Prevention of Temper Embrittlement in 2¼ Cr-1 Mo Weld Metal by Metallurgical Actions

A significant improvement in toughness properties after step cooling allows the application of high performance processes such as tandem submerged arc welding

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Introduction

The increasing demand for energy in the future and interest in alternative processes like coal gasification, coal liquification, the processing of heavier crude feedstocks and different catalytic reformings will most likely lead to a growing utilization of Cr-Mo alloy steels for the construction of heavy wall pressure vessels.

Due to the 850 °F (454°C) primary design temperature and other requirements, 2¼ Cr-1 Mo steel will continue to be the most important material used in pressure vessels.

In the past 10 years, temper embrittlement of 2¼ Cr-1 Mo steel and the weld metal has become of considerable concern to the users and producers of these heavy wall vessels. The principal reason for the temper embrittlement is the segregation of impure elements such as phosphorus, arsenic, antimony and tin in the grain boundary region. The embrittlement manifests itself by an upward shift of the ductile-to-brittle transition temperature after a long time exposure in the temperature range of 750–1100 °F (399–593°C).

The literature describing this phenomenon is now very extensive. The step-by-step progress that has been made to improve the properties of the steel and the weld metal is very evident in the literature (Ref. 1-11).

In case of 2¼ Cr-1 Mo steel, the embrittlement problem can be solved by reducing the residual elements to an extremely low level. Further, the embrittling element silicon and the alloying element manganese must be limited, the latter due to its tendency towards cosegregation. The requirement for a temper embrittlement resistant steel is commonly expressed by the so called J-factor formulated by Watanabe (Ref. 5):

$$J = (Mn + Si) \times (P + Sn) \times 10^4$$

where the different elements are expressed in percent.

Most recent specifications require a J-number of less than 150; this can be effected, for example, by the following composition: 0.50% Mn, 0.10% Si, 0.010% P, and 0.010% Sn. The J-number is in this case 120.

Interacting Effects on the Temper Embrittlement of the Weld Metal

Due to the wide range of complex interacting effects, it is much more difficult to improve the resistance of the weld metal to temper embrittlement than to the equivalent extent in case of wrought or forged material. For this reason, welding consumables have lagged behind the development of the wrought steel despite the fact that it is of equal importance. Proposals have been made that circumvent the need for temper embrittlement resistance.

One proposal to circumvent resistance to temper embrittlement is to reduce the pressure within the lower range of temperature; another is to use only forged rings for the construction of vessels since, in this case, they are without welded longitudinal seams. However, forged rings have an inherent disadvantage compared to rolled plate rings because of surfacing coalescence difficulties caused by the higher carbon content and the temper embrittlement problem in the forged material. Thus, the best solution for construction of 2¼ Cr-1 Mo steel vessels is to improve the toughness properties of the weld metal to the same extent that has been achieved successfully with the base metal.

The first important step is to reduce the level of the residual elements of the weld metal as low as possible. However, this is not the only measure of toughness properties. After exposure within the critical range of temperature for a long time, the weld metal will have an overall lower quality level than the comparable clean steel, since the improvement is only gradual and not fundamental. This is due to a wide field of interacting effects, which must also be considered at the same time. Based on experience it is necessary to consider the following variables which are discussed further elsewhere in this paper:

1. Chemical composition with emphasis on residual elements.
2. Heat treatment.
3. Basicity of the electrode coating for shielded metal arc welding and flux for submerged arc welding.
4. Grain size and welding techniques.

Step Cooling Embrittling Treatment of the Test Material

Before discussing the different interacting effects, it is useful to briefly describe the conditions for the long-time exposure of the test material that is normally used to simulate the service behavior of the steel or weld metal. The extent of embrittlement depends on exposure time and temperature. SAE 3140 type steel is an example – Fig. 1. Each curve of the diagram in Fig. 1 represents a certain transition temperature. The diagram shows

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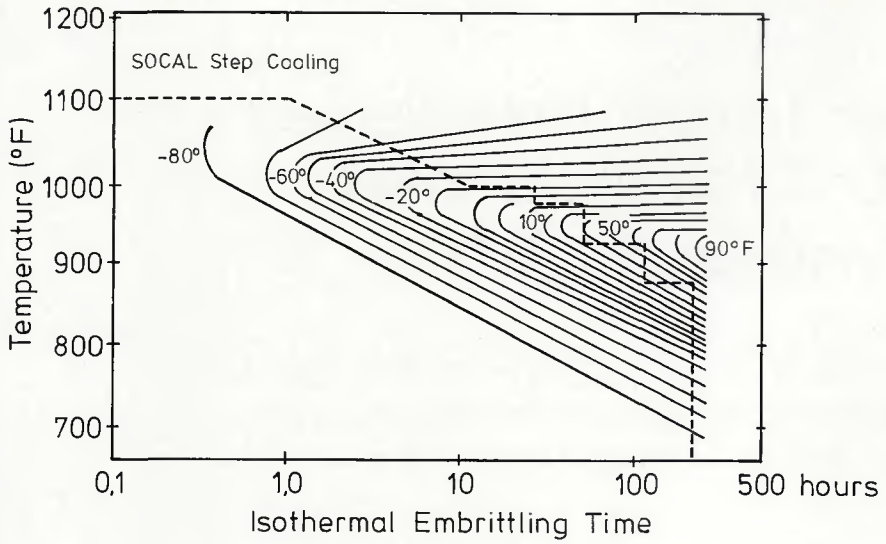

Fig. 1—Isothermal embrittlement of the steel SAE 3140 exemplifying the temper embrittlement phenomenon (Ref. 1)

Table 1—Specifications for the "Step Cooling" Embrittling Treatment Formulated by General Electric, C. F. Braun and Standard Oil of California

Temperature, °F	Exposure time, h			Rate of cooling, °F/h		
	GE	C. F. Braun	SOCAL	GE	C. F. Braun	SOCAL
1100	1	1	1	10	10	10
1000	15	15	15	10	10	10
975	24	24	24	10	10	10
925	60	60	60	5	5	10
875	125	100	100	50	50	50
600				Air cooling	Air cooling	Air cooling

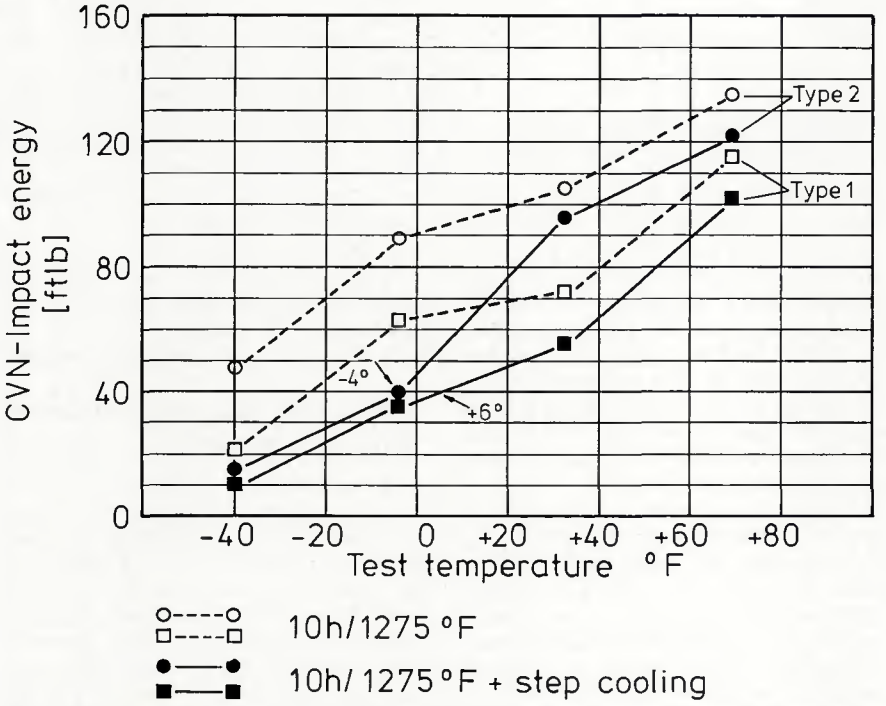

Fig. 2—Charpy impact curves of the weld metals of two E9015-B3 electrodes with different levels of residual elements

that, for the same effect, the exposure time can be shortened if the embrittling treatment temperature corresponds to the reversing point of the respective curves. For this reason, a so-called "step cooling" treatment has been formulated by General Electric as well as C. F. Braun and Standard Oil of California (SOCAL)—Table 1.

The small differences between each treatment shown in Table 1 refer only to the cooling rate from 925 to 875 °F (496 to 468 °C) and to the exposure time at 875 °F (468 °C). The extent of the resulting embrittlement is not influenced by these unimportant deviations. In Fig. 1 the SOCAL "step cooling" treatment is indicated by a dash line in order to show its trend compared to the different embrittlement curves. The "step cooling" line does not exactly follow the reversing points of these embrittlement curves due to the fact that the SAE 3140 Ni-Cr alloyed steel exhibits a slightly different although similar embrittlement behavior compared to the 2¼ Cr-1 Mo steel. However, the data show very impressively that, after 200-300 hours, the "step cooling" treatment produces the same extent of embrittlement at a much longer isothermal exposure at any temperature.

Interacting Variables and Their Effects

Influence of Chemical Composition and Heat Treatment

As previously mentioned, it is absolutely necessary to provide a very low level of residual elements. However, in the case of the weld metal, this precaution is but one of many others if temper embrittlement is to be prevented. Figure 2 shows two pairs of Charpy impact curves (before and after step cooling) for two different E9015-B3 electrodes. Weld metal from the type 1 electrode was deposited to a previous standard with a normal amount of impurities. The weld metal of the type 2 electrode has a very low level of residual elements, but the electrode coating is also standard. The weld metal compositions for both types, including the J-factor, are shown in Table 2. The welding parameters are also given in the same table.

Despite the extremely clean weld metal from the type 2 electrode, the improvement of the Charpy-impact values after step cooling is relatively small. In this case, the 40 ft-lb (54J) transition temperature is about −4 °F (−20 °C). This is higher than the transition temperature of a comparable clean steel which must be lower than −20 °F (−29 °C).

The postweld heat treatment of the weld metal before step cooling was 10 hours (h) at 1275 °F (691 °C). Based on prior experience, the results were not negatively influenced by this treatment, since the optimum range for the temper-

ing of 2¼ Cr-1 Mo weld metal is 1250–1300 °F (677–704 °C). Leaving this range of optimum PWHT temperatures, it must be expected that there will be a loss of toughness due to the incomplete tempering at a subcritical temperature on the one hand and the more coarse grained microstructure as a result of exceeding the advised temperature. Furthermore, we have found that the weld metal toughness can be improved by prolonging the postweld heat treatment within the optimum temperature range.

Merely reducing the unfavorable residual elements does not improve the impact properties to a sufficient level. Other influencing factors must be considered. The results of extensive experiments in our R&D department hint at the manganese content of the weld metal as being one of these factors. However, results point in a direction that is opposite from that implied by the Watanabe formula. Weld metal from the electrodes (Table 2) is characterized by a manganese content of about 0.6%; this is relatively low (*i.e.* complies with the AWS specification for E9015-B3 electrodes). Furthermore, this low Mn content also leads to a correspondingly low J-factor. However, it must be noted that the J-factor was originally introduced in order to describe the embrittling behavior of the base metal and not of the weld metal.

For the base metal, Watanabe considered manganese as a cosegregate with the residual elements. Using the Watanabe formula for the base metal, it is necessary to keep it within a limited range. However, in the case of the weld metal, manganese does not cosegregate due to rapid solidification and subsequent high cooling rates. Therefore, time for extensive diffusion to the grain boundaries is short, and it is not necessary to limit the manganese content to the same extent as in the case of the base metal. Practical experience shows that the toughness of the weld metal can be improved if the manganese content is increased up to 0.7–1.0% due to the increased formation of acicular ferrite in the microstructure.

In addition, the increase in manganese content provides even more advantages. The most important one is the increased hot tensile strength, plus better welding behavior of the electrode and the tendency toward fewer discontinuities and slag inclusions in the weld metal. With this in mind, it would appear prudent to use the J-factor for the specification of wrought steel composition and to use another formula for the specification of the weld metal.

In 1970 Bruscato (Ref. 3) formulated an embrittling factor without incorporating the element manganese. It considers only the critical residual elements according to the following formula:

Table 2—Weld Metal Analysis and Welding Conditions Relating to the Results Given in Fig. 2

Weld metal analysis, %

	Type 1 electrode	Type 2 electrode
C	0.06	0.07
Si	0.26	0.29
Mn	0.58	0.60
Cr	2.26	2.18
Mo	0.96	0.94
Cu	0.04	0.04
Ni	0.03	0.04
P	0.017	0.006
S	0.016	0.007
As	0.013	0.006
Sb	0.003	0.002
Sn	0.006	0.007
V	0.01	0.01
J-Factor	193	116

Welding conditions:

Electrode size, mm	4.0 × 350
Welding position	Flat
Current, A	170
Voltage, V	23
Length of bead deposited, in.	10
Heat input, kJ/in.	26
Interpass temperature, °F	390
PWHT	10 h at 1275°F

$$X = \frac{10\,P + 5\,Sb + 4\,Sn + As}{100}$$

The different elements are expressed in ppm. Furthermore, the Bruscato formula has the advantage that not only phosphorus and tin but the other influencing elements, including antimony and arsenic, are considered. This should provide a better approach for describing the embrittling behavior of the weld metal (Ref. 12).

Increased Basicity of the Electrode Coating for Shielded Metal Arc Welding

The recommended increase in the manganese content is not the primary measure to employ in order to prevent temper embrittlement of the 2¼ Cr-1 Mo weld metal. More importantly, temper embrittlement of this and similar alloys cannot really be excluded; it can only be controlled within a limited but acceptable range.

An important requirement is to increase the Charpy impact values before step cooling (after postweld heat treatment) to the highest achievable level. The consequence of this measure is that the impact values after step cooling will be characterized by a remarkably high level despite a partial loss of toughness due to the unavoidable temper embrittlement. The necessary metallurgical action is to increase the basicity of the electrode coating (Ref. 13-19); the residual elements must be kept low as recommended previously. The results of this measure are shown in Fig. 3.

Table 3—Weld Metal Analysis Relating to Results Given in Figs. 3 and 4, %

C	0.06	Ni	0.03
Si	0.25	P	0.010
Mn	0.79	S	0.009
Cr	2.36	As	0.004
Mo	1.04	Sb	0.002
Cu	0.02	Sn	0.003
		V	0.01
	J-factor	135	
	Bruscato-factor	12.6	

The 40 ft-lb (54 J) transition temperature after step cooling is, in this case, −53 °F (−47 °C) and is comparable with the behavior of the low residual steel. The corresponding weld metal analysis, including J-factor and Bruscato embrittlement factor, is shown in Table 3. Postweld heat treatment and welding conditions are the same as shown in Table 2.

Since electrode coating basicity has a significant influence on the toughness, it would be helpful if the degree of basicity could be defined by a generally applicable formula. As yet, the best approach is given by the Boniszewski (Ref. 14 and 15) formula that summarizes the influence of the different ingredients as follows:

$$B = \frac{\begin{array}{c}CaO + MgO + CaF_2 + \\ Na_2O + K_2O + \\ \tfrac{1}{2}\,(MnO + FeO + BaO)\end{array}}{\begin{array}{c}SiO_2 + TiO_2 + \tfrac{1}{2} \\ (Al_2O_3 + ZrO_2)\end{array}},$$

where all oxides and CaF_2 are expressed in mole fractions.

The problem with this formula is that it gives too much weight to the nonbasic ingredient fluorspar (CaF_2) which is added as a neutral salt and used to reduce the high melting point of the basic slag. Therefore, the degree of basicity calculated by the Boniszewski formula cannot be considered as absolutely correct; this makes it very difficult to compare the actual basicity of different manufactured electrode coatings.

In the case of the special type of electrode shown in Fig. 3, the calculated degree of basicity is 2.8. This high degree of basicity is the main key to understanding the high impact values at low temperatures, even after step cooling. Due to the significant amount of basic ingredients, the slag absorbs more of the small spherelike SiO_2 particles out of the liquid weld metal than in normal cases. Since the rest of the non-extracted SiO_2 influences the impact values to a very high degree, it should be kept as low as possible.

The amount of included SiO_2 can be

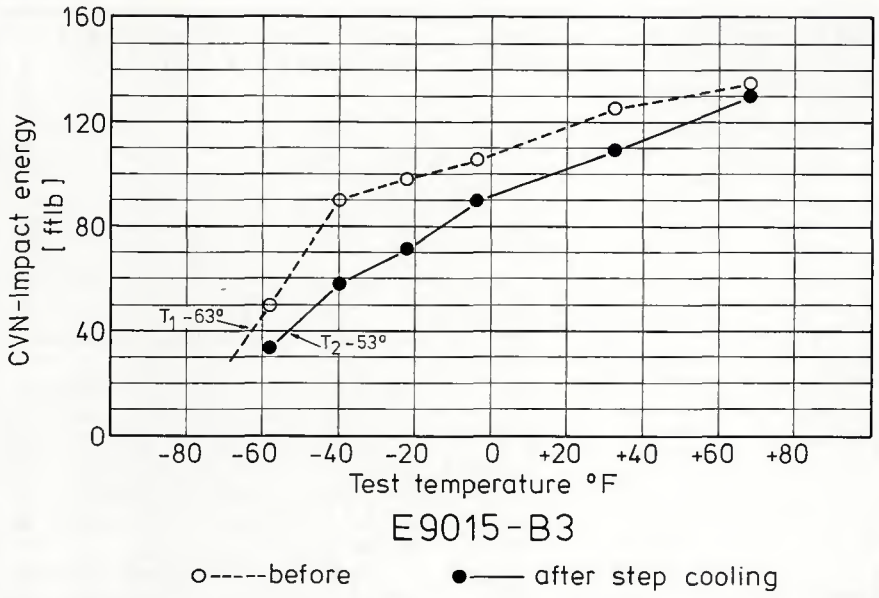

Fig. 3 – Charpy impact curves of the weld metal of an improved E9015-B3 electrode with increased coating basicity

expressed by the oxygen content of the weld metal; thus, this value may also be seen as an expression of the real basicity of the electrode coating. In this case, the oxygen content of the weld metal was about 0.030%.

Referring to the Charpy impact curves of Fig. 3, it can be noted that, besides the 40 ft-lb (54J) transition temperature, there is another approach common in specifications for materials to resist temper embrittlement. This is to use the formula, $T_1 + f$ (ΔT) = maximum temperature where T_1 is the 40 ft-lb (54J) transition temperature before step cooling and ΔT is the shift of the curve due to step cooling ($\Delta T = T_2 - T_1$).

The formula recommended by C. F. Braun is the most critical one. Braun uses a multiplicator of ΔT which is 3 and the maximum temperature 100 °F (38 °C). In the case of Fig. 3, the above mentioned equation has to be evaluated by using the following values: $T_1 = -63$ °F; $T_2 = -53$ °F; $\Delta T = 10$ °F; $T_1 + 3 \times \Delta T = -33$ °F.

The result is, in this case, even a negative value due to the extremely low transition temperature before step cooling and due to the relatively small shift after step cooling.

Figure 4 supplements the information for covered electrodes with increased basicity by providing corresponding graphs for lateral expansion and shear fracture.

Increased Flux Basicity to Guarantee Successful Submerged Arc Welding

With the submerged arc process, it is also necessary to increase the basicity of the flux (Ref. 13-19). Otherwise it would not be possible to raise the level of Charpy impact values after step cooling, even with the use of an extremely clean electrode. A further requirement is to minimize the pickup of residual elements from the flux; one of the most important, phosphorus, must be maintained as low as possible.

If these preconditions are fulfilled, weld metal toughness can be expected to be as shown in Fig. 5. In this case, the 40 ft-lb (54J) transition temperature was −49 °F (−45 °C) after step cooling. The corresponding figures according to the formula $T_1 + 3 \times \Delta T$ were $-63 + 3 \times 14 = -21$ °F. The chemical compositions of the electrode and weld metal, including J-number and Bruscato embrittling factor, are indicated in Table 4; welding and PWHT conditions are also shown in the table.

Results comparable to those in Fig. 5 have been confirmed by using other heats of electrode and lots of flux based on the same requirement for weld metal purity and flux basicity.

Flux basicity used is 2.8 according to the Boniszewski formula. The corresponding oxygen content of the weld metal was also about 0.030%. This solution for successful submerged arc weld metal behavior when using a single electrode can also be utilized with the tandem-arc technique. The Charpy impact values before and after step cooling are, in this case, slightly lower due to the higher heat input but will exceed all present requirements.

The results are shown in Fig. 6 where the electrode wire heat and the lot of flux were the same as in Fig. 5. For tandem-arc welding, it is necessary to keep the welding variables within a reasonable range. The tandem arc welding conditions are shown in Table 5 and can be used as recommendation for shop-floor welding.

Influence of Grain Size and Welding Technique

Grain size and the percentage of fine grained microstructure are also very

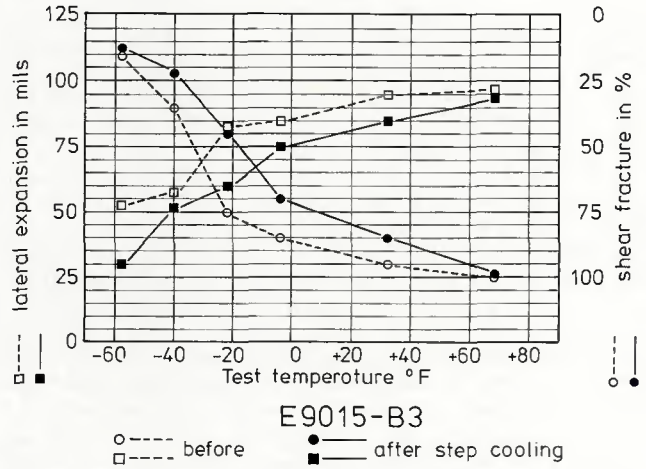

Fig. 4 – Lateral expansion and shear fracture relating to the Charpy impact curves of Fig. 3

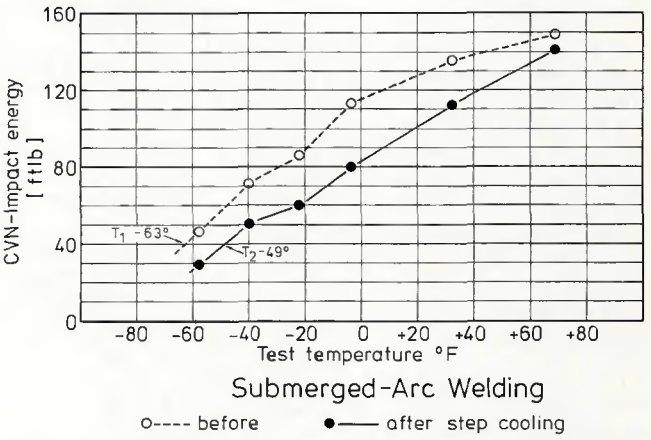

Fig. 5 – Charpy impact curves of the 2¼ Cr-1 Mo weld metal deposited by single electrode submerged arc welding

Table 4—Solid Electrode and All-Weld-Metal Analyses As Well As Welding Conditions Relating to Figs. 5 and 6

Chemical Composition, %

	Solid electrode	Weld metal
C	0.11	0.08
Si	0.08	0.21
Mn	0.52	0.82
Cr	2.53	2.33
Mo	0.97	0.95
Cu	0.05	0.09
Ni	0.02	0.02
P	0.005	0.007
S	0.006	0.009
As	0.004	0.004
Sb	0.002	0.002
Sn	0.003	0.003
V	0.01	0.01
J-factor	—	103
Bruscato-factor	—	9.6

Welding conditions:

Electrode diameter, mm	4.0
Current (DC, electrode positive), A	550
Voltage, V	30
Travel speed, ipm	24
Heat input, 42 kJ/in.	42
Interpass temperature, °F	390
PWHT	10 h at 1275 °F

important factors if the Charpy impact values of the weld metal are to be pushed to the highest level. Due to the fact that the primary grains, after solidification, are partially refined by each following pass during welding, the extent of this refinement influences the weld metal properties. Thus, the geometry of each single bead has to be considered as a decisive factor of influence, since the extent of refinement depends directly on the thickness of each bead – or, in other words, on its resultant width-to-thickness ratio. The thinner the weld passes, the larger are the areas which are refined by each following weld pass. For this reason, it is very important to adhere closely to proper welding procedure.

With shielded metal arc welding, best results are to be expected if the welding can be carried out in the flat position. In this case the thickness of the single weld passes will normally have the right dimension of approximately 2 mm (0.08 in.) if the diameter of the electrodes is not larger than 5.0 mm (0.2 in.) and if the welding speed is not too low. The 2 mm (0.08 in.) thickness is also a good recommendation for all other shielded metal arc weldments. If this is not exceeded, optimum Charpy impact curves can be expected for each respective type of electrode. The level of these curves is, of course, dependent on the quality of electrodes available from each manufacturer.

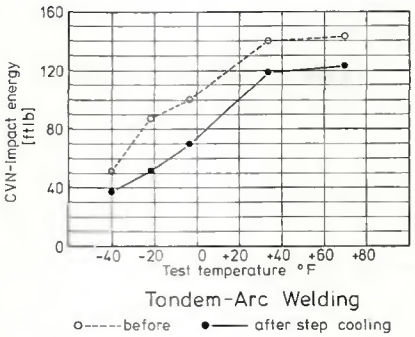

Fig. 6 – Charpy impact curves of the 2¼ Cr-1 Mo weld metal deposited by tandem-arc welding

Clearly, it is much more difficult to approach the 2 mm (0.08 in.) single weld pass thickness in the vertical-up (3G) or other restrictive positions. If it can be approached by a specific weaving technique, nearly the same toughness properties can be expected as in the flat position. If not, the results tend to scatter in a very wide range depending on the extent of how far the recommended single weld pass thickness is exceeded.

The following test results demonstrate the beneficial influence of the proposed welding technique. Figure 7 shows four different microstructures produced with type E9015-B3 4 mm (0.16 in.) diameter electrodes; the welding parameters are indicated in Table 6.

Test A was welded in the flat position (1G), test B in the vertical-up position (3G) but with the same single bead thickness; C and D were welded purposely with thicker passes, adopting a welding technique that is normally preferred by the welders. Due to their previous education, welders generally control heat input and do not concern themselves with the thickness of the beads. The heat input is much less important, since it mainly influences the primary microstructure while the single weld pass thickness influences the extent of the subsequent grain refinement. Thus, the increased heat input by applying the weaving technique has no negative effect on the toughness properties of the weld metal; this is because it will not reverse the advantage of the grain refinement, based on this special kind of welding technique.

The graphs in Fig. 8 show the Charpy impact values at 0, −20 and −40 °F (−18, −29 and −40 °C) after postweld heat treatment for 10 h at 1275 °F (691 °C). Under the conditions of test B, the results of the vertical-up position almost match those of the flat position. As shown, this modified welding technique has a distinct advantage over the normal welding

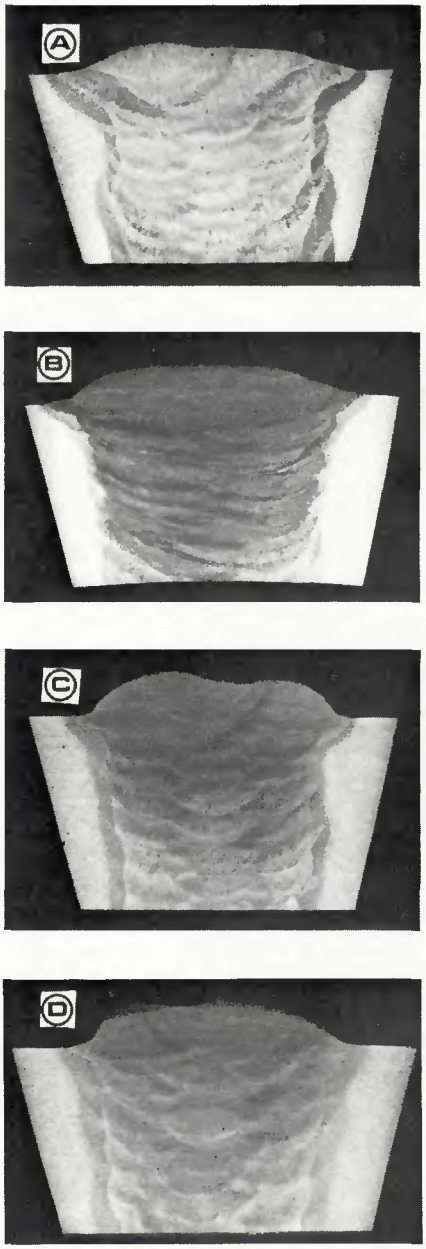

Fig. 7 – Microstructure of 4 weld metals of an E9015-B3 electrode deposited in different welding techniques

Table 5—Welding Conditions Relating to Fig. 6

Electrode diameter, mm	4.0
Current	AC each electrode
Amperage, A	600 each electrode
Voltage, V	32 each electrode
Travel speed, ipm	28
Heat input, kJ/in.	83
Interpass temperature, °F	390
Electrode distance, in.	1

Table 6—Welding Conditions Relating to the Microstructures of Fig. 7 and Charpy Impact Values of Fig. 8

	Electrode diameter, mm	Position	Amperage, A	Voltage, V	Heat input kJ/in.	Number of layers[a]
Test A	4.0	1 G	175	23	27	10
Test B	4.0	3 G	140	23	50	10
Test C	4.0	3 G	140	23	35	7
Test D	4.0	3 G	140	23	43	5

[a]The thickness of the base metal was 20 mm (0.79 in.)

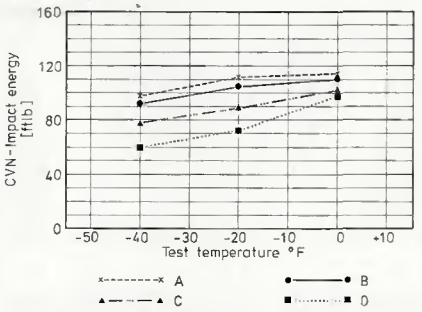

Fig. 8—Dependence of the Charpy impact values on different welding techniques after stress relieving

technique in the vertical-up position. This is the only feasible way to get high Charpy V-notch values at very low temperatures.

The same influence of the single weld pass geometry must be considered for submerged arc welding. It is necessary to define the right welding conditions. For optimum performance, a maximum of 550 A should be judged as a shop-floor guideline, not to be exceeded without strong reasons. The corresponding voltage should be approximately 30 V. The travel speed should be at least 20 ipm (8.47 mm/s).

If for any reason the amperage exceeds 550 A, the voltage must also be increased in order to keep the same ratio between width and thickness of each bead. Of course, the voltage must be decreased if the submerged arc welding is carried out with a lower amperage. As previously mentioned, Tables 4 and 5 give a useful recommendation for any shop-floor welding.

Conclusions

The toughness properties of 2¼ Cr-1 Mo weld metal after step cooling can be improved to the same level that can be reached for wrought steel, if the following conditions are fulfilled:

1. The amount of the residual elements have to be limited by specifying low maximum values. The influencing elements are phosporus, arsenic, antimony and tin. In the case of manganese, there is an adverse influence if its content is kept as low as in the wrought steel. The recommended range for the weld metal is 0.7–1.0% Mn.

2. The best temperature range for the PWHT is 1250–1300 °F (677–704 °C). The Charpy impact values can be improved by prolonging the time of PWHT.

3. The grain refinement of each single bead is optimized if its thickness is not greater than 2 mm (0.08 in.). In the case of shielded metal arc welding, it is relatively easy to fulfill this requirement in the flat position. Vertical-up welding requires a weaving technique despite the higher heat input. For submerged arc welding, it is necessary to optimize the welding conditions.

4. One of the most important metallurgical actions is to increase the basicity of the electrode covering and of the SAW flux to the highest degree and have it compatible with the weldability requirements.

Under these conditions, at least 40 ft-lb (54 J) can be guaranteed by a safe margin for the weld metal at −20 °F (−29 °C) after step cooling. This is true for both shielded metal arc and submerged arc welding.

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