

PHYSICAL METALLURGY OF ALLOYS 718, 725, 725HS, 925 FOR SERVICE IN AGGRESSIVE CORROSIVE ENVIRONMENTS

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ABSTRACT

Processing conditions were designed to produce alloys 718 (UNS N07718), 725 / 725HS (UNS N07725), and 925 (UNS N09925) with essentially clean grain boundaries, partial coverage of grain boundaries by the precipitates, and full coverage of grain boundaries by the precipitates. Grain boundary precipitates were found to degrade room temperature impact strength. Partial coverage of grain boundaries by second phase particles did not adversely affect the properties in slow strain rate (SSR) tests conducted in the oil patch environments. However, the materials having grain boundaries fully covered with second phase particles had inferior properties in SSR testing.

Key Words: UNS N07718, UNS N07725, UNS N09925, slow strain rate, oil patch, microstructure, time-temperature-transformation diagram, grain boundary precipitates, processing

INTRODUCTION

Corrosion environments encountered in oil and natural gas production are rather aggressive ⁽¹⁾. They may contain significant levels of hydrogen sulfide, carbon dioxide, chlorides, and free sulfur. Further, some of these environments are at high pressure and temperature, up to 450°F (232°C). Processing of oil and natural gas under these environmental conditions requires special materials.

Nickel-base alloys 718, 725, and 925 are commonly used in oil and natural gas production ⁽¹⁾. These alloys contain high Cr/Mo contents for aqueous corrosion, and also considerable levels of hardeners like Ti/Nb/Al to form gamma prime and gamma double prime precipitates for strength. Being heavily alloyed multi-component systems; these materials require special consideration for processing and heat treatments. Time-Temperature-Transformation (TTT) diagrams can be used as road maps to determine precipitation of various phases under different processing conditions. This paper shows the effect of intergranular precipitates on mechanical properties and SSR test results in sour oil patch environments.

EXPERIMENTAL PROCEDURE

Nominal chemical compositions of alloys 718, 725 / 725HS, and 925 are listed in Table 1. Solution annealing and age hardening treatments of these alloys are listed in Table 2.

Alloy 925 was produced in the mill with two different microstructures. Standard material containing isolated grain boundary carbides and non-standard material containing heavy continuous grain boundary eta and carbide precipitates, Figures 1a and 1b. The former will be referred to as 925-S and the latter will be referred to as 925-T. Processing of material 925-T was specially designed to generate the above mentioned microstructure.

Commercially produced alloys 725 and 725HS were used for the testing. Alloys 725 and 725HS have the same UNS chemical composition but differ in the way they are processed and heat treated. Alloy 725 had essentially clean grain boundaries whereas 725HS had isolated eta precipitates on the grain boundaries, Figures 2a and 2b. The purpose of grain boundary eta in alloy 725HS is to refine the grain size for higher strength. In addition, a lower temperature solution anneal of alloy 725HS compared to the regular alloy 725 (Table 2) results in a higher residual work which enhances age hardening on subsequent heat treatment. Fine grain size and a specially designed age hardening treatment of alloy 725HS is responsible for its higher yield strength compared to regular alloy 725.

Commercially produced hot worked alloy 718 was solution annealed and age hardened in the lab to produce two different microstructures, Figures 3a and 3b. Heat treatment conditions are listed in Table 2. The material for Figure 3a was heat treated using the standard oil patch specification conditions. This material will be referred to as 718-S. The material for Figure 3b was subjected to a specially designed heat treatment to precipitate continuous fine grain boundary delta precipitates. This material will be referred to as 718-M.

Fully heat-treated specimens were subjected to room temperature tensile, impact, and hardness testing. Mechanical properties are listed in Table 3. These were SSR tested in a severe sour brine environment representing Mobile Bay type conditions. The SSR test results are listed in Tables 4 to 6.

RESULTS

Mechanical Properties: Continuous grain boundary precipitates shown in Figures 1b and 3b degrade impact strength and reduction of area, Table 3. However, the hardness and the rest of tensile properties are essentially unaffected.

Slow Strain Rate Testing

Based on extensive laboratory testing, a pass/fail criteria was initially developed for SSR testing of stainless alloys⁽²⁾ and was later verified for precipitation strengthened Ni-base alloys⁽³⁾. According to this technique, the material is tested under SSR test conditions in a simulated oil patch environment and also in inert (air or nitrogen) atmosphere. The acceptance of the material is decided by the ratio of time to failure (TTF), ratio of % reduction of area (RA) and/or ratio of % elongation (El) of the oil patch environment tests versus inert atmosphere tests. The exact value of the ratio, which decides pass/fail, depends on the material and the severity of the environment. For Ni-base precipitation strengthened alloys, a ratio of 0.70 or greater typically passes the material⁽³⁾. If the ratio is between 0.70 to 0.80, the specimen is examined under scanning electron microscope (SEM). A predominantly ductile fracture

surface passes. All specimens are examined for secondary cracking in the gage length, away from the fracture surface. The presence of secondary cracks rejects the material even if all other criteria are satisfied.

Alloy 925: Table 4 shows the SSR test data on the materials designated as 925-S and 925-T at 300°F (150°C) in 25% NaCl + 400 psig (2.8 MPa) H₂S + 400 psig (2.8 MPa) CO₂. This environment represents Mobile Bay type conditions. Material 925-S, which was processed under standard oil patch specified processing conditions had SSR ratio of over 1.0 for TTF, %EL, and %RA. This material had very few isolated grain boundary precipitates. In contrast, the material 925-T, which was specially processed to dump out thick continuous grain boundary precipitates failed due to low SSR ratios for TTF and %EL.

Alloys 725 and 725HS: Table 5 shows the SSR test data on materials designated as 725 and 725HS at 400°F (204°C) in 100,000 ppm Cl⁻ (as NaCl) + 200 psig (1.4 MPa) H₂S + 200 psig (1.4 MPa) CO₂. This environment also represents Mobile Bay type conditions. Materials 725 and 725HS exhibited SSR ratios close to 1.0 for TTF, %EL, and %RA. These materials were processed in the mill using standard oil patch specified conditions. It should be mentioned that the material 725 was devoid of grain boundary precipitates, whereas the material 725HS contained intentionally produced discontinuous grain boundary precipitates.

Alloy 718: Table 6 shows the SSR data for alloy 718 in two different heat-treated conditions in 10% NaCl + 358 psig H₂S + 200 psig CO₂ at 300°F (150°C). This environment represents Mobile Bay type conditions. A hot finished bar was annealed and aged in the lab to produce material 718-S. This material had acceptable SSR ratios for TTF, %RA and %EL. However, the material 718-M, which was subjected to a specially designed heat treatment to dump out thin continuous grain boundary precipitates failed due to low SSR ratio for % RA.

DISCUSSION

Matrix and grain boundary second phase particles are preferentially attacked in a corrosive environment due to their different crystal structures, chemical compositions, and depletion of precipitate-forming elements at the precipitate / matrix interface ⁽⁴⁾. Continuous grain boundary precipitates are more harmful since these form a continuous network of weak sites. This could explain low SSR ratios for 925-T and 718-M materials, which contained continuous grain boundary precipitates. These two materials were specially produced for this investigation.

Microstructural Development in Alloys 718, 725, 725HS and 925

TTT diagrams can be used to determine presence of various phases in any alloy. Figures 4 to 6 show the most recent TTT diagrams of alloys 925, and 725, 718 ⁽⁵⁻⁷⁾. These diagrams do not account for segregation and residual work in the materials. Further, the accuracy of phase field boundaries depends on the heat treatment intervals and the detection limits of the analytical tools used for these investigations. It can be inferred from the TTT diagrams that the well-processed standard 718, 725, and 925 (Table 2) will be essentially free from grain boundary precipitates (carbides/eta/delta). Significant volume fraction of grain boundary precipitates in the fully heat treated condition of these alloys suggests improper processing at one or more of the following steps: raw materials, melting / remelting, homogenization, hot working, solution annealing and aging.

Scrap or raw materials containing high levels of impurities will result in higher content of undesirable elements. Proper melting ensures desired chemical composition and effective

desulfurization / deoxidation. The purpose of remelting is to minimize macro-segregation. An optimum remelt rate ensures least segregation and an economic process. A high melt rate tends to result in a high degree of segregation and a low melt rate tends to result in remelt defects and poor ingot surface quality. Homogenization is carried out to minimize micro-segregation. It involves heat treating an alloy for extended times close to the melting point. A high homogenization time / temperature can result in incipient melting and subsequent hot working problems. A low homogenization time/temperature can result in only partial elimination of segregation resulting in hot workability problems and poor properties in the fully processed material. The cast structure produced by melt / remelt processes has to be worked at a certain minimum reduction ratio to develop a fully wrought structure. A too high or too low hot working temperature results in poor hot workability. Alloys hot worked at a rather low temperature tends to have a high volume fraction of second phases which needs longer time at temperature to dissolve on subsequent solution annealing. A material hot worked at a rather high temperature is prone to grain coarsening and degradation in strength. In addition to all the factors discussed above, different size products have to be evenly exposed at the specified time / temperature throughout the cross section for solution annealing and age hardening to develop the required microstructure and properties.

CONCLUSIONS

The origin of second phase grain boundary precipitates can be related to any of the following processing stages: raw materials, melting / remelting, homogenization, hot working, solution annealing and age hardening. In the well-processed materials, TTT diagrams can be used as road maps to figure out the presence of various phases under the given time/temperature conditions. The data showed that the intentional presence of isolated grain boundary precipitates helped to increase the yield strength of alloy 725HS by grain refinement without degrading SSR properties in oil patch environment. However, intentionally produced continuous grain boundary precipitates in alloys 718 and 925 degraded SSR ratios.

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Table 1. Nominal Chemical Composition in wt% of Alloys 718, 725 / 725HS, and 925.

Alloys	UNS Numbers	Ni	Cr	Fe	Mo	Nb	Ti	Al
718	N07718	53.4	18.5	18.5	3.0	5.0	1.0	0.5
725 / 725HS	N07725	58.5	20.8	7.6	8.0	3.5	1.5	0.2
925	N09925	43.0	20.0	28.0	3.0	-	2.2	0.2

Table 2. Solution Annealing and Age Hardening Conditions.

Material Designation	Process Condition	Solution Anneal	Age	Mill or Lab Heat Treatment
925-S	Standard	1850°F (1010°C), 90 minutes, WQ	1365°F (741°C) - 8h, FC 100°F (56°C) / h to 1150°F (621°C), hold at 1150°F for 8h, AC	Complete Mill processing
925-T	Non-standard	1850°F (1010°C), 90 minutes, WQ	1365°F (741°C) - 8h, FC 100°F (56°C) / h to 1150°F (621°C), hold at 1150°F for 8h, AC	
725	Standard	1900° F (1038C°), 1 hour, WQ	1350°F (732C°) - 8h, FC 100°F (56°C) / h to 1150°F (621°C), hold at 1150°F for 8h, AC	
725HS	Standard	1825°F (996°C), 2 hours, WQ	1400°F (760°C) - 2h, FC 100°F (56°C) / h to 1200°F (649°C), hold at 1200°F for 6h, AC	
718-S	Standard	1875°F (1024°C), 90 minutes, WQ	1450°F (788°C) / 7h, AC	Hot worked mill material was annealed and aged in the lab.
718-M	Non-standard	1875°F (1024°C), 90 minutes, WQ	1725°F (941°C) - 4h, AC + 1450°F (941°C) - 7h, AC	

Note: AC, WQ, and FC in the table stands for air cooling, water quenching, and furnace cooling respectively. “h” stands for hours.

Table 3. Room Temperature Mechanical Properties.

Material Designation	Tensile Properties				Impact Strength, ft-lbs (joules)	Hardness, Rc
	Yield Strength, ksi (MPa)	Tensile Strength, ksi (MPa)	% Elongation	% Reduction of Area		
925-S	114.7 (791)	166.3 (1047)	26.3	39.9	87.3 (118)	34.0
925-T	122.4 (775)	169.3 (1167)	21.9	26.1	43.0 (58)	37.0
725	128.0 (883)	183.0 (1262)	28.0	48.0	69.3 (94)	37.0
725HS	155.8 (1074)	199.1 (1373)	24.6	44.0	36.0 (49)	41.0
718-S	128.0 (883)	173.6 (1197)	29.6	45.0	44.5 (60)	35.5
718-M	123.3 (850)	177.9 (1227)	25.2	36.6	27.3 (37)	36.7

Table 4. SSR tests of materials designated as 925-S and 925-T at 300°F (150°C) in 25% NaCl + 400 psig (2.8 MPa) H₂S + 400 psig (2.8 MPa) CO₂. The environment values are the averages of 2-3 tests. None of these tests showed secondary cracks.

Material Designation	Atmosphere	TTF hours	TTF Ratio	%RA	%RA Ratio	% EI	%EI Ratio
925-S	Inert	16.2	-	27.5	-	23.3	-
	Environment	17.3	1.07	28.6	1.04	24.9	1.07
925-T	Inert	14.1	-	23.6	-	20.3	-
	Environment	8.6	0.61	18.4	0.78	12.4	0.61

Table 5. SSR tests of alloys 725 and 725HS at 400°F (204°C) in 100,000 ppm Cl⁻ (as NaCl) + 200 psig (1.4 MPa) H₂S + 200 psig (1.4 MPa) CO₂. The environment values are the averages of 2-3 tests. None of these tests showed secondary cracks.

Material Designation	Atmosphere	TTF hours	TTF Ratio	%RA	%RA Ratio	% EI	%EI Ratio
725	Inert	23.7	-	54.9	-	34.1	-
	Environment	23.6	1.00	53.0	0.97	34.0	1.00
725HS	Inert	22.9	-	45.9	-	28.2	-
	Environment	23.1	1.01	45.0	0.98	28.5	1.01

Table 6. SSR tests of materials designated as 718-S and 718-M at 300°F (150°C) in 10% NaCl + 358 psig (2.5 MPa) H₂S + 200 psig (1.4 MPa) CO₂. The environment values are the averages of 2-3 tests. None of these tests showed secondary cracks.

Material Designation	Atmosphere	TTF hours	TTF Ratio	%RA	%RA Ratio	% EI	%EI Ratio
718-S	Inert	22.8	-	38.1	-	28.7	-
	Environment	20.0	0.88	27.5	0.72	24.6	0.86
718-M	Inert	20.2	-	34.9	-	24.7	-
	Environment	16	0.80	21.3	0.61	19.0	0.76

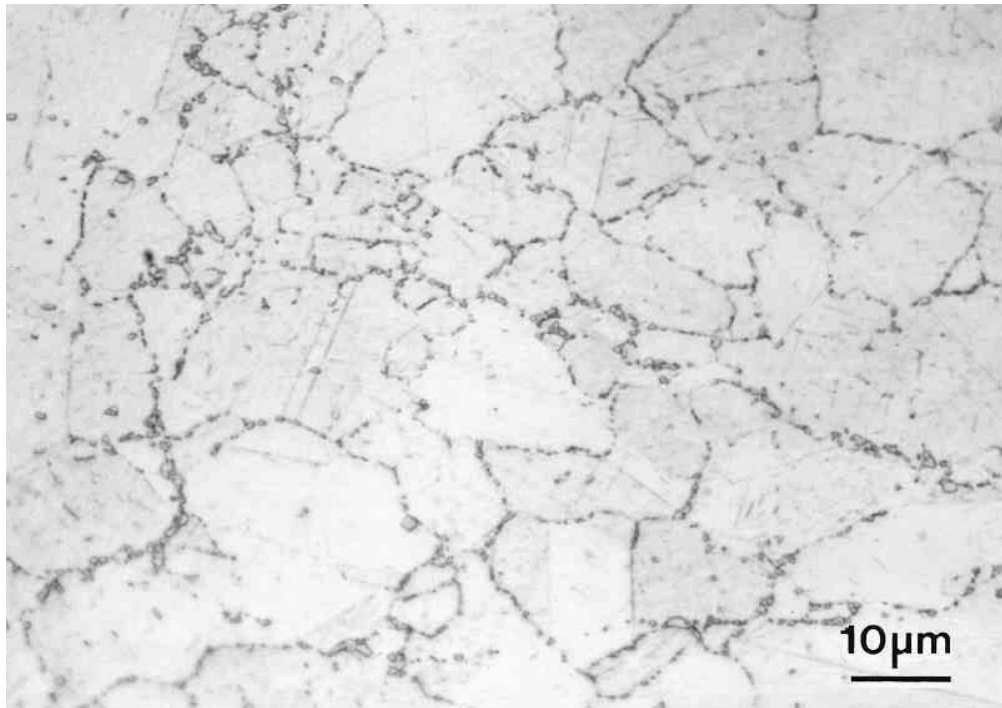
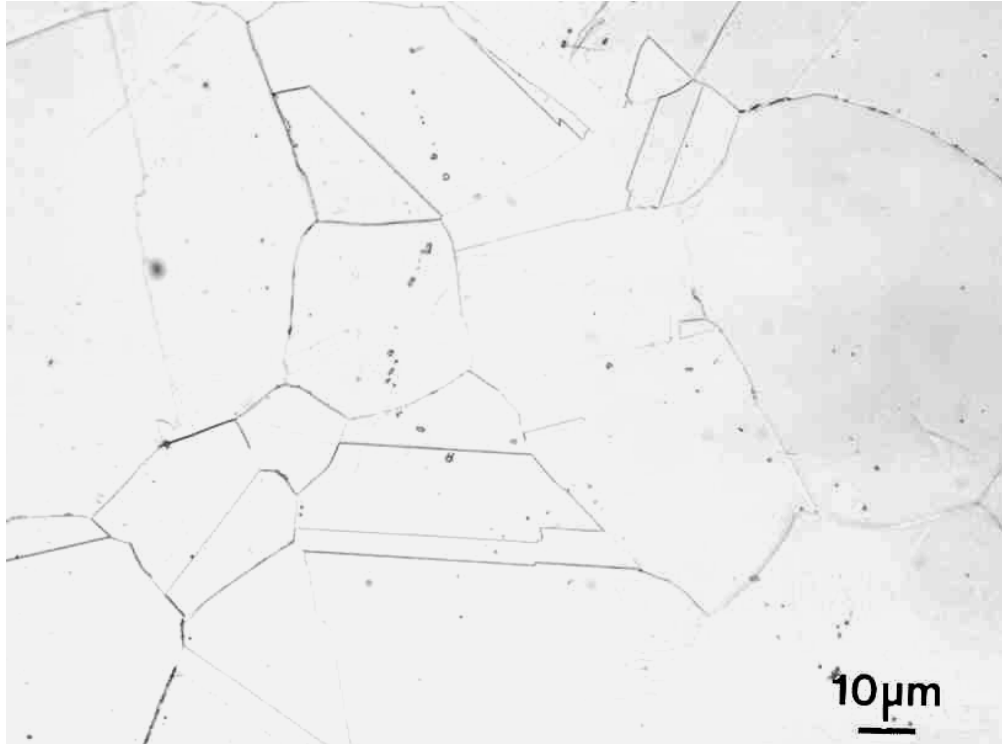


Figure 1. a) Photograph of the material designated as 925-S (Top); b) Photograph of the material designated as 925-T (Bottom). Material 925-S was obtained from standard mill production. Processing for material 925-T was specially designed to dump out thick continuous grain boundary precipitates.

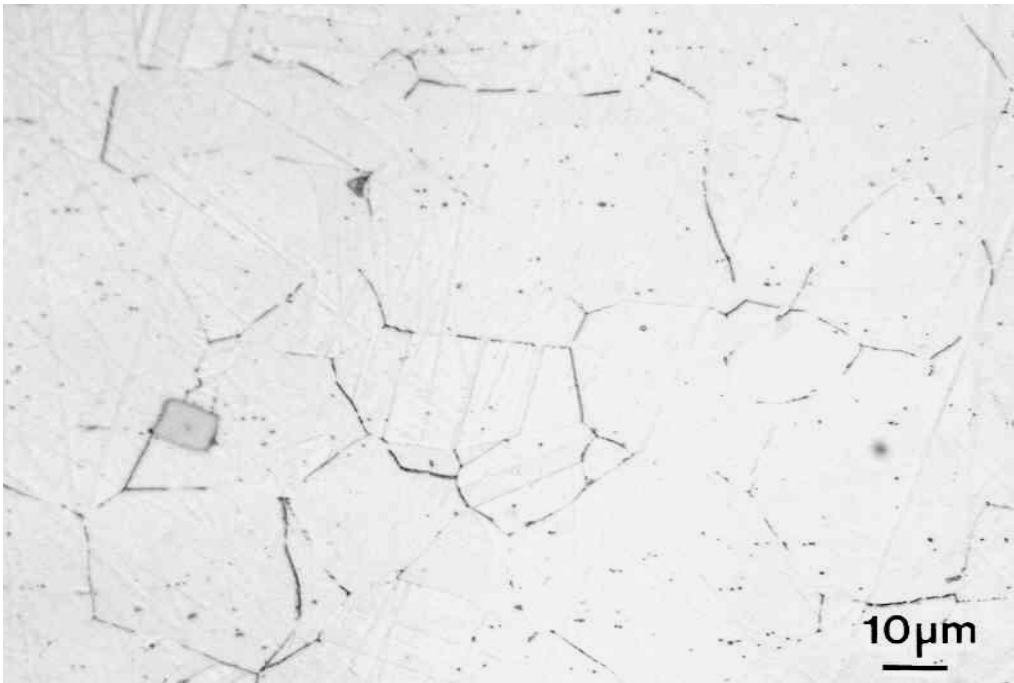
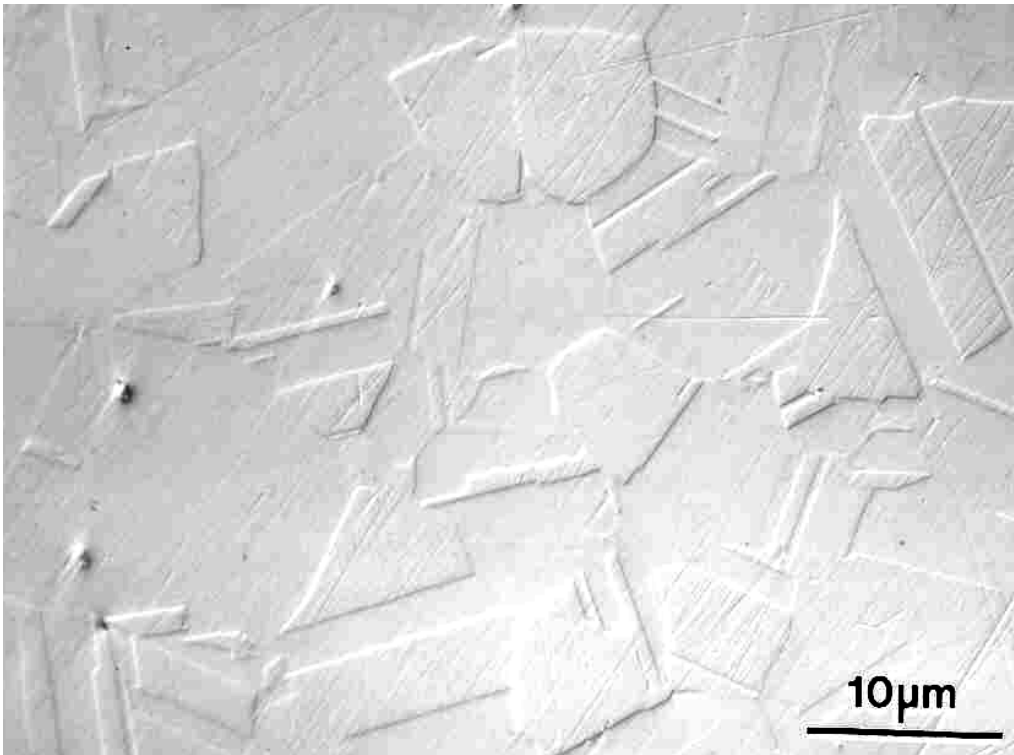


Figure 2. a) Photograph of the material designated as 725 (Top); b) Photograph of the material designated as 725HS (Bottom). The materials for alloys 725 and 725HS were obtained from the standard mill production.

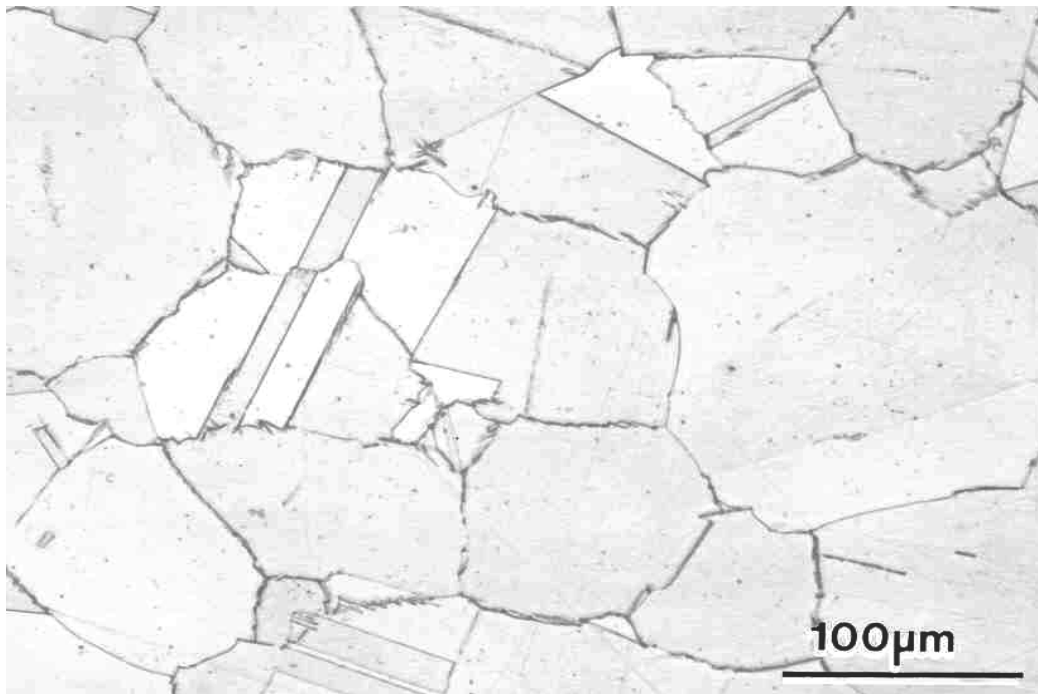
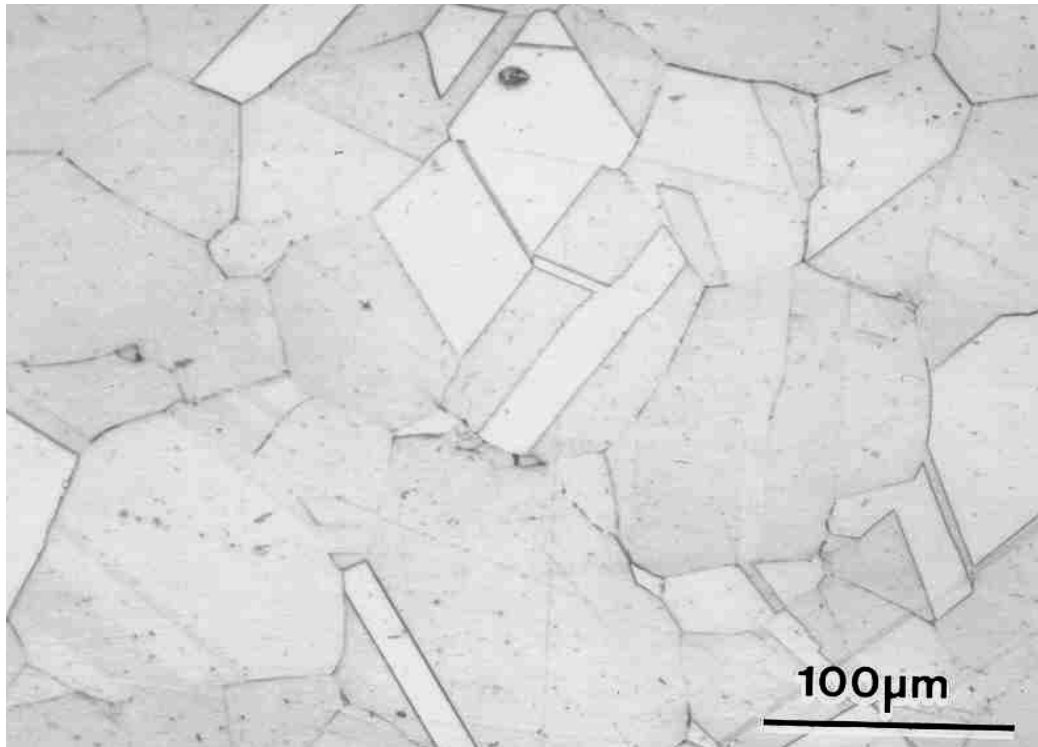


Figure 3. a) Photograph of the material designated as 718-S (Top); b) Photograph of the material designated as 718-M (Bottom). A mill produced hot worked bar was solution annealed and aged in the lab to produce materials 718-S and 718-M. Heat treatment for 718-M was specially designed to dump out continuous grain boundary precipitates.

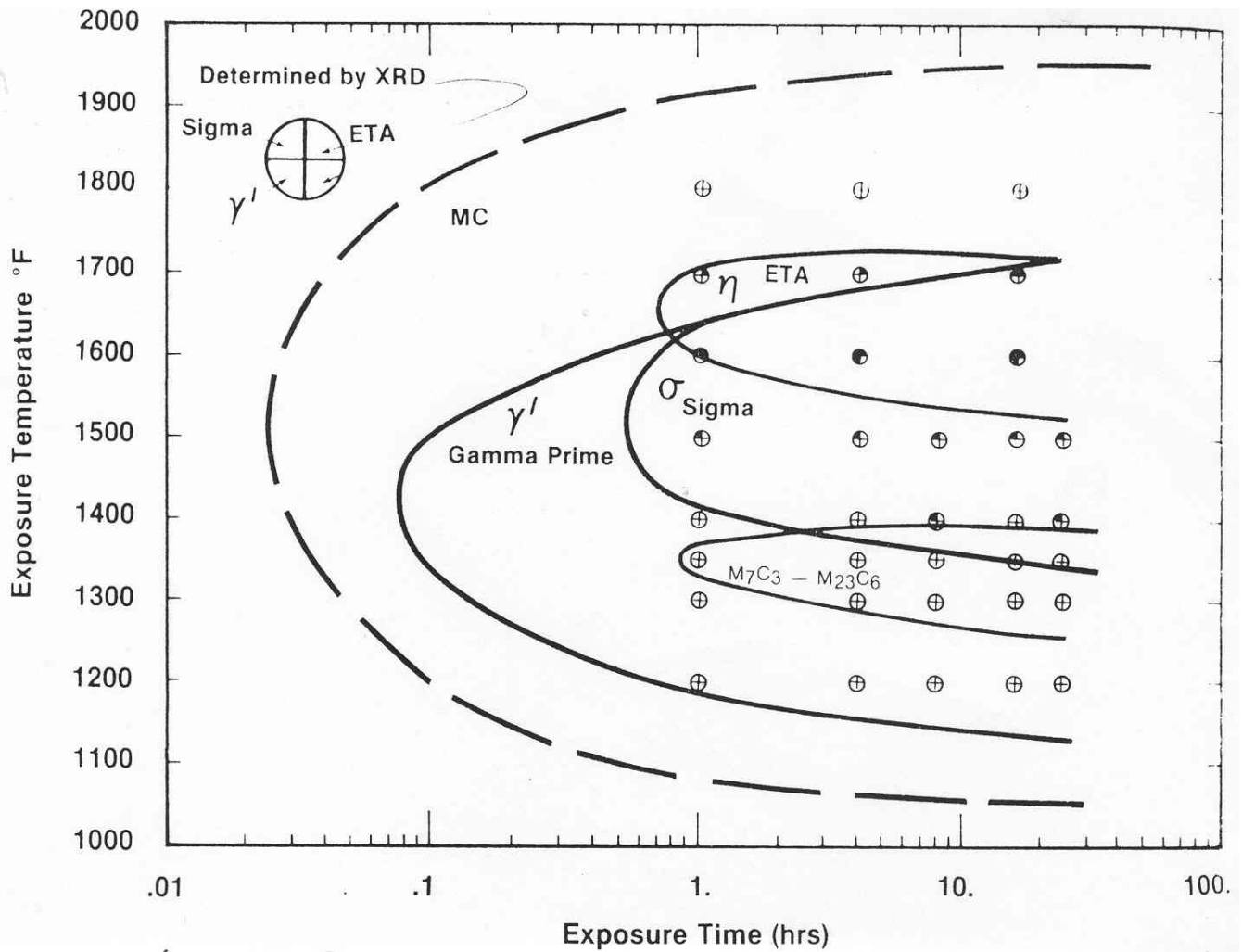


Figure 4. Time-Temperature-Transformation diagram of alloy 925 from reference (5).

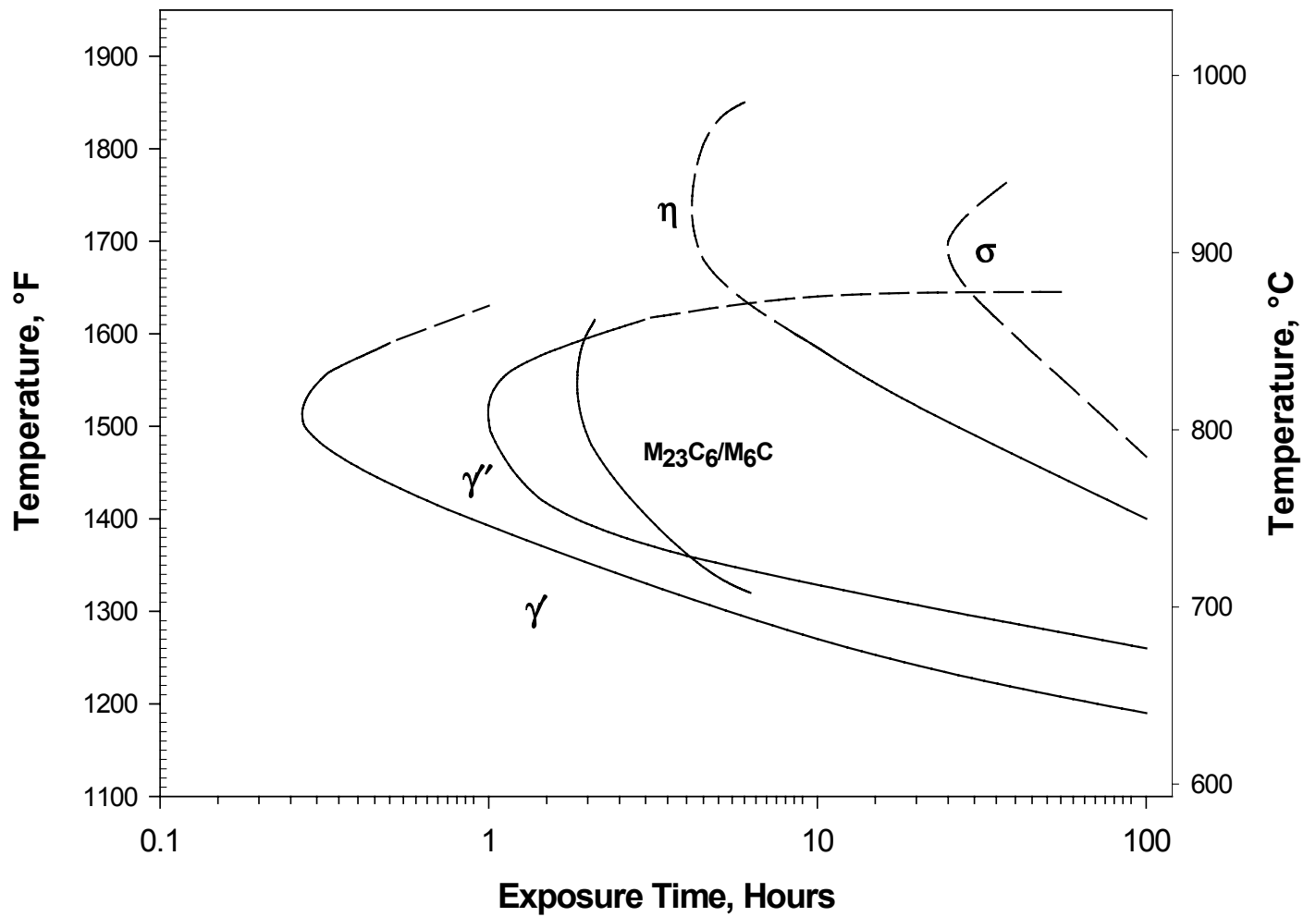


Figure 5. Time-Temperature-Transformation diagram of alloy 725 from reference (6)

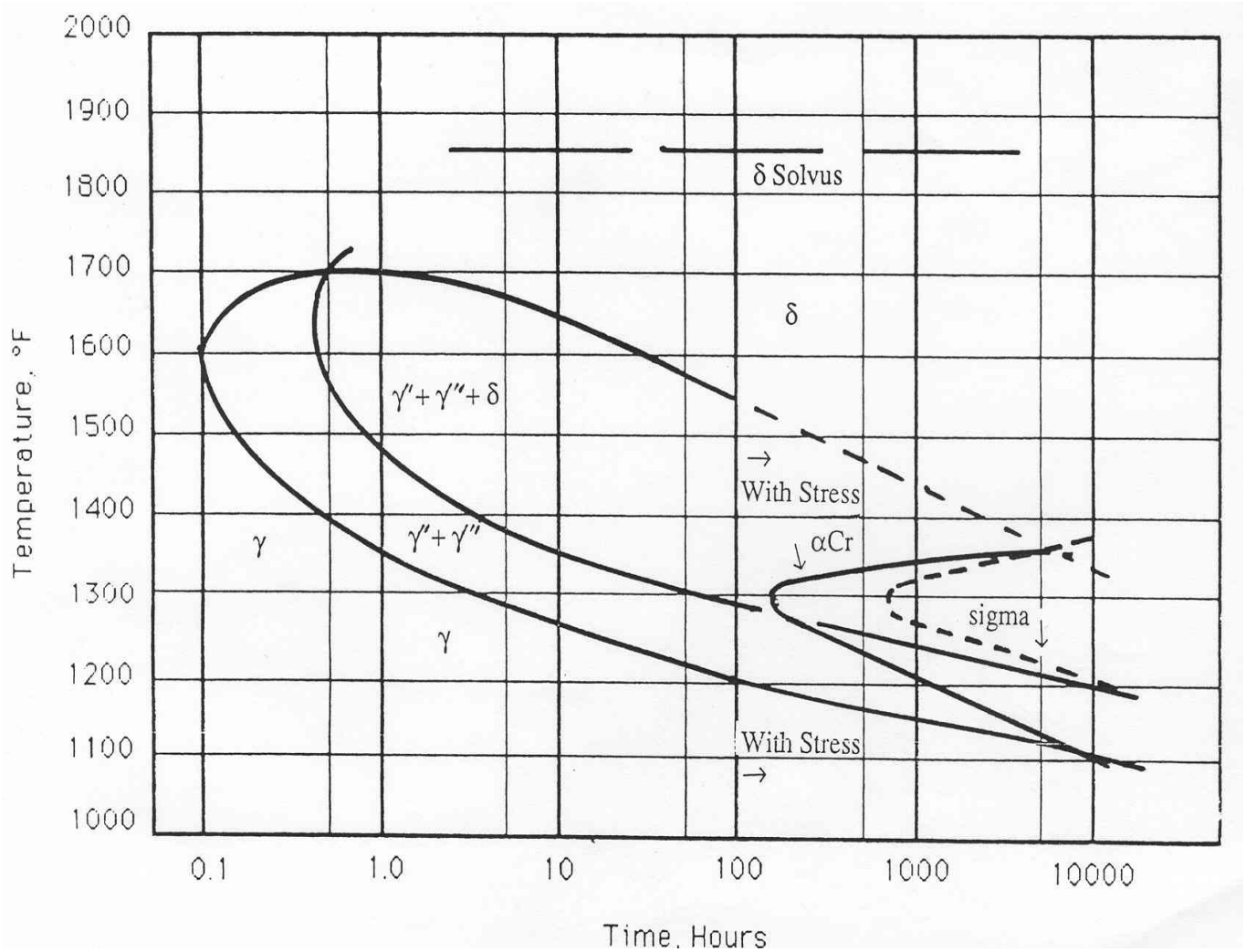


Figure 6. Time-Temperature-Transformation diagram of alloy 718 from reference (7).