.C. + 900°C/10h/A.C.

Long time structural stability study has been done in alloys T1-T7 at 750-900°C for 1500h exposure. Alloy T6 with 4.3% Ta was also long time exposured at 750-900°C for 10000h and selected specimens of alloy T6 after exposure were conducted for tensile test at 760°C and stress rupture test at 760°C, 647MPa. Furthermore, long time stress exposure was also conducted for alloy T6 at 750°C, 338MPa; 816°C, 245MPa; 870°C, 118MPa and 900°C, 98MPa almost till to 10000-20000h.

The effect of Ta on micro-structure and alloying element partitioning among the phases in alloys was studied by optical and quantitative metallography, DTA, TEM and chemical phase analyses after electrolytic extractions (7). As mechanical property criteria were selected tensile test at 760°C, stress rupture at 760°C, 647MPa and 980°C, 200MPa. Except these, creep tests at 760°C were conducted for selected alloys with various additions of Ta and Nb respectively and solid solution strengthened alloys with and without tantalum. After creep tests the fracture surfaces and thin foil specimens were also examined by SEM and TEM respectively.

Thermal fatigue tests were directly conducted on cast blades, and thermal fatigue crack lengths on the blades were measured for comparison after 180 cycles from 900°C to ambient temperature through water cooling. The influence of marine-gas corrosion resistance was conducted under salted fog (50ppm 10% NaCl + 90% Na_2So_4 solution) atmosphere for 25h at 900°C and average corrosion weight loss was measured.

Results

Mechanical Properties

The role of Ta. Ta addition in superalloys not only increases tensile strength at 760°C but also the ductility, as shown in Fig1. The stress rupture strength and ductility at 980°C, 200 MPa and 760°C, 647 MPa are increased remarkably with the increasing Ta content in alloys. Particularly the increment of ductility at 760°C, 200 MPa is even more apparent (Fig.2).

The mechanical properties of alloy with 4.3% Ta after long-time exposure for 10000 hours at 750°-900°C were determined, as shown in Fig3. The tensile strength tends to slightly increase after long-time exposure at 750°C, but mildly decreases at 800°-900°C with prolonging exposure time. The stress rupture life continuously increases with exposure time at 750°, 800°C, but decreases at 850°C, 900°C.

The creep curves of alloys with various contents of Ta are shown in Fig4. The creep rupture life is prolonged with the increasing Ta in alloys and creep ductility is also raised. Meanwhile, the steady-state creep rate is decreased. The begining of the tertiary stage creep is also retarded. So that, the creep property is entirely improved by Ta addition as shown in Fig5. Ta addition can also improve thermal fatigue and marine-gas corrosion resistances, as shown in Fig6.

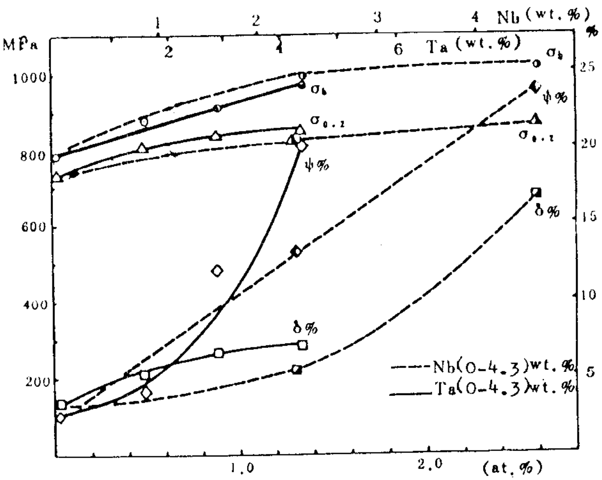

Fig.1. The influence of Ta and Nb in alloys on tensile properties at 760°C.

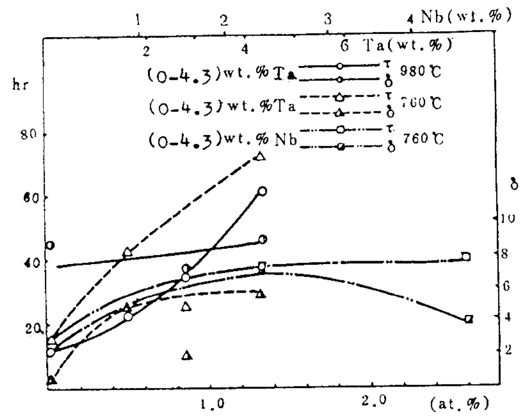

Fig.2. The influence of Ta and Nb in alloys on stress rupture properties at 760°C, 647 MPa; 980°C, 200 MPa.

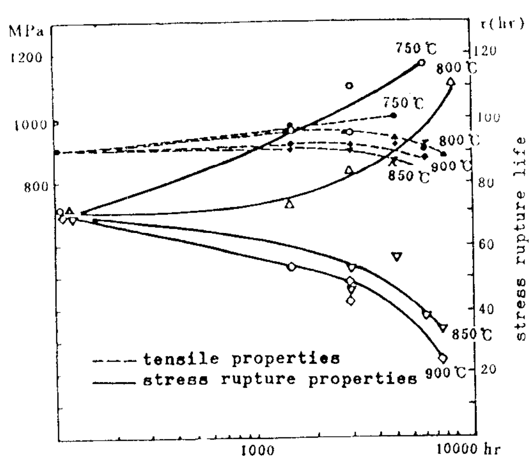

Fig.3. The influence of long-time exposure at 750-900°C on 760°C, 647 MPa stress rupture properties and ultimate strength of alloy T6 with 4.3%Ta.

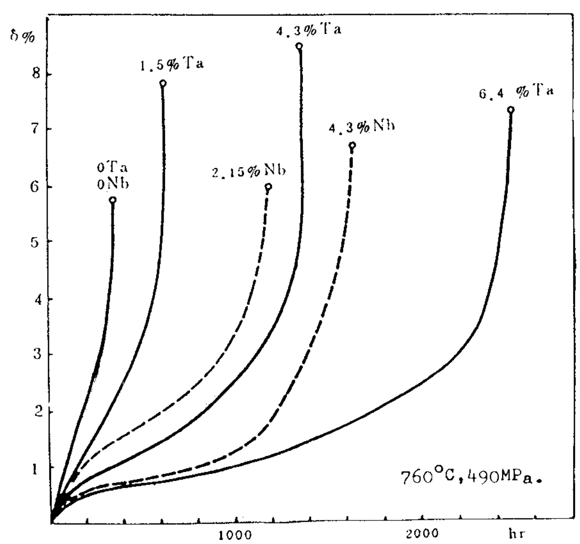

Fig.4. The creep curves of alloys with various contents of Ta and Nb.

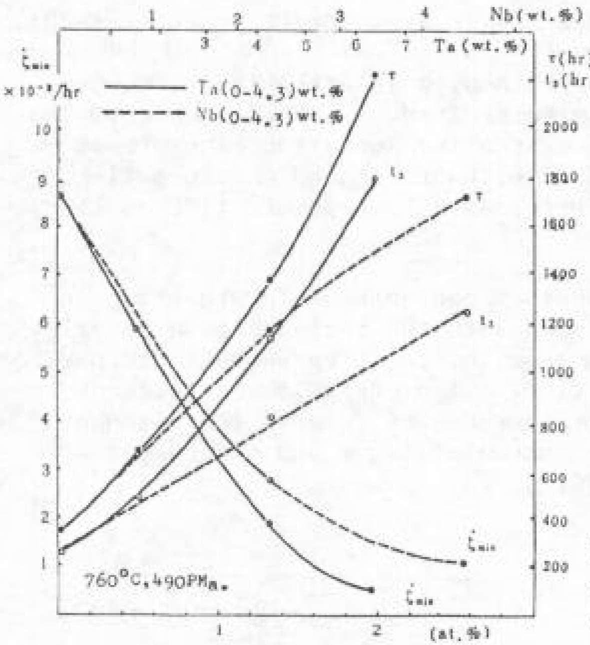

Fig.5. The influence of Ta and Nb in alloys on steady-state creep rate $\dot{\xi}_{min}$, time begining on tertiary creep t3 and creep rupture life τ.

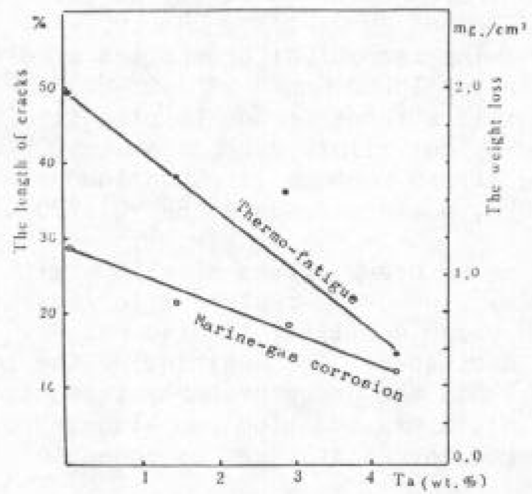

Fig.6. The influence of Ta in alloys on thermo-fatigue and marine-gas corrosion resistance.

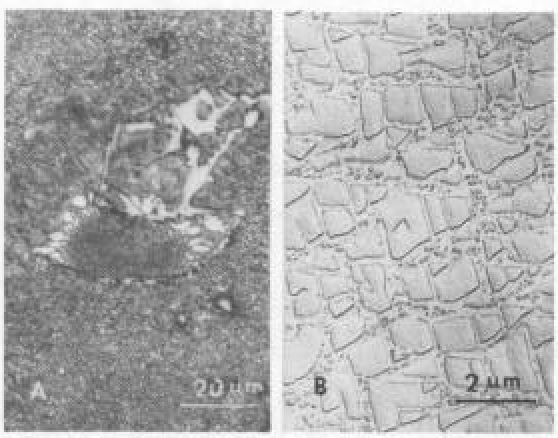

Fig.7. Microstructures of B1900 type alloy.

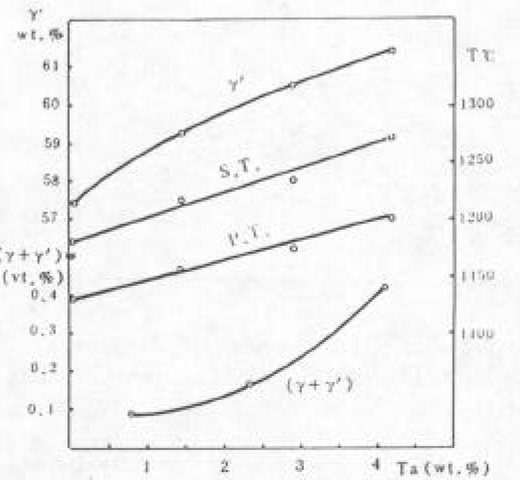

Fig.8. The influence of Ta in alloys on γ' fraction, (γ+γ') eutectic, γ' solution (S.T.) and precipitation (P.T.) temperature at heating and cooling respectively.

The role of Nb. The tensile properties, stress rupture properties and creep curves at 760°C of the alloys with various contents of Nb are shown in Fig1,2 and 4 in comparision with various Ta addition alloys. The atomic equivalent Nb increases the tensile strength, stress rupture strength and creep resistance as similar as Ta does. Both 760°C tensile and creep ductility are enhanced, but the increment of creep ductility by Nb addition is not so large as in case of Ta. It is possible to make substitution of Nb for Ta from the viewpoint of improving strength and ductility. However, the Nb effect on thermo-fatigue, oxidation and marine-gas corrosion is still unknown; it is currently being studied.

Structure and its stability

The influence of Ta on as-heat-treated microstructure. As-heat-treated microstructure of (T1-T7) alloys with various contents of Ta (0.6.4%Ta) consists of γ-solid solution, large and small γ' precipitates in γ-matrix, MC, M_6C, $M_{23}C_6$ carbides, M_3B_2 boride and primary eutectic (γ+γ') located both in grains and at grain boundaries, as shown in Fig7A, b. Ta addition in alloys increases γ' fraction apparently, slightly increased primary carbide MC, but decreases the total amount of secondary carbides M_6C and $M_{23}C_6$. About 70-80% total amount of Ta in alloys dissolves in γ' phase as Ni_3 (Al,Ti,Ta). For instance, in a 4.3% Ta-containing alloy, 3.5%Ta dissolves in γ' phase. The γ' fraction, amount of primary eutectic phase (γ+γ'), γ' phase solution temperature at heating (S.T) and precipitation temperature at cooling (P.T) all increase with Ta contents in alloys, as shown in Fig8. As a result of solution of Ta in γ' phase, Ta content in γ' increases apparently with the increasing amount of Ta in alloys, but the amounts of Al, Mo, and Cr decrease as shown in Fig9. A great deal (about 4/5) of the main and minor phases (MC, M_3B_2, M_6C, and $M_{23}C_6$) in as-heat-treated alloys is MC. About 15% total

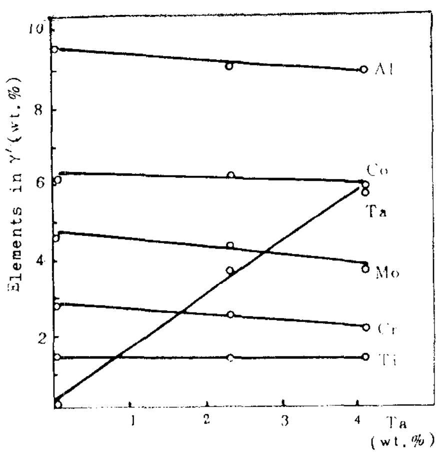

Fig.9. The influence of Ta in alloys on γ'composition.

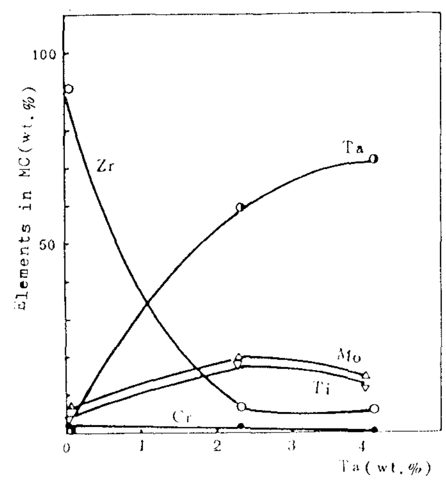

Fig.10. The influence of Ta in alloys on MC composition.

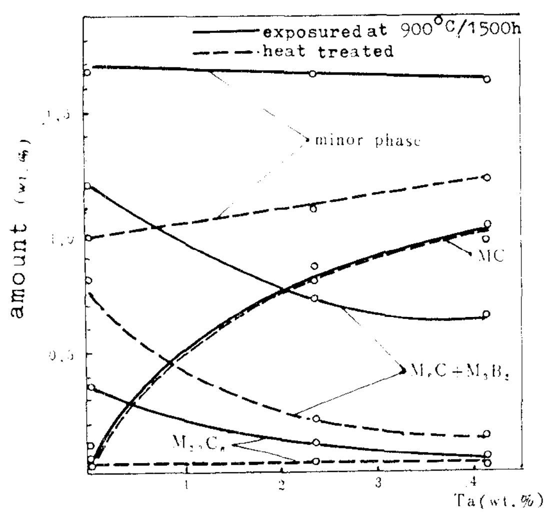

Fig.11. The influence of Ta in alloys on the amounts of MC, (M_6C+M_3B_2) and $M_{23}C_6$ phases at as-heat-treated state and after 900°C 1500h exposure.

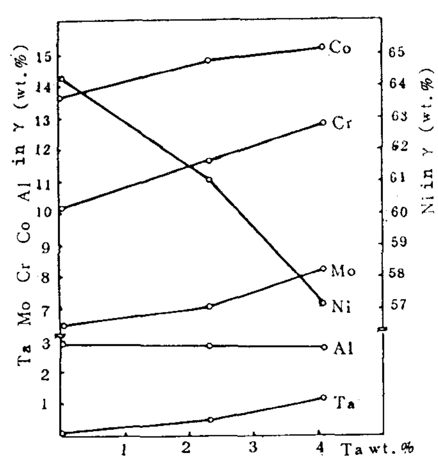

Fig.12. The influence of Ta in alloys on γ matrix composition.

amount of Ta in experimental alloys appears in MC carbide. Fig10 is the MC carbide compositions in alloys with various contents of Ta. It is obvious that Ta content in MC increases but the Zr, Ti, Mo and Cr all decrease with the increasing Ta in alloys as shown in Fig10. Fig11 shows that the total amount of the minor phases increases with the increasing Ta in as-heat-treated alloys, but the main increase is only MC carbide. The $M_{23}C_6$ carbide fraction does not change basically, but the amount of M_6C carbide decreases significantly with the increasing Ta in alloys. Thus, Ta addition in alloys can depress M_6C phase precipitation and enhances structural stability. The remaining part (about 10% total amount of Ta in alloy) is soluted in matrix. It is worthwhile to mention that the solution of Ta in the matrix does not decrease but increases the solubility of main solid solution strengthening elements such as Co, Cr and Mo etc. For instance, the solubility of (Co+Cr+Mo) is 35% in Ta-free alloy, but 43% in alloy containing 4.3%Ta.

The influence of Ta on structural stability. The T.C.P. phase does not appear in the alloys with various contents of Ta after 1500h exposure at 800°C,850°C,900°C and also does not appear in alloy T6 with 4.3% Ta after long-time exposure at 750°C,800°C,850°C,900°C for 10000h and long-time stress exposure at 750°C, 338 MPa for 20144h,816°C,245MPa for 15240h, 870°C, 118 MPa for 12434h, 900°C, 98 MPa for 25576h either. It indicates good stability. However, the γ' phase and carbides ($M_{23}C_6$ and M_6C) change apparently. The coagulation rate of γ' phase is depressed by Ta addition in alloys during high temperature exposure. The γ' fraction increases with the exposure time at 750°C and 800°C, but oppositely decreases at 850°C and 900°C (6). After long-time exposure at 900°C for 800h the small γ'phase dissolves in matrix of the alloy without Ta but in alloy with 4.3% Ta the small γ'phase does not dissolve. After long-time exposure at 850°C for 800h, the γ'phase coagulates and grows evidently in the alloy without Ta, but in alloy with 4.3% Ta these phenomena does not significantly show (Fig13).

The MC carbide is stable and does not decompose at long-time exposure at different temperature. Fig11 indicates the MC fraction does not change in the alloys with various contents of Ta after 900°C,1500h exposure, but

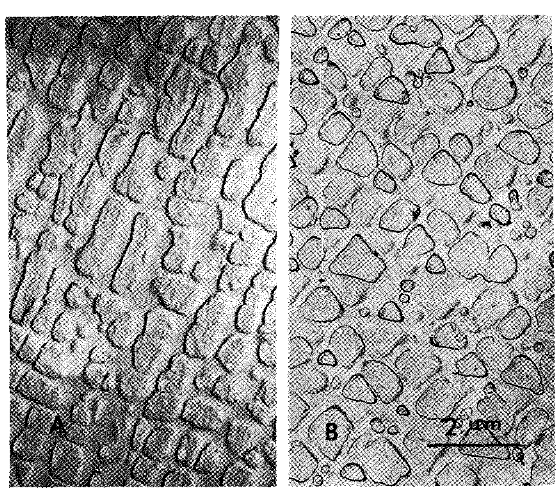

Fig.13 The influence of Ta in alloys on γ' stability after 850°C, 800h exposure (a-0%Ta, b-4.3Ta)

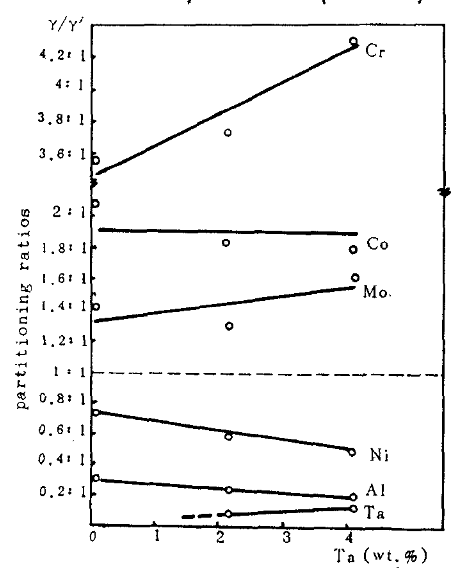

Fig.14. The influence of Ta in alloys on alloying element partifioning ratios between γ and γ' phases.

the increment of carbides after long-time exposure (mainly $M_{23}C_6$) decreases with the increasing Ta in alloys. It means Ta has the beneficial effect to resist the secondary carbide precipitation.

As shown in Fig 14 the partitioning ratio of Ta itself between γ and γ' phase is increased by the Ta addition in alloys, while the partitioning ratios of Ni,Al, in γ/γ' decrease and the partitioning ratios of Cr, Mo in γ/γ' increase and partitioning ratio of Co in γ/γ' does not show significantly change with the increasing Ta in alloys. These partitioning phenomena will induce important effect on strengthening of alloys.

Discussion

Ta in B1900 type alloy not only increases the tensile and streses rupture strength, prolongs creep fracture life, decreases steady-state creep rate, but also increases the tensile, stress rupture and creep fracture ductilities. It indicates the complex beneficial effect on strengthening and ductility improvement. Moreover, Ta improves the thermo-fatigue and marine-gas corrosion resistances. The beneficial effect of Ta is closely related to the partitioning ratio of Ta in each phase. About 70-80% total amount of Ta in alloy enters into γ' phase, 15%Ta goes to form MC carbide. The remaining part of Ta is soluted in γ matrix. Thus, the role of Ta is directly related to the γ' phase strengthening, γ solid solution strengthening and also closely related to structural stability of precipitated carbides from γ solid solution. First of all Ta enhances γ' phase strengthening effect, i.e. increases γ' phase fraction, enhances γ' solution temperature and changes γ' composition. For instance, in comparison T1 alloy (0%Ta) with 4.3%Ta addition T6 alloy in as-heat-treated state, it can increase γ' weight fraction from 57.4% to 61.5%1, γ' solution temperature from 1180°C to 1270°C and the $(\gamma+\gamma')$ eutectic volume fraction from 0.16% to 0.42%. Oppositely, the γ' size tends to decrease with the increasing Ta in alloys, thus, the stability of γ' phase is increased. Chemical composition of γ' changes with Ta addition in alloys because of substitution Ta for partial Al, Mo, Co and also Ni. For instance the stoichiometrical form of γ' in T1 (0%Ta) and T6(4.3%Ta) alloys are $(Ni_{0.93}Co_{0.07})_{2.92}$ $(Cr_{0.11}Al_{0.74}Ti_{0.08}Mo_{0.10})$ and $(Ni_{0.93}Co_{0.07})_{2.86}(Cr_{0.09}Al_{0.71}Ta_{0.07}Ti_{0.06}Mo_{0.08})$ respectively. TEM observation on thin foil of the creep specimens indicates similar behaviour of alloys with and without Ta addition. As shown on Fig.15, dislocations cut the large cubic γ' and around them dislocation tangles are formed.

It is surprising that the solution of Ta in γ matrix does not decrease but actually enhances the solubility of the main solid solution strengthening elements such as Cr, Mo and Co etc. Thus, the strengthening effect of Ta not only enhances γ' strengthening effect, but also shows the duplicate beneficial effect of the solid solution strengthening effect of Ta itself and superimposed enhanced strengthening effect of other main solid solution hardeners. According to the chemical phase analyses results of alloys T1 and T6, without Ta and with 4.3% Ta, the simple solid solution experimental alloys S1 and S2 were specially melted. Typical creep curves of S1, S2 alloys sufficiently indicate that the duplicate solid solution strengthening effect of alloy S1 containing Ta and higher contents of Cr, Co and Mo can prolong creep fracture life and also creep strength and ductility strongly. It is obvious the improvement of ultimate strength and ductilities in comparision S1 with S2 alloy as shown on Fig 18. This beneficial solid solution strengthening effect may be contributed by the stacking fault energy decrease in γ matrix because of high solubility of alloying elements such as Ta, Co,Cr and Mo.

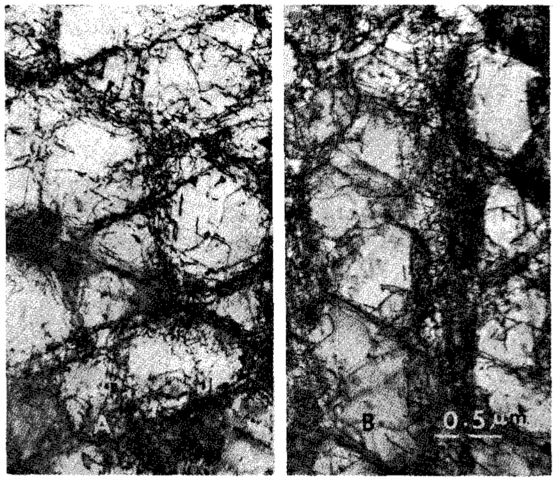

Fig.15. TEM micro-graphs of T1 (0% Ta, a) and T6 (4.3% Ta, b) alloys

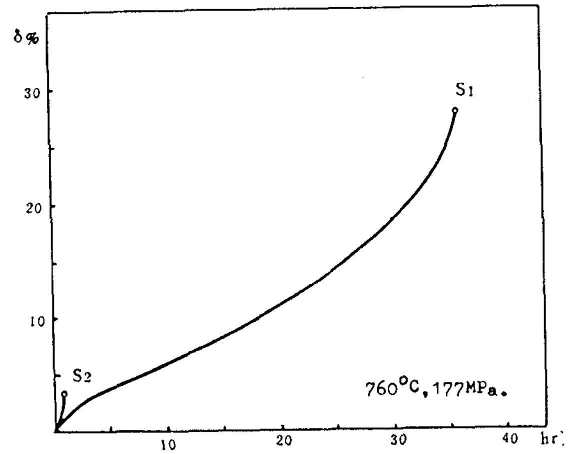

Fig.16. The creep curves of alloys S1(1%Ta) and S2 (0%Ta).

Ta addition in alloys increases structure stability in several ways. The stability of γ' after long-time exposure is increased by Ta addition. It can be seen from Fig.13 that after 1500h exposure at 900°C coagulation and growth rate of large cubic γ' and dissolution of small γ' in alloys with various content of Ta have been more or less depressed by Ta addition. Some investigations (8,9,10) reported the carbide reaction $MC+\gamma \rightarrow \gamma'+M_{23}C_6$ occurs in B1900 alloy containing Ta during high-temperature exposure. Our results based on quantitative chemical phase analyses after electrolytic extractions show MC carbide in alloys containing Ta is still stable and the amounts of MC carbide do not change after 900°C 1500h exposure (See Fig.14). Additionly, the solubility of Cr and Mo etc (main constituents in secondary carbides $M_{23}C_6$ and M_6C) is increased with Ta addition in γ solid solution, hence the amount of precipitated carbides in γ matrix is decreased and structure stability increased. Meanwhile, after long-time stress-free (10000h) or stress (10000-20000h) exposure at different high tempratures there is no TCP phase precipitation in the alloy containing 4.3% Ta which shows good structure stability.

Ta addition in alloys has another unique beneficial effect, Ta not only raises high temperature tensile strength, stress rupture life and creep resistance but also obviously improves ductility at high temperature tensile, stress rupture and creep tests (see Fig 1,2,4 and 5). SEM fractograph study on creep fracture surfaces is shown in Fig 17. Low creep fracture ductility alloy T1(0% Ta) specimen characterizes low ductility intergranular fracture (Fig 17a) and Ta-containg alloy T6 (4.3% Ta) with high creep fracture ductilily characterizes transgranular and intergranular mixed fracture behaviour with apparent dimples, more secondary cracks and plastic ridges (Fig 17b).

We would like to suggest the ductility improvement of Ta-containing alloys is closely related to their γ solid solution matrix behaviour. Typical creep curves (Fig 16) and tensile properties (Fig 18) of two special prepared solid solution strengthened alloys S1 (1% Ta) and S2 (0%Ta) have confirmed our suggestion that S1 solid solution single phase alloy with 1% Ta and higher content of Cr and Mo characterizes not only much higher creep and tensile strengths but also higher ductilities than S1 alloy without Ta. SEM fractographs of creep specimens are shown in Fig 19. Tantalum-free S2 alloy with low ductilities characterizes typical almost brittle intergranular fracture (Fig 19a). However, Ta-containing S1 alloy shows ductile fracture with apparent dimples.

Niobium is in the same group of the periodic table as tantalum and niobium behaviour is also very similar to tantalum. Mechanical property test results including tensile, stress-rupture and creep (see Fig1,2,4 and 5), show equivalent atomic content on Nb is possible to replace Ta in alloys for obtaining relevant strength and ductility. However, the creep ductility improvement of Nb is not such high as Ta does, but the degree of ductility improvement is still quite good in comparison to the alloy without Ta. It seems, the substitution of Nb for Ta from the viewpoint of strengthening effect is quite promising. Further investigations are continuing.

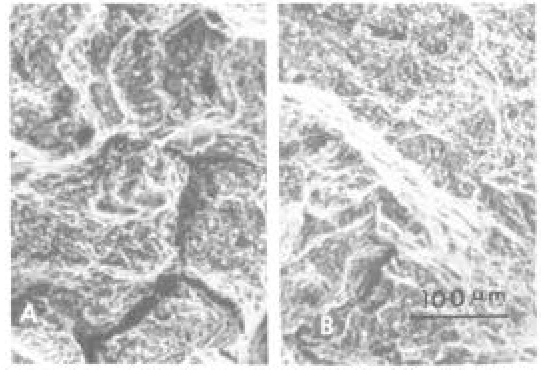

Fig.17. SEM fractographs of alloys T1 (0% Ta, a) and T6,(4.3% Ta, b) on creep specimens at 760°C, 490MPa.

Conclusions

1. The beneficial effect of tantalum on nickel-base superalloys is not only to raise high-temperature tensile strength and creep resistance but also obviously to improve ductility in high-temperature tensile and stress rupture tests. Simultaneously, tantalum addition can also enhance thermal fatigue and marine-gas corrosion resistances.

2. The partitioning of tantalum in experimental alloys is as following: about 70-80% Ta enters into γ'phase and forms Ni_3 (Al, Ti, Ta) type strengthening phase; about 15% Ta goes to carbide and forms high tantalum-containing MC phase; the remaining part of tantalum is soluted in γ matrix. Thus, the beneficial strengthening effect is contributed by enchanced γ'strengthening effect, stabilizing carbides and duplicated solid solution strengthening.

3. Tantalum addition can increase γ'fraction in investigated nickel-

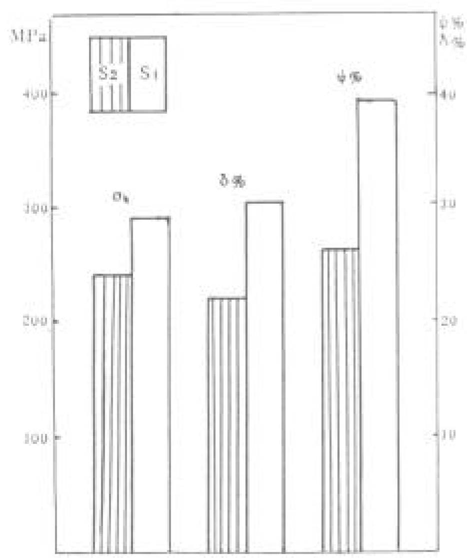

Fig.18. The tensile properties of alloys S1 (1%Ta) and S2 (0%Ta).

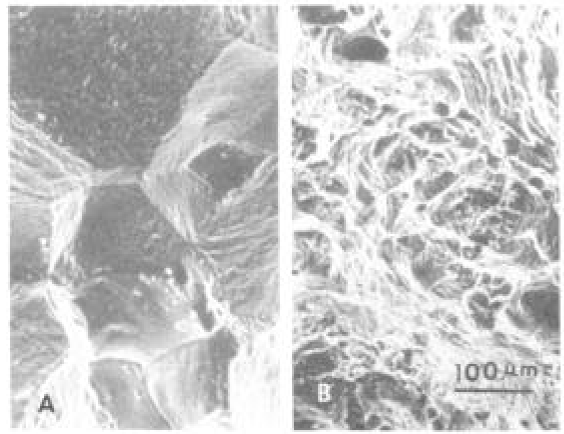

Fig.19. SEM fractographs of alloys S2 (0% Ta, a) and S1 (1% Ta, b) on creep specimens at 760°C 177MPa.

base superalloys, increase γ'solution temperature, decrease the cubic size of γ' particles and improve γ'stability at high temperature long-time exposure.

4. The solution of tantalum in γ solid solution matrix does not decrease but oppositely increasesthe solubility of main solid solution strengthening elements such as Cr, Mo and Co etc., that not only enchances solid solution strengthening effect but also intensively improvesthe ductility of γ solid solution phase.

5. Tantalum addition can improve structural stability in the investigated nickel-base superalloys as follows: decreases the coagulation and growth rate of γ'phase, no decomposition of MC carbide and decreases the amount of precipitated $M_{23}C_6$ and M_6C carbides at high-temperature long-time exposure.

6. It is hoped that the substitution of atomic equivalent Nb for Ta will provide a similar strengthening effect in investigated nickel-base superalloys. Systematic research on Nb substitution is continuing.

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