TECH FRONTIERS

475°C embrittlement and 550ºC re-dissolution effect of duplex stainless steel

BARUNDEB RAHA

Mr Raha is with Peekay Steel Castings (P) Limited

Duplex stainless steel is susceptible to brittle fracture under certain conditions of temperature and time. Between 700-900°C, deleterious phases like sigma, chi, carbides, and nitrides form, which are hard and brittle. A study has been undertaken to evaluate this embrittlement effect of duplex, super duplex and hyper duplex stainless steel of grades like 4A, 5A, 6A, and 7A of ASTM A890 external

DUPLEX stainless steel is widely used in various conditions where strength and corrosion resistance are dominant factors for selecting material. Duplex stainless steel consists of equal proportion of ferrite and austenite in solution annealed condition. Ferrite imparts strength and austenite gives corrosion resistance property. Because of its higher PREN[1] values, duplex stainless steel is preferred for application in highly corrosive environments. Both from the strength and corrosion resistance point of view it is superior to austenitic stainless steel; and because of its lower Ni, higher N content, and higher strength/weight ratio than austenitic stainless steel, duplex stainless steel is more cost effective than austenitic and super austenitic grades.

On cooling from liquid stage, duplex steel solidifies as ferrite and at around 1400°C complete transformation of liquid phase to solid (ð-ferrite) is over. On further cooling, part of ð-ferrite transforms to austenite and at around 1000°C, phase balance is established. Cooling below 1000°C, ferrite decomposes to various intermetallic phases which are called deleterious phases. They are shown in the TTT[2] curve of duplex stainless steel. Among all such phases, sigma and chi phases have a strong embrittlement effect.

In the lower portion of **Figure1**, some other intermattalic phases, like alpha prime (α1), □, and G form. They are also deleterious phases and make the steel brittle. They form between 280-500°C and, at 475°C, embrittlement effect is very clear.

For this reason, this phenomenon is termed as 475°C embrittlement as the rate of embrittlement is highest at this temperature.[3] Reidrich and Loib[4] were first to report such embrittlement by exposing iron-chromium alloy at elevated temperatures and concluded that embrittlement is sensitive to temperature in a very narrow range. Fisher et al.[5] suggested the decomposition of the ferrite phase to chromium-rich alpha prime phase (α1) and iron-rich alpha phase (α) in the temperature range of 280-500°C. William[6] proposed the existence of a miscibility gap in Fe-Cr phase diagram in temperature range of 280-500°C as the cause of precipitation of α^{1} as shown in

Figure1: TTT Diagram of Duplex SS

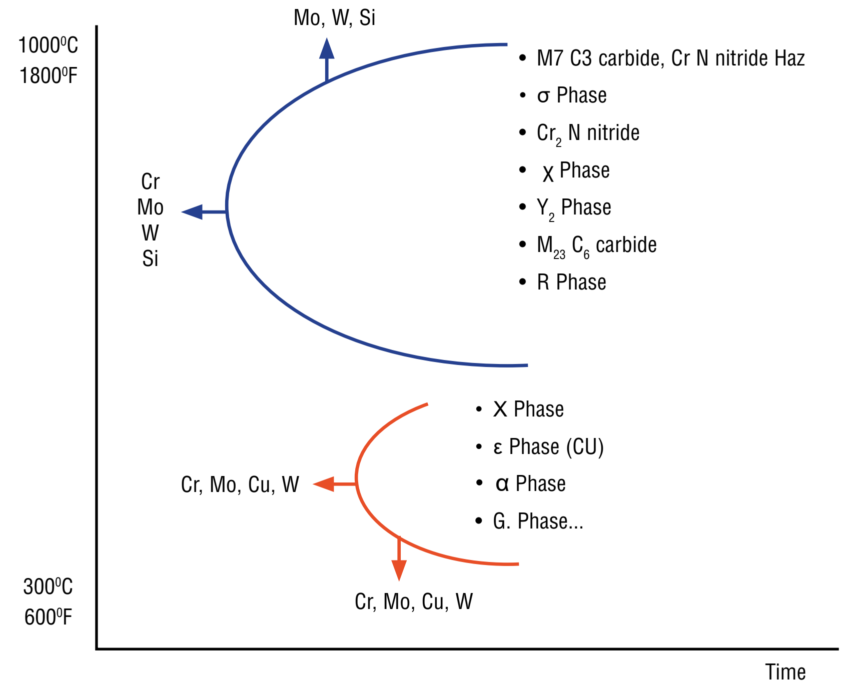


Figure2: Cr content Vs Temp. showing Alpha Prime Phase

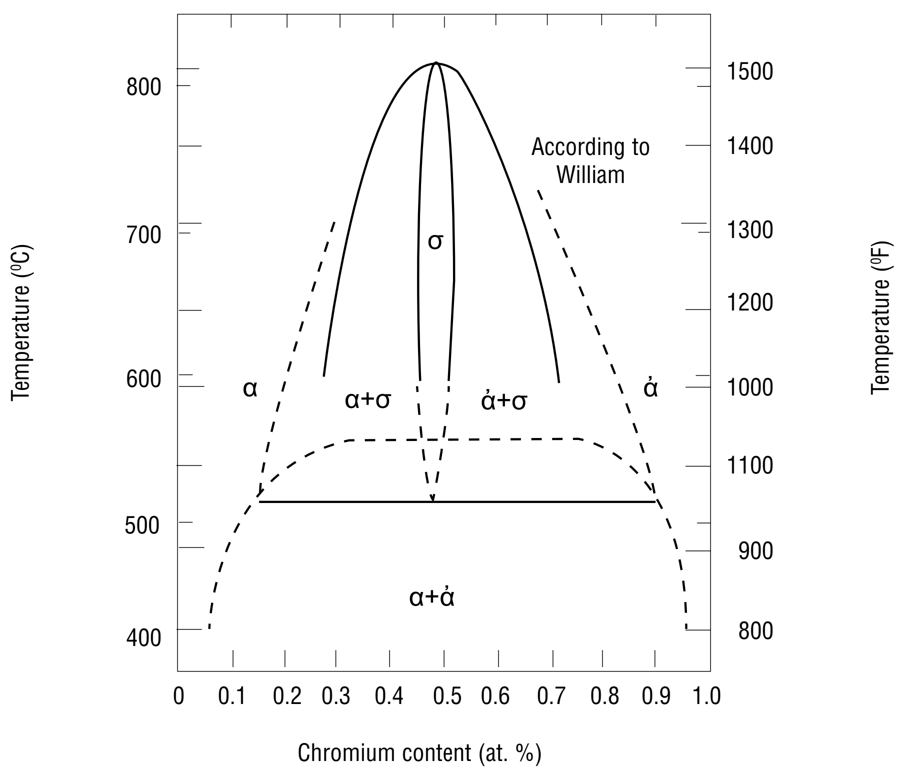


Figure3: Spinodal Decomposition

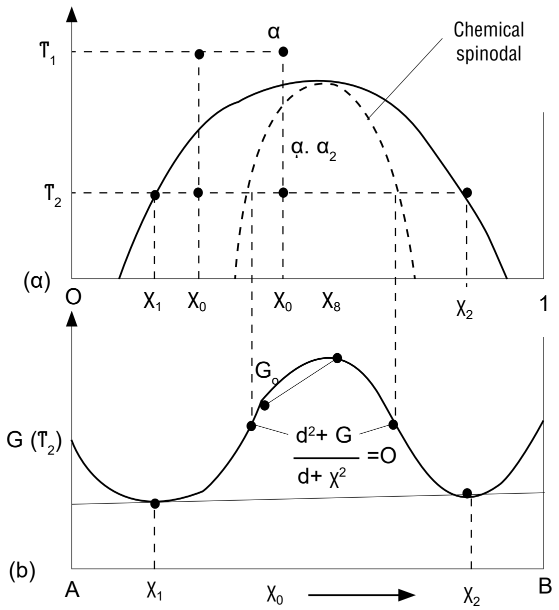


Figure3A: Schematic Plot at different times in an alloy (a) Inside Spinodal (b) Outside Spinodal

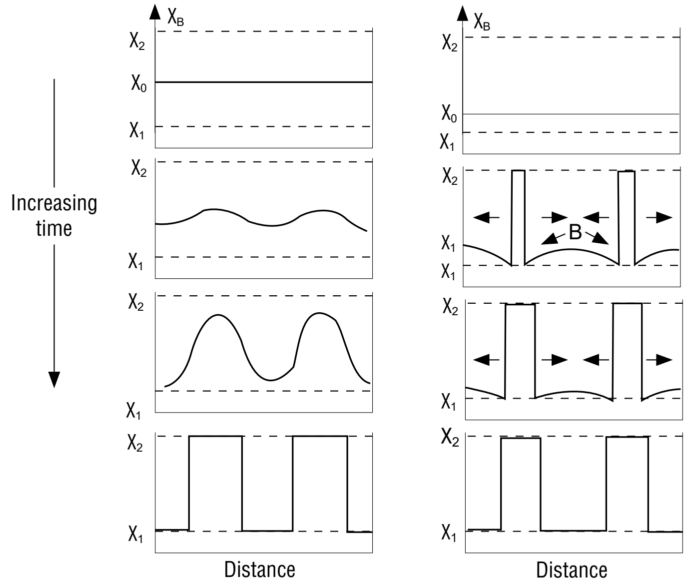


Figure2. According to this phase diagram, 475°C embrittlement may be expected at temperatures below 516°C in the composition range of 12-92% chromium in iron-chromium binary alloy system. Blackburn and Nutting[7] completely re-dissolved the α[1] after 24-hour aging at 550°C.

Miscibility gap and spinodal regions on phase diagram

Spinodal reaction occurs in a miscibility gap of the phase diagram. Let us consider a phase diagram with miscibility gap as shown in **Figure3**. When an alloy of composition X_o is homogenised at T_1 and then quenched to T_2, originally it has uniform chemical composition and its Gibbs energy is equal to Go on the diagram. This alloy is unstable at T_2 because of composition fluctuations, creating regions rich in A and rich in B and these lead to a decrease in total Gibbs energy of the system. Subsequently uphill diffusion occurs and continues until a two-phase structure with equilibrium compositions of X_1 and X_2 is achieved. Such transformation occurs at any composition for which the free energy-composition curve has negative curvature, mathematically: $d^2G/dX^2 < 0$ and it takes place through the diffusion process unlike the nucleation and growth processes. This is called a spinodal decomposition of a phase. The diffusion mode of spinodal decomposition is shown in **Figure3A.**[8]

In this study, we evaluated embrittlement effect at 475°C by varying aging time for various duplex grades like 4A, 5A, 6A, and 7A of ASTM A890[1]. These grades are in regular production line of Peekay Steel, Calicut Plant. Also we studied corrosion test[9] and welding test after both 475°C embrittlement and 550°C treatment.

EXPERIMENTATION

Test blocks from production heats of grades 4A, 5A, and 6A of ASTM A890 were selected for experimentation. All these production heats were processed through Induction + AOD melting route. We also made a hyper duplex grade 7A heat in an induction furnace for carrying out experimentation and to establish this new grade. Test blocks were heat treated originally in industrial furnace along with castings as per cycle mentioned in ASTM A890. For experimentation, test pieces were further heat treated in a muffle furnace in the laboratory for 475°C embrittlement and 550°C re-dissolution test.

475°C embrittlement test

The chemical composition of various grades of duplex steels selected for this study is shown in **Table1**. Mechanical properties after heat treatment are shown in **Table2**.

The microstructure of a grade 7A is shown in **Figure4**. The SEM of fractography images of ductile fracture of broken impact sample of grade 7A is shown in **Figure4A**.

Next 25x25x30 mm test pieces were cut from heat treated test blocks and they

Table1: Chemistry of various duplex grades

Grade	C	Mn	Si	P
4A	0.024	1.074	0.520	0.028
5A	0.023	1.131	0.497	0.026
6A	0.020	0.812	0.521	0.019
7A	0.030	2.808	0.887	0.005
	S	Cr	Ni	Mo
4A	0.003	22.42	5.79	3.04
5A	0.003	24.35	7.51	4.29
6A	0.003	24.07	7.83	3.82
7A	0.006	26.36	7.74	2.45
	Cu	W	N	Other
4A	0.275	-	0.168	
5A	-	-	0.191	
6A	0.549	0.592	0.204	
7A	0.512	3.924	0.382	B:0.003 Ce + La: 0.0055 Ba:0.001

Table2: Mechanical properties after annealing

Grade	UTS MPa	0.2% MPa	%EL	ISO-V -50°C	BHN
4A	697	500	35.85	120	217
5A	748	507	28.86	110	235
6A	765	577	39.15	110	248
7A	868	591	32	40	265

were aged in a muffle furnace for 1, 5, and 10 hours at 475°C. After that, hardness and impact test were carried out. The test result is shown in **Table3**. Here we can see increase in hardness with corresponding decrease in impact values with aging time and their trend is shown in **Figures5&6**. It is interesting to note that there was drop of impact values after holding the sample at 475°C. In this line we carried out further experimentation by holding fresh sample of 4A, 5A, and 6A at 475°C for 1 minute, 10 minutes, and 30 minutes. **Table4** shows hardness and impact values.

Effect of embrittlement was noticed after holding sample for 1 minute for 5A and 6A grades. However after 10 minutes, there was sharp drop in impact values as shown in **Figure7**.

The microstructure of broken impact sample after 10-hour soaking is shown in **Figure8**. The structure is normal Ferrite + Austenite. Other precipitates like α^1could not be seen by SEM analysis because of their fineness.

Effect of 475°C on tensile values

We carried out experimentation to find out the effect of 475°C treatment on tensile and corrosion resistant property.

Figure4: Normal Ferrite + Austenite

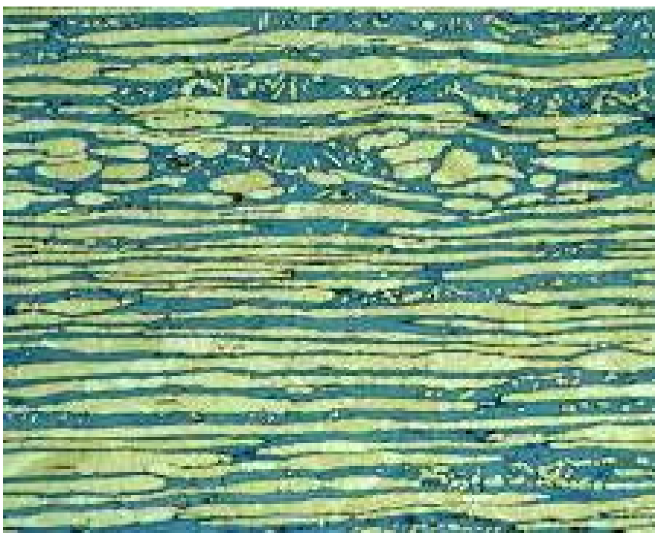


Figure4A: Dimple fracture of broken impact sample

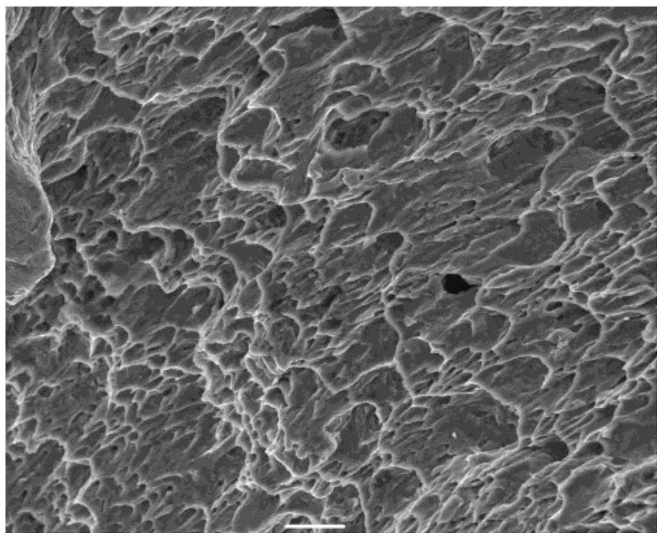


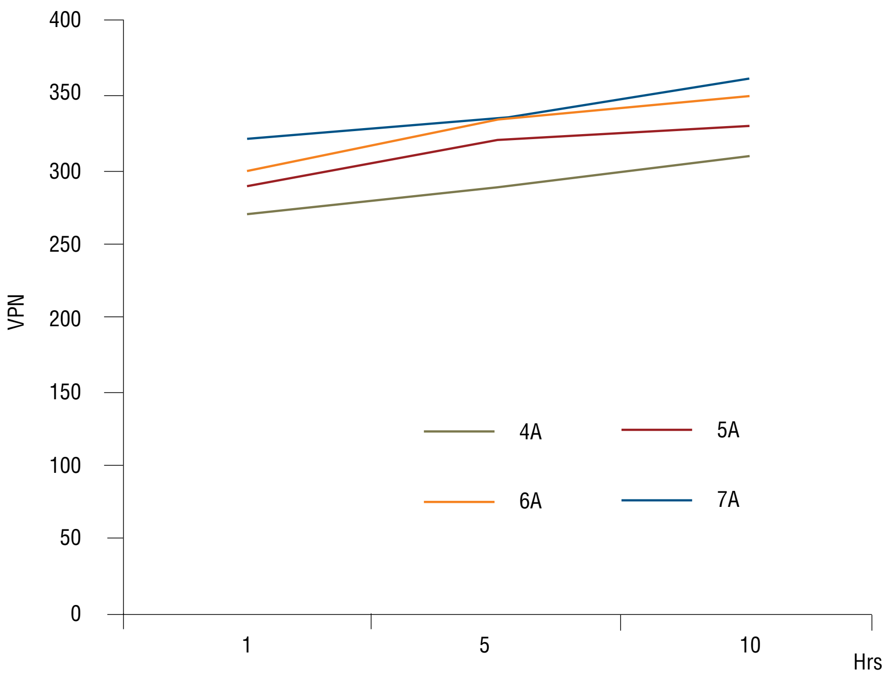
Table3: Effect of 475°C aging on duplex grades

Hours	VPN	J, -50°C	VPN	J,-50°C
	4A		**5A**	
1	265	66	300	30
	6A		**7A**	
1	305	44	320	20
	4A		**5A**	
5	290	32	320	20
	6A		**7A**	
5	335	58	335	16
	4A		**5A**	
10	310	28	354	18
	6A		**7A**	
10	350	26	360	10

Table4: Sample aged for 1 minute to 30 minutes

Time, minutes	4A	5A	6A
	VPN/J @ -50°C		
1	249/102J	285/134	297/102
10	264/48J	294/102	299/92
30	276/28	319/84	322/80

Figure5: VPN vs Holding Time



ere we took 50x50x250 mm length pieces from grade 4A, 5A, and 6A from solution annealed block and made tensile sample first as per ASTM A3708. After that, finished tensile samples from each grade of 4A, 5A, and 6A were aged at 475°C for 30 minutes. After treatment, heat tint yellow colour was noticed on each sample as shown in **Figure9**. The degree of heat tinting is more in case of 6A than other grades. Tensile values are shown in **Table5**.

From Table5, we find that there was increase in tensile values after 30-minute ageing. However, ductility as measured by %E and %RA showed declining trend when compared with original value. Similar trend was noticed for 10-hour aging time.

Corrosion test

We carried out pitting corrosion test of grade 4A sample after ageing at 475°C for 30 minutes. The test was carried out as per ASTM G48, method A in FeCl3 solution at 70°C for 24 hours. Pitting was noticed as shown in **Figure10**.

Re-dissolution test

We carried out re-dissolution treatment at 550°C for 5 and 10 hours of earlier 10-hour aged samples at 475°C. Hardness values of samples after re-dissolution treatment are shown in **Table7**.

From this we find that after 10-hour re-dissolution treatment at 550°C, grade 4A has almost reached its original hardness values. However, for other grades more soaking is required. Further dissolution treatment for 20 hours was done. For 5A and 6A there were marginal drop in hardness. For 7A, there is no drop in hardness after 20 hours.

Welding test

Here we took a grade 4A plate and made a groove at the middle of the plate and filled it up by SMAW welding process as per established process for grade 4A. **Table8** shows the test results.

From this experiment, we find that the

Figure6: Toughness vs Holding Time

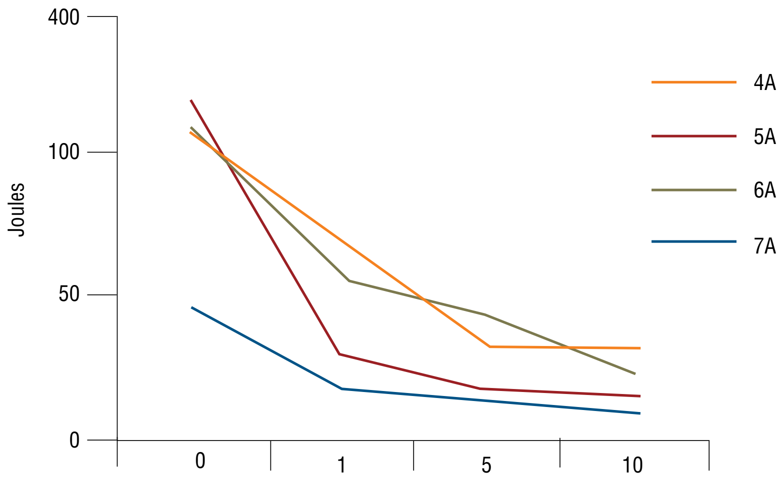
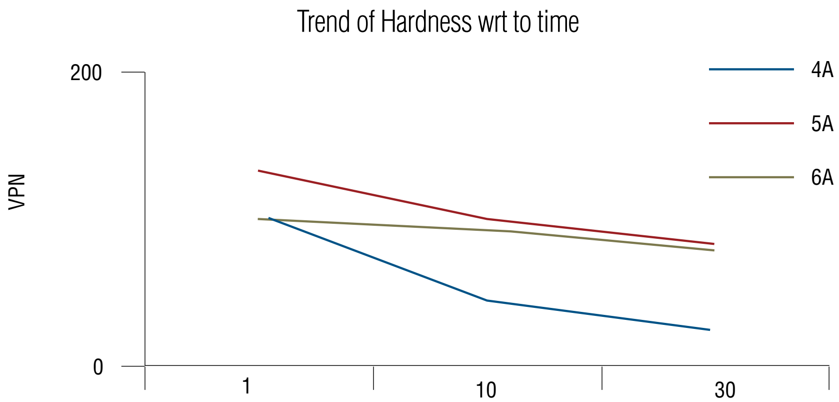


Figure7: Time in mins



475°C effect is clearly visible after welding on HAZ, WM, and BM in terms of increase in hardness. The same sample, when exposed for 10 hours at 550°C, showed marginal decrease in hardness value. However, the sample did not show any effect when exposed at 550°C after welding.

Conclusion

We have carried out experimentation on 475°C embrittlement of duplex stainless steel. Based on our experiments, the following conclusions are drawn.

1. Embrittlement effect as measured in terms of increase in hardness and reduction in toughness was observed even after holding the samples at 475°C for 10 minutes only.
2. This was reflected by sharp drop in impact values and increase in tensile values with corresponding decrease in elongation values.
3. There was no change in microstructure from original solution annealed structure as seen under optical and SEM
4. Re-dissolution treatment was carried out at 550°C for all grades up to 20 hours. For grade 4A, re-dissolution effect was noticed in terms of decrease in hardness after 10-hour soaking.
5. Pitting corrosion noticed on samples treated at 475°C.

Figure8: Normal structure after 10-hour aging

Figure9: Tensile sample with heat tint mark

Table5: Tensile test result after 30 minutes aging at 475°C

	4A	5A	6A
0.2%YS MPa	508 (523)	598 (549)	602 (516)
UTS MPa	749 (683)	829 (771)	843 (796)
%E	30.5 (31.2)	22.2 (31.6)	38.5 (41.5)
%RA	63.18	46.56	66.57

Figure10: Heavy pitting observed

Table7 Effect of re-dissolution treatment

Grade	475°C VPN after 5 hr	5 hr aging at 550°C	10 hr aging at 550°C
4A	306-312	251-262	242-253
5A	351-358	302-314	281-289
6A	354-363	312-319	302-306
7A	363-374	352-361	304-312

Table 8 Hardness of various welding zones of cross section of test piece (VPN)

SN	Condition	HAZ	WM	BM
1	As weld	270	272	230
2	475°C, 5 hr	314	316	250
3	475°C, 5 hr + 550°C, 10Hr	297	302	240
4	550°C, 10 hr	266	280	238

6. There is further scope to study embrittlement and re-dissolution effect during welding of cast duplex steel.

Notes

1 ASTM A890/A890M-13 standard specification for castings, Iron–Chromium–Nickel–Molybdenum Corrosion Resistant, Duplex
2 Charles J (1991). Proceedings of the Conference Duplex Stainless Steels '91, Beaune, France, vol.1, pp.3-48
3 Solomon HD, LM Levinson (1978). Acta Metallurgica 26,3, pp.429-42
4 Reidrich G, F Loib (1941). Archiv fur das Eisenhuttenwesen, 15, pp.175-82.
5 William RO (1958). Trans TMS-AIME 212, pp.497-502
6 Fisher RM, EJ Dulis, KG Carrol (1953). Transactions AIME 197 pp.690-5
7 Blackburn JM, JJ Nutting (1964). Iron and Steel Institute 202, pp.610-13
8 Porter DA, KE Easterling and MY Sherif, Phase Transformation in Metals and Alloys, CRC Press, Third Edition
9 ASTM G-48–11 Standard test methods for pitting and crevice corrosion resistance of stainless steels and related alloys by use of ferric chloride solution

This article first appeared in the Indian Foundry Journal, Volume 65, Issue 4, April 2019. Reprinted with permission of the publishers

The author can be contacted at Peekay Steel Castings (P) Limited, Calicut, Kerala. Email: b.raha@peekaysteel.in; phone: +91 495 2420724

The author is grateful to the management of Peekay Steel Castings for allowing this work to be carried out, particularly to Mr AK Rastogi, Chief Technology Officer, and Mr KE Shanavaz, Joint Managing Director, who showed keen interest and offered constant encouragement during experimentation. The author is also grateful to the National Institute of Technology (NIT), Calicut for support in carrying out SEM work in their laboratory during the course of experimentation