Whitepaper
CA6-NM

Weld Procedure Qualification to NACE Requirements

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Introduction

Originally developed as a friendlier alternative to CA-15, CA6-NM became the alloy of choice for many industries: power generation, marine, oil extraction and refining, chemical.

Both alloys have a martensitic structure and exhibit similar properties when considered for their corrosion resistance to most environments.

The low carbon levels as well as the addition of 4% Ni and up to 1% Mo made the CA-6NM grade more resistant to damages caused by sea water cavitation when compared with its older relative, CA-15. The power generation industry, especially Francis Runner manufacturers, embraced the CA-6NM right from its creation for its superior machining and welding properties.

Used in the normalized and tempered condition, the alloy has excellent strength, ductility, hardness and toughness. However, various heat treatment cycles can be employed in order to improve certain parameters. CA-6NM has a medium resistance to general corrosion compared to other grades, but the low carbon/low hardness version is very resistant to sulphide stress corrosion cracking and this is what the oil and gas industry was looking for: an alloy resistant to fluids containing various combinations of CO_2 and H_2S.

It is recognized that grades with higher hardness levels or hard zones occurring in fusion welds become susceptible to sulphide stress corrosion cracking. In order to maintain superior performance in such applications and limit the alloy sensitivity to sulphide stress corrosion cracking (SCC), NACE standards limit the maximum hardness of CA-6NM alloy to HRC 23.

There is a wealth of literature recommending ideal chemistries, proper heat treatment cycles and welding techniques, best welding methods and filler materials so that the HRC 23 maximum hardness can be achieved. But is it achievable?

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Acknowledgements

I would like to thank Bradken Energy for its support and the Steel Foundry Society of America.

References

1. T.G. Gooch – Heat Treatment of Welded 13%Cr-4%Ni Martensitic Stainless Steels for Sour Service, Supplement to the Welding Journal, July 1995.
2. Steel Castings Handbook, Supplement 8, Corrosion Series, SFSA, 2004
3. Loveless, R.W., Smith, W.C. and Templeton, N. C. 1982, Weld Procedure Filler Metal and Post Weld Heat Treatment - Their Effect on Hardness and Quality of Welds in CA6NM Cast Stainless Steel Alloy.

Description

This work is intended to present parameters and reveal results obtained during the qualification of two CA6-NM weld procedures to NACE requirements.

T.G. Gooch's recommendations in his article "Heat Treatment of Welded 13%Cr – 4%Ni Martensitic Stainless Steel for Sour Service" published in the Supplement to The Welding Journal of July 1995 were followed to a tee. T.G. Gooch was a recognized authority in the field of metal joining. He carried out extensive and comprehensive research on the welding of steel, in particular of duplex and martensitic stainless steel. He was the author of numerous books and published numerous articles, many of them in the American Welding Journal.

T.G. Gooch's recommendations for a successful NACE procedure qualification were as follows:

1. The carbon content of the base metal should be as low as possible, provided that specified strength levels can be maintained. Carbon should be below 0.03% for the greatest chance of meeting maximum hardness.
2. The filler metal should be carefully selected. The carbon content of the filler metal should be as low as possible.
3. Prior to welding, the base metal should be in a normalized and double tempered condition. Ideally, the base metal must already meet the maximum hardness requirement before the welding takes place.
4. After welding, the test coupons should receive a double temper treatment. Following each tempering cycle the test coupons should be allowed to cool well to room temperature.

Experimental Procedure

The experiment covered two welding processes: Shielded Metal Arc (SMAW) and Gas Metal Arc (GMAW) solid wire.

The base metal used for qualification consisted of cast plates. Several 12" X 6" X 1.75" plates were moulded and poured in no bake moulds (Figure 1). The CA6NM alloy was prepared in an induction furnace. The charge was carefully selected using 100% virgin materials, no returns. Pure chromium was used instead of Fe-Cr in order to attain the lowest carbon content possible.

To further prevent carbon contamination, a new Kaltek disposable ladle was used for the pour. Moulds were coated with a water base ZrO_2 wash. The gating system was provided with filters. Deoxidizers were not intentionally added. Elements were analyzed using an Optical Emission Spectrometer.

The composition of the base metal is given in Table 1.

Figure 1 – Cast weld test plates

Table 1 – Composition of base metal

	C	Si	Mn	P	S	Cr	Ni	Mo	V
Ladle analysis	0.018	0.559	0.584	0.010	0.007	11.973	3.904	0.452	0.0235
Product analysis	0.0220	0.563	0.583	0.0123	0.009	11.980	4.060	0.454	0.0236

	Ti	Al	Zr	Ca	Cu	Sn	Co	N	O
Ladle analysis	0.007	0.008	0.0038	0.0019	0.044	0.003	0.0082	0.019	0.019
Product analysis	0.005	0.006	0.0034	0.0009	0.045	0.003	0.0085	0.018	0.014

Prior to welding, the weld test plates were normalized and double tempered. Normalizing was performed at 1850°F for 7 hours followed by air cooling to room temperature. The intermediate temper was performed at 1250°F for 4 hours followed by air cooling while for the final temper the test plates were heated at 1100°F, held for 17 hours then air cooled. Table 2 shows Brinell hardness readings measured on each plate after the completion of each tempering cycle.

Table 2 – Base metal hardness measurements after the intermediate and the final temper

	66131 (BHN)		66132 (BHN)	
	After IT	After FT	After IT	After FT
1	262	255	269	248
2	262	248	262	255
3	262	255	262	248
4	262	248	269	248
5	269	248	269	248
6	269	248	262	255

After the final temper all test plates were softer than 255 BHN.

Consumables of the lowest carbon content available for both shielded metal arc (SMAW) and gas metal arc (GMAW) were purchased from BOHLER. When selecting the filler metal, all major alloying elements were considered and special attention was paid to the carbon content.

Table 3 shows the chemical composition of the filler metal as certified by the vendor in his Material Test Certificate provided with the shipment, as well as the actual chemistry of the weld analyzed on the foundry spectrometer after the completion of the weld. Most of the elements tested at the foundry were found to be in line with the certificate except for the carbon. Both, the wire and the stick electrodes revealed higher carbon content when tested at the foundry.

Table 3 – Certified chemistry vs. chemical composition of the filler metal as analyzed at the foundry

		C	Si	Mn	P	S	Cr	Ni	Mo	V
GMAW - solid wire electrode	**Cert**	<0.01	0.7	0.7	0.02	<0.01	12.4	4.9	0.5	
	Act	0.054	0.571	0.541	0.017	0.003	12.41	4.918	0.434	0.048
SMAW – stick electrode	**Cert**	0.03	0.33	0.5	0.014	0.005	11.58	4.22	0.49	
	Act	0.044	0.39	0.54	0.015	0.005	11.71	4.35	0.46	0.020

		Ti	Al	Zr	Ca	Cu	Sn	Co	N	O
GMAW - solid wire electrode	**Cert**					0.12				
	Act	0.0002	0.0051	0.0037	0.0003	0.112	0.0055	0.044	0.044	0.052
SMAW – stick electrode	**Cert**					0.12				
	Act	0.0165	0.0152	0.0034	0.0002	0.016	0.0023	0.016	0.025	0.043

Single run bead welds were deposited along the base metal. Multipass deposits were produced in a single "V" groove of 1.75" depth and 70° angle in flat position. Prior to welding the plates were preheated in the oven at 300°F for 3 hours. The interpass temperature was maintained below 350°F. All welding electrodes for SMAW were 3.2 mm (0.125") diameter and the GMAW wire was 1.2 mm (0.047") diameter. A mixture of 75% Argon and 25% CO_2 gas was used as shielding atmosphere for the GMAW process.

Heat Treatment

After the completion of the welding, the test plates were double PWHT-ed as follows:

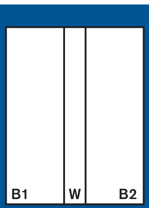
1. Intermediate Temper: 650oC (1202ºF) for 10 hours.
2. Final Temper: 600oC (1112ºF) for 20 hours.

Both HT cycles were followed by cooling in still air to room temperature.

Hardness Measurements

Brinell hardness measurements were taken before and after the second PWHT. Representative measurements are shown in table 4.

Table 4 – Base metal and weld deposit Brinell hardness measurements after each PWHT



		6631 / 66131 - GMAW		6632 / 66132 - SMAW	
		After IT	After FT	After IT	After FT
	B1	262	255	269	248
	W	262	248	262	255
	B2	262	255	262	248

After this work was completed at the foundry, the weld test plates were sent to an independent laboratory for further testing, including Vickers hardness measurements using a 10kg load.

Vickers hardness was measured on the base metal weld and heat affected zone in accordance with NACE MR0175, as shown in Figure 2. Tensile strength tests across the weld and bend tests were carried out in accordance with ASME Section IX, in order to complete the qualification of the weld procedure.

Table 5 illustrates the actual Vickers hardness measurements while the values shown in Table 6 represent the average Vickers hardness in the base metal, weld and HAZ.

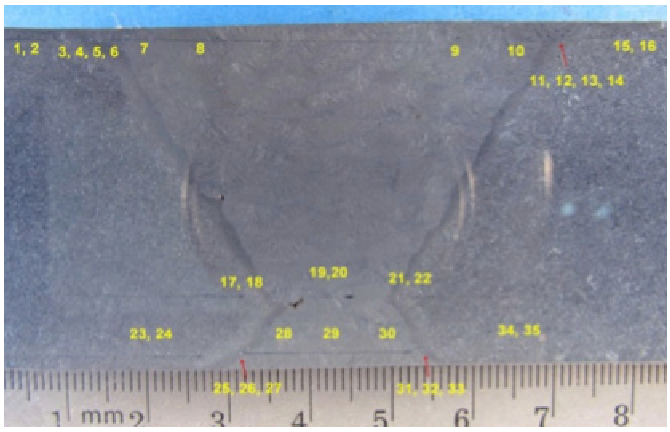


Figure 2 – Vickers hardness survey. Locations.

Table 5 – Vickers hardness results after post weld double tempering

Reading No.	Location	GMAW (HV 10Kgf)	SMAW (HV 10Kgf)	Reading No.	Location	GMAW (HV 10Kgf)	SMAW (HV 10Kgf)
1	Base Metal - 1	248	253	19	Weld Metal	291	287
2	Base Metal - 1	248	248	20	Weld Metal	289	294
3	HAZ - 1	279	281	21	HAZ – 2	283	287
4	HAZ - 1	279	291	22	HAZ – 2	276	296
5	HAZ - 1	285	294	23	Base Metal – 1	253	251
6	HAZ - 1	279	292	24	Base Metal – 1	250	252
7	Weld Metal	286	290	25	HAZ – 1	279	283
8	Weld Metal	292	281	26	HAZ – 1	287	280
9	Weld Metal	291	296	27	HAZ – 1	276	282
10	Weld Metal	296	289	28	Weld Metal	283	287
11	HAZ - 2	296	290	29	Weld Metal	284	290
12	HAZ - 2	298	282	30	Weld Metal	283	281
13	HAZ - 2	286	274	31	HAZ – 2	290	284
14	HAZ - 2	288	274	32	HAZ – 2	285	289
15	Base Metal - 2	250	248	33	HAZ – 2	276	274
16	Base Metal - 2	249	253	34	Base Metal – 2	250	252
17	HAZ - 1	286	288	35	Base Metal – 2	246	254
18	HAZ - 1	294	288				

Table 6 – Average hardness after post weld double tempering

Location	GMAW (HV 10Kgf)	SMAW (HV 10Kgf)
Base Metal	249	252
Weld Metal	288	289
HAZ	284	286

The Vickers hardness readings were found acceptable at all locations in the base metal. However, in the weld metal and HAZ, the survey revealed values higher than 253 HV (HRC 23)

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Microstructure

The microscopic examination of the weld, HAZ, and base metal revealed microstructural characteristics typical to a low carbon tempered martensite. The weld metal revealed coarser, columnar grains, typical to re-solidification of the weld and HAZ while the base metal regions exhibited a finer, more equiaxed shaped structure: figures 3 to 8.

GMAW

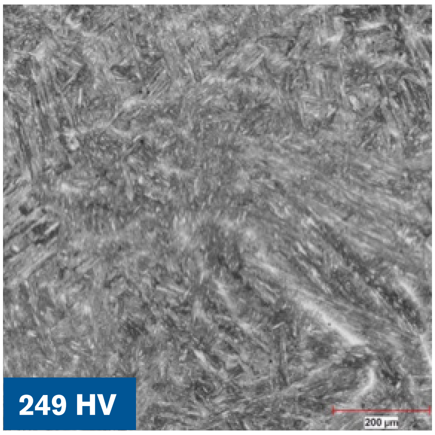

Figure 3 – Base Metal. Normal tempered martensite typical to low carbon martensitic stainless steel.

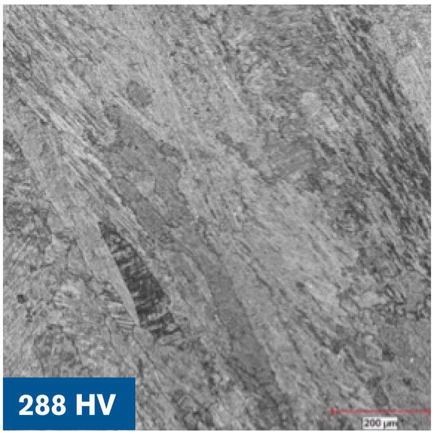

Figure 4 – Weld Metal. Tempered martensite with columnar shaped grains.

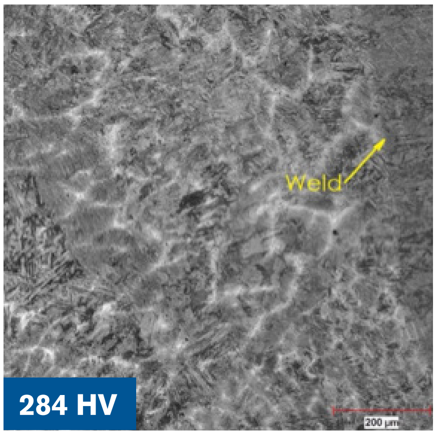

Figure 5 – HAZ. Tempered martensite with grains coarser than the base metal.

SMAW

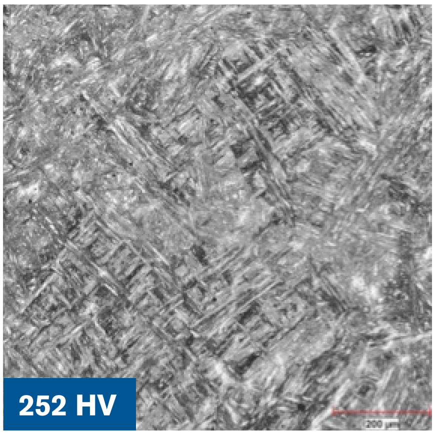

Figure 6 – Base Metal. Normal tempered martensite typical to low carbon martensitic stainless steel. Martensite needles are arranged in parallel forming blocks.

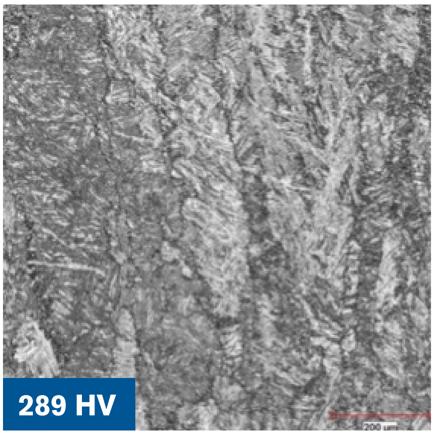

Figure 7 – Weld Metal. Tempered martensite with columnar shaped grains.

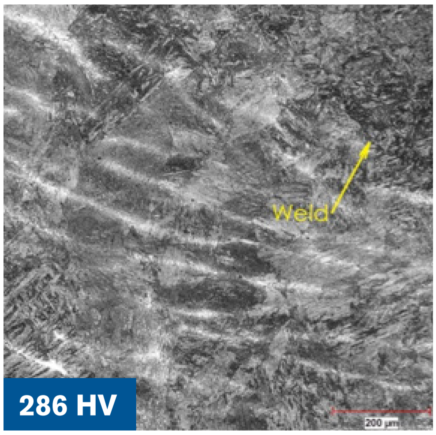

Figure 8 – HAZ. Tempered martensite with grains coarser than the base metal.

Subsequently, the test coupons used for the Vickers hardness testing were re-polished and re-tested for hardness, this time using the Rockwell hardness method. The hardness measurements were performed in accordance with ASTM E18-12 using a load of 15 Kgf. Coupons were tested on the same surface and the location of each measurement was carefully selected so that it coincided with the initial Vickers hardness testing.

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Table 7 shows comparative hardness results using the two methods converted to Rockwell C in accordance with ASTM E140-12b, Table1.

Table 7 – HV 10Kgf and HR 15N results converted to HRC

		GMAW				SMAW			
Reading No.	**Location**	**HV10Kgf**	**(HRC*)**	**HR15Kgf**	**(HRC*)**	**HV10Kgf**	**(HRC*)**	**HR15Kgf**	**(HRC*)**
1	Base Metal - 1	248	22	68.0	< 20	253	< 23	67.0	< 20
2	Base Metal - 1	248	22	67.0	< 20	248	22	67.5	< 20
3	HAZ – 1	279	> 23	68.5	< 20	281	> 23	67.0	< 20
4	HAZ – 1	279	> 23	69.0	< 20	291	> 23	69.5	< 20
5	HAZ – 1	285	> 23	69.0	< 20	294	> 23	67.5	< 20
6	HAZ – 1	279	> 23	68.5	< 20	292	> 23	67.5	< 20
7	Weld Metal	286	> 23	68.5	< 20	290	> 23	70.5	22
8	Weld Metal	292	> 23	69.0	< 20	281	> 23	70.5	22
9	Weld Metal	291	> 23	69.5	< 20	296	> 23	70.5	22
10	Weld Metal	296	> 23	69.0	20	289	> 23	70.5	22
11	HAZ – 2	296	> 23	69.0	< 20	290	> 23	66.5	< 20
12	HAZ – 2	298	> 23	69.5	20	282	> 23	66.5	< 20
13	HAZ – 2	286	> 23	69.5	20	274	> 23	68.5	< 20
14	HAZ – 2	288	> 23	70.0	21	274	> 23	70.5	22
15	Base Metal - 2	250	< 23	68.5	< 20	248	22	66.5	< 20
16	Base Metal - 2	249	< 23	66.5	< 20	253	< 23	67.5	< 20
17	HAZ – 1	286	> 23	70.5	22	288	> 23	69.0	< 20
18	HAZ – 1	294	> 23	70.5	22	288	> 23	69.5	20
19	Weld Metal	291	> 23	68.5	< 20	287	> 23	69.5	20
20	Weld Metal	289	> 23	70.5	22	294	> 23	70.5	22
21	HAZ – 2	283	> 23	70.5	22	287	> 23	70.5	22
22	HAZ – 2	276	> 23	70.0	21	296	> 23	70.5	22
23	Base Metal - 1	253	< 23	68.5	< 20	251	< 23	68.0	< 20
24	Base Metal - 1	250	< 23	68.0	< 20	252	< 23	68.0	< 20
25	HAZ – 1	279	> 23	70.0	22	283	> 23	70.5	22
26	HAZ – 1	287	> 23	70.5	22	280	> 23	69.5	20
27	HAZ – 1	276	> 23	70.5	22	282	> 23	70.0	21
28	Weld Metal	283	> 23	70.5	22	287	> 23	70.5	22
29	Weld Metal	284	> 23	70.5	22	290	> 23	70.5	22
30	Weld Metal	283	> 23	70.5	22	281	> 23	70.5	22
31	HAZ – 2	290	> 23	70.5	22	284	> 23	70.0	21
32	HAZ – 2	285	> 23	70.0	21	289	> 23	69.5	20
33	HAZ – 2	276	> 23	70.0	21	274	> 23	69.0	< 20
34	Base Metal - 2	250	< 23	67.0	< 20	252	< 23	68.0	< 20
35	Base Metal - 2	246	< 22	68.0	< 20	254	23	68.0	< 20

The HRC converted results were consistently lower and well under the maximum NACE limit of 23HRC when the Rockwell 15N method was used. The data in Table 7 suggest that the Vickers to Rockwell C hardness conversion as per ASTM E140-12b is not applicable to this alloy, in this hardness range.

Triple-Cycle Post-Weld Heat Treatment

In an attempt to obtain a more homogeneous microstructure at all locations and determine whether or not the grain size and shape of the martensitic structure has a significant impact on the final hardness, test coupons from the same weld test plates were subjected to a triple cycle post-weld heat treatment as follows:

1. Normalizing: 1850°F for 6 hours
2. Intermediate Temper: 250°F for 10 hours
3. Final Temper: 1112°F for 20 hours

Superficial hardness surveys were performed on the normalized and double tempered samples. Vickers 10 Kgf and Rockwell 15Kgf methods were both used at identical locations. Results are shown in Table 8.

Table 8 – Vickers (HV10Kgf) and Rockwell (HR15Kgf) hardness results converted to Rockwell C obtained on the normalized and double tempered samples.

		GMAW				SMAW			
Reading No.	Location	HV10Kgf	(HRC*)	HR15Kgf	(HRC*)	HV10Kgf	(HRC*)	HR15Kgf	(HRC*)
1	Base Metal - 1	266	> 23	69	< 20	262	> 23	68	< 20
2	Base Metal - 1	261	> 23	69.5	20	260	> 23	67.5	< 20
3	HAZ – 1	268	> 23	69.5	20	262	> 23	68	< 20
4	HAZ – 1	268	> 23	69	< 20	264	> 23	69	< 20
5	HAZ – 1	267	> 23	69.5	20	262	> 23	68	< 20
6	HAZ – 1	261	> 23	69	< 20	266	> 23	69.5	20
7	Weld Metal	281	> 23	68.5	< 20	267	> 23	69.5	20
8	Weld Metal	282	> 23	70	21	266	> 23	70.5	22
9	Weld Metal	280	> 23	69.5	20	274	> 23	70.5	22
10	Weld Metal	280	> 23	69	< 20	269	> 23	70.5	22
11	HAZ – 2	263	> 23	69	< 20	264	> 23	69.5	20
12	HAZ – 2	262	> 23	68.5	< 20	260	> 23	69.5	20
13	HAZ – 2	260	> 23	69	< 20	260	> 23	69	< 20
14	HAZ – 2	261	> 23	68	< 20	260	> 23	69	< 20
15	Base Metal - 2	259	> 23	69	< 20	261	> 23	69	< 20
16	Base Metal - 2	262	> 23	69.5	20	262	> 23	69.5	20
17	HAZ – 1	265	> 23	69.5	20	267	> 23	69.5	20
18	HAZ – 1	262	> 23	69	< 20	265	> 23	69	< 20
19	Weld Metal	280	> 23	69.5	20	274	> 23	70.5	22
20	Weld Metal	280	> 23	70	21	273	> 23	70.5	22
21	HAZ – 2	263	> 23	70	21	270	> 23	69.5	20
22	HAZ – 2	259	> 23	69	< 20	270	> 23	69.5	20
23	Base Metal - 1	269	> 23	69.5	20	268	> 23	69	< 20
24	Base Metal - 1	266	> 23	69.5	20	268	> 23	69	< 20
25	HAZ – 1	259	> 23	69.5	20	262	> 23	69.5	20
26	HAZ – 1	262	> 23	69.5	20	263	> 23	69.5	20
27	HAZ – 1	261	> 23	69	< 20	260	> 23	69.5	20
28	Weld Metal	277	> 23	69	< 20	282	> 23	70.5	22
29	Weld Metal	278	> 23	69	< 20	280	> 23	70.5	22
30	Weld Metal	270	> 23	69.5	20	281	> 23	70.5	22
31	HAZ – 2	261	> 23	69	< 20	263	> 23	69.5	20
32	HAZ – 2	259	> 23	69	< 20	267	> 23	69.5	20
33	HAZ – 2	263	> 23	69	< 20	267	> 23	69.5	20
34	Base Metal - 2	263	> 23	69	< 20	272	> 23	69	< 20
35	Base Metal - 2	268	> 23	69.5	20	274	> 23	69.5	20

The overall results after the normalizing and double tempered cycle were less scattered due to a more homogeneous martensitic structure but still too high when considering the HV measurements. The base metal appeared to be harder, but this could be attributed to a more advanced precipitation of micro-carbides in a softer matrix.

The Rockwell C hardness results converted from Rockwell 15 Kgf measurements were consistently lower than the HRC results converted from Vickers 10 Kgf substantiating once again the inapplicability of the ASTM E140-12b Vickers to Rockwell C hardness conversion.

The Struggle is in the Method

This work shows that, in reality, a weld procedure qualification may fail just because the wrong testing method was adopted.

When the Vickers testing method was performed and the ASTM E140 was used for converting HV10Kgf readings to HRC, **almost all converted results revealed values higher than 23 HRC**; as a result, the qualification of the weld procedure to NACE MR0175 was considered a **fail.** However, when the same test coupons were tested using the Rockwell HR 15N testing method and the HR 15N results were converted to HRC using the same ASTM E140-12b, table 1, **all converted results were lower than 22 HRC**. In this case the very same weld procedure qualification **complied** with the NACE MR0175 maximum hardness requirement of 23 HRC.

Both Table 7 and Table 8 substantiate that the Rockwell-Vickers hardness correlation given by ASTM E140 is not applicable to CA-6NM and possibly to other martensitic grades. In his work, T.G. Gooch concluded that 23 HRC is equivalent to 275 HV10Kgf. This work indicates that the NACE hardness limit of 23 HRC is equivalent to 285 HV10Kgf. The difference could be attributed to the fact that Gooch's work was performed on 13%Cr-4%Ni wrought materials while for this project cast plates were used.

Conclusions

Summary

1. In general, castings made in CA6NM alloy, when produced with a low carbon content (0.03% or less) in normalized and double tempered condition, meet the maximum hardness limit of 23 HRC.

2. The problem arises when the NACE maximum hardness limit of 23 HRC is applied to welds and heat affected zones. This work confirms the practical struggle in achieving the maximum hardness limit of 23 HRC in welds and heat affected zones even when CA6NM base metal with very low carbon content is welded using low carbon filler materials and even when the weld is followed by a double post weld heat treatment.

3. The maximum hardness limit of 23 HRC can consistently be achieved in the base metal, weld, and HAZ after a double temper cycle only when the Rockwell C values are taken as equivalents of HR 15N readings and not of HV readings. This is especially helpful when weld procedures are qualified to NACE MR0175 in which case both HV and HR 15-N methods are accepted.

4. Things become more complicated when having to qualify a weld procedure to NACE MR0103. Both NACE specifications, MR0175 and MR0103, serve the same oil and gas industry establishing requirements for materials resistant to stress corrosion cracking in environments containing wet H2S. MR0175 regulates the oil and gas field operations while MR0103 is tailored to refinery environments and applications. The two standards are generally the same, however HR 15N is a testing method in full compliance with NACE MR0175 but not in compliance with NACE MR0103. According to NACE MR0103 the only accepted hardness test method for welding procedure qualification is the Vickers method with a load of 98 N (10 kgf) or less.

5. The tensile strength is not significantly impacted by the low carbon content. All four tensile strength tests across the weld performed on coupons removed from the post-weld double-tempered test plates passed the minimum strength required.

6. The triple-cycle post-weld heat treatment (normalizing and double tempering) does not have a significant impact on the final hardness. Current results suggest that maximum softening can be obtained after a double tempering treatment.

7. This work shows that the low carbon content of the base and filler metal is a major compositional factor in determining the maximum hardness. However, a carbon content lower than 0.02% has no practical value. This was substantiated by the fact that the carbon content of the wire used for GMAW qualification barely made the spec.

8. Welding electrodes ordered for NACE jobs must be tested immediately upon receiving. The material certificate alone is not enough, as there can be significant discrepancies between the reported and tested values.

9. This work also indicates that there should be no difference between a base metal AOD refined and a metal produced in an induction furnace. There may be various issues related to the metallurgy of the weld and HAZ that could make the qualification a difficult task, but the real challenge here is the hardness testing method selection limitation.

10. In the author's opinion, the key to success in meeting NACE hardness requirements for CA6NM castings is not having to weld at all. In order to achieve this performance one should resort to all available tools: MagmaSoft, a sound foundry practice and expertise, generous feed pads. Also one should be prepared to settle for a lower casting yield, increased machining stocks, a lot more work in the grinding room, etc. Welding does not seem to be an option.

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BK-Sales & Marketing- Global-Whitepaper-MP-Carbon Segregation in CA6-NM Castings