NEW RESULTS CONCERNING THE INFLUENCE OF HEAT TINTS DURING WELDING ON THE CORROSION RESISTANCE OF STAINLESS STEELS

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ABSTRACT

High alloyed stainless steels stand out for a high corrosion resistance due to a protective passive layer which is formed when the content of chromium exceeds 13%. When welding these steels, heat tints arise in the area of the weldment. They may occur from faint yellow to intensive blue in the spectrum depending on the applied welding process and the quality of the backing gas used. Due to their structures, they partly drastically reduce the corrosion resistance of stainless steels so that they may lead to damages of the technical application of welded components. In the following the pitting resistance by different backing gases and the chemical composition of the stainless steel itself are described.

KEYWORDS

stainless steels, heat tints, pitting corrosion, pitting resistance, oxidation, backing, welding

1. Introduction

The main reason for the existence of the stainless steels is their resistance to corrosion. The corrosion resistance and mechanical properties vary over a broad range, so that these steels are often used for pipes and equipment in agressive media or environments. Further processing and in particular welding has to be done carefully. A countless variety of instructions and guidelines exist, which allows high qualitive and reproducible weldments as required. Admittedly minor carelessness lead to inadequate weldments and to strong surface oxidations, which further lead to corrosion damages in the area of the weldment. For no other material category so many references, clues, rules and research-activity are to be found, with the purpose of assuring the handling of stainless steels.

The pitting resistance of stainless steels

The corrosion resistence of stainless steels is based on the spontaneous formation of passive layers when the steel contains at least 13 % of chromium. When storing stainless steels in oxidic surroundings or at atmospheric conditions these passive layers are built homogeneously and protect the underlying base material against corrosive solutions. Passive layers have a thickness of approximently 2 to 10 nm, are made up of chrome oxides and reduce the corrosion rate to a minimum. Figure 1 indicates a typical anodic dissolution behavior of an active-passive metal. Up to the primary passivation potential ε_{pas} and the assigned critical anodic current density for passivity i_{pas} the metal is in the active state. Above the primary passivation potential ε_{pas} the current density drops and keeps a constant low level above the flade potential ε_F. After the passive state, where the current density is diminutive for a wide area, follows the transpassive state. This state is characterised by an exponential increase of the current density above the breakdown potential ε_D, where the metal is dissolved rapidly.

If the surrounding media contain chlorides, the metal passes at minor potentials, then named pitting potential ε_L, over into the transpassive state. The pitting potentials have minor amounts the more chlorides [Cl^-] the media contain, see Figure 1. The chlorides themselves are not involved in dissolving the passive layer, but they operate as a catalyst and form complex transitions, which are better dissoluble than the metal oxide. The stability of the passive layer is disturbed and local corrosion processes appear. Inhomogeneity in the surface such as segregations, inclusions or violations of the passive layer, for example if heat tints occur, operate as initiators for local corrosion.

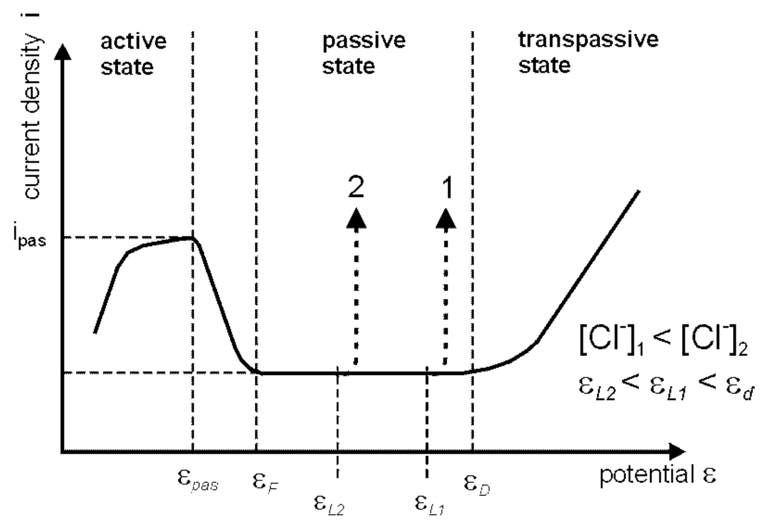

Figure 1: corrosion characteristic of an active-passive metal as a function of electrode potential[1]
ε_{pas}: primary passivation potential; ε_F: Flade potential; ε_L: pitting potential;
ε_D: breakdown potential; i_{pas}: current density for passivity

The corrosion resistance of a stainless steel depends on the stretch and position of the passive potential range and the value of the current density i_{pas} when the material is in the passive state. These are based on the concentration of the alloying elements. Chromium, nickel and molybdenum reduce the current density when the material is in the passive state in a way that a strong passive layer is built in less oxidic environments. Additionally the chromium and nickel reduce the primary passivation potential ε_{pas}. The varying influence of the alloying elements on the pitting resistance of the metal is obvious when using the pitting resistance equivalent (PRE) [2].

There exists a linear correlation for stainless steels between pitting resistance, which can be measured by the pitting potential or by the critical pitting temperature, and the PRE, which only depends on the chemical composition of the examined metal, as shown in figure 2.

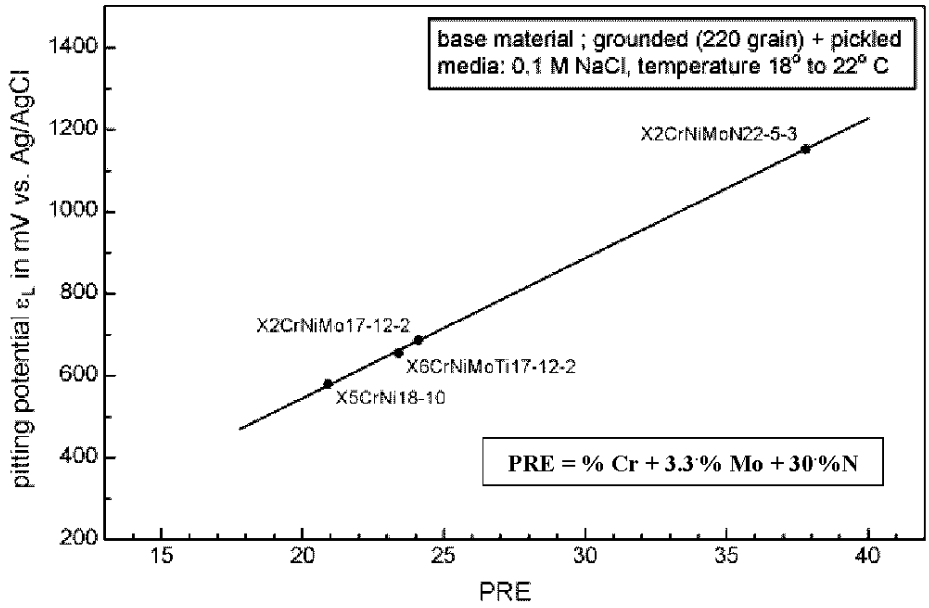

Figure 2: correlation between PRE and pitting potential ε_L of examined materials [6]

Arrangements to avoid heat tints

Supreme purpose is always to avoid heat tints by means of all available technical instruments and personal ability in the first place. This is relevant if the boundary conditions of the later use are inadequately known. Careful process engineering and accurate handling during the welding process are more cost-effective, than reworking or removing heat tints by pickling or grinding. Heat tints can be avoided by a clean preparation of the joint, use of suitable flexible tubes, selecting backing gases with a minimum of remaining oxygen content, compliance with the necessary rinse times and reducing the heat input during welding.

If unforeseen interruptions during the welding process and therefore heat tints have occurred, they have to be removed, when the component with heat tints is unable to resist in the corrosive environment. There exist numerous publications, work instructions and guidelines that describe different techniques of removing heat tints. The more gently the after-treatment is, the better is the achieved corrosion resistance.

Best corrosion resistance is achieved by pickling. Figure 3 shows that nearly the corrosion resistance of the base material can be obtained by using a suitable pickling solution, just as no better resistance is performed, if the pickling solution is not able to remove the heat tints completely. Brushing or rough grinding should be avoided generally if the component is exposed to corrosive environments. It is demanded to match the after-treatment to the boundary conditions for later use.

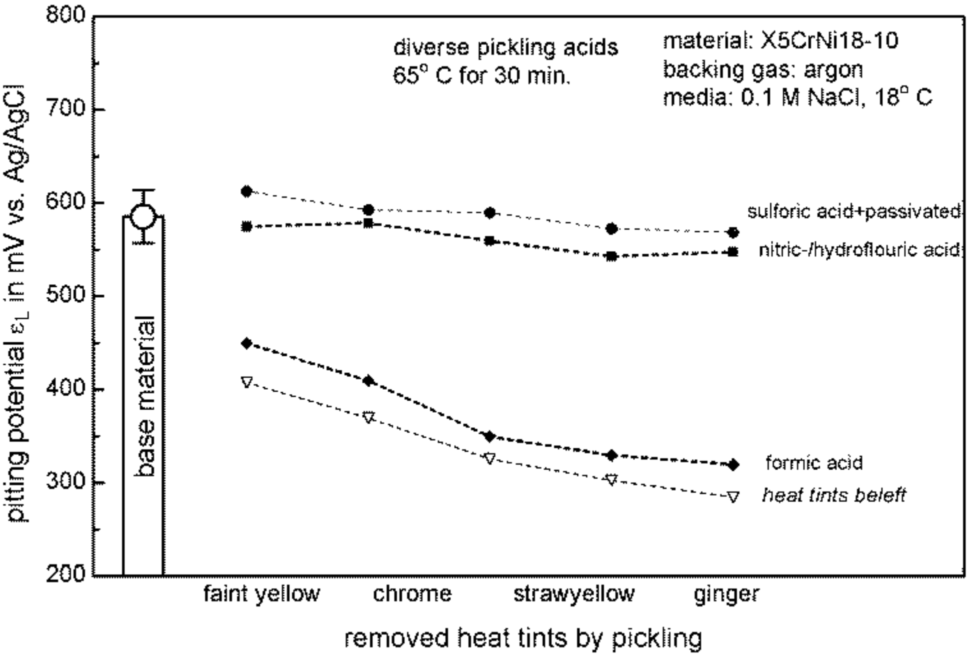

Figure 3: effects of different pickling soltions on heat tinted test specimen

The effects of heat tints as an initiator for pitting corrosion are known and important for the functional integrity of the total device. Different evaluations exist in norms and regulations to value the different heat tints, its effect on the corrosion resistance and to define them. In some norms and regulations these evaluations contradict each other [3, 4]. Our own examinations lead to the result, that there are distinctive differences in the surface structure and therefore in the corrosion resistance between faint yellow and, for example, red heat tints.

While faint yellow heat tints have a slightly reduced chromium amount in the outermost layer compared to the passive layer, the red heat tints have principally iron in the surface layer [5]. Thus the different corrosion resistance of a faint yellow heat tint, which is equal to the base material, or a red heat tint, with its extremely bad corrosion resistance, is explainable. Experiments within this research project [6] lead to statements as to which faint yellow heats tints can be tolerated in known corrosive environments and which have to be entirely removed to guarantee the operativeness of the device.

2. Experimental methods

Materials and the effect of heat tints on the corrosion resistance of stainless steels

Stainless steels need a special authorization for their use in a regulated installation or building site, as for example the authorization Z-30.3-6 of the German institute for building techniques in Berlin [7]. Such authorizations exist for the X5CrNi18-10 and for the X5CrNiMoTi17-12-2, which is stabilised with titanium. Because the pitting resistance of the weldment with heat tints obviously depends on the chemical composition of the alloy, four different materials with greatly diverging pitting resistant equivalents (PRE=%Cr+3.3%Mo+X%N; X=0 bis 30) were selected [8]:

The X5CrNi18-10 and the X5CrNiMoTi17-12-2 are often used for pipes in drinks installations. The X2CrNiMoN22-5-3 as a representative of the duplex steels with a ferritic-austenitic structure and a high corrosion resistance linked with improved mechanical strength was chosen and the X2CrNiMo17-12-2 as aquivalent for the X5CrNiMoTi17-12-2 with less carbon and the increasing use of molybdenum steels was taken into account.

Examining the different base materials all steels show the known linear correlation for stainless steels between pitting resistance and PRE, which is helpful and often used for the selection of a stainless steel for technical equipment. Other significant influencing factors on the pitting resistance of stainless steels are temperature, pH-value and chloridic content of the aggresive media. It is known and has been published accordingly [9] that a linearity exsists between these influencing factors and the pitting potential.

Backing gases

The different materials were grounded, pickled and air-stored to passivate. TIG-dummy weldments were made, whereas the root side which has to be examined was shielded with different backing gases, that are commonly used in technical processes for stainless steels. Argon and nitrogen are particulary suitable to reduce heat tints. But it is possible that faint yellow heat tints may occur, because standard qualities of argon and nitrogen include a remaining oxygen amount of approximately 100 vpm (volume per million) or more. Nitrogen with additions of up to 10 % hydrogen is a well-priced standard backing gas, which can be used for austenitic stainless steels and nowadays even for duplex steels [10].

Table 1: parameter of measurements

examined materials	X5CrNi18-10 - X6CrNiMoTi17-12-2 X2CrNiMo17-12-2 - X2CrNiMoN22-5-3
preparation of the material	grounded (220 grain), pickled in nitric-/hydroflouric acid (65 °C for 30 min.), airpassivated
welding parameter	TIG-process, feed rate: 25 cm/min, energy input: E = 2.35 kJ/cm, backing gas flow rate: 3-5 l/min
used backing gases	Argon 5.0 - Nitrogen 5.0 - Ar + 10 % H_2 - N_2 + 10 % H_2
measuring the pitting potential	quasi-static polarisation circuit; media: 0.1 M NaCl room temp., rinse thoroughly with O_2; reference electrode: Ag/AgCl

The use of argon as backing gas leads to a well developed root side, but argon is unable to displace the entire remaining oxygen, which is adsorbed on the surface. Argon with additions of 6.5 to 10 % hydrogen leads to a well developed root, too, and is often used for austenitic stainless steels. In present examinations Ar + 10 % H_2 was used. To produce specific heat tints in different shades of yellow defined amounts of oxygen were added into the backing gases mentioned above.

The influence of the remaining oxygen is of particular importance from the technical point of view, because an ideal backing of the weldments can often not be guaranteed during fabrication and on-field production. As a result different shades of yellow heat tints may occur near the welded seam. Backing gases with specific additions of 0, 25, 50, 75, 100 vpm O_2 for argon or nitrogen and 0, 100, 200, 300 vpm O_2 for Ar + 10 % H_2 and N_2 + 10 % H_2 were used. Different shades of yellow from uncolored to ginger were created.

The pitting potential was measured for all welded specimens by using a quasi-static polarisation circuit. At room temperature an aqueous solution of 0.1 M NaCl was used. The results gained in these experiments can be transferred and easily compared with former results of comparable materials, where results exist for different chloridic concentrations and different temperatures [9]. A summary of examined materials, welding parameter, used backing gases and the way of measuring the pitting potential is given in table 1.

3. Experimental results

Influence of oxygen content and composition of the backing gas on the pitting resistance of heat tints

In international norms and regulations a total removal of these faint yellow heat tints is required if the weldment is exposed to corrosive environments [3, 4]. Despite the use of backing gases the welding process leads to heat tints in the area of the heat-affected zone and the seam itself, depending on the content of the remaining oxygen. When the backing gas has approximately 0 vpm of oxygen the heat-tinted surface occurs as a faint yellow, but the shade of the heat tints increases the more oxygen remains in the backing gas, Figure 4.

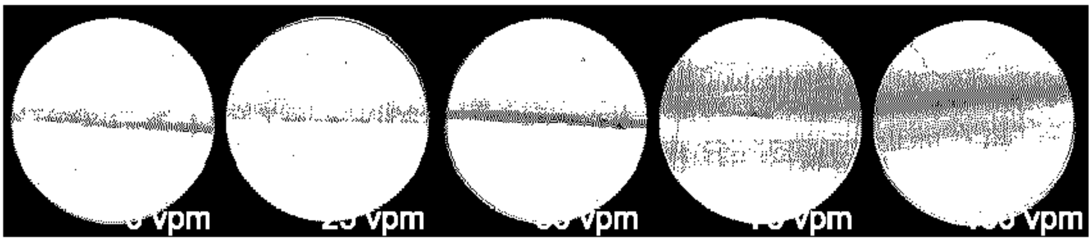

Figure 4: occurring heat tints, material X2CrNiMo17-12-2, backing gas: nitrogen, oxygen content as specified

Using nitrogen as backing gas for materials which are stabilized with titanium in the range of the welded seam titan nitrides are separated. The welded seam with the titan nitrides shines yellow, but it has no effect on the pitting resticance, contrary to the heat tints. With the vpm-amount of the oxygen that are used in these examinations no validation of pitting resistance in practice is possible. Here dummy-welds in laboratory conditions were made. A more useful possibility to estimate the pitting resistence of a weld is to value the heat tint itself. For these examinations a correlation between oxygen amount and occurring heat tint is possible, tables No. 2 and 3 [6].

Table 2: correlation between heat tints and oxygen amount using argon and nitrogen

	Ar and N_2
0 vpm	faint yellow
25 vpm	chrome
50 vpm	straw yellow
75 vpm	gold yellow
100 vpm	ginger

Table 3: correlation between heat tints and oxygen amount using argon/hydrogen and nitrogen/hydrogen

	Ar+10 %H_2 and N_2**+10 %H_2**
0 vpm	uncolored
100 vpm	faint yellow
200 vpm	straw to gold yellow
300 vpm	ginger

With increasing shades of the heat tints the pitting resistance of the material is decreasing, Figure 5. The resistance of all materials, in this figure exemplary for the X2CrNiMo17-12-2, drops with the increasing amount of oxygen in the backing gas. Otherwise an influence of the different backing gases on the pitting resistance is determined. The most utilised backing gas for welding stainless steels is argon. Due to its inert characteristic, argon has no ability of displacing the entire remaining oxygen, humidity or carbondioxide. Consequently backing the weldment with argon always leads to faint yellow heat tints even with accurate root side shielding. Therefore welded samples, where argon was used as backing gas, have the least pitting resistance compared with the other backing gases used. Much better pitting resistance is realised using, for example, nitrogen as backing gas.

In examinations of heat tints with Auger-electron spectroscopy an enrichment of nitrogen in the surface up to 75 nm was verified [11] when welded with the backing gas nitrogen. These surface layers enriched with nitrogen have a significant effect on the corrosion resistance, because the initiation of pits is inhibited. The nitrogen enrichment compensates the chromium depletion in the surface layers, and therefore the nitrogen is considered with the coefficiant up to 30 in the calculation of the PRE. The use of the Nitrogen as well as backing gases with a content of hydrogen cause a better pitting restistance. At temperatures that appear during welding the hydrogen reacts with the existing amount of oxygen and turns to water. No other oxydation is possible and the surface shows no heat tints – it is uncolored. A comparison between heat tints that occur during welding with argon on the one hand and on the other hand Ar + 10 %H_2 shows, that similar yellow heat tints are generated, only with higher contents of oxygen, when using Ar + H_2 as backing gases.

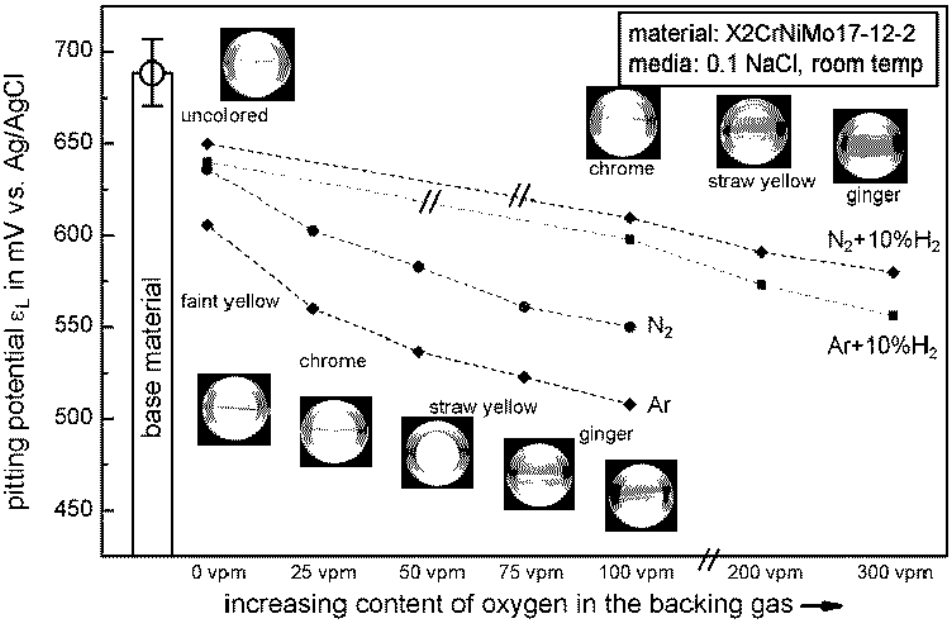

Figure 5: pitting potentials of samples using the X2CrNiMo17-12-2, TIG-dummy-welded with assigned backing gases versus occurred heat tints [6]

Influence of material composition on the pitting resistance of heat tints

If the different base materials are compared to each other, the pitting potential behaves equally for all materials in dependence of the oxide layer. Figure 6 shows these correlations for the different stainless steels X5CrNi18-10, X5CrNiMoTi17-12-2 and X2CrNiMo17-12-2 where nitrogen was used as backing gas.

The graph showing pitting potential versus color intensity of the heat tints shows no distinctive minimum, but decreases continously. The less the PRE of the material is the stronger is the loss of pitting restistence due to faint yellow heat tints. Admittedly the pitting resistance itself depends on the chemical composition of the base material.

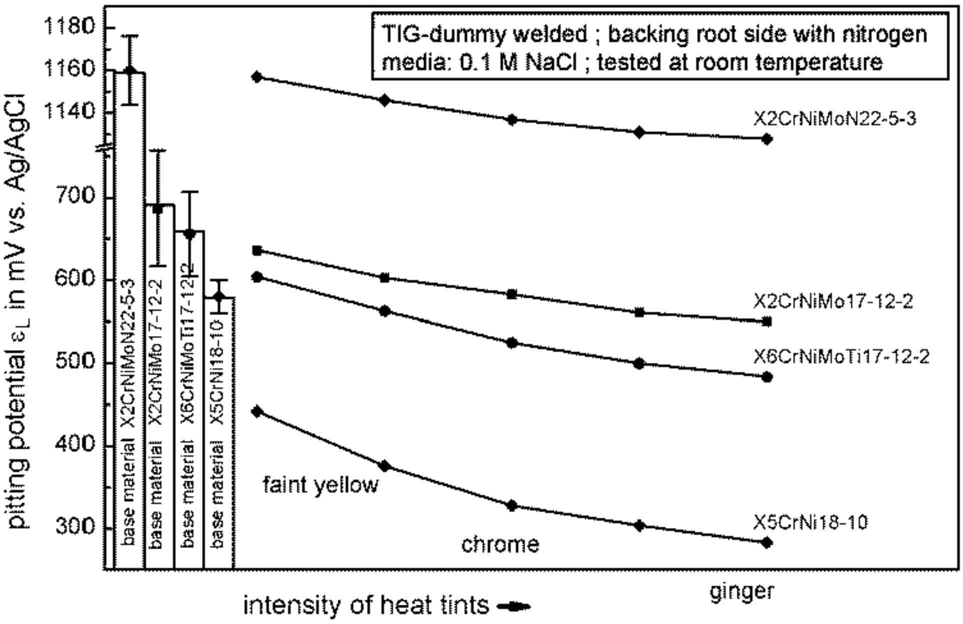

Figure 6: pitting potential versus color intensity of heat tint, backing gas nitrogen, TIG-dummy welded [6]

4. Conclusion

The fundamental question is „Which yellow heat tints can be tolerated under known corrosive environments or are seams without any heat tints to be demanded?". Therefore an exact differentiation between the different shades of yellow, for example faint yellow or strawyellow heat tints, is necessary. Faint yellow heat tints have nearly no effect on the pitting resistence as shown by available results [5, 6, 11]. The difference in pitting resistence between base material and heat tints with brown colors is more severe.

At any time engineering researches allow a differentiation between critical and noncritical heat tints by measuring the thickness of these oxide layers and surface analysis with e.g. Auger-electron spectroscopy or electron microprobe analysis. These methods fail when field estimation concerning the intensity of heat tints has to be done. An easy method has to be generated which helps to estimate present heat tints in practice. An easy color classification of present heat tints could indirectly be done by measuring the amount of oxygen in the backing gas during the welding process. This procedure can be applied to examine welds whose root sides are difficult to access visually. For weldments which are accessible can be visually expertised and similar samples with known heat input, surface condition and backing gases can be created and tested.

In spite of all the results concerning the use of stainless steels in present or former work, it has to be taken into account, that the effect of heat tints on the resistence of welded structures is mostly unclear. Heat tints and other defects made before, during and after the welding interfere with the resistance of the entire structure. To transfer the results a plain graphical presentation is needed. One possibility is the correlation between the pitting potential of each material and its PRE, and indicating the loss of resistance due to heat tints by arrows. Figure 7 shows this chart for the examined materials, where argon was used as backing gas and strawyellow heat tints occur. If heat tints cannot be avoided and using argon as backing gas, a welded X2CrNiMo17-12-2 has a pitting resistance which is worse than the resistence of X5CrNiMoTi17-12-2 (non-welded base material), but the resistance is better than the non-welded base material of the X5CrNi18-10. Thus the user is given a support tool for material selection depending on the application.

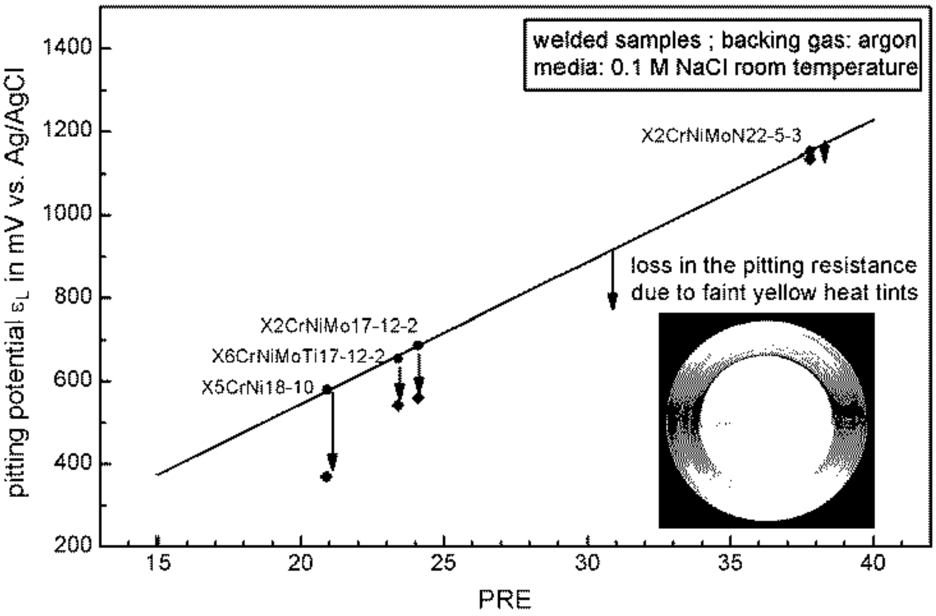

Figure 7. loss in the pitting resistance of examined samples due to straw yellow heat tints [6]

The loss in pitting resistance seems serious, but the aqueous solution has a large chloridic content of about 0.35 weight-%, which is severe referring to contents that can appear in cooling or drinking water. A known logarithmic dependency between pitting potential and chloridic content allows to transfer these results to media with less chloridic quantity. The loss in pitting resistance is therefore less distinct.

The faint yellow heat tints, that occur with the use of backing gases, resist less aggressive media such as drinking water. Slight amounts of remaining oxygen in the backing gas lead to faint yellow heat tints, which barely reduce the pitting resistance of the welded material. It must be taken into consideration that the corrosion resistance of a heat affecting zone with heat tints is characteristic of the whole system. It depends on the base material, the welding process and mostly on the aggressiveness of the media. Using backing gases with higher quality, which solely lead to faint yellow heat tints, a subsequent pickling of the surface can be skipped. Faint yellow heat tints have no effect on the pitting resistance in some cases. But the question as to whether heat tints have to be pickled or can be retained on the surface so that the pitting resistence of the whole system is guaranteed is to be answered individually in most cases.

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