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CORROSION2001

WHY SHOULD ONE CONSIDER ALLOY 59 (UNS N 06059) FILLER METAL IN MARINE APPLICATIONS?

M. Eckhardt, J. Klöwer
Krupp VDM GmbH
P. O. Box 1820
D - 58778 Werdohl / Germany

D. C. Agarwal
VDM Technologies Corp.
11210 Steeplecrest Drive, Suite 120
Houston, Texas 77065, USA

ABSTRACT

Out of the Ni-base-alloy spectrum for marine applications Ni-Cr-Mo alloys present the highest resistance against local and uniform corrosion.

One alloy of this family is alloy 59, developed in the late 1980s and has been in the market for over 10 years. Due to its nominal chemical composition of 59 % nickel, 23 % chromium, 16 % molybdenum and an iron content below 1 %, alloy 59 has excellent corrosion resistance, evidenced by its high PRE (Pitting Resistance Equivalent) number and confirmed in various investigations and field studies.

The absence of W and Cu in alloy 59 accounts for its high thermal stability. Together with its low sensitivity to hot cracking, alloy 59 shows very good weldability, verified for all technical welding processes by the German TÜV and the American Bureau of Shipping.

Corrosion test results obtained in lab trials in standard test solutions and in natural seawater show that the resistance to pitting corrosion, crevice corrosion and uniform corrosion of joint and overlay weldments is comparable to the behaviour of the base material.

This paper presents an overview of the corrosion resistance and potential applications of alloy 59 as a filler metal for marine industries.

Key words: Alloy 59 UNS N06059, filler metal, nickel alloy, marine, offshore, localized corrosion,uniform corrosion

INTRODUCTION

In marine applications resistance to high localized and uniform corrosion is usually desireable. Seawater can be characterized as a medium with a high chloride content and traces of other halogens at a pH-level of 6 to 8, containing ions of heavy metals such as Cu, Zn, Pb, Fe , ions of alkali metals and sulfur [1]. However, differences in temperature, salinity and marine life create a wide range of different seawater conditions all over the world. Crevices, which in most constructions cannot be avoided (e. g. at flanges) or which are formed by marine life create areas, in which the metal is more sensitive to localized corrosion. Depending on severity of corrosion, the requirements for marine applications are met by specific stainless steels, duplex and super duplex steels as well as Cu-Ni- and Ni-alloys.

Table 1 shows alloys whose behaviour in different corroding media including seawater environments in many investigations was evaluated [2-9]. Out of this group the most versatile alloys with the highest resistance against localized and uniform corrosion as well as stress corrosion cracking are the Ni-Cr-Mo alloys. While the Cr makes these alloys resistant towards oxidizing media, the Mo- and/or W- content favour corrosion resistance in reducing environments. In addition, Mo and W are significant strengthening agents, due to their large atomic sizes.

The development of this alloy group, the so called C-family, started in the nineteen-thirties with alloy C (now obsolete), eventually leading to the work horse alloys such as C-276 and 22. Successful attempts to improve corrosion resistance by increasing the alloying elements like Cr, Mo and/or W have been made. Investigations revealed that corrosion resistance in seawater [10] is suitable to low Fe, high Mo and high Cr containing alloys. A measure of the influence of Cr, Mo and N content on the corrosion behaviour is the pitting resisting equivalent (PRE), i. e. % Cr + 3.3 % Mo + 30 % N.

A development of the late 1980's is alloy 59. By dropping the Fe-content below 1% and increasing the Cr-content to 23 % and the Mo-content to 16 % an alloy was created with the highest PRE of the Ni-Cr-Mo alloys (Table 1). Since this alloy only consists of the four elements Ni, Cr, Mo and a small amount of Fe it is an only ternary alloy within the C-family of alloys.

Ideally, the corrosion resistance of weld metal and heat affected zones should be equivalent to that of the base metal. Extensive studies have been performed to characterize the corrosion resistance of welded nickel base alloys and superaustenitic steels to intergranular and pitting corrosion[12]. In most cases the corrosion resistance was nearly the same for weldments and base material. However, in some cases it is necessary to weld with an overalloyed filler metal in order to meet the corrosion resistance of the base metal.

A cost effective alternative to the application of solid Ni-Cr-Mo base metal is the application of weld cladded material. In this case corrosion resistant weld metal is overlayed on to carbon steel. For economical production highly efficient processes as well as filler metals with a good weldability must be available. After 10 years of application in the CPI, in FGD plants and in offshore service, filler metal 59 has proven effective welding all Ni-Cr-Mo alloys and 6Mo, Duplex and Super Duplex stainless steels[11].

ALLOY 59

Thermal Stability

As already mentioned, alloy 59 is the purest ternary alloy of the C-family, containing only Ni, Cr, Mo and a small amount of Fe. Due to this composition alloy 59 has very good thermal stability which has a positive impact on the weldability compared to other Ni-Cr-Mo alloys (Figure 1). Especially when thicker dimensions must be welded or in overlay welding processes with a high energy input the high thermal stability prevents formation of micro structures sensitive towards intergranular corrosion. The time to start sensitization for alloy C-276 is a few minutes while for alloy 59 it only starts after appr. 2 hours. Recent investigations show that alloy 59 after heat treatments associated with welding, cladding, annealing etc. exhibited the lowest corrosion rates compared to the new C-family alloys 686 and C-2000 in tests acc. to ASTM G-28 A and B[14]. Table 2 presents data of different Ni-Cr-Mo-alloys tested after annealing at 1600 °F (871 °C)[15]. The non-tungsten and non-copper containing alloy 59 did not incure any localized or intergranular attack. The other alloys suffered deep pitting and intergranular attack due to detrimental inter-metallic phases precipitated during the annealing process.

Weldability

It has shown[16, 17] that one criterion for the weldability of super stainless steels and nickel-base alloys is resistance to hot cracking as evaluated in the Modified Varestraint-Test (MVT). In this test the specimens are heated with a TIG burner and bent mechanically as shown in Figure 2. To measure sensitivity of the alloy to hot cracking the total length of the visible surface cracks is measured at a magnification of 25. The results of this test in Figure 3 show that the Ni-Cr-Mo alloys are in the lower part of the graph. With the exception of alloy C-4, alloy 59 shows the lowest sensitivity to hot cracking.

Together with the high thermal stability the good hot cracking behaviour makes alloy 59 suitable for all technical welding processes, such as PAW, GTAW, GTAW-HW, GMAW, MAG, MAG Tandem Welding etc., verified by the German TÜV and by the ABS. Increased requirements for weld bead quality and for more economical welding processes has led to advances in automatic welding processes, especially with GTAW-HW and MAG-Tandem process[18].

However, all weld beads show a heterogenuous cast structure with more or varying degrees of segregation. In the case of the Ni-Cr-Mo alloys, Mo-segregation can lead to selective corrosion of the welding bead. So the aim must be to adjust the welding parameters in a way that suppresses segragation. This can be achieved by keeping the energy as low as possible. High corrosion rates were observed [19] with energy inputs $\geq$ 6 kJ/cm while the mass loss was negligible for weldments which were produced with a heat input $\leq$ 5 kJ/cm. While the weld bead is attacked by selective corrosion, the heat affected zone of the base metal is susceptible to intergranular corrosion. Alloys which are not as thermally stable as alloy 59 exhibit greater intergranular corrosion susceptibility with an increasing heat input.

The heat input, temperature of intermediate layers and diameter of wire electrode and rod electrode have an impact on the corrosion resistance of the weld [11]. The experience of the producers of semi finished products, filler metal producers and of the fabricators should be taken into account. For alloy 59 detailled information about these parameters for all welding processes are given in reference 20.

CORROSION RESISTANCE

Joint Welding

The resistance of alloy 59 base metal to localized and uniform corrosion in marine environments has been reported in several investigations [10, 21, 22]. In reference 23 corrosion resistance of GTAW and PAW weldments were compared to that of the base metal. Critical pitting temperature (CPT) and critical crevice temperature (CCT) were evaluated in Green Death solution and the uniform corrosion was measured after 21 days of exposure in a boiling solution, containing H_2SO_4 and 70,000 ppm Cl^- at a pHvalue of 1. Table 3 shows, that the corrosion resistance of alloy 59 weldments is similar to that of the base metal. Therfore, corrosion resistance in marine environments is also expected to be excellent.

In another investigation [24] the influence of different welding processes on the corrosion resistance of alloy 59 weldments was evaluated. For this purpose Alloy 59 base metal was joint welded with alloy 59 filler metal. The welding processes were GTAW, PAW, MAG and MAG Tandem Welding. Critical pitting temperatures were measured in Green Death solution at a starting temperature of 80 °C which was increased by 5 °C every 24 hours of exposure. The results in Table 4 show that the CPT to some extent is dependent on the welding process. So the best results are obtained by the GTAW and the PAW process. However, the MAG and MAG tandem processes also produce weldments with high corrosion resistance and CPTs of up to 125 °C. Variations within the CPTs of the different welding processes can be attributed to different welding parameters. Table 5 shows results for MAG welding, in which the shape of the weld seam (X seam and V seam) and within the V seam welding the amperage and welding speed were varied. It can be seen that the change of the seam shape from X to V leads to an increase of the CPT of at least 5 °C. The lower resistance to pitting corrosion of the X seam ascribed to the bigger weld bead and a higher heat input. The variation of amperage and welding speed in this trial had no impact, while a higher energy input reduced the CPT of the PAW weldments.

The principle of the GTAW-HW process is presented in Figure 4. In this process the welding wire is preheated at a temperature below the melting point. Higher welding speeds can be achieved and the energy input can be reduced to a minimum. Table 6 presents the localized and uniform corrosion behaviour of GTAW-HW joint welded samples in comparison to the base metal evaluated in Green Death solution and acc. to ASTM G-28A [25]. Like the base metal both welded samples showed a high CPT of >130 °C and a low uniform corrosion rate of 0.92 mm/y. The uniform corrosion rate of the base metal was 0.86 mm/y.

A comparison of the corrosion resistance of various Ni-Cr-Mo alloys is given in Table 7. In this comparison, alloy 59 gave the best performance amongst all the Ni-Cr-Mo alloys tested. Both alloy C-276 and 22 not only had significantly higher corrosion rates than alloy 59 but also suffered crevice corrosion attack [23].

The corrosion behaviour of some cast Ni-based alloys was investigted in [26] to compare different alloys for naval seawater valves. The results show that in quiescent seawater only cast 59 was fully resistant to localized corrosion while cast 625, cast C-276 and cast 22 showed significant crevice attack. In flowing seawater cast alloy 59 and cast C-276 were the only alloys fully resistant, whereas cast 625 and cast 22 showed severe crevice attack. These results seem to be transferable to the behaviour of weldments since the weld beads have a cast micro structure.

Overlay Welding

Extensive crevice corrosion on 6Mo stainless steel flanges in the North Sea were repaired by weld overlaying the flange surfaces with alloy 625 [27]. The corrosion behaviour of several Ni-based alloys was compared to that of 6Mo stainless steels in chlorinated seawater. Weld overlays of different Ni-Cr-Mo alloys and different welding methods were tested for pitting and crevice corrosion resistance. The specimens were tested per ASTM G-48 C (for pitting corrosion) and procedure MTI-2 [28] and SINTEF's test method for crevice corrosion [27]. It has been shown by Garner [29] that the ASTM G-48 C ferric-chloride test provides a conservative prediction of crevice corrosion behaviour in seawater for a wide range of alloys. The SINTEF's test method simulates the start up of a chlorinating plant [27]. The results are shown in Table 8. The best pitting resistance was obtained for alloy 59 overlays with CPTs above 85 °C. The CPT of alloy C-276 was remarkably lower and explained by its high W content which can cause intermetallic precipitation during welding. Compared to 6Mo base material only alloy 59 and alloy 22 showed improved pitting corrosion resistance while alloys C-276, C-4 and 625 had lower CPTs than the base material.

The crevice corrosion behaviour evaluated in tests per MTI-2 procedure showed similar results. Again the CCTs of alloy 59 and 22 were the highest (Table 8). These two alloys were the only ones which showed an advantage of 6Mo base metal while the weld overlays of alloys C-276, C-4 and 625 showed lower CCTs than the base metals and so cannot be considered as an alternative to improving crevice corrosion behaviour of a 6Mo stainless steel flanges in chlorinated seawater.

Essential for the corrosion behaviour of an overlay weldment is prevention of iron dilution of the base metal. For economical reasons high capacity welding processes are required. Both requirements were considered in investigations, described in reference 30. For a two layer weldoverlay of alloy 59 on carbon steel the MAG tandem process was chosen. With the MAG double burner a welding speed of 1.2 m/min at a melting rate of 9.2 kg/h was realized. Figure 5 shows the scheme of this welding process. The quality of the bonding was checked in torsion and bending tests, as presented in Figure 6. In Table 9 the analysis of the filler metal 59 in comparison to the overlay layers is presented. It can be seen that the second layer nearly shows the composition of the filler metal. The sample preparation for corrosion investigations was done by sawing and planing off the carbon steel. The CPTs, evaluated in Green Death solution, are given in Table 10. With a CPT of 115 °C the overlay weldments showed excellent resistance towards pitting corrosion. This behaviour even can be improved to >130 °C by a mechanical treatment of the layer surface, which in this case was carried out by grinding. That means the corrosion resistance of weldoverlayed flange surfaces, which must be ground or milled in order to get a plane surface, is improved by mechanical treatment.

DISCUSSION

The Ni-Cr-Mo alloys were designed for the highly corrosive environments of the CPI, for FGD plants, offshore and similar applications. For evaluating the different alloys and for checking the delivery condition of semi finished products testing methods were developed for testing corrosion resistance in Cl-containing acidic solutions. More severe tests for the Ni-Cr-Mo alloys than the existing tests for the stainless steels were tested, e. g. to ASTM G-28 A and B, ASTM G-48 and in the "Green Death"-solution. Special tests for the applicability in marine environments use natural or artificial seawater (ASTM D1141-90) or similar specifications.

Beside the base metals welded materials are checked under the same conditions. In order to evaluate resistance to crevice corrosion crevice formers are used. In addition, uniform, pitting and crevice corrosion resistance in marine environments are evaluated in open or closed loop piping with flanges, welds etc.

The aim of the test methods mentioned is to evaluate the behaviour of the alloys in the application environment. However, each user must decide, how far the test methods meet the reality of his application and the ranking methods used.

CONCLUSION

Corrosion resistance of alloy 59 in marine applications has been shown to be excellent in a number of investigations. Reasons as to why also alloy 59 filler metal should be considered for marine applications include:

- Due to its good thermal stability and low sensitivity to hot cracking weldability using filler metal 59 is very good.

- The German TÜV and ABS have verified that filler metal 59 is suitable for all technical welding processes, including GTAW-HW and MAG Tandem.
- Weldments of filler metal 59 have the same corrosion resistance as the base metal
- When optimized welding parameters are applied the corrosion behaviour of the welds are nearly independant of the welding process. Detailled information is given in reference 20.
- Weld overlays with alloy 59 exhibits better pitting and crevice corrosion resistance to 6Mo stainless steel than other Ni-Cr-Mo alloys.
- Alloy 59 exhibits very high resitance to crevice corrosion for critical areas in marine applications.

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Table 1
Nominal Compositions of Some Marine Alloys

		Nominal Composition					
Alloy	**Structure**	**Cr**	**Ni**	**Mo**	**Fe**	**Others**	**PRE**
29-4-2	Ferritic	29	2	4	Bal		42
29-4		29		4	Bal		42
904 L	Austenitic	20	25	4.5	Bal	Cu	35
825		22	40	3.2	31	Cu	33
25 Cr	Duplex	25	6	3	Bal	Cu 1.7	35
926	Superaustenitic	21	25	6.5	Bal	Cu 0.9, N 0.2	42
31		27	31	6.5	Bal	Cu 1.2, N 0.2	48
90/10	Copper Alloys		10		1.5	Cu Bal	0
70/30			30		0.1	Cu Bal	0
400	Nickel Alloys		66		1	Cu Bal	0
K-500			66		1	Al 2.7, Cu Bal	0
625	Ni-Cr-Mo Alloys	21	61	9	3	Cb 3.5	51
C-4		16	16		2		69
C-276		16	58	16	5	W 4	69
22		21	57	13	3	W 3	65
59		23	59	16	< 1	Al 0.3	76
686		21	56	16	2	W 4	74
C-2000		23	57	16	2	Cu 1.6	76

Table 2
Thermal Stability per ASTM G-28A and ASTM G-28B after Sensitization for 1 h at 871 °C (1600 °F) [21]

	Corrosion Rate in mpy or mm/y/0.0254				
Medium	**C-276**	**22**	**686**	**C-2000**	**59**
ASTM G-28A	> 500	> 500	872	116	40
ASTM G-28 B	> 500	339	17	> 500	4
Pitting Attack	Severe	Severe	Severe	Severe	None
Intergranular Attack	Severe	Severe	Severe	Severe	None

Table 3
Corrosion Resistance of Alloy 59 Base Metal vs. Weldment [21]

Medium		**Unwelded**	**GTAW**	**PAW**
Green Death	CPT	> 130 °C*	>120 °C	> 115 °C
	CCT	110 °C	110 °C	105 °C
H_2SO_4, 70,000 ppm Cl^-, Boiling, 21 days		0.003 mm/y No Pitting	0.007 mm/y No Pitting	0.003 mm/y No Pitting

* decomposition of the solution

Table 4
Pitting Corrosion Resistance of Alloy 59 Weldments of different Welding Processes [24]

Welding Process	**CPT**
GTAW	120 - 130 °C
PAW	115 - 130 °C
MAG	115 - 125 °C
MAG Tandem	115 - 125 °C

Test Medium: Green Death Solution

Table 5
Pitting Corrosion Resistance of Alloy 59 Weldments of different Welding Processes and Welding Parameters in Green Death Solution [24]

Process	**Seam Shape**	**CPT**
MAG	X	115 °C
MAG	V	125 °C
MAG	V*	120 °C
	Energy Input	**CPT**
PAW	11.3 kJ/cm	> 130 °C
PAW	12.8 kJ/cm	115 °C

* Higher Amperage, Higher Welding Speed

Table 6
Uniform and Pitting Corrosion Resistance of Alloy 59
GTAW-HW Weldments in Comparison to Alloy 59 Base Metal [25]

Sample	CPT (Green Death Solution)	Uniform Corrosion rate (acc. to ASTM G-28A)
GTAW-HW	>130/>130 °C	0.92/0.92 mm/y
Base Metal	>130 °C	0.86 mm/y

Table 7
Corrosion resistance of Various Ni-Cr-Mo alloy Weldments
in a High Chloride, Low pH Medium* [23]

Base Metal	Filler Metal	Corrosion rate mm/y	Pitting Corrosion	Crevice Corrosion
625	625	1.15	No**	No**
C-4	C-4	0.58	No**	No**
C-276	C-276	0.32	No	Yes
22	22	0.44	No	Yes
59	59	0.007	No	No

* 70,000 ppm Cl-, pH 1, Temperature 105 °C, 21 days
** High corrosion rate masks any loclized attack

Table 8
Critical Pitting and Critical Crevice Corrosion Temperatures of some Ni-based alloys,
Overlay Welded by different Welding Processes, in Comparison to 6Mo Stainless Steel
Base Metal [27, 31]

Alloy	Overlay Welding Process	CPT (ASTM G-48 C)	CCT (MTI-2)	CCT (SINTEF)
625	SMAW	45 °C	25 °C	12 °C
625	PAW	90 °C	25 °C	4 °C
59	GTAW	> 85 °C*	85 °C	33 °C
59	SMAW	> 85 °C*	90 °C	38 °C
59	SMAW	> 85 °C*	80 °C	38 °C
C-276	PAW	55 °C	30 °C	28 °C
C-4	SMAW	30 °C	25 °C	8 °C
22	SMAW	> 85 °C*	65 °C	27 °C
6Mo		60 °C	45 °C	30 °C

*decomposition of the solution

Table 9
Analysis of Weld Overlays on Carbon Steel in Comparison to the Analysis of the Filler Metal
Welding Process: MAG Tandem [30]

	Ni	Cr	Mo	Fe	Mn	Si	Al	P	S	C
Filler Metal	R	22.45	15.35	0.35	0.15	0.4	0.15	0.002	0.004	0.004
1st Layer	R	22.05	15.35	1.94	0.15	0.5	0.15	0.002	0.002	0.007
2nd Layer	R	22.45	15.60	0.47	0.15	0.5	0.16	0.002	0.002	0.004

Table 10
CPTs of Overlay Weldments of Alloy 59 on Carbon Steel
Test Medium: Green Death Solution [30]

Treatment	CPT
as welded	115 °C
wet ground, grain # 80	>130 °C

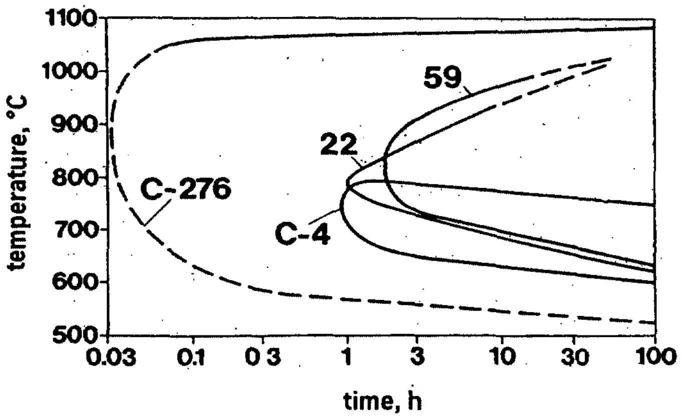

Figure 1: Time-Temperature-Sensitization Diagram of several Ni-Cr-Mo Alloys (13)

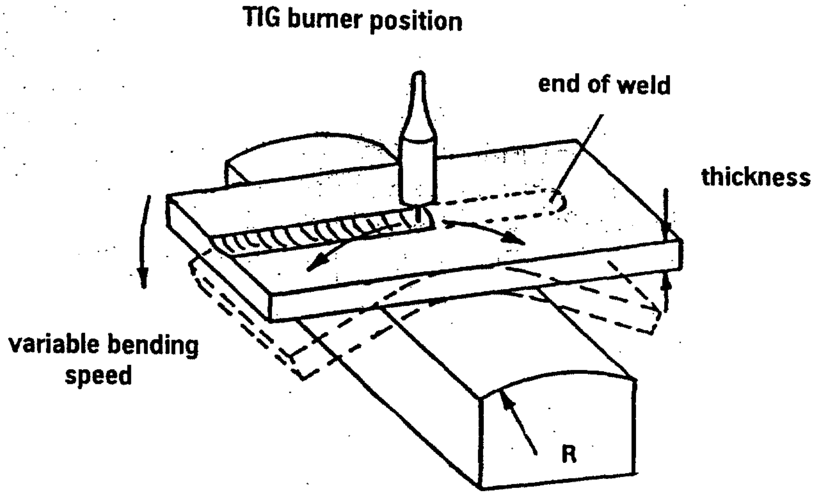

Figure 2: Modified Varestraint-Test (MVT) for the Evaluation of the Hot Cracking behaviour (16)

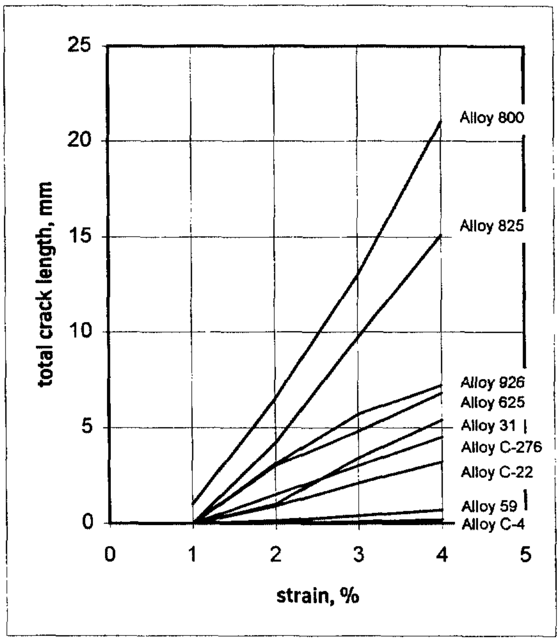

Figure 3: Hot Cracking Bevaviour of different Ni-Cr-Mo Alloys

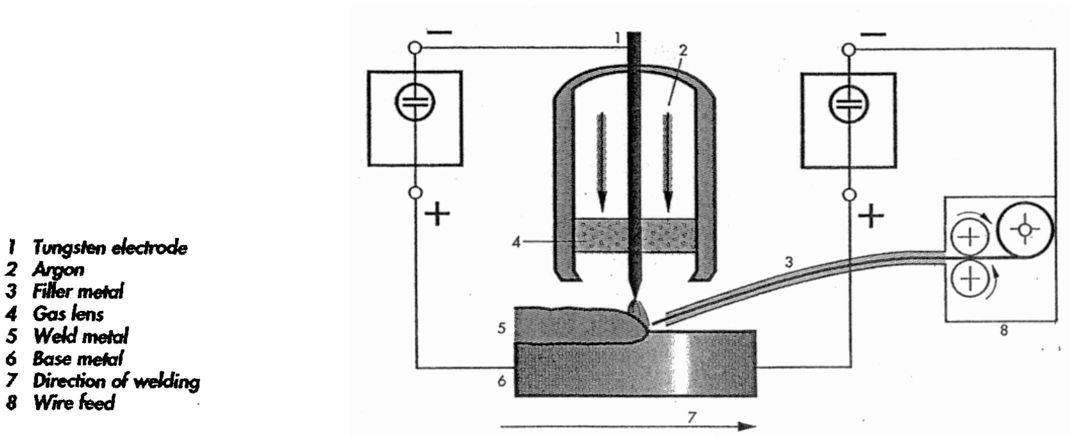

Figure 4: Gas Tungsten-Arc Hot Wire Welding (GTAW-HW)

1 *Wire electrode 1*
2 *Wire electrode 2*
3 *Wire feed rollers*
4 *Shielding gas*
5 *Contact tube*
6 *Gas nozzle*
7 *Base metal*
8 *Direction of welding*

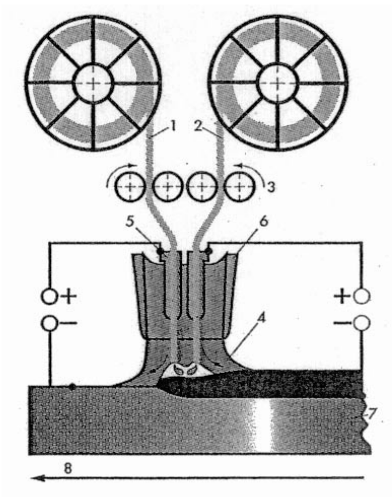

Figure 5: Metal Active Gas Tandem Welding (MAG Tandem Welding)

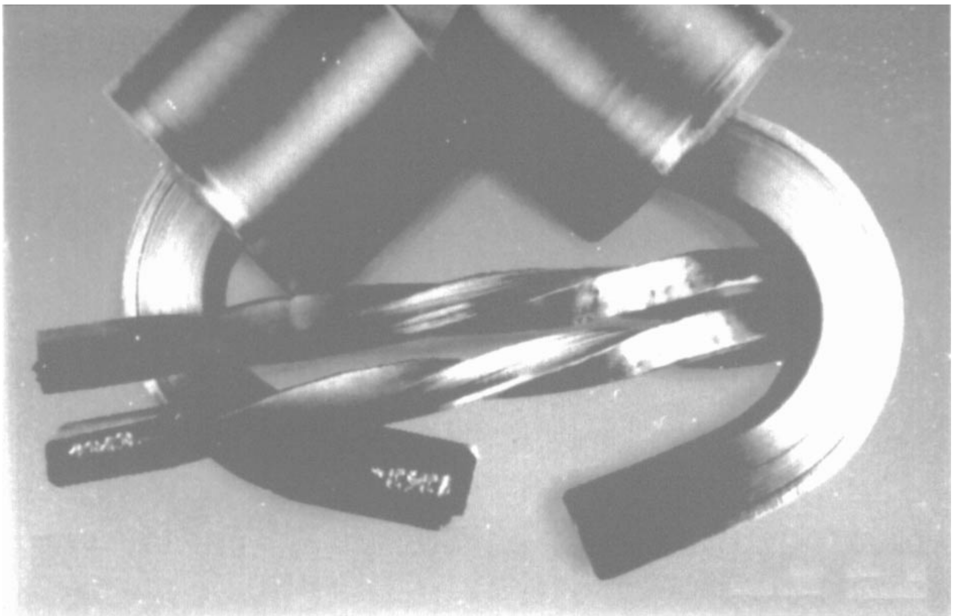

Figure 6: Specimen for Checking the Bonding Quality of Overlay Weldments [29]