A Study of Inter-relationship Between Metal Processing, Grain Boundary Segregation and Impact Toughness of 17–4 Precipitation Hardened Stainless Steel

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ABSTRACT

An assessment of 17-4 precipitation hardened martensitic stainless steel has been attempted in terms of processing steps with a view to obtain a rationale of the quantitative effects of grain boundary segregation processes on impact toughness. Auger electron spectroscopy (AES) studies have enabled an understanding of the striking variation in impact toughness as a function of carbon content to emerge on the basis of Nb-C-P interaction processes. It is recommended that in order to obtain good toughness in conjunction with high strength, it is necessary that Nb/C ratio in the steel be maintained at a value less than 6. AES analysis of grain boundaries strongly suggest that elemental phosphorus is responsible for the low value of toughness of 17-4PH stainless steel. It is therefore essential that the processing steps be designed in a manner to prevent diffusion of the embrittling element phosphorus to the grain boundary for a tough material to be obtained. The influence of post-aging quenching on impact toughness is also discussed in this paper.

KEYWORDS

Stainless steel, impact toughness grain boundary segregation, phosphorus, Auger electron spectroscopy.

INTRODUCTION

17-4 PH stainless steel belongs to the family of precipitation hardening martensitic stainless steel (AISI, 630), containing 17%Cr, 4%Ni and 4%Cu as the main alloying elements; carbon content in the steel is normally maintained below about 0.05 wt%. The stainless steel is used in applications requiring superior mechanical properties combined with corrosion resistance (Wolf and Brown, 1976). The material inherently retains a useful strength/toughness combination at temperatures up to about 753K. The precipitation hardening reaction in the steel is attributed to copper which is taken into solution during high temperature annealing (~ 970K). On cooling to room temperature the material completely transforms to martensite (which has a low solubility for copper), although a small amount (~10%) of delta ferrite is frequently observed in the solution annealed condition. The heat treatment broadly consists of homogenisation at about 1320K followed by cooling to room temperature and aging in the temperature range of 698-868K (Wolf and Brown, 1976). Aging in the temperature range of 698-868K results in the precipitation of a copper-rich phase, which is responsible for the high yield strength and tensile strength of the material.

However, it is now widely realised that the segregation of impurity elements, notably P, S, Sn, Sb and As in commercial steels, even when their bulk concentrations are low in the range of 50-200ppm, can dramatically influence mechanical properties. Studies on iron and iron-based alloys in the temperature range of 670-1070K (Erhart and Grabke, 1981) have indicated that the segregation of P at the grain boundaries decreases grain boundary cohesion and causes temper embrittlement of low alloy steels. In Fe-C-P alloys, C also segregates to the grain boundaries, reducing P segregation through site competitive process and thereby enhances grain boundary cohesion by counteracting embrittlement.

The study reported here concerns the inter-relationship between metal processing, grain boundary chemistry and impact toughness of 17-4 PH stainless steel. One serious difficulty in regard to the toughness of this steel was experienced during the course of processing the steel, which has not been attended to in the past. The manufacturing of the low carbon 17-4 PH stainless steels, containing niobium, at the special alloys manufacturing company at Mishra Dhatu Nigam (MIDHANI), Hyderabad (India) appeared straightforward, the impact toughness values of the product material showed a wide variation and presented a baffling problem. There was heavy scatter in toughness values from heat to heat and from batch to batch within the same heat, even though the testing was done in the same heat-treated condition. The impact toughness values were found to scatter over a large range from 5 to 120 Nm. The primary objective was therefore an understanding of the large variation in impact toughness values observed during processing of 17-4 PH stainless steel. The secondary objective was to study how processing steps have bearing on grain boundary segregation characteristics and, in turn, the impact toughness of the industrially important 17-4 PH stainless steel.

EXPERIMENTAL

In order to understand the factors responsible for the large variation in impact toughness, a series of steels (Table 1) with varied percentage of carbon (0.02 - 0.09 wt%C) but about the same levels of Nb (~0.28 wt%) and P (~0.03 wt%) were selected, since it was felt that the Nb/C ratio may play a pivotal role in influencing impact toughness. The experimental material was made at Mishra Dhatu Nigam (MIDHANI) Ltd., Hyderabad, (India) through the arc furnace and vacuum arc remelting (VAR) route. The ingots (400-500mm dia) were forged and subsequently rolled to section sizes of ~100-130 mm dia. The commercial heat treatment of these steels consisted of solution annealing in the temperature range of 1295-1325K for 30 minutes per 25mm section thickness, followed by an air cool to 305K and then quenching in ice water. Aging was carried out at 825K for 4hrs. (H1205 condition; Wolf and Brown, 1976).

Table 1. Chemical composition and impact toughness for selected heats of 17-4 PH stainless steel with varied % of carbon content (and Nb/C ratio).

Heat	C	S	P	Mn	Si	Cr	Ni	Cu	Nb	Nb/C	Impact Toughness (Nm)
A	0.024	0.005	0.030	0.42	0.19	16.85	4.22	3.08	0.27	11.25	41
B	0.030	0.009	0.028	0.38	0.48	15.81	4.01	3.11	0.29	9.67	32
C	0.035	0.007	0.029	0.39	0.36	16.22	4.11	3.10	0.31	8.86	24
D	0.042	0.006	0.032	0.44	0.27	15.84	4.02	3.22	0.27	6.43	44
E	0.048	0.005	0.029	0.49	0.39	15.81	4.13	3.56	0.29	6.04	89
F	0.057	0.007	0.031	0.52	0.58	16.40	4.35	3.70	0.31	5.44	110
G	0.089	0.007	0.032	0.60	0.40	16.66	4.31	3.49	0.30	3.37	108

Besides studying the striking variation in impact toughness with %C, two series of heat treatments were performed with the following intentions: (i) to study the variation in impact toughness over the extreme ends of aging temperature available for 17-4 PH stainless steel, (ii) to study the effect of rate of cooling after aging, since the nature of post aging cooling treatment is expected to alter toughness values without any significant loss in tensile strength.

In the first series, one set of solution annealed specimens (1310 ± 15K for 90 min) were aged for each of the three aging temperatures: 890K for 4h (H 900 condition), 825K for 4h (H1025 condition) and 750K for 4h (H 900 condition) (Wolf and Brown, 1976). In all the cases the material was fully austenitic with complete dissolution of copper after holding for 90 mins. at 1310K and became martensitic after cooling to room temperature. In the second series, one set of solution annealed samples were water-quenched and other set furnace cooled after aging.

The technique of Auger electron spectroscopy (AES) in a scanning Auger microprobe (Physical Electronics, Inc., 545C) was used to study the grain boundary composition. Fresh fracture surfaces were obtained by impacting notched samples at liquid nitrogen temperature within the ultrahigh vacuum (~10^{-7} Pa) system of the Auger electron spectrometer. By scanning the electron beam on the fracture surface and monitoring the secondary electron emission we were able to obtain a secondary electron image of the in-situ created fracture surface on the T.V. monitor on which intercrystalline and transcrystalline cleavage facets could be distinguished. Fracture surfaces were primarily intercrystalline for specimens with low toughness values, whereas they were intercrystalline + transcrystalline for specimens with moderate and high impact toughness values.

AES spectra were obtained from intercrystalline and transcrystalline fracture facets using a beam current of 1-3μA. The peak-to-peak height of the elements was used to quantify the spectra in terms of atomic concentration, using standard spectra for pure elements. The toughness of each heat (austenitic grain size 30-40 μm) was characterised by fracture energy in a room temperature Charpy V-notched (CVN) test on heat-treated specimens.

RESULTS AND DISCUSSION

Effect of Carbon Content (and Nb/C ratio) on Impact Toughness

Room temperature tensile properties, notably 0.2% proof strength (1075-1115MPa), ultimate tensile strength (1100-1150MPa) and % reduction in area (53-64%) of heats A to G (Table 1) did not show any significant variation with change in carbon content of the steel, while a striking variation in impact toughness was observed as the carbon content of the steel was increased from 0.02% - 0.09% (Fig.1). Fig.1 shows that there is probably a tendency for the impact toughness to decrease in the range of 0.02% - 0.032%C, beyond which it increases and attains a maximum at 108 Nm at ~ 0.06%C. Further increase in carbon content does not indicate any variation in impact toughness. AES spectra of a grain boundary facet of heat C is shown in Fig.2a, on which are indicated predominant peaks of elements. Only P was found to be locally enriched at the grain boundaries; Nb was detected only in very small concentrations at the grain boundaries. On the other hand, AES spectra of transcrystalline fracture surface did not show any evidence of P (Fig.2b).

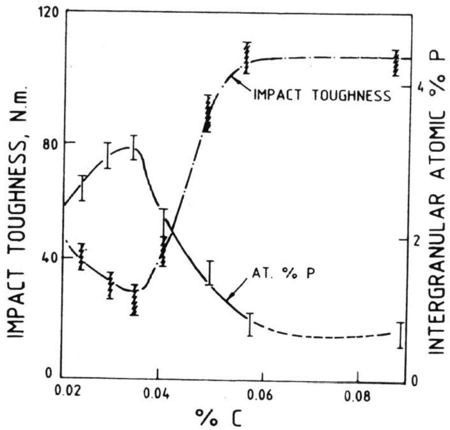

Fig.1. Variation of impact toughness and intergranular at.% P with bulk % C in 17-4 PH stainless steel

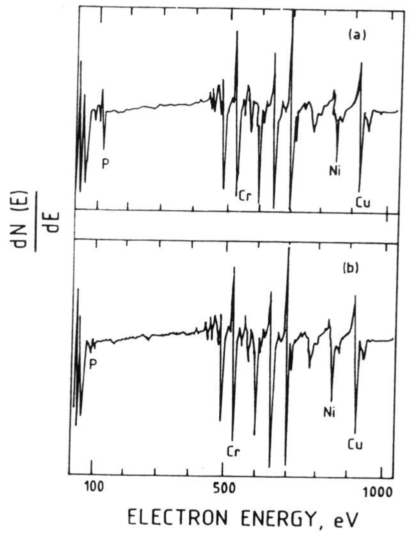

Fig.2. Auger spectrum of (a) intergranular and (b) transgranular fracture surface.

The effect of carbon content (also Nb/C ratio) on the grain boundary segregation of phosphorus for the selected seven melts (A-G) is summarised in Fig.1; P and Nb contents of the melts were about the same level (~0.03% P and approx. 0.28% Nb, Table 1). The grain boundary concentration of phosphorus is slightly on the lower side for low carbon content (~ 0.02%) melt in comparison to heat C (0.035% C) which yielded in AES maximum phosphorus segregation at the grain boundary. This is caused by the chemical interaction of Nb and P to form NbP (Erhart and Grabke, 1981).

This formation of NbP, either in the form of clusters or precipitates is most likely to occur during aging (Möller and Grabke, 1984). With an increase in carbon content, the grain boundary concentration of phosphorus is increased, since Nb locks up C in NbC, thereby allowing the phosphorus segregation to increase. Phosphorus segregation is a maximum at a carbon concentration of 0.035%, corresponding approximately to the value necessary to precipitate all of the niobium as NbC. This is in view of the fact that at carbon and niobium concentrations of ~0.035 and ~ 0.28 wt.% respectively, there is no availability of either free niobium, which could tie up phosphorus in the form of NbP, or free dissolved carbon which could displace phosphorus from the grain boundaries, so that the grain boundary concentration of phosphorus is a maximum. In melts with carbon contents greater than ~ 0.035%, the presence of free or excess carbon will displace phosphorus effectively from the grain boundary through site competition (Erhart and Grabke, 1981). Thus, at carbon concentrations greater than ~ 0.035 wt.%, the grain boundary concentration of phosphorus is low.

The striking variation in impact toughness as a function of carbon content (Fig.1) can therefore be explained on the basis of Nb-C-P interactions discussed in the foregoing. One can, in fact, delineate the data presented in Fig.1 into two distinct regimes: (a) a low-toughness regime (Nb/C ratio > 6 but less than, say 20) characterised by high grain boundary concentration of phosphorus and NbC formation owing to strong Nb-C interaction, (b) a high toughness regime (Nb/C < 6), where grain boundary P is displaced by C through site competition. This segregation of C has two important effects; it alleviates the harmful effect of P and also enhances grain boundary cohesion. Thus, the Nb/C ratio very significantly plays an important role in influencing toughness. It is important to note here that, even though elements Nb and C may be within the specified range, it is the ratio that is more important as far as the property requirement is concerned.

Role of Molybdenum on Impact Toughness of Precipitation Hardened Stainless Steel

There is, however, another way to approach the problem of impact toughness variation with Nb/C ratio by the addition of small amounts of an alloying element, say, molybdenum, which possesses a high interaction energy for phosphorus. The presence of ~ 1.4% molybdenum in almost similar grade of martensitic steel (Table 2) led to improvement in toughness and did not indicate any significant variation in both room temperature tensile properties, namely 0.2% proof strength (1110-1170 MPa), ultimate tensile strength (1250-1300 MPa) and % reduction in area (53-66%) and in impact toughness (85-102 Nm). This observation is in contrast to that obtained for molybdenum-free stainless steel (Table 1 and Fig.3a). A comparison of the grain boundary phosphorus segregation for molybdenum-free (Fig.3a) and molybdenum-containing (Fig.3b) steels clearly suggests that the improvement in impact toughness is solely caused by the removal of phosphorus from the grain boundary. In fact, the AES study indicated the presence of small concentrations of phosphorus in a few grain boundary regions; Nb and Mo were detected only in very small amounts at the grain boundaries. On the other hand , transcrystalline fracture surfaces did not show any evidence of phosphorus.

In practise, one would generally expect NbP formation in preference to Mo_3P, since the Nb-P interaction energy is greater than Mo-P. However,

Table 2. Chemical composition ,and impact toughness of molybdenum containing precipitation hardened stainless steels with varying Nb/C ratio

Heat	C	S	P	Mn	Si	Cr	Ni	Cu	Mo	Nb	Nb/C
H	0.052	0.001	0.034	0.93	0.40	14.47	5.55	1.52	1.67	0.23	4.42
I	0.067	0.001	0.035	0.53	0.54	14.23	5.38	1.84	1.45	0.40	5.97
J	0.044	0.002	0.028	0.61	0.58	13.45	5.44	1.68	1.52	0.35	7.95
K	0.041	0.003	0.028	0.66	0.25	13.39	5.51	1.82	1.53	0.33	8.05
L	0.041	0.001	0.027	0.71	0.33	14.35	5.42	1.65	1.70	0.39	9.51

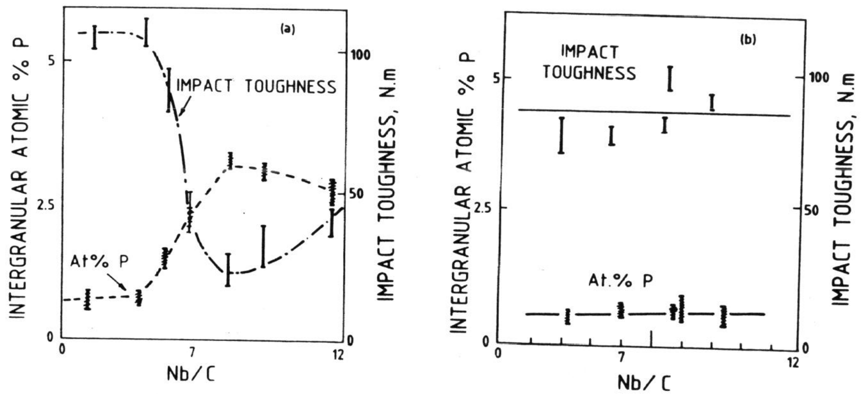

Fig. 3. Variation of impact toughness and atomic % P with Nb/C ratio in precipitation hardened stainless steel. (a) Mo-free steel, (b) Mo-containing steel.

Nb is a strong carbide-former, as compared to the phosphide, hence in the presence of carbon (low Nb/C ratio, < 6), Nb will tend to form NbC first, thereby allowing Mo to lock up phosphorus in the form of Mo_3P or $(FeMo)_3P$ (Yu and McMahon 1980). Even at a Nb/C ratio of ~ 8.87, when all Nb is tied up with C sufficient Mo will be available to lock up P as Mo_3P, either in the form of clusters or precipitates during aging (Möller and Grabke, 1984). The strong coupling of Mo-P therefore retards considerably the rate of build up of phosphorus at the grain boundary, so that the free phosphorus level is low. the presence of any free or excess molybdenum will, in fact, further enhance cohesion by segregating to the grain boundary (Dumoulin et al., 1980). In the present case, the possibility of excess molybdenum causing precipitation of Mo_3C such that the remedial effect is lost is unlikely. Since the Nb-C interaction is greater than the Mo-C interaction, NbC will therefore form in preference to Mo_3C. In melts with high Nb/C ratio (> 6), the presence of excess Nb will precipitate Nb as NbP in a manner similar to that of Mo, thereby eliminating P segregation. It can be inferred from the results that good toughness in conjuction with high strength can be obtained when the Mo/C ratio is greater than 25, in accordance with Table 2.

Effect of Aging Temperature on Impact Toughness

In regard to the effect of aging temperature on mechanical properties

of 17-4 PH stainless steel, once again the room temperature tensile properties namely, 0.2% proof stress, ultimate tensile strength and % reduction in area did not show any significant variation for heats with adverse and favourable Nb/C ratios of 8.5 and 3.8 respectively for identical heat treatments. There was, however, an appreciable difference in impact toughness values for all there aging treatments (Table 3).

Table 3. Effect of aging temperature on impact toughness and grain boundary concentration of P and C in 17-4 PH stainless steel

	HEAT M (Nb/C = 3.8)			HEAT N (Nb/C = 8.5)			
	at.%P	at.%Cu	Impact Toughness(Nm)	at.%P	at.%Cu	Impact Toughness(Nm)	0.2% Proof Stress(MPa)
H900 (750)*	1.8	4.3	79	3.2	5.0	8	1210-1250
H1025 (825K)*	0.7	3.5	110	3.0	4.1	25	1075-1115
H1150 (890K)*	0.5	2.3	120	1.1	2.7	90	1010-1020

In Table 3, grain boundary concentration of P and Cu are also presented. It shows that impact toughness increases with increase in aging temperature (for both the Nb/C ratios), which appears to be clearly associated with a decrease in P segregation. The decrease in P concentration is, however, accompanied by a small decrease in grain boundary Cu concentration. This may well be caused by a strong interaction of the two elements as suggested by the presence of the relatively high melting Cu_3P phase in the Cu-P phase diagram (M. Nageswararao et al., 1985). The effect of a high grain boundary Cu concentration on the effect of embrittlement of P is not known as of today. The dependence of a decrease in grain boundary phosphorus concentration on an increase in aging temperature can be described by the well-known McLean equation (McLean, 1957). Similar trends have been observed in iron-base alloys containing small amounts of chromium (Erhart and Grabke, 1981). In view of the fact that the study of the effect of C content on impact toughness (Table 1, Figs.1 and 2) do not seem to suggest that the grain boundary segregation of Cu has any bearing on toughness values, thus the improvement in toughness with increase in aging temperature can be attributed largely to the decrease in grain boundary segregation of P and lowering of the 0.2% proof stress (Table 3), which was observed to decrease with increase in aging temperature. Table 3 also shows that the material with the adverse Nb/C ratio of 8.5 always indicates a higher grain boundary P segregation (and lower toughness) as compared to that with favourable Nb/C ratio of 3.8 for all three aging temperatures.

Effect of Post-Aging Quenching on Impact Toughness

The effect of the cooling rate after the aging treatment on toughness is presented in Table 4. Table 4 clearly demonstrates a pronounced beneficial effect of cooling rate on toughness, both for favourable and adverse Nb/C ratios. The use of water-quenching in lieu of normal air-cooling practice, yields substantial enhancement in impact toughness. It may be noted at this stage that the increase in toughness occurred without impairing tensile properties, confirming that post-aging quenching does not alter the alloy's normal response to aging.

Table 4. Effect of post-aging quenching treatment on impact toughness of 17-4 PH stainless steel

Aging Temp.	Heat J (Nb/C = 3.96)		Heat K (Nb/C = 8.6)	
	at.%P	Impact Toughness(Nm)	at.%P	Impact Toughness(Nm)
770K (WQ)	0.9	61	--	--
770K (AC)*	--	38	--	--
770K (FC)	2.5	16	--	--
800K (WQ)	0.4	94	1.5	45
800K (FC)	1.1	81	3.6	11

WQ-Water Quenched, AC-Air Cooled, FC-Furnace Cooled, *-Wolf and Brown,1976

AES study of slow cooled samples indicated local enrichment of P at the grain boundaries, whereas no such evidence of P was noted in the case of water-quenched samples. It can be inferred from the AES study that the post-aging quenching prevents diffusion of the embrittling element P to the grain boundaries, as a consequence of which a tougher material is obtained. Thus, an important effect of post-aging quenching treatment is that impact toughness can be improved without changing the aging temperature, which is expected to eliminate variations in tensile strength.

CONCLUSIONS

1. The Nb/C ratio predominantly influences impact toughness of 17-4 PH stainless steel; in order to obtain good impact toughness in conjunction with high strength, it is necessary to control the chemistry of steel with a value of Nb/C ratio of less than 6.
2. The low toughness regime (Nb/C ratio>6 but less than 20) is characterised by high grain boundary concentration of P, which increases with the C concentration up to a maximum at the C content necessary to precipitate all Nb as NbC. The high toughness regime (Nb/C ratio $<$ 6) is characterised by low P segregation, in view of displacement of P from grain boundaries by C via the site competition process.
3. The presence of a small % of Mo ($\sim$ 1.4 wt.%) in the PH stainless steel ensures complete locking of embrittling element, P, presumably in the form of phosphides yielding a tougher material, irrespective of Nb/C ratio.

REFERENCES

Erhart, H. and H.J.Grabke (1981), Equilibrium segregation of P at grain boundaries of Fe-P, Fe-C-P, Fe-Cr-P and Fe-Cr-C-P alloys. Met. Sci., 15, 401-412.

Guttman, M., Ph. Dumoulin and M. Wayman (1982). The thermodynamics of interactive co-segregation of P and alloying elements in iron and temper-brittle steels. Met. Trans., 13A, 1693-1711.

McLean, D. (1957). Grain Boundaries in Metals, Clarendon Press, Oxford.

Moller, R. and H.J.Grabke (1984). Grain boundary segregation of phosphorus in Fe-Nb-P and Fe-Nb-C-P alloys. Scripta Met., 18, 527-530.

Nageswararao, M., B.Lerch and V.Gerold (1985). Factors influencing the toughness of a 17-4 stainless steel. Z.Metallkde., 76, 330-337.

Rossi, D.J. and J.D. Rossi (1987). PH Stainless steel is tougher than you thought. Adv. Matls. and Processes, 3, 45-47.

Wolf, J. and W.F. Brown (1976). Aerospace Structural Metals Handbook, Vol.2, Mechanical Properties Data Centre, Belfour Stulen Inc., pp. FeAH 1-7.

Yu, J. and C.J. McMahon (1980). The effects of composition and carbide precipitation on temper embrittlement of 2.25Cr-1Mo steel. Met. Trans. 11A, 277-289.