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Heat Treatment of Welded 13%Cr-4%Ni Martensitic Stainless Steels for Sour Service

The roles of welding procedure, material composition and postweld heat treatment are examined in relation to producing the minimum hardness levels in the weld zone

BY T. G. GOOCH

Introduction

For many years, the petroleum industry has employed martensitic stainless steels for wellhead and valve applications, and increasing use has been made of 13%Cr-4%Ni alloys. This material type was originally developed as a cast alloy (*e.g.*, ASTM A487/A487M-89a Grade CA6NM), especially for heavy-section water turbine components, and replacing the older 12% Cr cast steels to CA15 and similar specifications. The combination of a low-carbon content and the addition of 3.5 to 4.5% nickel produces a fine, lath martensite structure which, after a tempering heat treatment, can exhibit superior mechanical properties. Thus, CA6NM and its forged variant ASTM A182/A182M-91 F6NM (UNS S41500 or S42400) find application for production fluids containing CO_2 and H_2S, but it must be recognized that such alloy steels are potentially susceptible to sulfide stress corrosion cracking (SCC) in H_2S environments (Ref. 1), particularly when hardening occurs, as is the case with fusion welds.

Sensitivity to sulfide SCC increases at higher material hardness levels, and the NACE MR0175 (1993 revision) standard limits 13%Cr-4%Ni alloys to HRC 23 maximum for sour service. Attainment of such a hardness level requires careful consideration of tempering procedure. The presence of nickel depresses the A_{c1} temperature of the steel, and hence CA6NM is necessarily tempered at lower temperatures than employed for CA15 (perhaps 620°C as opposed to 720°C). This retards the tempering reactions, and, depending on the precise steel composition, may still involve a temperature in excess of the A_{c1}, with resultant partial reaustenization and subsequent hardening on coolout.

Work by Nalbone (Ref. 2) showed that the NACE hardness limit for CA6NM base metal was achievable with carbon contents below 0.03%, but this could result in tensile and yield strengths below those specified in ASTM A487/A487M-89a. Single- and two-stage heat treatments were examined, and, in this regard, Kane, *et al.* (Ref. 3), found the SCC resistance of CA6NM to be improved by double tempering (Ref. 2). An initial high-temperature heat treatment at perhaps 670°C (*i.e.*, above the Ac_1) causes softening of untempered martensite but, at the same time, results in partial retransformation to austenite. On cooling, the austenite reverts to fresh martensite, producing a mixed structure of tempered and untempered martensite. A second heat treatment is then carried out at a lower temperature, but high enough to produce sufficient tempering of the fresh martensite (*ca.* 600°C). With such a cycle, about 15 vol-% retransformed austenite is stable and does not transform to martensite at room temperature (Ref. 4).

Even with double tempering, experience has shown that production of welded components in 13%Cr-4%Ni steels poses considerable difficulties in holding weld area hardnesses below the NACE maximum value of 23 HRC. For weld procedure qualification tests, the Vickers scale is frequently used, and the 23 HRC limit is taken as equivalent to about 253 HV, following, for example, BS860: 1967. Difficulty in meeting such hardness maxima has arisen with both

KEY WORDS

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Table 1 — Composition of Base Steel

Material Identity	C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Nb	Ti	Al	O	Co
	Element, wt-%														
Pipe (as-received)	0.025	0.012	0.026	0.27	0.45	3.8	14.0	0.46	0.040	0.06	<0.01	<0.01	0.015	0.019	0.03
ASTM A182/A 182m F6NM	0.05 max	0.030 max	0.030 max	0.60 max	0.5–1.0	3.5–5.5	11.5–14.0	0.5–1.0	—	—	—	—	—	—	—

— = not specified
Heat treatment: 1035°C, 7 h, air cooled; 675°C, 3 h, air cooled; 605°C, 3 h air cooled

Table 2 — Range of Welding Conditions Employed

Welding Process	Number of Welds	Voltage, V	Current, A	Travel Speed, mm/min	Arc Energy kJ/mm
		Range of conditions			
SMA: single pass	5	19–26	145–150	195–245	0.83–0.95
	5	21–27	150–175	105–140	2.0–2.4
GTA: single pass	2	8.8–9.2	145–150	90–100	0.81–0.86
	2	8.3–8.9	200–205	50–55	1.9–2.0
SMA: multipass	5	19–21	145–150	220–230	0.79–0.85
	5	20–26	155–180	105–130	2.0–2.3
GTA: multipass	2	8.6–8.9	145–150	95–100	0.75–0.80
	2	8.1–8.6	200–205	45–55	2.0–2.0

cast and forged products, while weld deposits of nominally matching composition have consistently been found to be harder than the base metal (Refs. 2, 4, 5). Accordingly, the present investigation was carried out to examine the roles of welding procedure, material composition and postweld heat treatment practice, with the aim of defining conditions giving minimum hardness.

Attention was paid to the base steel, weld metal and surrounding heat-affected zone (HAZ), although with an emphasis on the final weld metal run, which was not tempered by subsequent beads and has given particular problems in practice. Representative base material was obtained and weld beads were deposited using the shielded metal arc (SMA) and gas tungsten arc (GTA) processes, with a number of consumable compositions and under varying welding conditions. Single and double heat treatment cycles were employed, and Vickers hardness was determined, which was related also to Rockwell scale measurements.

Experimental Procedure

Sample Preparation

The base metal was pipe prepared to the F6NM specification, with 250-mm (10-in.) OD and 25-mm (1-in.) wall thickness, and supplied in the double-tempered condition. The composition is given in Table 1, with the reported heat treatment procedure. Major elements were analyzed by x-ray fluorescence. Carbon and sulfur were determined by combustion in oxygen, and oxygen and nitrogen by inert gas fusion.

Shielded metal arc and GTA consumables were obtained from commercial manufacturers to cover a range of the major alloying elements identified by the specification, *viz.* carbon, chromium, nickel and molybdenum. All SMA electrodes were of 4-mm (0.16-in.) diameter, and the GTA wires were 1.6 (0.063 in.) and 2.4-mm (0.125-in.) diameter.

Single run bead-on-plate welds were deposited along the base metal pipe. In addition, multipass deposits were produced in a groove of 20-mm (0.8-in.) depth and 70-deg included angle, to obtain different dilution levels and hence deposit composition. To obtain weldments which had experienced relatively short or extended thermal cycles, beads were deposited nominally either at 0.8 kJ/mm (20 kJ/in.) with 100°C (212°F) preheat or at 2 kJ/mm (51 kJ/in.) with 150°C (302°F) preheat and interpass. A total of 28 welds was produced. The range of welding conditions for individual runs is given in Table 2.

Heat Treatment

Transverse slices, approximately 10 mm thick, were cut from each test bead and heat treated to cover a range of PWHT cycles. Single and double tempering were carried out. In the former case, samples were heated to 580°, 600° or 620°C (1076°, 1112°, 1148°F) for either 10 or 20 h. For double tempering, the first cycle was at 650°, 670° or 690°C (1202°, 1238°, 1274°F) for 10 h, with a second cycle at 600° or 620°C for 20 h. The intermediate temperature between cycles was 0°, 20° or 150°C (32°, 68°, 302°F). Throughout, heating and cooling rates were held at a nominal 200°C/h (392°F), while temperature was monitored and controlled by direct attachment of thermocouples to the specimens.

Hardness Measurement and Examination

Hardness measurement was carried out mainly using a Vickers machine with 10-kg indenting load. Hardness of the final weld metal run deposited was measured on sections from all as-welded and heat-treated samples. Vickers hardness was also determined on the base steel and on the heat-affected zone (HAZ), corresponding to the final run for both arc energies, after all heat treatment cycles. Rockwell C scale hardness measurements were performed on the base metal and heat-treated weld metals, giving a range of Vickers hardness.

Optical metallographic examination was carried out on as-welded and heat-treated samples. Chemical analyses were undertaken on the final deposited weld metal runs, as well as for the base metal.

Results

Material Analyses and Microstructure

The base steel met specification requirements except for manganese and molybdenum — Table 1. Both of these elements were slightly low, but this discrepancy was not considered significant for the present study.

The compositions of the different consumables used are illustrated by Table 3, corresponding to the lowest dilution samples produced. These generally comply with the base metal specification requirements, although variations can be noted. The GTA wire F gave a silicon content above the base steel maximum of 0.6%, while wire G had a manganese level below the 0.5% minimum. Deposits made using SMA consumables C and D, and both GTA wires F and G, were below the specified minimum molybdenum content of 0.5%. The chromium and

Table 3 — Compositions of 0.8kJ/mm Heat Input Multipass Weld Metals

Consumable designation	Welding process	Element, wt % C	S	P	Si	Mn	Ni	Cr	Mo	V	Cu	Ti	Co	N
A	SMA	0.021	0.008	0.007	0.30	0.87	4.46	12.6	0.59	0.03	0.03	<0.01	0.02	0.013
B	SMA	0.030	0.010	0.010	0.35	0.89	4.57	12.3	0.60	0.02	0.03	<0.01	0.02	0.015
C	SMA	0.037	0.006	0.021	0.17	0.55	3.51	12.9	0.47	0.03	0.05	0.01	0.02	0.027
D	SMA	0.046	0.012	0.012	0.55	0.73	4.47	13.0	0.48	0.03	0.03	0.01	0.02	0.012
E	SMA	0.036	0.010	0.021	0.52	0.67	4.42	12.3	0.60	0.03	0.02	0.02	0.03	0.021
F	GTA	0.014	0.007	0.010	0.65	0.53	5.01	13.5	0.44	0.03	0.03	<0.01	0.04	0.016
G	GTA	0.005	0.006	0.018	0.13	0.46	4.93	12.8	0.37	0.02	0.05	<0.01	0.03	0.024

nickel contents of all deposits were within specification limits, while carbon content varied from 0.005 to 0.046% and nitrogen from 0.010 to 0.027%.

A summary of the total weld metal compositional range obtained is given in Table 4. A spread of deposit analysis was achieved, although it is noted that no samples were of a minimum chromium level or of maximum nickel and molybdenum contents. Notwithstanding the above variations from the base metal compositional requirements, the deposits were produced using commercial consumables, and thus should reflect the practical situation.

Base metal and HAZ microstructures are shown in Fig. 1. The as-received steel showed a martensitic matrix with roughly 5 to 10% retained delta ferrite. Some delta ferrite was evident also in the HAZs and in most as-deposited weld metal samples (Fig. 2). Following single-cycle heat treatment, all samples displayed a normal tempered martensite structure, with the ferrite phase being less well defined (Fig. 3A and 3B). This was observed also with double-cycle samples having an intermediate cooling to 0°C. Samples cooled only to 150°C, and to a lesser extent those to 20°C, displayed irregular light etching islands, apparently untempered martensite, after the final 620°C cycle, while the matrix lath structure was well defined giving a pearlitic appearance at high magnification — Fig. 3C.

Hardness Results

General comments

Representative Vickers hardness measurements are shown in Table 5 in terms of the maximum, minimum and average values. The total spread observed was from over 400 HV10 to below 240 HV10. However, as indicated by Table 5, the range for a single sample was fairly small, say 10-15 HV points, the greatest variation being noted for as-welded specimens, especially HAZs.

As-welded Condition

The hardness data for the various test beads were related to composition by linear regression analysis, as in Table 6. The only element having a clear and constant effect on hardness was carbon, increasing carbon giving higher hardness — Fig. 4. As-deposited hardness was not consistently influenced by any other elemental factor, including nitrogen — Fig. 5. From Fig. 4, as-deposited weld metal hardness was not affected by the welding conditions employed nor by the welding process.

Single Postweld Heat Treatment Cycle

After heat treatment, weld metal hardness again increased with carbon level, but the results showed much more scatter than for the as-welded condition — Fig. 6A. Generally, hardness decreased at higher PWHT temperatures over the range studied (Fig. 6B and 6C), but, with a 20-h cycle, hardness of the higher carbon deposits was lower after 600°C than 620°C treatment. For both HAZ and weld metal, heat treatment reduced hardness relative to the as-welded situation, the shift being greater with higher original

Table 4 — Weld Metal Compositional Range Obtained

Element	Range, wt % SMA	GTA
C	0.017-0.046	0.005-0.020
Cr	12.3-13.3	12.7-13.9
Ni	3.51-3.53	4.20-5.01
Mo	0.45-0.62	0.36-0.44
N	0.010-0.027	0.015-0.024
Si	0.15-0.55	0.13-0.65
Mn	0.49-0.89	0.46-0.53

hardness (Fig. 7) and with higher carbon content in the weld deposit (Fig. 8).

The best-fit lines in Fig. 8 indicate the hardness reduction at high-carbon contents to be greater after 600°C than 620°C PWHT, especially for 20-h cycles.

The hardness data were related to a Hollomon-Jaffe parameter, P, as in Fig. 9:

$$P = T\,(20 + \log t) \times 10^{3}$$

where T = heat treatment temperature (K), t = heat treatment time (h).

There was considerable variation in the behavior of individual welds, but, taking all weld deposits to represent a single population. Figure 9A presents av-

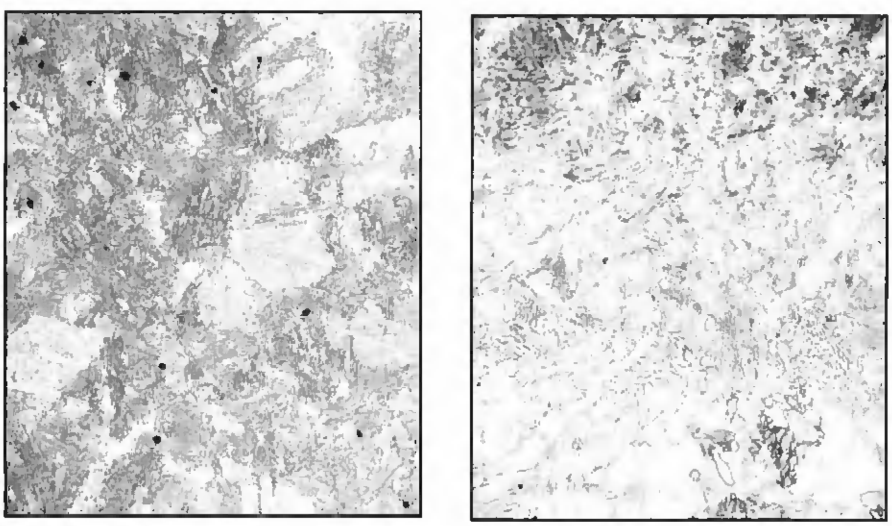


Fig. 1 — A — Base metal microstructure, electrolytic H_2SO_4 etch, 200X; B — fusion boundary and HAZ microstructure, electrolytic H_2SO_4 etch, 125X.

Fig. 2 — A — As-deposited SMA weld metal microstructure, 0.8 kJ/mm, 0.024%C, picral etch, 200X; B — as-deposited GTA weld metal microstructure, 0.8 kJ/mm, 0.016%C, picral etch, 200X.

erage hardness values for each heat treatment condition. While hardness decreased at higher P values, an inflexion is evident at a P value of about 18.8. From examination of the results, they could be divided on the basis of carbon content. As shown in Fig. 9B, low-carbon deposits displayed consistent reduction in hardness as P increased. In contrast, the higher carbon weld metals showed a minimum hardness as indicated in Fig. 9A.

Double Postweld Heat Treatment Cycle

Application of an initial heat treatment at 650° to 690°C before tempering at 600° to 620°C induced a change in weld metal hardness. However, hardness did not invariably fall relative to that obtained with a single PWHT cycle, as shown in Fig. 10 for a second heat treatment at 620°C. Using an intermediate cool to 0°C, the final hardness was generally reduced by application of double heat treatment, but was actually increased with intermediate cooling only to 150°C. Further, initial heating to 650°C gave the maximum reduction in hardness, with hardness gain being most evident using an initial cycle at 670°C. Similar trends in hardness change were observed also for the base metal and HAZ data (Table 7).

Figure 10A indicates that, given 0°C intermediate cooling, softening from a two-stage heat treatment was most marked for deposits that were hardest after a single cycle. This was the case for tempering at both 600° and 620°C, as indicated in Fig. 11.

Weld metal hardness levels recorded after double postweld heat treatment are plotted in Fig. 12 against carbon content. The high final hardness levels observed for an initial cycle at 670°C are evident, particularly with intermediate cooling to 20° or 150°C when hardness was consistently over 300 HV 10 — Fig. 12C and D. Using an initial cycle at 650°C, final hardness increased slightly with carbon content, but this was not evident for 670° or 690°C PWHT cycles employing a 150°C intermediate stage — Fig. 12D.

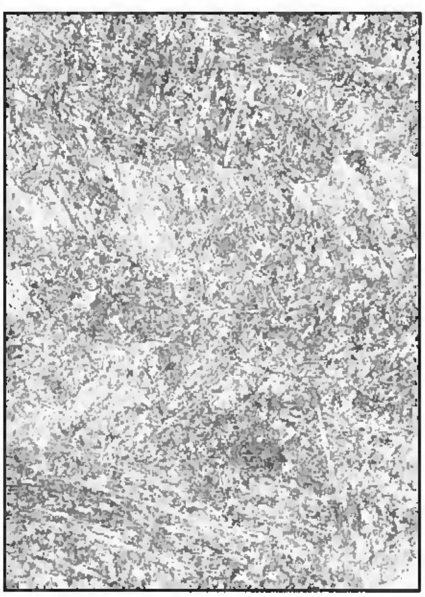
Hardness Correlations

The results of Rockwell hardness measurements are plotted against Vickers hardness in Fig. 13. In principle, the Rockwell C scale is limited to a minimum of 20 HRC, but, to aid location of the lower end of the correlation, values are shown down to a measured Rockwell hardness of 18.5 HRC. Although there is some overlap of data, the weld metals displayed rather higher Vickers hardness at a given Rockwell level than was the case for the base metal.

Discussion

As-Welded Condition

It is generally considered that the major factor determining the hardness of martensite is the carbon content, since this controls the lattice dilation, and, in large part, whether transformation occurs



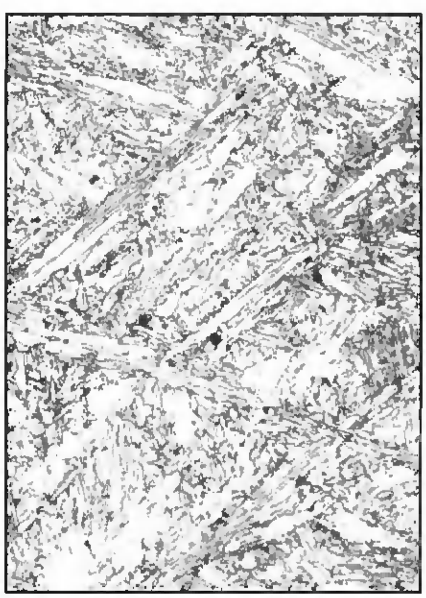


Fig. 3 — A — SMA weld metal microstructure, tempered at 620°C/20 h, 2 kJ/mm, 0.031%C, picral etch, 200X; B — SMA weld metal microstructure, tempered at 620°C/20 h, 2 kJ/mm, 0.031%C, picral etch, 1000X; C — SMA weld metal microstructure, tempered at 670°C/10 h, 150°C, 620°C/20 h, 2 kJ/mm, 0.031%C, picral etch, 1000X.

to give a slipped or twinned product. Thus, in the present fully hardenable 13%Cr-4%Ni material, it would be expected that hardness of the as-welded structure developed at welded joints will depend mainly on carbon content, as exemplified by Fig. 4, and indeed, while substitution elements will play a role in determining the absolute level of martensite hardness, the range of element contents in the present materials is too small to have a readily discernible effect. Other investigators have found that nitrogen does not have a directly similar effect to that of carbon in determining hardness (Ref. 5), and the present findings are consistent with this view — Fig. 5.

Given cool out to room temperature following welding, with subsequent virtually complete transformation, it can be argued that welding conditions will influence hardness only via autotempering during the cooling cycle. It would seem that autotempering is fairly minor at the present low carbon levels, since there was no clear evidence that higher arc energy and preheat temperature, with attendant slower cooling, produced any major influence on the final deposit hardness — Fig. 4.

Single-Cycle Postweld Heat Treatment

The hardness results for all weld metals were examined using multiple regression analysis to relate hardness to composition for each heat treatment cycle employed. In a number of cases, fairly high multiple correlation coefficients were obtained, but there was no consistent trend in the resultant elemental coefficients between the different heat treatment data sets. Not only did the magnitude of the coefficient vary considerably, but so also did the sign. The only exception to this inconsistent effect on hardness was carbon, as illustrated in Fig. 6. It must be assumed that overall composition will affect hardness after heat treatment, both by determining the rate and extent of tempering reactions, and by influencing the A_{c1} temperature; however, no consistent influence of substitution elements was observed, indicating that, for the elemental ranges studied, their effect on hardness after single cycle heat treatment is secondary to that of carbon.

As would be expected, the hardness drop on PWHT was greatest with high carbon levels and high as-welded hardnesses. Overall, reduction in carbon gave decreased hardness after PWHT, although the slopes of the carbon-hardness plots were less than for the as-deposited data.

Accepting scatter in the results, hardness of low-carbon weld metals decreased monotonically with increasing Hollomon-Jaffe parameter, P, indicating progressive tempering — Fig. 9. This was not the case for higher carbon deposits. While the magnitude of the hardness change is small, at high P values an additional reaction evidently took place. This is most likely to involve partial reaustenization and formation of virgin martensite on cool out, i.e., the material A_{c1} temperature was exceeded at 620°C, at least locally, possibly in association with segregation of alloying elements remaining from solidification. In most cases, PWHT at 620°C for 10 h served to reduce hardness relative to 600°C, but extending the time to 20 h sometimes in-

Table 5 — Weld Metal Hardnesses of 0.8 kJ/mm Multipass Welds: Single-Cycle PWHT

Consumable type	As-welded	Hardness+, HV10 580°C, 10 h	600°C, 10 h	620°C, 10 h
A	330-314	294-292	292-258	279-258
	321	292	287	268
B	397-366	294-283	287-283	283-262
	379	290	285	273
C	397-383	279-268	268-262	279-245
	389	273	264	263
D	420-420	309-306	309-304	297-281
	420	307	306	290
E	387-370	302-299	285-281	292-281
	379	300	285	288
F	342-325	290-283	283-276	268-258
	324	287	281	262
G	333-325	264-258	268-251	272-271
	325	261	258	272

+ presented as $\frac{\text{max-min}}{\text{mean}}$

Table 6 — Results of Regression Analysis of Hardness of As-Deposited Weld Metal

Arc Energy, kJ/mm	Regression Coefficients Constant	%C	%Si	%Mn	%Ni	%Cr	%Mo	%V	%N	Correlation Coefficient, R
0.8	514.8	3005	17.5	−36.2	−4.3	−5.2	−82.2	−2831	−634.3	0.9924
2.0	102.9	1938.6	8.5	113	12.6	0.4	8.2	1081.5	2464.1	0.982
All welds	134.03	2735.2	−19.1	−8.34	23.87	1.53	47.63	−7.17	1162.8	0.922

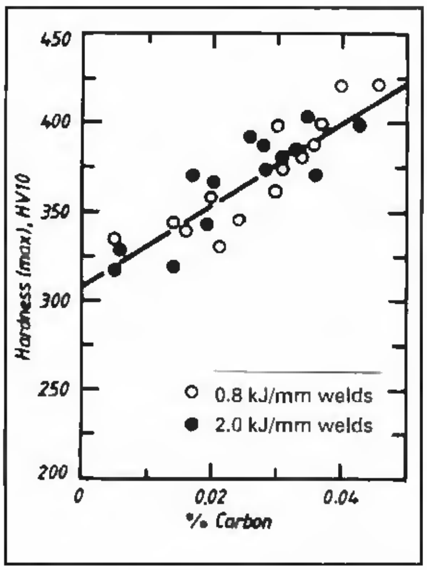


Fig. 4 — Maximum as-welded weld metal hardness vs. carbon content.

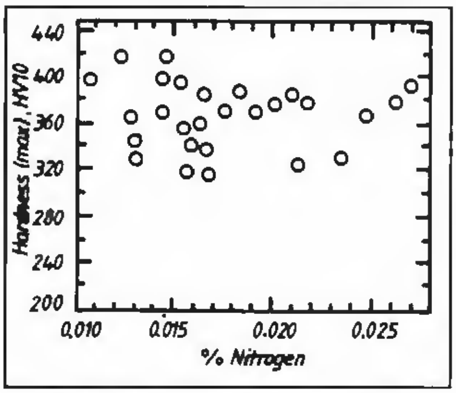


Fig. 5 — Maximum as-welded weld metal hardness vs. nitrogen content.

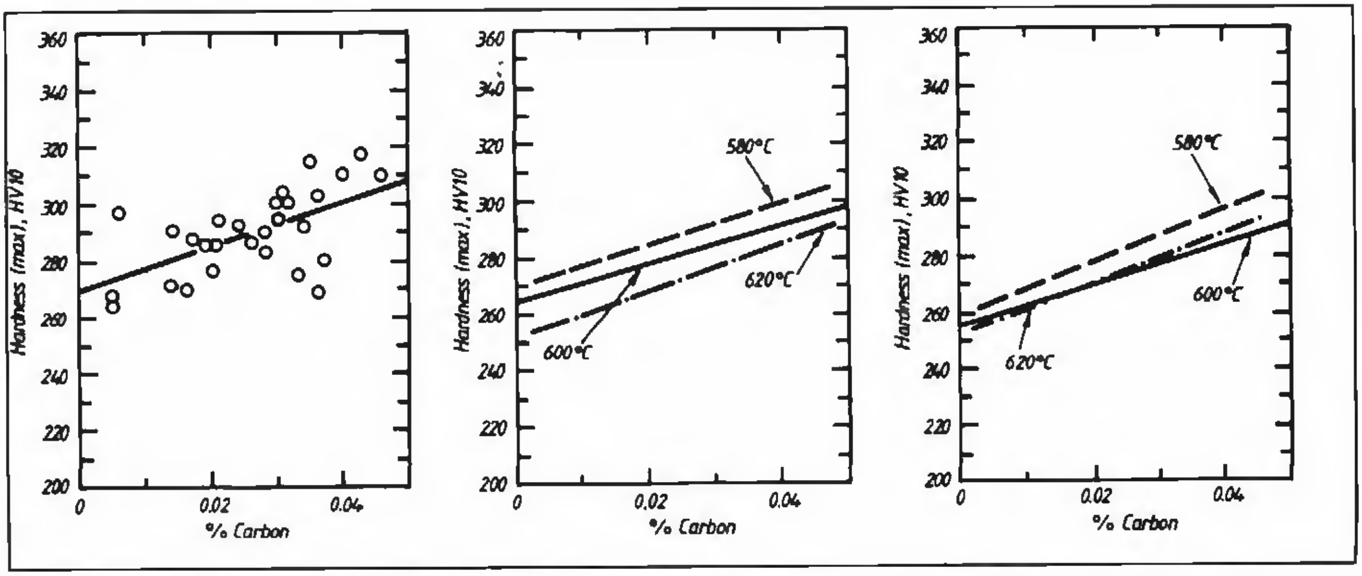


Fig. 6 — Maximum hardness vs. carbon content for single-cycle PWHT weld metal samples. A — Data for 580°C at 10 h, with best-fit line; B — best-fit lines for 10 h PWHT; C — best-fit lines for 20 h PWHT.

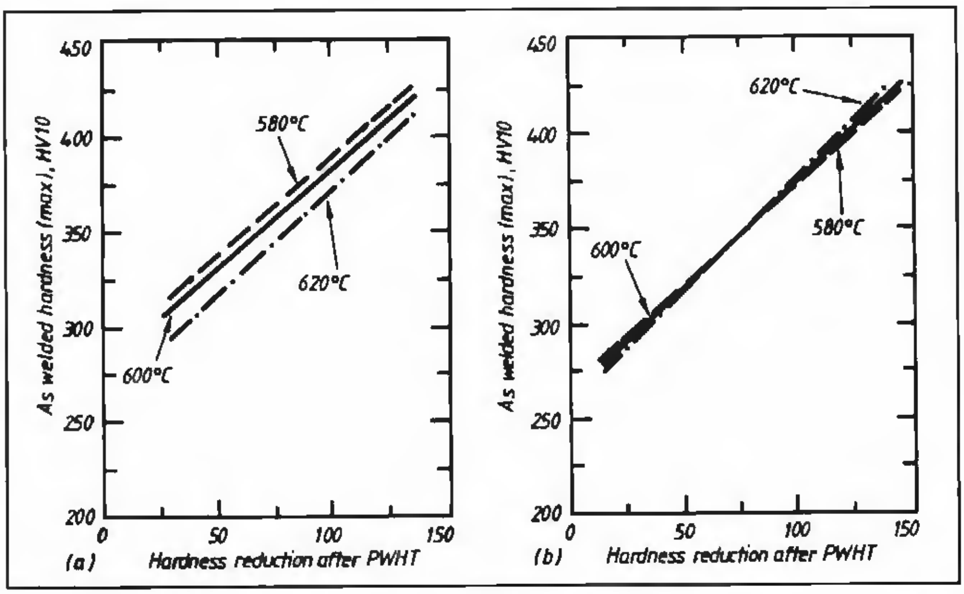


Fig. 7 — Maximum as-welded weld metal hardness against measured hardness reduction after single-cycle PWHT. Best-fit lines. A — 10 h; B — 20 h.

duced a higher hardness, especially for the higher carbon deposits — Fig. 9B. This implies either sluggish austenite reformation at 620°C or that the longer heat treatment time destabilized the austenite relative to martensitic transformation on cooling. The hardness increase after 20 h heat treatment is unlikely to be due to secondary hardening from carbide formation, since this time should cause overaging of alloy carbides, while, accepting the presence of chromium and molybdenum, the levels of other carbide-forming elements (vanadium, niobium and titanium) were low.

Fischer and Larson (Ref. 4) pointed out that the A_{c1} of 13%Cr-4%Ni steel can be low, ca. 550°C, and that discernible hardening after a heat treatment occurs only when the A_{c1} is exceeded by a temperature interval sufficient to induce some 20% austenite. This view follows other work, notably by Leymonie, *et al.* (Ref. 6), and Kulmburg, *et al.* (Ref. 7), although both these studies involved steels containing 5 to 6%Ni, as opposed to the present 4%Ni. Bartoli (Ref. 8) commented on the extreme sensitivity of the microstructure of 13%Cr-4%Ni steels to small changes in analysis and heat treatment, suggesting that the A_{c1} point could be about 620°C (Ref. 7), and unfortunately a reliable relationship between composition and A_{c1} does not seem to have been produced for these alloys. Thus, further study of the tendency for 13%Cr-4%Ni steel to undergo reaustenization during tempering heat treatment cycles remains necessary. Nonetheless, while individual weld metals may show greatest softening after 20 h at 620°C, Fig. 9 indicates that overall lowest hardness will most often be produced by tempering for a shorter time, or at a temperature nearer 600°C, although, for practical purposes, the variation in final hardness over this temperature range is negligible.

Double-Cycle Postweld Heat Treatment

Two points can be made regarding the two-stage heat treatment operation. First, to obtain minimum hardness, there is benefit in cooling to 0°C between the heating cycles. In fact, the reduction in hardness relative to a 20°C intermediate cool is remarkable, indicating substantially more transformation to martensite at the lower temperature, and implying that, for the materials studied, the Mf temperatures were within this range.

Second, it is clear that an initial heat treatment can actually give a higher final hardness after a second heat treatment than with a single cycle alone. The effect was most pronounced with a first cycle at 670°C, and in some cases the final hardness was as high as in the as-welded condition. This marked hardening, together with the fact that hardness was not dependent on carbon (at least for 670°C and 690°C cycles, as in Fig. 12) indicates

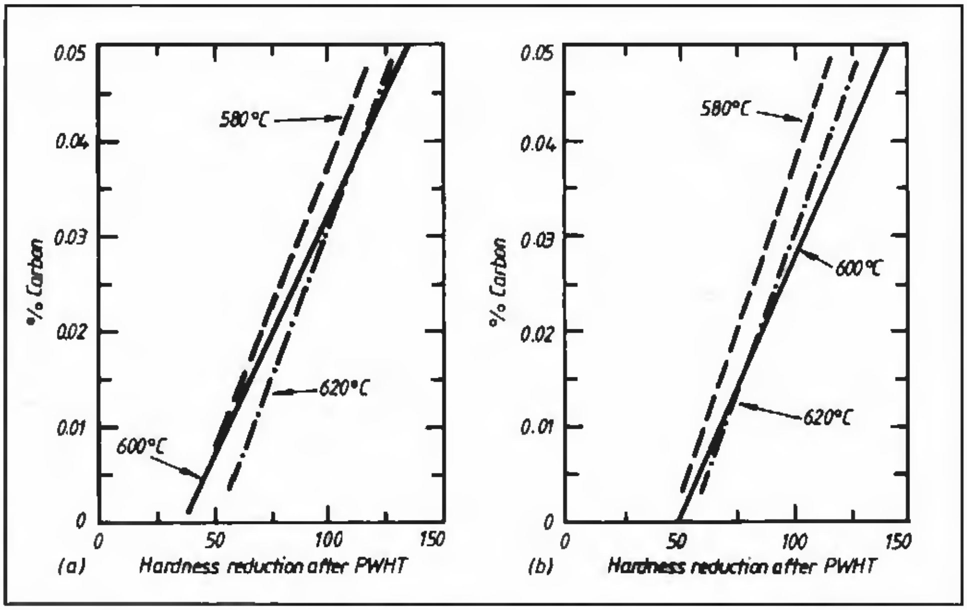


Fig. 8 — Weld metal carbon content against measured hardness reduction after single-cycles PWHT. A — 10 h; B — 20 h.

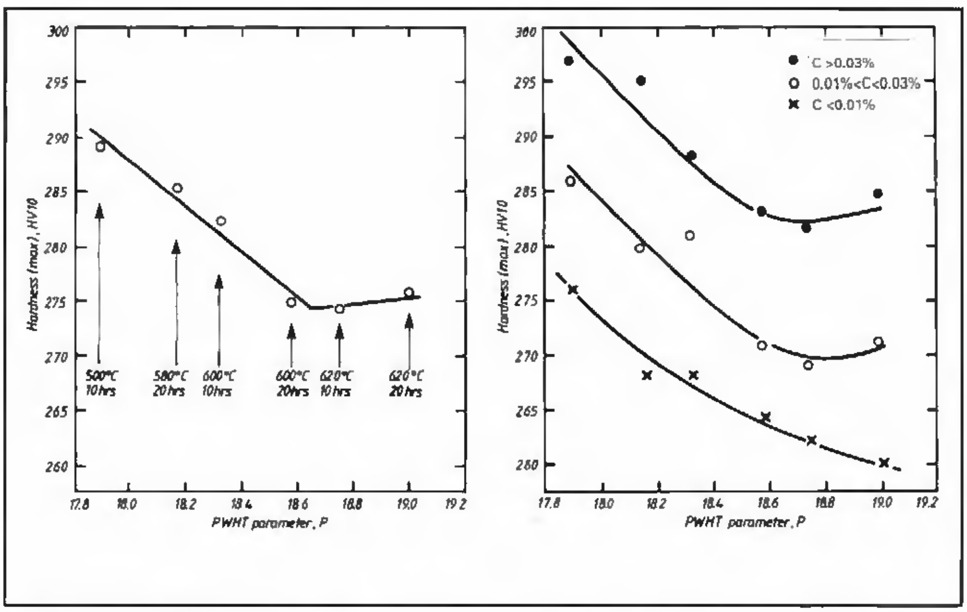


Fig. 9 — A — Relationship between average weld metal hardness levels (maximum value for each weld) and PWHT parameter, $P = T (20 + \log t) \times 10^3$; B — same as 9A except hardness data divided in terms of deposit carbon content.

that the final hardness was determined by the formation of appreciable amounts of martensite on cooling from the second stage at 620°C (or 600°C). In effect, the initial heat treatment "conditioned" the material in terms of its transformation behavior during the second cycle.

This must reflect 1) the amount of austenite produced during the first cycle that is retained on cool out, 2) the composition of the first cycle austenite, especially in terms of Cr, Ni and C (Ref. 6), and 3) the degree to which the austenite is destabilized during the second cycle by $M_{23}C_6$ precipitation. Hence, the singular effect of a 670°C treatment will be to induce the maximum amount of austenite that is stable prior to the 620°C stage (possibly 50%) (Ref. 6), the final hardness being largely determined by the volume fraction of low-carbon virgin martensite. With intermediate cooling to only 150°C, and greater austenite retention, there may also be a contribution to the final hardness from some isothermal transformation after 20 h at 620°C.

The hardness increase manifest for a 670°/20°/620°C cycle in Fig. 12C is not consistent with work by Kane, *et al.* (Ref. 3), on base metal, who found a 677°/20°/607°C treatment to give softening relative to single tempering at 607°C. These authors do not give the times at temperature, but the reason for the disparity is not clear. It is not due to a difference between base metal and weld deposits, as shown by Table 7. Kane, *et al.*, used material of fairly high carbon content (0.06–0.08%), and it may stem from variations in transformation temperatures, both A_{c1} and Ms. Evidently, selection of an optimum temperature for the first stage of double-cycle tempering must be approached with caution, and, in the context of achieving minimum hardness (and optimum SCC resistance), the benefit of intermediate cooling to 0°C must be noted.

Hardness Correlations

The Rockwell and Vickers hardness data are plotted in Fig. 13 in terms of both maximum and average results for a single sample. The two sets appear to form part of the same population. Figure 13 also shows correlations for 13%Cr-4%Ni materials from other sources, the Fisher-Larson (Ref. 4), Hays-Patrick (Ref. 8) and Sherman-Nalbone-Scott (Ref. 5) results having the original Brinell measurement converted to the Vickers scale using BS 860: 1967.

Neither the base metal nor the weld metal results, or those from the other sources in Fig. 13, are described by the ASTM E140-88 hardness scale conversion, and this correlation is evidently inappropriate for 13%Cr-4%Ni materials. Similar comment can be made for the BS 860: 1967 Rockwell-Vickers curve for steels. Even the base metal data lie on the high Vickers side of the Fisher-Larson relationship (Ref. 4). These authors do not give the origin of the correlation cited in their work. The apparent discrepancy could indicate a difference between cast and wrought products, but this is unlikely since the present data on forged steel fall in the same area as the Hays-Patrick and Sherman-Nalbone-Scott results on cast materials.

The present results fall in a similar position to those from Sherman, *et al.*, and Hays and Patrick. At higher hardnesses, the weld metal results deviate from the curve derived by Hays and Patrick from a direct round-robin hardness measure-

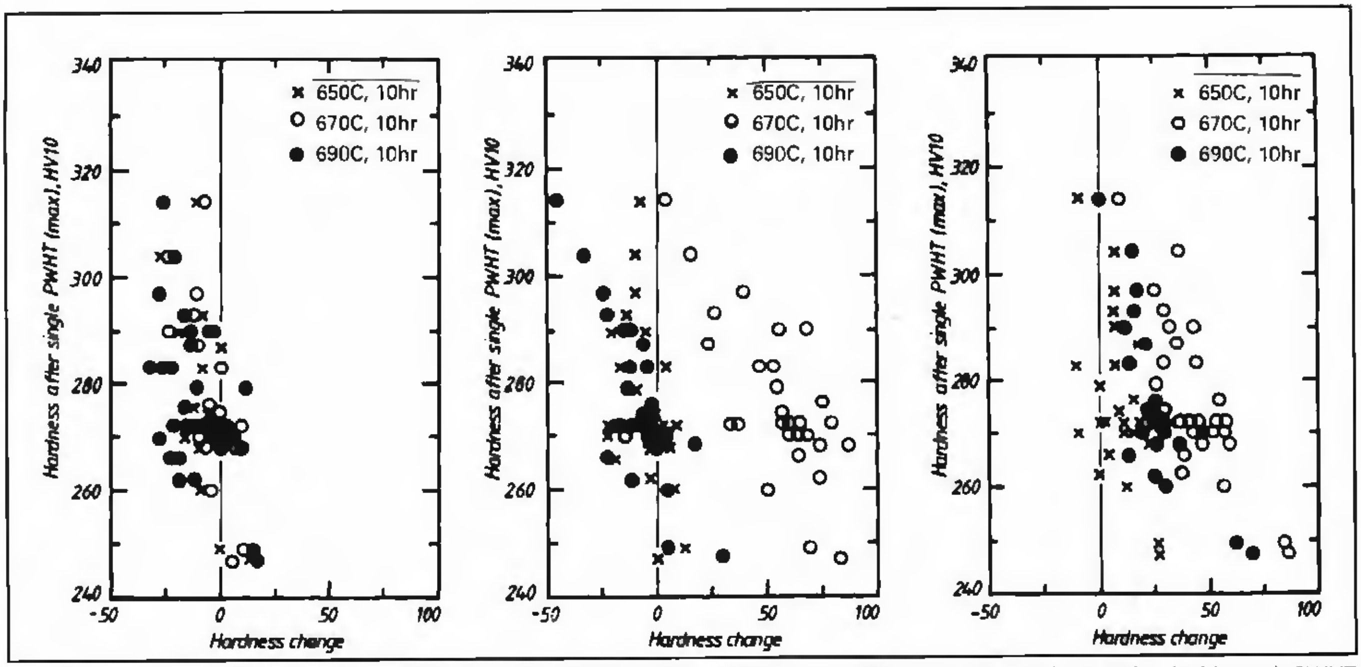


Fig. 10 — Maximum weld metal hardness after single PWHT of 620°C, 20 h, against measured Vickers hardness reduction after double- cycle PWHT, the final stage also being 620°C at 20 h. A — 0°C intermediate cool; B — 20°C intermediate cool; C — 150°C intermediate cool.

ment program on cast 13%Cr-4%Ni steels. Nevertheless, up to 30 HRC there is reasonable agreement between the two studies, and, while the scatter of the present data must be noted, it would seem that below this limit the Hays-Patrick relationship can be employed for 13%Cr-4%Ni materials to convert Rockwell hardness to the Vickers scale and vice versa, at least for castings and weld metals.

Practical Implications

A feature of the hardness data generated in this study is that the majority of the maximum HV levels recorded are above 253 HV, which would normally be taken as equivalent to Rockwell 23 HRC from BS 860: 1967. This is the case, moreover, for a range of deposit compositions and postweld heat treatment conditions, and the program thus effectively underlines the difficulty experienced by industry (Ref. 10) in meeting the 23 HRC maximum limitation as commonly derived from Vickers measurement.

However, the ASTM E140-88 and BS 860: 1967 Rockwell-Vickers correlations are clearly not applicable to 13%Cr-4%Ni materials, and, if the Hays-Patrick relationship is accepted, the NACE limit of 23 HRC can be taken as equivalent to 275 HV. In this case, there is a much better prospect of meeting the specification requirement. Final hardness was not influenced by welding conditions or process over the range studied, and viewed overall, the results indicate that the following measures should be pursued to achieve weld metal hardness below 275 HV:

1) The material carbon content should be reduced as far as possible (provided that specified strength levels can be maintained). Results from single and double PWHT cycles giving lowest hardness are shown in Fig. 14. Using a single cycle, carbon should be below about 0.02% for the greatest chance of meeting a 275 HV maximum criterion, whereas up to 0.03% appears tolerable for a double cycle with intermediate cooling to 0°C.

2) The present results suggest that maximum softening can be obtained at 600–620°C for most materials, but the time at higher temperature in this range must not be too long. More especially for higher carbon materials, 600°C for 20 h may give more reliable attainment of low hardness, although a preference for 605°C (1121°F) will be noted from American work (Refs. 4, 10).

3) Lowest hardness can be obtained with a double temper treatment, at least for high-carbon weld metals — Fig. 10.

Table 7 — Base (BM) Metal and HAZ Hardness after Final Heat Treatment at 620°C for 20 h, HV10

	Condition										
			Double Cycle								
			Intermediate Cool to 0°C			Intermediate Cool to 20°C			Intermediate Cool to 150°C		
Region	As-welded	Single cycle	650°C, 10h	670°C, 10h	690°C, 10h	650°C, 10h	670°C, 10h	690°C, 10h	650°C, 10h	670°C, 10h	690°C, 10h
BM	262-251 / 255	243-242 / 243	242-230 / 237	254-247 / 250	233-230 / 231	240-238 / 239	304-299 / 301	247-240 / 243	276-264 / 268	276-274 / 275	270-260 / 266
HAZ, 0.8 kJ/mm	351-304 / 333	270-266 / 268	260-254 / 257	262-252 / 255	262-258 / 261	260-251 / 256	317-302 / 309	254-247 / 250	285-270 / 275	306-297 / 300	302-287 / 293
HAZ, 2 kJ/mm	360-357 / 358	262-260 / 261	272-258 / 267	245-240 / 243	254-251 / 252	262-256 / 260	306-302 / 304	249-247 / 248	276-264 / 268	306-285 / 297	302-287 / 290

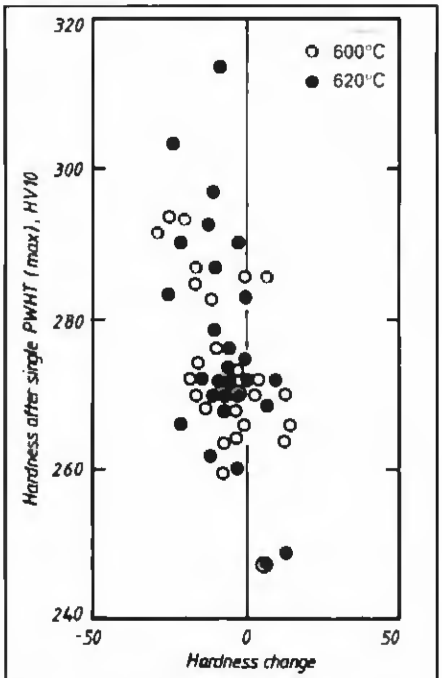


Fig. 11 — Hardness difference between single- and double-cycle PWHT. Single cycle: 20 h at 600°C or 620°C; double cycle: 10 h at 670°C, cool to 0°C, 20 h at 600° or 620°C.

However, the temperature for the first cycle should be held fairly low, say 650°C, while intermediate cooling to 0°C is strongly preferred — Fig. 10A. Indeed, subzero cooling to promote complete transformation to martensite may well give an even better response to tempering, and could be considered directly after welding, prior to a single heat treatment cycle. Double tempering does not necessarily guarantee that a 275 HV maximum will be achieved. Higher carbon deposits, of higher original hardness, may still exceed this value, as indicated by Fig. 14. The data in Fig. 12 suggest that use of a midrange temperature of 670°C for the first cycle can increase the final hardness. In principle, therefore, higher or lower temperatures are to be recommended, but it will be noted that material of composition outside the present range may show rather different behavior.

The present observations are consistent with those of other workers (Refs. 3–8), especially in indicating the fine balance that must be struck between achieving a temperature high enough to give tempering, but not inducing too much austenite formation, which will revert to virgin martensite on cool out. It is, thus, unfortunate that it is not possible to predict the A_{c1} temperature from material composition with any confidence at the present time. This work shows the role of composition to be complex, and further study of the transformation behavior of commercial 13%Cr-4%Ni steels and

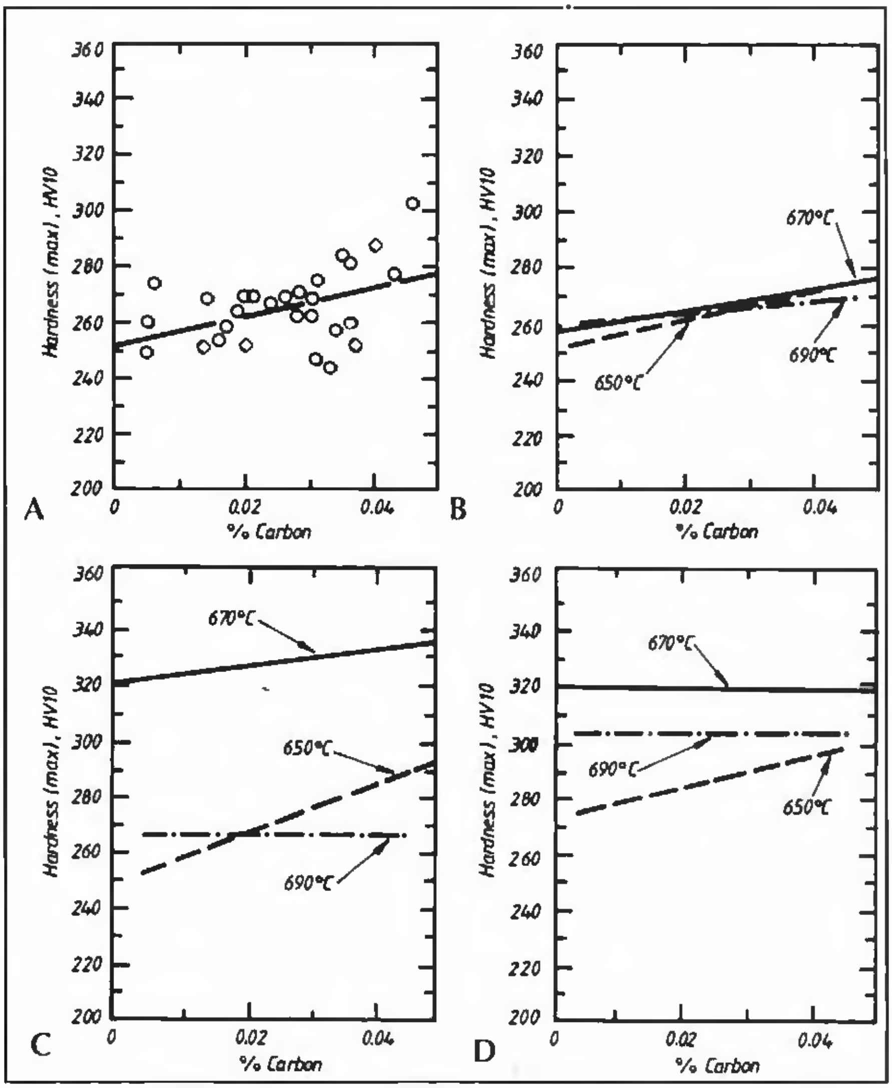


Fig. 12 — Maximum hardness vs. carbon content for double-cycle PWHT weld metal samples. Final cycle at 620°C at 20 h. A — 650°C at 10 h, 0° intermediate cool, showing scatter in results; B — 0°C intermediate cool, best-fit lines, varying temperature of initial cycle; C — 20°C intermediate cool, best-fit lines, varying temperature of initial cycle; D — 150°C intermediate cool, best-fit lines, varying temperature of initial cycle.

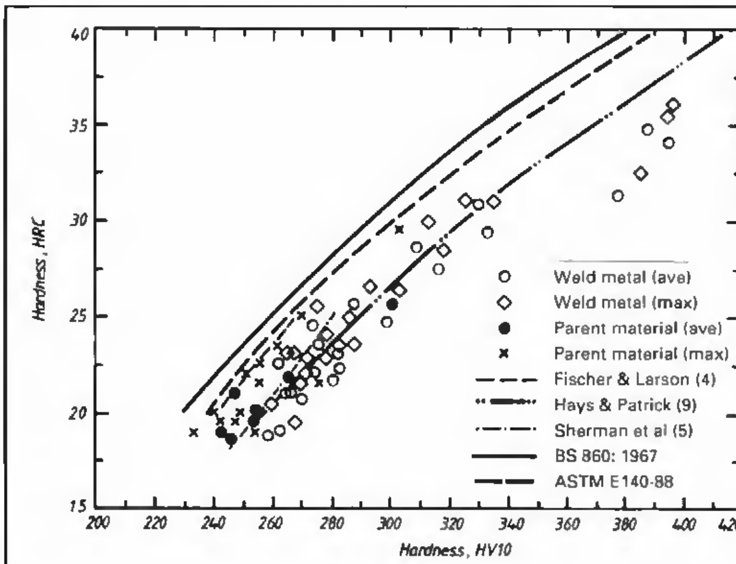
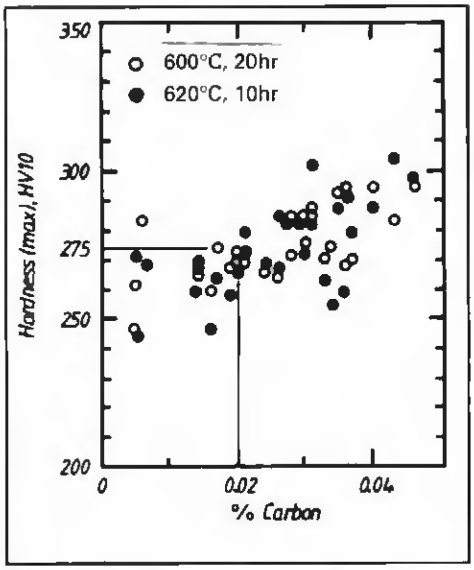


Fig. 13 — Comparison of Rockwell and Vickers hardness for weld metal and base metal.



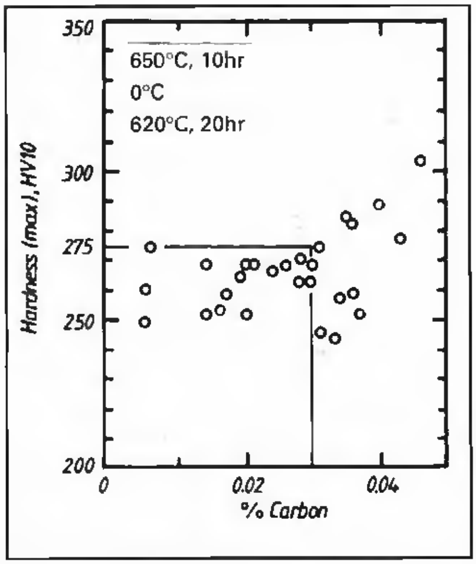


Fig. 14 — Hardness results indicating maximum carbon levels to attain 275 HV maximum after PWHT. A — Single cycle; B — double cycle.

weld metals is required, in terms of both the A_{c1} and Ms/Mf temperatures. Since nickel in particular is recognized as a strong depressant of the A_{c1} point, consideration could well be given to the use of consumables of fairly low nickel level to obtain effective tempering and low hardness, assuming that adequate deposit toughness can be maintained. Loveless, *et al.* (Ref. 10), observed that lower hardness could be more readily obtained with molybdenum-free steel. This approach would necessitate attention to corrosion behavior, but could be viable for most sour service conditions.

In principle, lower hardness can be obtained with extended heat treatment times at temperatures of 600°C. However, this may cause unacceptable loss in tensile properties, especially yield strength (Ref. 4).

Summary and Conclusions

Work has been carried out to clarify factors influencing the final hardness achieved at welded joints in 13%Cr-4%Ni steels. Bead-on-plate and bead-in-groove welds were produced using the SMA and GTA processes under high and low arc energy/preheat conditions. Different consumables were employed to obtain a range of deposit composition within that likely to be encountered by industry. Vickers and Rockwell hardness measurements were carried out on the base metal, HAZs and weld deposits, both as-welded and after single and double postweld heat treatment cycles. The following conclusions were reached:

1) The work confirms the practical difficulty in meeting a maximum hardness limit of 253 HV, taken as equivalent to 23 HRC from ASTM E140-88 and BS 860: 1967. However, it is concluded that 23 HRC is equivalent to 275 HV for 13%Cr-4%Ni materials, and this limit can generally be met by appropriate control of material composition and heat treatment schedule.

2) The major compositional factor determining hardness was carbon content. Higher hardness was associated with increased carbon contents, both as-welded and following postweld heat treatments, although the effect of carbon was least with double PWHT cycles.

3) Hardness was not consistently related to any other single element, including nitrogen.

4) As-welded HAZ and weld metal hardness was reduced by single postweld heat treatment at 580 to 620°C. Minimum hardness was generally achieved following heat treatment at 600°C/20 h or 620°C/10 h; hardness tended to increase for higher carbon (>0.03%) deposits on extending PWHT time at 620°C to 20 h.

5) Further decrease in hardness could be obtained with a double postweld heat treatment cycle. However, to obtain maximum softening, it was essential for the intermediate temperature between heat treatment stages to be as low as possible. Cooling to 0°C gave significantly lower hardness than cooling only to room temperature. Final hardness was decreased by use of a lower temperature for the first cycle, within the range of 650 to 690°C.

6) The results did not indicate that welding process, arc energy or preheat temperature had a significant effect on the final HAZ or weld metal hardness levels achieved, either as-welded or after postweld heat treatment.

7) The ASTM E140-88 and BS 860:1967 Rockwell-Vickers hardness correlations for wrought steels were found to be inapplicable to 13%Cr-4%Ni materials. Up to 30 HRC, the present weld metal results were consistent with a Rockwell-Vickers hardness relationship derived following Hays and Patrick.

8) The present results and the Hays-Patrick data indicate that, for 13%Cr-4%Ni steels, the NACE hardness limit of 23 HRC is equivalent to 275 HV.

9) To hold weld area hardness below 275 HV, the materials should be of minimum carbon content, with final temper at 600 to 620°C but not for excessive times. Lower hardness can be obtained with a double heat treatment, with an intermediate cool to 0°C being recommended. With a double PWHT cycle, carbon levels substantially below 0.03% are not of particular benefit.

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References

1. Hudgins, C. M., McGlasson, R. L., Mehdizadeh, P., and Rosborough, W. M. 1966. Hydrogen sulfide cracking of carbon and alloy steels. *Corrosion* 22(8): 238–251.
2. Nalbone, C. S. 1982. Effects of carbon content and tempering treatment on the mechanical properties and sulphides stress corrosion cracking resistance of AOD (argon oxygen decarburization) refined CA6NM (cast stainless steel). ASTM STP 756, pp. 315–331.
3. Kane, R. D., Watkins, M., and Greer, J. B. 1977. The improvement of sulfide stress cracking resistance of 12% chromium stainless steels through heat treatment. Corrosion 33(7): 231–235.
4. Fischer, R. B., and Larson, J. A. 1982. Experiences and some pitfalls in processing CA6NM. *Trans. Amer. Foundrymen's Soc.* 90: 103–133.
5. Sherman, E. T., Nalbone, C. S., and Scott, W. D. 1983. Processing low-carbon

CA6NM (steel) to meet NACE (National Association of Corrosion Engineers) hardness requirements. *Proc. of 1983 SCRATA Annual Conf*, Paper 4.

6. Leymonie, C., Ottmann, M-C., Risacher, R., and Thauvin, G. 1979. Contribution a l'Etude des transformation structurales des aciers a 13%Cr-4%Mi, *Rev. de Met.* 76: 815–826.

7. Kulmburg, A., Korptheuer, F., Koren, M., Gründler, O., Hutterer, K., *op cit*, Folkhard, E. *Welding Metallurgy of Stainless Steels*. Springer-Verlag Wien New York, English Translation 1988, Ref. 194.

8. Bartoli, M. 1984. Considerations on the weldability of Cr-Ni martensitic stainless steel castings of type 13%Cr-4%Ni and 16%Cr-5%Ni. Fonderia 33 (4/5): 47–52.

9. Hays, C., and Patrick, D. H. 1983. Hardness conversion data for CA6NM alloy. *Metallography* 16 (2): 229–233.

10. Loveless, R. W., Smith, W. C., and Templeton, N. C. 1982, Weld procedure, filler metal, and postweld heat treatment — their effect on the hardness and quality of welds in CA6NM alloy (cast stainless steel). ASTM STP 756, pp. 394–402.

INTERPRETIVE REPORT ON DYNAMIC ANALYSIS AND TESTING OF PRESSURIZED COMPONENTS AND SYSTEMS — FIFTH EDITION

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Dynamic analysis of pressurized components is a key element in satisfying specified safety and economical requirements in the design process. Recognizing this, PVRC initiated work to establish needs and priorities, recommend research programs, and help direct research activities toward industrial applications.

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