EXTRA LOW CARBON AGE-HARDENABLE ALLOYS FOR TUBULAR APPLICATION IN OIL AND GAS INDUSTRY

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ABSTRACT

Alloy 718 with extra low- and normal-carbon contents have been produced for tubular applications in hostile environments in oil and gas industry, using vacuum induction melting followed by vacuum arc remelting. The tubes have been obtained using hot-extrusion and cold-drawing processes, and then solutionized and aged to achieve 120ksi to 150ksi minimum yield strength. Taking the hot-extrusion process, the microstructure obtained is homogeneous and the average grain size becomes finer than that obtained by a conventional forging process. Reduction in carbon content improves pitting corrosion resistance. This is attributed to reduction in the amount of carbo-nitride stringers. Overaging is detrimental in ductility, toughness and intergranular corrosion resistance.
Alloy PH3(23%Cr-52%Ni-4%Mo-5%Nb) has been found superior to alloy 718 in corrosion resistance, which is mainly the consequence of higher Cr and Mo contents and the absence of non-metallic inclusions associated with lower C content and trace level of Ti as well as the absence of γ'-Ni_3Ti precipitation.

Superalloys 718, 625, 706 and Various Derivatives
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INTRODUCTION

Age-hardenable alloy is used as a corrosion resistant material in the oil and gas industry because of its combination of high strength, corrosion resistance, and ability to be heat treated to various strength levels. While several new alloys have been developed for this particular purpose[1)2)3)], there is no doubt that alloy 718 is most widely applied in certain sour gas environments[4)5)]. However, alloy 718 was originally developed for high temperature use, so its properties have not been optimized enough for oil industry.

The effect of extra low carbon composition was previously reported to improve the low cycle fatigue only for high temperature application[6)].

The NACE specification MR0175 limits the maximum hardness of alloy 718 to HRC 40. This implies that the very high strength levels achieved through dual aging treatments used in the aerospace industry cannot be used in the oil and gas application. Therefore, single-aging treatments especially underaging may be preferred.

This paper will focus on the effects of extra low carbon and the underaging of alloy 718 on the mechanical properties and the corrosion resistance in the oil industry comparing with alloy PH3 characterized by higher Cr and Mo contents and the absence of γ'-Ni_3Ti precipitation[1)]. The relative characteristics of underaging, overaging and dualaging treatments of alloy 718 would provide the basis of preferred heat treatments which optimize desired properties.

PROCEDURE

Materials

Materials for testing came from new facilities of VIM and VAR introduced to the Steel Tube Works in order to manufacture superalloys averse to gas elements all the way through. The chemical compositions of the alloys are given in Table I. Here, 718L designates alloy 718 with low C content and 718H with high C content. Cr and Mo contents of alloy PH3 are higher than those of alloy 718 and C content level is low as 718L. Ti is kept trace level in PH3 to avoid γ'-Ni_3Ti precipitation. They were vacuum induction melted followed by vacuum arc remelting to 500mm diameter ingot. The tubes were obtained using hot-extrusion and cold-drawing processes to 93mm diameter and 7.5mm wall thickness. Then they were solutionized at 1025°C. Taking the hot-extrusion process, the microstructures obtained are homogeneous and the average grain sizes become ASTM grain size No.5.5-7.5. Those are finer than that obtained by a conventional forging process. The aging conditions were selected by a preparatory examination as mentioned later.

Table I Chemical Composition (wt.%)

Alloy	C	Si	Mn	Ni	Cr	Mo	Ti	Nb	Al	Fe
718L	0.003	0.01	0.02	52.1	18.7	3.0	0.9	5.0	0.55	Bal.
718H	0.044	0.01	0.02	52.2	18.8	3.1	0.9	4.9	0.53	Bal.
PH3	0.004	0.04	0.37	51.9	22.7	3.6	0.0	4.8	0.19	Bal.

Mechanical Properties Test

Tensile tests were performed at room temperature with 6mm diameter and 30mm gage length specimens. Charpy impact tests were performed at 0°C with half size specimens(10mm depth, 5mm width and 2mm V-notch depth). Vickers hardness tests(HV10) and Rockwell hardness tests scale C(HRC) were also performed.

Corrosion Test

Immersion tests were performed in non-deaerated solutions of reagent grade acids with 3mm thickness, 10mm width and 40mm length specimens.

Crevice corrosion tests were performed in 10% $FeCl_3 \cdot 6H_2O$ at 30°C for 24h exposure with 3mm thickness, 30mm width and 50mm length specimens. The specimens were fitted with multiple crevice devices produced by TFE-fluorocarbon washers.

Anodic polarizations were measured in 5% NaCl with 0.1atm H_2S solution at 80°C with 15mm diameter and 2mm thickness specimens. Anodic polarization curves were obtained potentiodynamically at a sweep rate of 20mV/min with a potentiostat. The potential at which the anodic current density attained $1mA/cm^2$ by the occurrence of pitting was adopted as the pitting potential.

Slow strain rate tensile tests(SSRT) were conducted by 4mm diameter and 30mm gage length specimens with a strain rate of $4.0 \times 10^{-6}s^{-1}$ in H_2S-Cl^- environments.

Stress corrosion cracking tests were performed by C-rings and four-point bent-beams(2mm thickness, 10mm width and 75mm length) exposed in H_2S-Cl^- environments.

All specimens except for C-rings were finished to 120-grit surface and cleaned with acetone. C-rings were cut from mill-pickled tubes and cleaned with acetone.

Microstructure Observation

The microstructures after aging were examined with thin foils by TEM in the JEOL-2000EX.

RESULT

Aging Condition

Before mill aging, general aging behavior has been examined using solutionized tubes. Figure 1 shows the isochronous age-hardening behavior of alloy 718. The hardness of 718L is higher than that of 718H for all the conditions tested and the peak hardness temperature gets high with low C content. PH3 shows the peak hardness around 700°C for 20h.

Three aging conditions were chosen for 718L and 718H. The underaging and overaging conditions are 700°C for 8h and 785°C for 8h respectively. The dualaging condition is 720°C for 8h followed by 620°C for 8h as described in ASTM B670 for high temperature service. This condition is applied to compare with the single aging conditions.

The aging condition of PH3 chosen is 690°C for 20h around the peak aging.

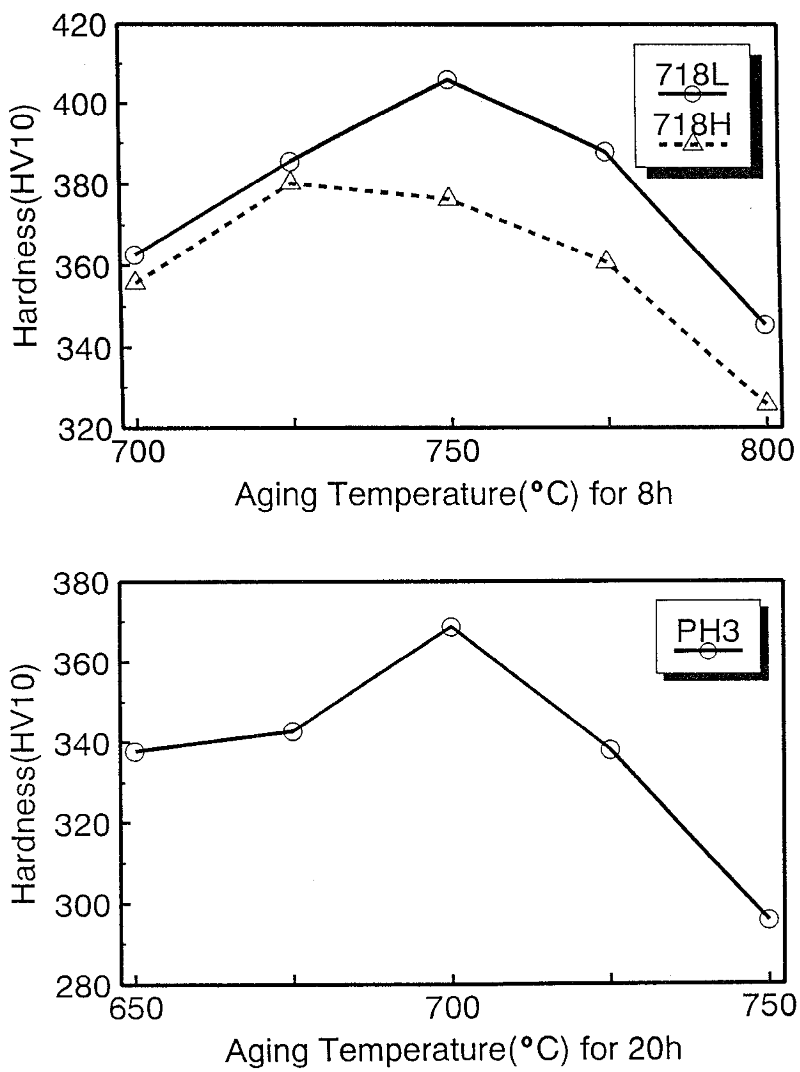

Figure 1 Age-hardening behavior of 718L, 718H and PH3

Mechanical Properties

Mechanical properties obtained are summarized in Table II. Single(under- and over-) aged 718L and 718H satisfy 120ksi minimum yield strength as well as PH3. The yield strength of 718L is higher than that of 718H for the same single aging condition. Dual aged 718L and 718H satisfy 150ksi minimum yield strength but exceed HRC 40. Even though all of the fracture are ductile, over- and dual-aging are harmful not only for ductility but also for impact toughness of 718L and 718H. Ductility and impact toughness of PH3 are as same as those of overaged 718L.

Table II Mechanical Properties of Mill Aged Tubes

Alloy	Aging	Mark	YS (MPa)	YS (ksi)	TS (MPa)	El (%)	RA (%)	HRC	Absorbed Energy (J)*
718L	Under	L-U	916	133	1242	32	64	38	85
	Over	L-O	938	136	1273	26	56	38	50
	Dual	L-D	1079	157	1338	26	61	42	67
718H	Under	H-U	838	122	1212	34	55	34	57
	Over	H-O	873	127	1218	26	52	37	41
	Dual	H-D	1104	160	1351	24	48	44	37
PH3	Peak	PH3	879	128	1146	31	56	37	41

*Half size specimen at 0°C

Corrosion Resistance

Immersion Test Figure 2 shows the corrosion resistance in 5% $FeCl_3$ + 10% NaCl solution. In this solution the specimens are corroded in a pitting type. The corrosion resistance depends mainly on the content of C for alloys 718. PH3 are scarcely attacked.

Figure 3 shows the corrosion resistance in 2.5% $Fe_2(SO_4)_3$ + 50% H_2SO_4 solution. This condition measures the susceptibility to intergranular attack as described in ASTM A262 Practice B. The corrosion resistance mainly depends on aging condition. Over- and dual-aging are harmful for alloys 718. The corrosion resistance of PH3 is as same as that of the underaged alloy 718 regardless of 20h aging.

Figure 4 shows the corrosion resistance in boiling 10% HCl solution. This condition expects the uninhibited acidizing environments and shows general corrosion. The corrosion rate of alloys 718 is about 35g/m^2/h(1500mpy) not depending on both C content and aging condition. The corrosion resistance of PH3 is higher than that of alloys 718.

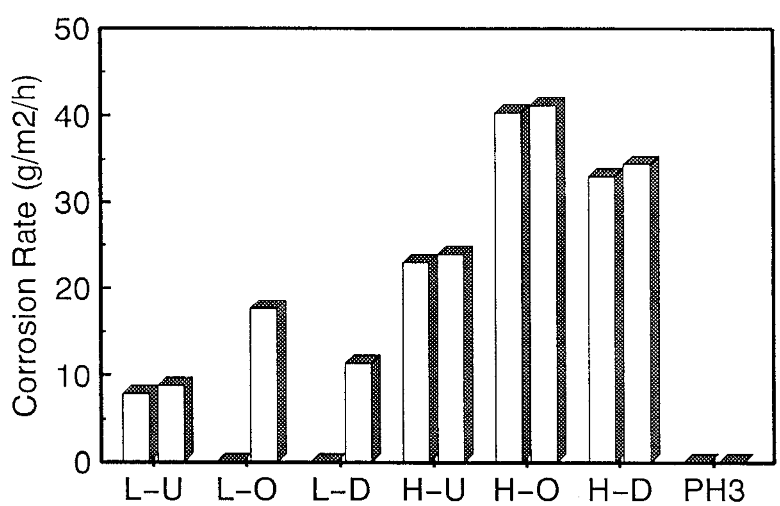

Figure 2 Corrosion resistance in 5% $FeCl_3$ + 10% NaCl at 50°C for 24h

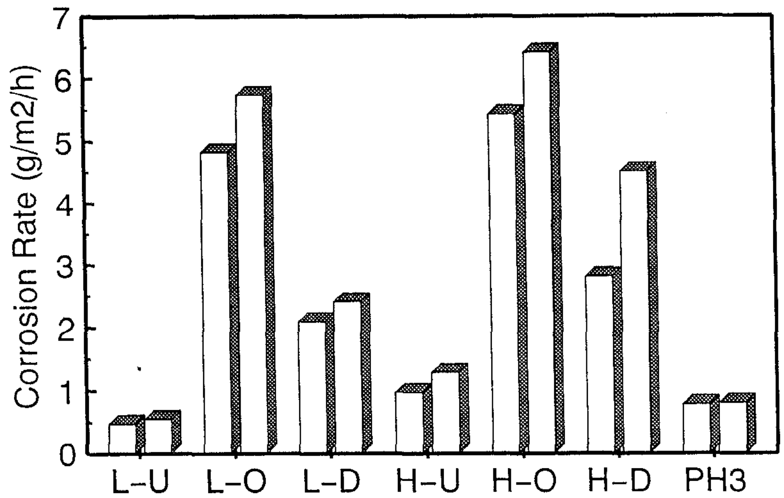

Figure 3 Corrosion resistance in boiling 2.5% $Fe_2(SO_4)_3$ + 50% H_2SO_4 for 120h

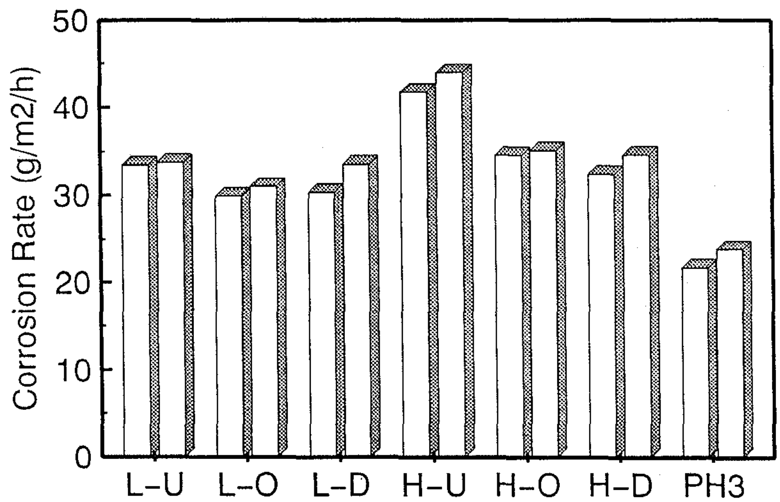

Figure 4 Corrosion resistance in boiling 10% HCl for 24h

Crevice Corrosion Figure 5 shows crevice corrosion resistance in 10% $FeCl_3 \cdot 6H_2O$ at 30°C for 24h. Higher C content is detrimental as same as to pitting resistance.

Pitting Potential Figure 6 shows pitting potential in 5% NaCl + 0.1atm H_2S + N_2 balance at 80°C. The pitting potential of alloy 718 is about 450mV not depending on both C content and aging condition. PH3 shows higher potential level.

Slow Strain Rate Test Figure 7 shows SSRT results of 718L and PH3 evaluated in 25% NaCl + 2atm H_2S + 30atm CO_2 at 177°C. The ratio of the time to failure(TTF) in H_2S to that in air corresponds to the susceptibility to stress corrosion cracking(SCC). Underaging condition for 718L exhibits higher resistance for cracking. Although the cracking resistance of PH3 is as same as that of dualaged 718L, PH3 is superior to alloy 718 in another environments as shown in Table III. This is attributed to the absence of γ'-Ni_3Ti precipitation[1].

Stress Corrosion Cracking Test results are shown in Tables IV and V. Exposed in H_2S-Cl^- environments, every specimen shows no cracks in these conditions. Further studies are now in progress in this area.

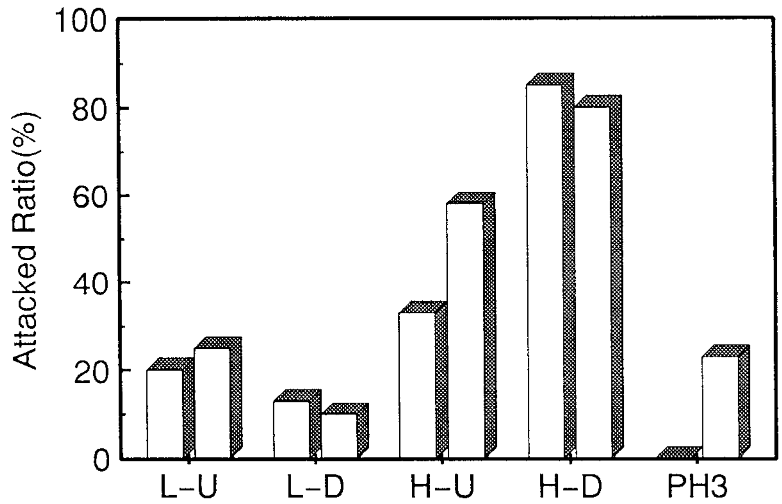

Figure 5 Crevice corrosion resistance in 10% $FeCl_3 \cdot 6H_2O$ at 30°C for 24h
*Attacked ratio is percent of attacked sites in eighty sites per two specimens.

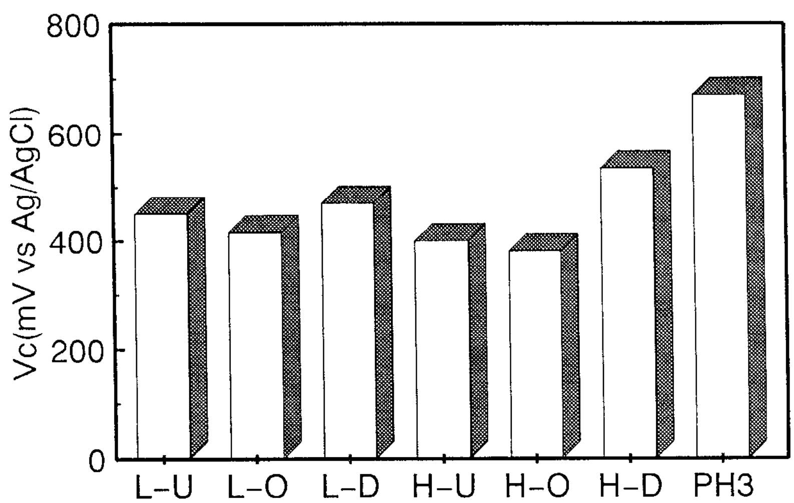

Figure 6 Pitting potential in 5% NaCl + 0.1atm H_2S + N_2 at 80°C

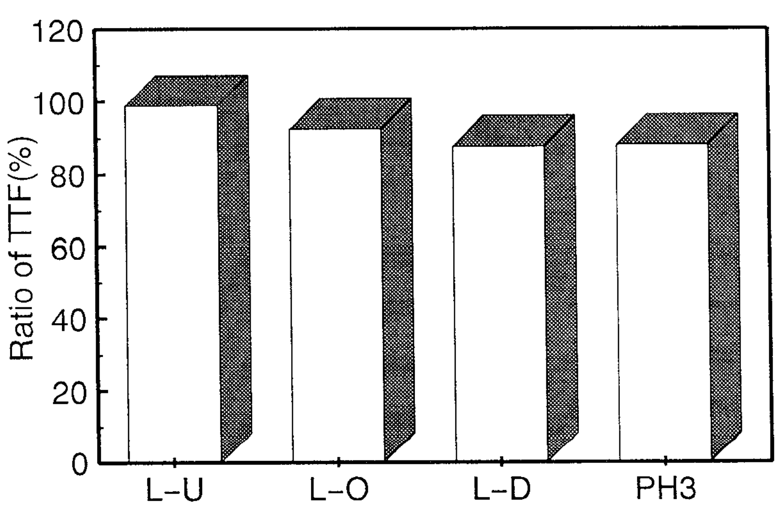

Figure 7 Ratio of TTF evaluated by SSRT in 25% NaCl + 2atm H_2S + 30atm CO_2 at 177°C

Table III SSRT results of 718L and PH3
Evaluated in 25% NaCl + 0.5% CH_3COOH + 7atm $H_2S^{1)}$

Alloy	TTF(h) in air	TTF(h) in H_2S	Ratio(%)
718L	17.7	6.3	36
PH3	16.8	16.7	99

*Both alloys were aged at 700°C for 20h.
It corresponds to peak aging for 718L in this work.

Table IV Stress Corrosion Cracking Data for Four-Point Bent-Beams
Evaluated in 20% NaCl + 0.5% CH_3COOH + 10atm H_2S + 10atm CO_2

Alloy	Aging	Applied Stress*	Temperature (°C)	Duration (h)	Cracking
718L	Under	80%,100%YS	200	720	No
	Over	80%,100%YS	200	720	No
	Dual	80%,100%YS	200	720	No
718H	Under	80%,100%YS	200	720	No
	Over	80%,100%YS	200	720	No
	Dual	80%,100%YS	200	720	No
PH3	Peak	80%,100%YS	200	720	No

*Duplicate specimens for each applied stress

Table V Stress Corrosion Cracking Data for C-rings
Evaluated in 20% NaCl + 1g/l S + 10atm H_2S + 10atm CO_2

Alloy	Aging	Applied Stress	Temperature (°C)	Duration (h)	Cracking
718L	Under	100%YS	120	720	No
718H	Under	100%YS	120	720	No
PH3	Peak	100%YS	120	720	No

DISCUSSION

Alloys 718 with different C content have exhibited different age-hardening behavior and the resultant mechanical and corrosion properties are diversified to a great extent. This has been discussed from the stand point of change in the microstructure.

Inclusion

Figure 8 shows optical micrographs of the non-metallic inclusion in 718L and 718H as solution.

Only TiN inclusions are observed in 718L. The inclusions of 718H are NbC as well as TiN. The difference is attributed to the difference in C content between two alloys. Higher density of inclusions in 718H is considered to be harmful to the impact toughness and the pitting corrosion resistance.

In order to estimate the amount of inclusions, Ti and Nb content in extracted residues were examined. The result is shown in Figure 9. PH3 which does not contain Ti was also examined and few inclusions are observed. About 5% of Ti and 10% of Nb are found to be already precipitated as inclusions in solutionized 718H. This results in the reduction of the effective Ti and Nb contents for the subsequent precipitation of γ' and γ'' phases and reduces the peak aged hardness as shown in Figure 1.

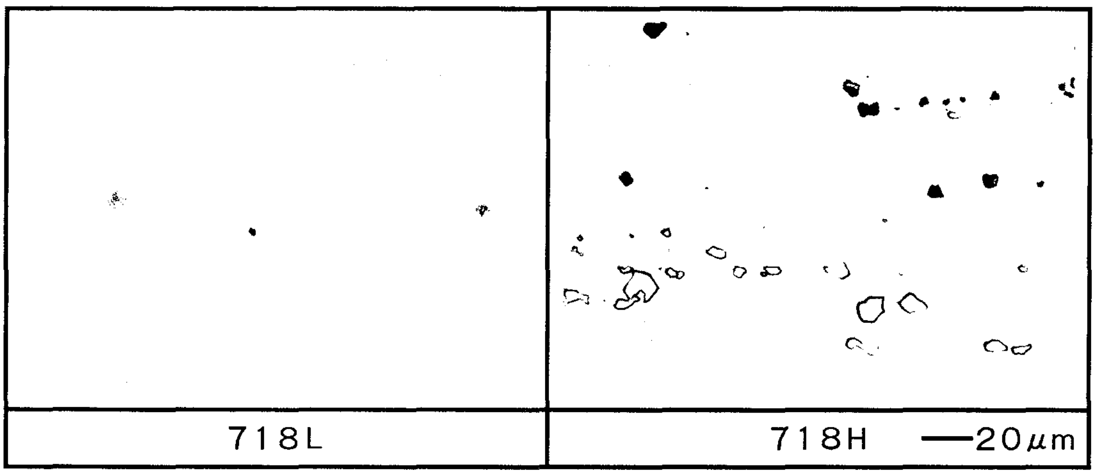

Figure 8 Non-metallic inclusion of 718L and 718H as solution

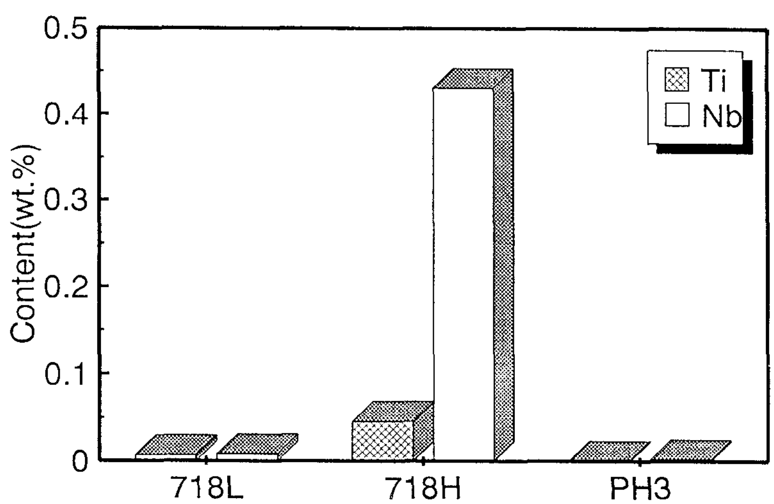

Figure 9 Ti and Nb content in extracted residues as solution

Microstructure after Aging

The microstructures after aging have been examined with thin foils by TEM. Figure 10 shows the bright images with the [100] zone axis of the matrix of the under(a)-, over(b)- and dual(c)-

aged 718L. After underaging, very fine γ' and γ'' particles are observed. The maximum diameter of the precipitate is less than 10 nm. The precipitates are coarsed over 100nm after overaging. The precipitates morphology after dualaging is similar to that in the underaging condition, while , the amount of γ' precipitates seems to be increased according to the electron beam diffraction pattern observation. The strength of the alloys are considered to depend on these precipitates morphology.

Figure 11 shows the bright images of the grain boundary region of the under(a)-, over(b)- and dual(c)-aged 718L. After under- and dual-aging, no precipitates are observed along grain boundaries. After overaging, a significant amount of δ-Ni_3Nb is observed with a precipitation free zone(PFZ). The difference of the grain boundary precipitation is attributed to the relation between the aging condition and the precipitation nose[7)]. It is concluded that the grain boundary precipitates affect the ductility, impact toughness and intergranular corrosion resistance.

718H shows the precipitate morphology similar to 718L. PH3 is characterized by very fine γ'' precipitates in the matrix without γ'-Ni_3Ti.

CONCLUSION

1. Reduction of C content in alloy 718 improves the strength, ductility, impact toughness and pitting corrosion resistance. This is attributed to reduction in the amount of inclusions and increase in the effective Ti and Nb.

2. Underaging condition is preferred for oil and gas application to avoid the grain boundary precipitate resulting in the improved ductility, impact toughness and intergranular corrosion resistance.

3. PH3 exhibits higher corrosion resistance, which is mainly the consequence of higher Cr and Mo contents and the absence of non-metallic inclusions associated with lower C content and trace level of Ti as well as the absence of γ'-Ni_3Ti precipitation.

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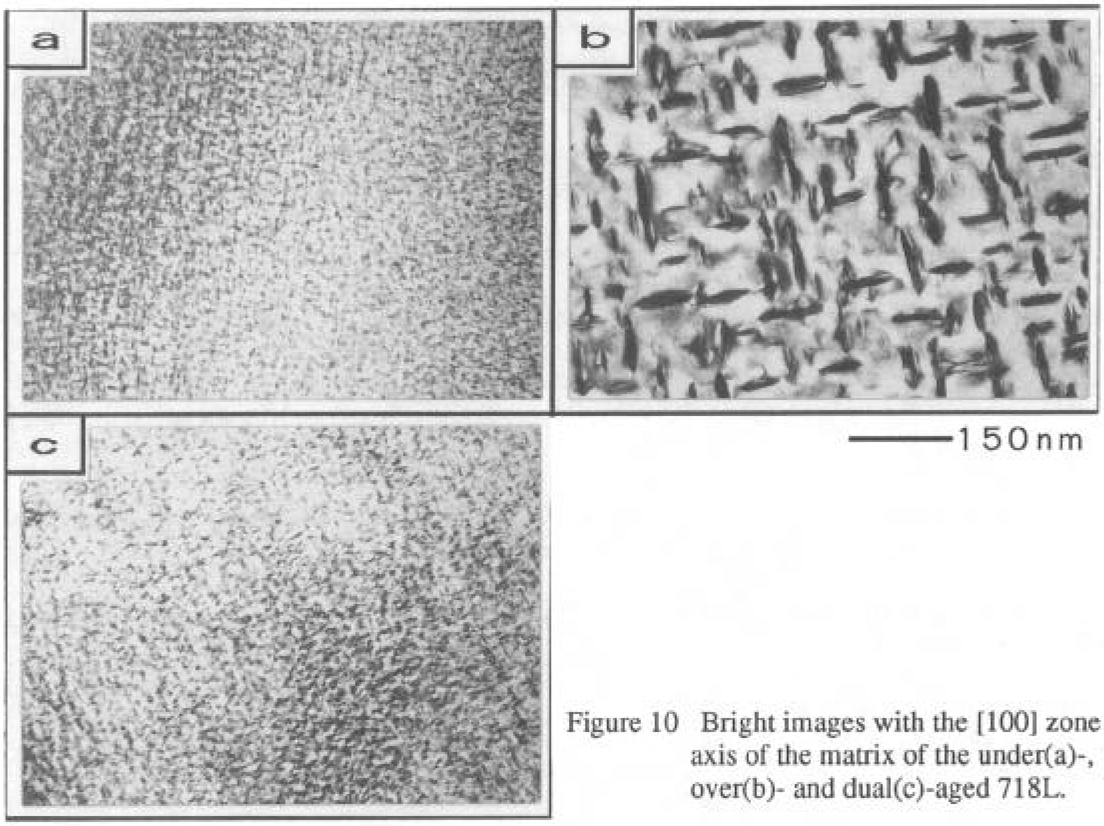

Figure 10 Bright images with the [100] zone axis of the matrix of the under(a)-, over(b)- and dual(c)-aged 718L.

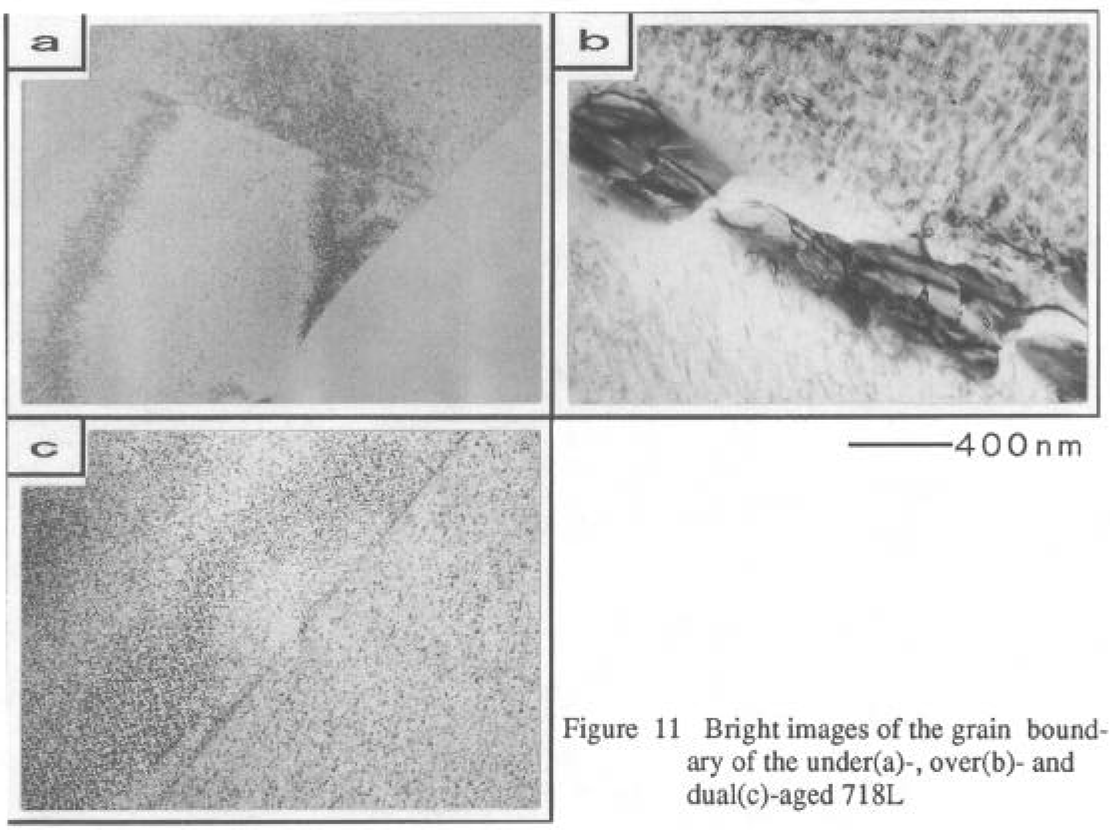

Figure 11 Bright images of the grain boundary of the under(a)-, over(b)- and dual(c)-aged 718L

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