CORROSION BEHAVIOUR OF HIGH ALLOYED STAINLESS STEEL WELD METALS, JOINTS AND OVERLAYS IN STANDARDIZED CORROSION TESTS WITH SOME EXAMPLES

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ABSTRACT

As already described earlier, stainless steels can form on their surface a protective, passive film on exposure to a service environment. This passive film, especially its stability and homogeneity, is responsible for the corrosion resistance of these materials. Welding can have a strong impact due to the typical segregated, multiphase weld metal structures and the additional influence of the weld heat cycle. This may result in a lower corrosion resistance of the weld metal compared to the base metal in case of a similar chemical composition. To describe the corrosion behaviour, many different tests have been developed, using different environments, different test temperatures and different test specimen preparation. But due to the variety of parameter settings and test conditions, the corrosion test results are often not comparable. To overcome this problem, standardized corrosion tests were established. Specimen preparation, test solution composition, test duration and temperature setting are defined to allow a "world wide" comparison. This paper gives an overview of which standardized tests are applied in practical use for typical types of material. Additionally some results of weld metal and joint testing are shown from which the influence of different thermal cycles, alloying concepts, surface conditions and shielding gases on the corrosion behaviour can be derived.

IIW-Thesaurus keywords: Corrosion; Intergranular corrosion; Pitting corrosion; Selective corrosion; Corrosion tests; Standards; Rules; Stainless steels; Steels; Austenitic stainless steels; Ferritic stainless steels; Duplex stainless steels; Weld metal; Welded joints; Cladding; Reference lists.

1 INTRODUCTION

The formation of a passive layer on the surface of stainless steels is the key for the excellent corrosion resistance of these steels. But the build-up of this layer is influenced in various ways, by:

– the chemical composition;

– microstructure and the homogeneity of the base material;

- the corrodent and its temperature;
- exposure time;
- corrodent flow conditions;
- different base material combinations.

Besides these basic factors, welding can affect the corrosion behaviour in a detrimental way too.

The weld metal solidifies with a similar segregation behaviour as a casting. This causes a "microstructural chemical inconsistency" within the dendrites and grains. Additionally, the weld metal has in most cases a multiphase microstructure, consisting at least of austenite and delta ferrite.

And also the heat input of the welding process can influence the corrosion resistance by activating precipitation

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processes within the weld metal and heat-affected zone. This leads in further consequence to additional phases in the microstructure and to a depletion of corrosionpreventing elements in the surrounding of the precipitates which enables corrosion attack.

There are a few metallurgical possibilities, like overalloying and stabilising of the weld metal, to overcome these problems. Nevertheless, weld metal and joints can have a different corrosion behaviour compared to the base material, which is in most cases a single phase, austenitic structure, established by a solution heat treatment.

An estimation concerning the success of the welded joint in practical use can be done by corrosion testing. To build up a base for comparison of test results, a few standardized corrosion tests are established, which allow a good description of the corrosion resistance of the material within the tested corrosion system (environment, temperature, time). But it could happen that materials with a bad performance in a standardized test can show a good performance in another environment whereas materials with high corrosion resistance in the standardized test fail. This aspect should be kept in mind when dealing with standardized tests and this makes a material selection from the corrosion point of view more complicated.

As already mentioned, these standardized corrosion tests allow a ranking among different materials and give a hand during corrosion material selection. To establish

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a useful ranking, only a few different types of tests, mainly divided by the applied corrosion mechanism and aggressiveness of the environment are necessary. In many cases, the test results are traced back to the chemical composition of the material. Besides the chemical composition, also a heat treatment, surface conditions of the joint, and shielding or backing gases can influence the corrosion behaviour. Some of these aspects are considered below in various examples.

2 STANDARD CORROSION TEST METHODS FOR WELDED JOINTS AND ALL-WELD METALS

Standard corrosion tests methods which are applied for testing of high alloyed stainless steels are characterized by their main corrosion mechanism:

- intergranular corrosion;
- selective corrosion;
- pitting corrosion.

To activate these different corrosion mechanisms, special environments and test conditions are applied. The common used corrosion tests and further details concerning environment, testing procedure and evaluation are described in various standards. The most important standards are EN ISO 3651-2, ASTM A 262 and ASTM G48.

In Figure 1 and Figure 2 a variety of, in Europe, commonly used stainless steels and applied corrosion tests are shown. In these tables, red dots mark tests which are commonly required, and circles mark tests which are seldom required. Unmarked sections show that the authors have no information about whether the mentioned test is applied for the considered type of base material. These test procedures have been developed

$\left($ regular $\left(\bigcirc\right)$ rare required $\right)$

Figure 1 – Common used corrosion tests for high alloyed steels, part 1

Steel acc. EN 10088-1	Base material No.	IGC-Test	IGC/Selektiv	Pitting corrosion
		ASTM A 262		ASTM G48
		Pract. B "Streicher-Test"	Pract. C "Huey-Test"	Methode A 24 hrs.
X2CrNi19-11	1.4306			
X1CrNiSi18-15-4	1.4361			
X2CrNiMo18-14-3	1.4435			
X1CrNiMoN25-22-2	1.4466			
X2CrNiMoN17-13-5	1.4439			O
X1NiCrMoCu25-20-5	1.4539			
X1NiCrMoCuN25-20-7	1.4529			
X2CrNiMoN22-5-3	1.4462	O	O	
X2CrNiMoN25-7-4	1.4410	\Box	o	
X2CrNiMoCuWN25-7-4	1.4501			

$($ regular $/$ \bigcirc rare required $)$

Figure 2 – Common used corrosion tests for high alloyed steels, part 2

for base materials, but now they are often used for testing of welded joints and weld metals. Especially in case of procedures according to ASTM A 262 Pr. E used for weld metals and joints failures can be caused by mechanical overload and not by corrosion attack what can cause a misleading interpretation of the test results.

It can be seen that, depending on their aggressivity, the tests are restricted to a typical group of stainless steels.

For comparison reasons a cross reference between the European and the American steels is shown in Figure 3.

3 LOCATION OF CORROSION TEST SAMPLES

For a corrosion test different types of test samples from the weld metal or welded joints can be used. In Figure 4 the location of possible test samples is shown in case of a multi-layer all-weld metal, Figure 4 b), and joint specimens of plates and tubes, Figure 4 a).

Due to a different sample extraction between all-weld metal and joints, slight differences in the corrosion test results can be expected. Additionally a strong influence caused by the welding process, the welding procedure, the heat input and the root pass sequence has to be taken into account.

Besides these "welding-related" influences also an additional heat treatment and the surface condition of the sample (ground, pickled, brushed, untreated) have a strong impact on the corrosion resistance.

But also the mechanical tooling during the specimen preparation can influence the results of the corrosion tests. If the cutting tool is not sharpened or the grinding material is too coarse, the local contact pressure between tool and specimen will be increased and the affected surface could be heated up in an unacceptable way. Especially uncontrolled cutting and grinding can cause a rapid oxidation of the surface, in worst cases also precipitation and phase transformation, which can

Figure 3 – Cross reference of different high alloyed steels

lead in further consequence to a reduced corrosion resistance of the specimen.

To enable corrosion testing of high alloyed overlays the un- or low alloyed base materials have to be removed mechanically before testing, otherwise the results of the corrosion test are detrimental because the un- or low alloyed base material has nearly no corrosion resistance. From the remaining high alloyed layer samples have to be worked out, typically with a total surface of at least 10 cm2. If no other specifications are available, the sample surface condition should be finished using abrasive paper. Before testing, a cleaning of the samples in acetone is also recommended.

In Figure 5 a possible sample of an overlay is shown, from which test specimens for the corrosion test can be worked out.

In the special case of a single overlay, established using SMAW, GMAW or FCAW the first welded seam on the un- or low alloyed base material has to be cut off and

Figure 4 – Specimens for corrosion tests of all-weld metal and joints

Figure 5 – High alloyed single overlays on un- and low alloyed base material produced with SMAW, GMAW, FCAW according to IIW-Doc. IX-2029-02

excluded from further corrosion investigations. It has been shown in [5] that the chemical composition of the first seam is quite different compared to the following seams due to changed dilution conditions. If the first seam is incorporated in the test, the corrosion results could be detrimental [6].

4 EXAMPLES FOR RELATIONSHIP BETWEEN MICROSTRUCTURAL CHANGES AND RESULTS OF STANDARDIZED CORROSION TESTS

4.1 Intergranular corrosion tests

4.1.1 EN ISO 3651-2 (DIN 50914)

As already discussed, the corrosion test results depend mainly on the chemical composition (carbon, chromium, molybdenum) and also on the stage of segregation and precipitation of these elements, which is influenced by the thermal history of the component. Corrosion attack can be expected in non-stabilised, carbon rich high alloyed materials after annealing in critical temperature ranges [7]. Due to a Cr-carbide precipitation Cr-depleted zones are formed and an intergranular corrosion attack can occur. From the metallurgical point of view the reduction of the carbon content is a very useful tool to shift the sensitisation curve to longer times. Nevertheless, sensitisation within a critical temperature range will occur.

Due to the high sensitivity of the corrosion test, the sensitisation behaviour during annealing at critical conditions can be shown. In this case intragranular corrosion (IGC) tests can be used to establish Time-Temperature-Sensitisation (TTS)-diagrams for stainless steels (see Figure 6).

The corrosion test procedure of EN ISO 3651-2 also incorporates a bending of the tested specimen to make the IC-cracks more visible under light microscopy. By measuring the crack length also a relation between the depth of the cracks and precipitation status is obvious, indicated in Figure 7.

Besides a reduction of the carbon content to reduce the chromium carbide formation, a further widely used method to prevent sensitisation is in alloying with strong carbide-forming elements like titanium and niobium. But especially in case of consumables the stabilisation with Nb is much better controllable. Due to its strong oxidation tendency, titanium has a high burn-off rate during the metal transfer in the arc. The arc length and the weld current density play thereby also an important role.

Insufficiently stabilised base materials and weld metals can show an intergranular corrosion attack after annealing in the critical temperature range. In Figure 6 the stabilising effect of Nb in weld metals of type E 19 9 Nb with different stabilising ratios Nb/C is shown. The TTS-

Figure 6 – Time-Temperature-Sensitisation (TTS)-diagrams of different Nb-stabilised, high alloyed all-weld metals

Figure 7 – Depth of IGC-attack (schematic) depending on the annealing time at 550 oC

diagrams were established using a reliable number of IGC-tests, in this case according to EN ISO 3651-2 which is close to DIN 50914.

It can clearly be shown that, with increasing Nb/C-ratio, the TTS-curve is shifted to lower temperatures and longer times. For a strong stabilisation, quite high Nb/Cratios are necessary.

Going into detail and taking into account that the allweld metal is more or less a "multi-layer compound" many heat-affected zones (HAZ) exist within the all-weld metal. According to the Cr-carbide precipitation theory, the high-temperature HAZ should be preferred attacked due to the additional heat input with temperatures in the critical range. The "Like a Knife-Line Attack"-picture on the right hand side in Figure 8 confirms this.

On the right hand side of Figure 8 an example for IGC in the HAZ of the base metal is shown, the weld metal is not affected. This could be explained by a better stabilisation of the weld metal and a more beneficial "thermal history". Related to the base material it can be said that, without an additional heat input, the stabilisation is sufficient, but, if there is an additional thermal treatment like welding, IGC can occur in the high temperature HAZ of the base material.

– IGC-test on overlays

This IGC-test method can also be used for testing high alloyed overlays on carbon steel if the requirements for the sample preparation as described before are considered. In [6] test results of single overlays produced with GMAW, FCAW and SMAW using filler metals of type 309L are discussed. So the real weld metal is like a 308-type with different C-content. In the as welded condition of the overlay in almost any case no IGC-attack occurred, independent of the base material, which was expected in the first run. But it must be kept in mind that, due to a possible higher dilution with the carbon-containing base material, which is strongly influenced by the welding process, welding procedure and shielding gas,

Figure 8 – "Knife-Line Attack"; IGC-Test according to DIN 50914

an unexpected higher carbon content in the overlay could exist. Furthermore it has to be considered that carbonrich base materials require a relatively high interpass temperature to prevent hardening effects and this also increases the amount of dilution. In a worst case scenario this could lead to IGC-attack in the HAZ of the welded overlay already in the as welded condition.

The investigations have confirmed also this theory. IGCattack in the single overlay produced with FCAW and 100 % $CO₂$ shielding gas on the carbon-rich (C: 0,45 %) base material was detected (see Figure 9).

4.1.2 ASTM A262 Pr. C. (Huey test)

As stated earlier, this test belongs to the intergranular corrosion tests, but it has to be considered that also some selective corrosion processes take place. As an example the Huey test results on weld metal of E 19 9L are shown. In the as welded condition no IGC according to EN ISO 3651-2 (see also Figure 7) was detected and so the measured weight loss in the Huey test has to be explained by a general corrosion process. After a short term heat treatment $(675 \degree C/1)$ h) the measured weight loss is increased and this is an indication for the start up of sensitisation.

If the weld metal is fully sensitised, for example after a heat treatment at 550 °C/10 h, the measured weight loss increases significantly. In Figure 10 these effects are shown for the as welded metal and different heat-treated weld metals.

Further investigations on Huey-tested specimens have shown that, related to other weld metals, single phase austenitic structures are less sensitive to general corrosion processes initiated by this special test solution compared to austenitic/ferritic-microstructures. But it has also to be mentioned, that also the Cr/Mo-ratio plays thereby an important role. The higher the Cr/Mo-ratio, the less the weight loss in this test. In Figure 11 some examples of tested weld metals after 5×48 hrs testing time are shown. The lowest weight losses are achieved with a single phase austenitic structure with a moderate Cr/Mo-ratio and an austenitic/ferritic-structure with a very high Cr/Mo-ratio.

Figure 10 – Huey-test: Weight loss after different conditions; all-weld metal E 19 9 L

4.2 Pitting corrosion tests

As seen in Figure 1 and Figure 2, highly alloyed stainless steels are often tested using a severe test to determine the pitting corrosion resistance. They are often tested in Ferric (III)-chloride solutions, but also the measurement of current density-potential curves can be used.

Based on the results of these tests, the Pitting Resistant Equivalent (PRE) or the Critical Pitting Temperature (CPT) can be derived, which are related in further consequence to the chemical composition of the base metal.

Figure 11 – Huey-test: Weight loss of different all-weld metals

base material, shielding gas: 100 % CO₂

b) No cracks in single overlays on low carbon/low alloyed steels

In ASTM G 48-97 an approach for the determination of the CPT in sour ferric-chloride-solution is defined:

CPT $[°C] = (2.5 \times Cr %) + (7.6 \times Mo %) + (31.9 \times N %)$ -41.0

In other literature different formulas for describing PRE in ferric-chloride-solution can be found:

PRE (1) =
$$
(2,5 \times Cr \%) + (7,6 \times Mo \%) + (31,9 \times N \%)
$$

PRE (2) = $(Cr \%) + (3,3 \times Mo \%)$

PRE (3)= (Cr %) + (3,3 \times Mo %) + ((16 [Duplex] or

30 [Austenite] $) \times N$ %)

From these PREs also a CPT can be derived. Various experiments have shown that a linear relation between PRE and CPT over a wide range exists. Knowing this correlation, the CPT can be estimated by the chemical composition of the material [11].

Most experience exists in the determination of CPT and PRE especially for solution-treated base metals. In this case no, or only small microstructural segregations effects are expected.

In the case of a non-solution treated weld metal, but also in case of cast material, solidification-related segregation especially of molybdenum, but also of chromium occurs within the microstructure. Investigations have shown that the Mo_{max}/Mo_{min} -ratio caused by this "natural" segregation for a variety of high-alloyed Mo-containing stainless steels is about 1,4 [2]. In other words, the minimal Mo-value in the weld metal is about 20- 25 % less than the nominal value due to this alloyingelement specific, microstructural segregation. Because of the nature of this segregation within the dendrites it can only be influenced by an additional solution heat treatment. From this point of view, it is clear that weld metals must have a lower measured CPT, compared to the PRE or CPT calculated from their chemical analysis based on formulas established from solution treated base metals. Filler metal producers take this effect already into account by "overalloying" the filler metal

with Mo, compared to the base material, to guarantee the same pitting resistance in the weld metal as in the base material.

Furthermore it must be considered, that beside the chemical composition also the surface condition (roughness, oxide layers) and inhomogeneous microstructures have a strong impact on the pitting corrosion resistance [1, 8-11].

– ASTM G48 Method A for standard austenitic and ferritic-austenitic steels

This test procedure plays a dominant role in determination of the pitting corrosion behaviour of stainless steels [12]. The aim of this test is the determination of the critical temperature, at which pitting occurs. In this standard a test duration of 72 hours is recommended, but especially in weld metal testing, a test duration of 24 hours is widely used. As many investigations have shown, this deviation from the specified test procedure has a negligible influence on the achieved results.

As mentioned earlier, corrosion effects are very sensitive to variations in the chemical composition and surface condition but also to different corrodents and temperatures. That is why these test results prefer to be used for a ranking of materials under these special corrosion conditions. Conclusions from this test concerning the corrosion resistance in other environments are not practicable.

The influence of dilution and weld heat inputs on corrosion test results are often investigated. But in case of welded joints the single information of the first pit appearance within the sample or the total amount of the measured weight loss is not sufficient.

To demonstrate this, an example of a tested joint in Figure 12 is shown. The base material was of type AISI 316L (ASTM G48 Method A is usually not used for testing such "low alloyed austenitics"). For a better visualization the pits are plotted in a geometric development

Figure 12 – Pitting test results on welded base metal 1.4404 (AISI 316L): Influence of different backing gases and pickling

of the joint. It can clearly be seen, that the pitting behaviour on nearly each side of this geometric development is different. Additionally the test temperature (22 \circ C vs. 25 \circ C) and the surface condition (as welded vs. pickling) play an important role.

Furthermore the influence of different backing gases was studied in this example. And due to this graphic visualization, the expected benefits of the $N₂ + 10$ % H₂ compared to the Ar backing, in case of the root pass, is obvious.

In the above discussed example a lot of information can be withdrawn from this corrosion test and from this kind of test report. Nevertheless it must be stated that this kind of report is very time-consuming and could not be used for specifications. In this case an actual measured value, the measured "weight loss" is often required. But the most important information is, where on the specimen pitting is present. So the weight-loss has always to be discussed.

An approach to describe the influence of different shielding and backing gases using actual measured weight losses of a joint is shown in Figure 13 in case of a duplex stainless steel (UNS S 31803). To figure out the influence of shielding and backing gases, it is additionally marked, where the pitting occurred. From the practical point of view the shift of about 10 \degree C in the CPT caused by optimisation of the shielding and backing gases is a very interesting possibility.

Although useful information regarding different influences on the pitting resistance can be generated, it is shown in the previous examples that there is a need for quantification of the pitting corrosion resistance, especially for material specification. In this case the determination of the CPT is not sufficient, only the measured weight loss can be taken into account. But as shown in Figure 14 for fully austenitic all-weld metals there is a measurable weight loss independent of pitting corrosion effects and e.g. a good example for a ranking. Once pit-

Figure 14 – Pitting test results according to ASTM G 48/Method A (24 hrs); comparison of fully austenitic weld metals

ting occurs, the measured weight loss increases rapidly. It can also be seen in Figure 14 that this increase is not linear, so that a mathematical extrapolation of a "measurable" critical pitting temperature based on two real measured weight losses is not allowable.

In a further example the influence of different gases (shielding, backing) and different surface conditions in case of a super duplex stainless steel (SDSS) is shown in Figure 15. Compared to the as welded condition brushed and pickled joints are much more resistant and, as expected, nitrogen in the shielding (3 %) and backing gas has a beneficial influence [13].

As an additional effect it can also be seen from this diagram that, due to the standardization of the test method, results of different labs (values from the steel mill; own investigations) are in good accordance and can be compared.

From the above discussed examples it is obvious that the results of this test method can be strongly influenced and the definition of a measured value out of this test for a technical specification as a go/no go-criterion is very difficult.

Figure 13 – Pitting test results according to ASTM G 48/Method A (24 hrs); weight loss depending on shielding and backing gas

Figure 15 – Pitting resistance of various welds and conditions of the SDSS 1.4410 (UNS S32750)

That is why in practical use many different requirements for the corrosion resistance have been established. This should be pointed out in case of the duplex stainless steel (1.4462; UNS S 31803). But these different specifications are not so simple to fulfil due to the need of different welding recommendations (see Figure 16).

– PC-tests on overlays

In case of overlay-testing, additional care has to be taken in preparation of the samples (the base metal has to be fully removed, otherwise the measured weight loss is wrong) and the effects of dilution with the base metal or prior welded layers has to be taken into account. As described in [6] especially for single overlays of type 308L, due to the dilution effects, the chemical composition of the overlay is more or less "lean" compared to the composition of the pure filler and this corrosion test is often too strong. In such a case the PC-test is only informative as the results of ASTM G 48-97, Method A in [6] point out. Although the samples failed under the test conditions at 22 °C, a relationship between the number of detected pits and the measured weight loss was found (see Figure 17).

The measured weight loss in Figure 17 was reasonable, but the detected pinholes on the surface were very tiny. A cross section through a pinhole pointed out that below the surface a severe corrosion attack often took place.

Figure 16 – Different requirements regarding pitting corrosion results of DSS 1.4462

This explains the measured weight loss although only a few tiny pits were detected on the surface $-$ a typical form of covered pitting corrosion (see Figure 18). In this picture the white high alloyed overlay is embedded in a homogeneous dark grey coloured plastic (bottom of the picture). The pinhole is on the right side down and the irregular grey shaded pit itself has a depth of about 700 μm and an extension of about 1 500 μm.

Figure 17 – Relationship between counted pits and measured weight loss [g/m2h] at 22 oC test temperature [6]

Figure 18 – Severe covered pitting corrosion on overlay [6]

5 CONCLUSION

In practical use, only some corrosion tests are established and standardized. Therefore two main reasons are responsible: the strength of a test should go in line with the corrosion resistance of the material and the need for a "world-wide" reproducibility of the test results. But due to the complexity of the corrosion process, which is influenced by the chemical composition, microstructure, precipitation behaviour and surface condition, a large set of requirements are defined, which makes a comparison of the achieved test results in general more complicated.

Besides checking against specifications, also the influence of different shielding and backing gases, surface conditions and various heat treatments on the corrosion resistance of joints and weld metals can clearly be shown with these standardized corrosion tests. Nevertheless in most cases the corrosion resistance of the weld is lower due to the cast-like, segregated microstructure compared to the base metal, which is mostly solution heat treated.

Special care has to be taken in corrosion testing of overlays. The low alloyed base material has to be removed carefully. Otherwise completely wrong test results would be achieved. Different base materials combined with different amounts of dilution, caused by the applied cladding technology (welding process and procedure, shielding gas, preheat and interpass temperature) can influence the corrosion test results.

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