PM ALLOY 625M - A HIGH STRENGTH MODIFICATION of ALLOY 625

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Abstract

The capability of PM A625 to be age hardened with conventional heat treatments, has prompted Crucible to develop a niobium modified version of the basic composition to achieve higher strength levels. There has long been a need in a number of corrosive environments for a material with good corrosion resistance and high strength. Alloy 718 has usually been the alloy of choice for these applications and with the corrosive media now being encountered, it is not an acceptable material. PM 625M exhibits the same precipitation phenomena present in PM A625. Mechanical properties, corrosion data and microstructural information are presented in this paper.

Superalloys 718, 625, 706 and Various Derivatives
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Introduction

It was determined during the past decade that the Oil and Gas Industry had a need for a high strength corrosion resistant material to replace alloy 718 for the types of environments being encountered in deep sour wells. During that time, Crucible was closely involved in the development of argon atomized PM A625 which is the powder metal chemical equivalent of alloy 625 (i.e., UNS N06625). However, Crucible discovered[1] early on that PM A625 could easily be age hardened to yield strength levels as high as 724 MPa (105 ksi) without any measurable decrease in corrosion resistance. This precipitation hardening capability made PM A625 a good engineering material for many of the thick section size parts needed for well completions since it did not rely on cold work to achieve the required strength levels.

While PM A625 has been and is continuing to be used for many wellhead applications, there were also a number of other critical components that could not use this material because they required a yield strength minimum of 827 MPa (120 ksi). Crucible embarked on a development program to find an alloy modification of PM A625 to get the best of both worlds - strength equivalent to alloy 718 and corrosion resistance on a par with alloy 625.

Early work[1,2] identified the hardening phase in PM A625 to be γ'' (i.e., Ni_3Nb). However, the strength of this alloy could not be consistently boosted to the 827 MPa (120 ksi) yield strength level. Since there was a good correlation between niobium content and hardening ability, the composition of argon atomized PM 625M (UNS N06626) was selected to contain about 1.25 percent more niobium (i.e., 5% versus 3.75%) than PM A625. Some other adjustments were also made to the PM A625 composition, but these were not designed to effect the strength.

Mechanical Properties

Initially, the work with argon atomized PM 625M centered around minor compositional adjustments and heat treatment optimization. Material was consolidated both by hot isostatic pressing (HIP) and extrusion. Either method was effective: bar products being conveniently made via extrusion and near net shapes through the HIP process. Table I lists the nominal chemical analysis of the alloy and those of some early production heats.

TABLE I. - CHEMISTRIES OF PM 625M LOTS

Weight Percent for:	Nominal	Material Identification Code							
		H352	H454	H455	H456	H457	H458	H461	B436
C	0.02	0.02	0.031	0.033	0.030	0.030	0.030	0.029	0.023
O	<0.01	0.004	0.003	0.003	0.002	0.003	0.003	0.003	0.010
N	0.01	0.015	0.009	0.017	0.006	0.008	0.013	0.013	0.012
Cr	20.50	20.51	20.65	20.65	20.61	20.65	20.48	20.42	20.44
Mo	8.75	8.49	8.73	8.73	8.76	8.68	8.69	8.74	8.78
Nb	5.00	5.00	5.06	5.06	5.00	4.90	4.95	4.89	5.06
Ti	0.05	<0.05	<0.02	<0.02	0.27	0.02	0.10	0.10	0.06
Al	0.50	0.50	0.45	0.45	0.54	0.62	0.50	0.47	0.53
S	<0.015	0.001	0.005	0.005	0.006	0.004	0.005	0.005	0.001
Si	<0.50	0.14	0.15	0.15	0.20	0.13	0.16	0.16	0.12
Mn	<0.50	<0.03	<0.05	<0.05	<0.05	0.18	0.09	0.16	0.27
P	<0.015	0.008	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.010
Fe	5.00	4.79	4.88	4.88	4.77	4.83	4.95	4.89	4.92
Ni	BAL	BAL	BAL	BAL	BAL	BAL	BAL	BAL	BAL

The mechanical property and corrosion test data from these heats was used to get this alloy approved for use in critical service environments such as sour oil and gas wells. The material was balloted and approved to be included in the NACE Standard MR-01-75. Table II shows some of the typical room temperature tensile properties of the heats used to obtain the NACE approval. The heat treatment used for most of this material was the direct age DA718 cycle: 718°C (1325°F)/8 hours/furnace cool to 621°C (1150°F)/8 hours/air cool. This treatment worked effectively at achieving the yield strength levels between 827 MPa (120 ksi) and 965 MPa (140 ksi) on a consistent basis with PM 625M.

TABLE II. - TYPICAL ROOM TEMPERATURE TENSILE PROPERTIES OF PM 625M AND ALLOY 718

Material Code	Heat Treatment	Room Temperature Tensile Properties			
		UTS MPa (ksi)	0.2% YS MPa (ksi)	EL %	RA %
H352	DA 718	1248 (181)	917 (133)	29	37
"	982°C (1800°F)/1 hr/WQ + DA 718	1248 (181)	924 (134)	30	34
"	1144°C (2100°F)/1 hr/WQ + DA 718	1206 (175)	889 (129)	28	27
H454	DA 718	1262 (183)	896 (130)	27.5	28
H455	"	1275 (185)	910 (132)	29	37
H456	"	1324 (192)	965 (140)	22	25
H457	"	1220 (177)	841 (122)	34	42
H458	"	1275 (185)	917 (133)	27	28
H461	"	1282 (186)	924 (134)	30	35
Alloy 718	1024°C (1875°F)/1 hr/AC + 788°C (1450°F)/8 hrs/AC	1220 (177)	814 (118)	35	53.5

Note: DA 718 = 718°C (1325°F)/8 hrs/FC 55°C (100°F)/hr to 621°C (1150°F)/8 hrs/AC

More recently, additional work was done with variations in the heat treatment cycle. The room temperature tensile results from this study are presented in Table III. A number of variations of the DA718 treatment were applied to PM 625M and the level was higher than had been experienced prior to that time. Some additional heat treatment work was done to look at solution treatment and at single direct age treatments. The cycle resulting in the best combination of strength and ductility from the study was a direct age treatment at 691°C (1275°F) for 16 hours. The study also showed that solution treatments did not significantly effect the room temperature tensile properties.

TABLE III. - ROOM TEMPERATURE TENSILE PROPERTIES OF PM 625M WITH HEAT TREATMENT VARIATIONS

Material Code	Heat Treatment	Room Temperature Tensile					
		UTS		0.2% YS		EL	RA
		MPa	(ksi)	MPa	(ksi)	%	%
B436	718°C (1325°F)/4 hrs/FC to 621°C (1150°F)/4 hrs/AC	1296	(188)	951	(138)	22	26
"	718°C (1325°F)/4 hrs/FC to 621°C (1150°F)/8 hrs/AC	1310	(190)	965	(140)	20	24
"	718°C (1325°F)/4 hrs/FC to 621°C (1150°F)/16 hrs/AC	1310	(190)	945	(137)	22	23
"	718°C (1325°F)/8 hrs/FC to 621°C (1150°F)/2 hrs/AC	1296	(188)	951	(138)	24	28
"	718°C (1325°F)/8 hrs/FC to 621°C (1150°F)/4 hrs/AC	1317	(191)	986	(143)	25	29
"	718°C (1325°F)/8 hrs/FC to 621°C (1150°F)/8 hrs/AC	1324	(192)	1007	(146)	22	28
"	718°C (1325°F)/8 hrs/FC to 621°C (1150°F)/16 hrs/AC	1337	(194)	1041	(151)	22	26
"	718°C (1325°F)/8 hrs/FC to 621°C (1150°F)/32 hrs/AC	1344	(195)	1048	(152)	23	28
"	982°C (1800°F)/1 hr/WQ + 649°C (1200°F)/16 hrs/AC	1165	(169)	758	(110)	36	38
"	982°C (1800°F)/1 hr/WQ + 732°C (1350°F)/16 hrs/AC	1234	(179)	938	(136)	31	36
"	996°C (1825°F)/1 hr/OQ + 663°C (1225°F)/16 hrs/OQ	1206	(175)	786	(114)	35	39
"	996°C (1825°F)/1 hr/OQ + 677°C (1250°F)/16 hrs/OQ	1241	(180)	834	(121)	29	36
"	649°C (1200°F)/16 hrs/AC	1213	(176)	814	(118)	33	33
"	677°C (1250°F)/16 hrs/AC	1241	(180)	848	(123)	33	36
"	691°C (1275°F)/16 hrs/AC	1262	(183)	876	(127)	29	34
"	732°C (1350°F)/16 hrs/AC	1255	(182)	951	(138)	26	31

Note: All results are the average of two tests.
FC - Furnace cool at 55°C (100°F)/hr.

Thermal stability as measured by changes in strength or ductility after exposure at elevated temperature for an extended period of time was determined for PM 625M at 649°C (1200°F) for times up to 1000 hours. These results are shown in Table IV. There was a slight (i.e., 62 MPa (9 ksi)) increase in room temperature yield strength after exposure with no change in ductility.

TABLE IV. - ROOM TEMPERATURE TENSILE PROPERTIES OF PM 625M BLEND B436 AFTER THERMAL EXPOSURE AT 649°C(1200°F)

Thermal Treatment	Room Temperature Tensile			
	UTS MPa (ksi)	0.2% YS MPa (ksi)	EL %	RA %
DA 718	1248 (181)	917 (133)	28	41
DA718 + 649°C(1200°F)/10 hrs/AC	1248 (181)	903 (131)	30	41
DA718 + 649°C(1200°F)/100 hrs/AC	1255 (182)	924 (134)	30	41
DA718 + 649°C(1200°F)/1000 hrs/AC	1275 (185)	979 (142)	30	41

Note: DA718 = 718°C(1325°F)/8hrs/FC 55°C(100°F)/hr to 621°C(1150°F)/8 hrs/AC

Corrosion Properties

A series of different types of corrosion tests were conducted on PM 625M material along with alloy 718 for a baseline comparison. Intergranular corrosion was measured by the standard ASTM A763 Practice Y method, the ASTM A262 Practice B method (i.e., ASTM G-48), and the ASTM A262 Practice C method. General corrosion rate was measured in boiling 10% sulfuric acid, a reducing solution, and boiling 50% formic acid, an organic solution. Critical pitting and crevice corrosion temperatures were determined in a 10% ferric chloride solution and in "Green Death", a solution of mixed acids and ferric and cupric chloride.

Table V gives the results for these intergranular corrosion tests. The ASTM A763 Practice Y results of several different heat lots of material showed a consistent 6 to 9 mils per month corrosion rate for PM 625M. The comparative alloy 718 result was in excess of 30 mils per month or roughly four times as fast. The results of the ASTM A262 Practice B tests showed PM 625M to have about half the corrosion rate of alloy 718 (44.5 mils per month versus 91.5 mils per month). The ASTM A262 Practice C data showed that alloy 718 had a slower corrosion rate than PM 625M by 22.5 mils per month to 12.5 mils per month.

TABLE V. - INTERGRANULAR CORROSION RESULTS FOR PM 625M AND ALLOY 718

Material Code	Heat Treatment	Corrosion Rate for:		
		ASTM A763 Practice Y mil/mo	ASTM A262 Practice B mil/mo	ASTM A262 Practice C mil/mo
H352	A	9.1	--	--
H454	"	8.0	--	--
H455	"	8.7	--	--
H456	"	7.6	--	--
H457	"	7.1	--	--
H458	"	6.8	--	--
H461	"	6.0	--	--
H352	B	14.8	--	--
"	C	12.5	--	--
B436	D	--	44.5	22.5
Alloy 718	E	32.7	--	--
"	F	--	91.5	12.5

Heat Treatment:
A = DA718 = 718°C(1325°F)/8 hrs/FC 55°C(100°F)/hr to 621°C(1150°F)/8 hrs/AC
B = 982°C(1088°F)/1 hr/WQ + DA718
C = 1149°C(2100°F)/1 hr/WQ + DA718
D = 649°C(1200°F)/16 hrs/AC
E = 1024°C(1875°F)/1 hr/AC+ 788°C(1450°F)/8 hrs/AC
F = 954°C (1750°F)/0.5 hr/AC + DA718

Table VI contains the general corrosion rate data. In the reducing acid (i.e., sulfuric) solution the corrosion rate of the PM 625M was 0.67 mils per month versus 3.75 mils per month for alloy 718. In the organic acid (i.e., formic) solution the corrosion rate for PM 625M was less than half that of alloy 718 - 0.13 mils per month versus 0.33 mils per month. Both materials showed good resistance to general acid attack.

TABLE VI. - GENERAL CORROSION RESULTS FOR PM 625M AND ALLOY 718

Material Code	Heat Treatment	Corrosion Rate for: 48 hrs. in Boiling 10% H_2SO_4 mils/mo	Corrosion Rate for: 48 hrs. in Boiling 50% Formic Acid mils/mo
B436	D	0.67	0.13
Alloy 718	F	3.75	0.33
Heat Treatments: D = 649°C (1200°F)/16 hrs/AC; F = 954°C (1750°F)/0.5 hr/AC + DA718			

The critical pitting and crevice corrosion temperatures were determined for both PM 625M and alloy 718 in 10% ferric chloride and "Green Death". The results of these tests are shown in Table VII. For all cases, PM 625M is significantly superior to alloy 718. In the ferric chloride solution, the critical pitting temperature of PM 625M is typically about 80°C (176°F) and the critical crevice corrosion temperature is 40°C (104°F). The corresponding values for alloy 718 are less than half these levels. In the "Green Death" solution, the same advantage exists for PM 625M over alloy 718. The critical temperatures of PM 625M are approximately twice those of alloy 718.

TABLE VII. - CRITICAL PITTING AND CREVICE CORROSION TEMPERATURES FOR PM 625M AND ALLOY 718

Material Code	Heat Treatment	Critical Temperature in: Ferric Chloride				Green Death			
		Pitting		Crevice Corrosion		Pitting		Crevice Corrosion	
		°C	(°F)	°C	(°F)	°C	(°F)	°C	(°F)
H454	A	73	(163)	--		78	(172)	--	
H455	"	73	(163)	--		73	(163)	--	
H456	"	85	(185)	--		63	(145)	--	
H457	"	82	(180)	--		78	(145)	--	
H458	"	73	(163)	--		73	(163)	--	
H461	"	79	(174)	--		78	(172)	--	
B436	D	80	(176)	40	(104)	65	(149)	60	(140)
Alloy 718	E	45	(113)	--		42	(108)	--	
"	F	30	(86)	<8	(<46)	35	(95)	23	(73)

Heat Treatment:
A = DA718 = 718°C(1325°F)/8 hrs/FC 55°C(100°F)/hr to 621°C(1150°F)/8 hrs/AC
D = 649°C(1200°F)/16 hrs/AC
E = 1024°C(1875°F)/1 hr/AC+ 788°C(1450°F)/8 hrs/AC
F = 954°C (1750°F)/0.5 hr/AC + DA718

Table VIII lists the results of C-ring tests to evaluate the stress corrosion capability of PM 625M. Again alloy 718 was included in the test program for a comparison. Tests were run in a simulated sour environment at temperatures from 177°C (350°F) to 232°C (450°F). The alloy 718 material failed in times less than 720 hours of exposure at all temperatures. The PM 625M material showed no cracking in 720 hours up to 204°C (400°F). However, at 232°C (450°F), the highest temperature tested, PM 625M failed in less than 720 hours the same as the alloy 718 material.

TABLE VIII. - C-RING TEST RESULTS FOR PM 625M AND ALLOY 718

Material Code	Heat Treatment	Test Temperature °C (°F)	Time to Failure hrs
H352	A	177 (350)	720 NF
"	"	204 (400)	720 NF
"	"	232 (450)	<720
Alloy 718	E	177 (350)	<720
"	"	204 (400)	<720
"	"	232 (450)	<720

Heat Treatment:
A = DA718 = 718°C(1325°F)/8 hrs/FC 55°C(100°F)/hr to 621°C(1150°F)/8 hrs/AC
E = 1024°C(1875°F)/1 hr/AC+ 788°C(1450°F)/8 hrs/AC

Test Solution:
25% NaCL + 15%H_2S + 15% CO_2 + 70% N_2 + 1g/l elemental S

Test Stress:
Specimens were loaded to 90% of their room temperature 0.2% yield strength.

Another test of the stress corrosion capability of PM 625M is a constant strain rate tensile test (CERT). Some tests were conducted on a fully heat treated production lot of material. Results from one such test are given in Table IX. The conditions simulate a sour well environment and the criteria are the ratios of the tensile ductilities in the sour environment to those in an inert atmosphere. The ratios were greater than 1 which indicates better ductility in sour conditions. SEM and light microscopic examinations of the failed test bars revealed no indications of brittle fracture or secondary cracking in the gage section.

TABLE IX. - CONSTANT STRAIN RATE TENSILE RESULTS FOR PM 625M

Material Code	Test Conclusion	Test Duration hrs	EL %	RA %	Envir/Inert Ratio	
					EL	RA
B436	**Inert**	42.1	31.7	30.5	--	--
"	**Environment**	42.9	32.5	31.6	1.03	1.04

Inert = 125°C(257°F), 3.5/4.8 MPa (500/700 psi) Nitrogen gas.

Sour Environment = 125°C(257°F), 25% NaCl + 15 g/l free S + H_2S/CO_2 ratio of 9:1 at 10.3 - 13.8 MPa (1500-2000 psi)

Strain rate = 2.4 x 10^{-6}/sec.

Microstructural Characteristics

Specimens were prepared for SEM analyses of PM 625M material in the solution treated (982°C (1800°F)) and aged (649°C (1200°F)) and the direct aged (two cycles) conditions. Figure 1 shows the solution treated and aged microstructure. It shows a random precipitation of carbides and little or no second phase in the matrix. Electrolytic extraction of the precipitates indicated that the carbides are a Nb-rich MC type and a Mo-rich M_6C type. No γ'' (Ni_3Nb) was detected in these samples.

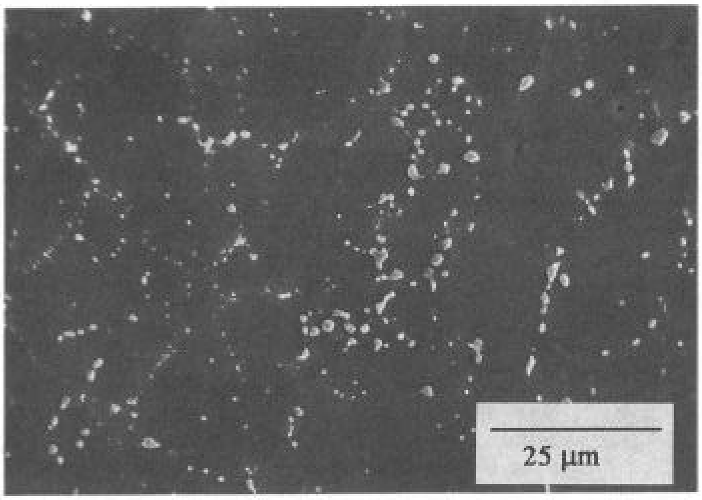
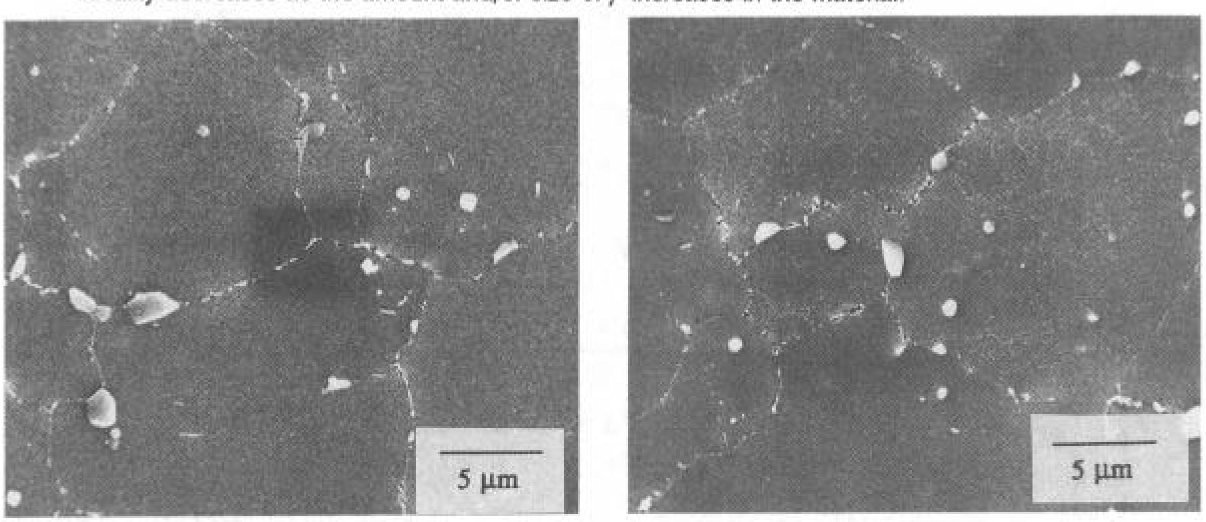


Figure 1. SEM Photograph of the Solution Treated and Aged Microstructure of PM 625M. Etchant: 10% HCl in Methanol Electrolytic

Figure 2 shows the two direct aged microstructures. One was a straight 691°C (1275°F) age for 16 hours and the other was a DA718 cycle of 718°C (1325°F)/8 hrs/furnace cool to 621°C (1150°F)/8 hrs/air cool. Both of these heat treatments resulted in a similar microstructure. The same carbides are present as in the as-HIP condition and the matrix for both treatments is filled with γ'' which has a slightly larger particle size in the DA718 treated material. Table X shows the corresponding room temperature tensile properties of all of these heat treated conditions. The strength increases and the ductility decreases as the amount and/or size of γ'' increases in the material.



(a) (b)

Figure 2. SEM Photographs of PM 625M in Two Direct Age Conditions: 691°C (1275°F)/16hrs (a) and 718°C (1325°F)/8hrs/FC to 621°C (1150°F)/8hrs/AC (b). Etchant: 10% HCl in Methanol Electrolytic

TABLE X. - ROOM TEMPERATURE TENSILE PROPERTIES OF PM 625M

Material Code	Heat Treatment	Room Temperature Tensile Properties UTS MPa (ksi)	0.2% YS MPa (ksi)	EL %	RA %
B436	982°C(1800°F)/1hr/WQ + 649°C(1200°F)/16 hrs/AC	1165 (169)	751 (109)	38	44
"	691°C(1275°F)/16 hrs/AC	1262 (183)	876 (127)	29	35
"	718°C(1325°F)/8 hrs/FC 55°(100°F)/hr to 621°C(1150°F)/8 hrs/AC	1324 (192)	979 (142)	22	30
Note: DA 718 = 718°C (1325°F)/8 hrs/FC 55°C (100°F)/hr to 621°C (1150°F)/8 hrs/AC					

TEM work[3] on PM 625M verified the findings of the SEM and extraction studies. The γ'' precipitates were determined to be approximately 15 nm to 25 nm in diameter and about 3 nm in thickness for material receiving the DA718 heat treatment. These particles were found in great abundance. The carbides were found to contain significant amounts of Nb and Mo with minor amounts of Ni, Cr, and Fe. They ranged in size from 0.2 μm to 1.5 μm.

Summary

Further development of the PM 625M alloy is currently on-going at Crucible. The goal was to find a composition with strength equivalent to alloy 718 and corrosion resistance similar to alloy 625. Each of these criteria were achieved. PM 625M, a niobium modified powder metallurgy composition of alloy 625 is a useful engineering material for applications requiring 827 MPa (120 ksi) minimum yield strength at room temperature and corresponding good corrosion resistance.

Acknowledgements

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References

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