

CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF TIG AND A-TIG WELDED JOINTS OF LEAN DUPLEX STAINLESS STEEL S82441 / 1.4662

This paper presents results of pitting corrosion resistance of TIG (autogenous and with filler metal) and A-TIG welded lean duplex stainless steel S82441/1.4662 evaluated according to ASTM G48 method, where autogenous TIG welding process was applied using different amounts of heat input and shielding gases like pure Ar and Ar+N₂ and Ar+He mixtures. The results of pitting corrosion resistance of the welded joints of lean duplex stainless steel S82441 were studied in as weld conditions and after different mechanical surface finish treatments. The results of the critical pitting temperature (CPT) determined according to ASTM G48 at temperatures of 15, 25 and 35°C were presented. Three different surface treatment after welding were applied: etching, milling, brushing + etching. The influence of post weld surface treatment was studied in respect to the pitting corrosion resistance, basing on CPT temperature.

Research on TIG welding of lean duplex stainless steel S82441/1.4662 showed a clear influence of the applied shielding gas mixtures, where the addition of 5 to 15% N₂ to Ar virtually no effect on the level of resistance to pitting corrosion, only 5% N₂ addition has a positive effect, while use of a mixture of 50% Ar + 50% He compared with welding at 100% Ar atmosphere, can significantly reduce the resistance to pitting corrosion. Definite good results were obtained during TIG welding with the participation of activation flux (A-TIG). The weld surface of lean duplex stainless S82441/1.4662 obtained in A-TIG welding without the addition of filler metal has a much lower tendency to pitting corrosion than traditional welds made by TIG method. Pitting corrosion resistance of welds made by A-TIG improved with the increase of the heat input in the tested range of welding current 100-200 A. It was also found that the intensity of the occurrence of pitting does not affect the method of cleaning welds after welding, but the mechanical removal of a thin surface layer of metal significantly reduces their intensity.

Keywords: lean duplex stainless steel, TIG, A-TIG, pitting corrosion, ASTM G48

1. Introduction

Evolution of duplex stainless steel grades (Fig. 1) runs in two-ways, on the one hand, the development is focused on increasing the levels of alloying elements that stabilize the passive layer such as chromium, molybdenum, and balance their impact by nickel. The hyper-duplex and super-duplex grade families were developed (i.e. grade: S32707). The second direction goes towards reducing the concentrations of nickel and replace it with another element of similar impact, which aims to reduce the material cost while maintaining the specific features of the two-phase structure. Economic considerations create the development of alloys with a lower share of expensive alloying elements such as nickel, which is replaced by manganese. This contributed to the emergence and development of a two-phase steel, so-called “lean duplex”. This type of grades develops, particularly active in recent years, which is due to the research for a lower cost of steel materials as compared to the classical grade of duplex stainless steel (EN 1.4462) and as a competitor to austenitic stainless steel (EN 1.4307, and 1.4401), which currently dominate the market for stainless steel. In contrast to traditional duplex stainless steel, the lean duplex stainless steel is characterized by a reduced

content of Mo and Ni and in the case of developing in the XXI century modern stainless steels S32101 (EN 1.4162) and developed in 2010 the S82441 steel (EN 1.4662) also increased content of manganese and nitrogen, which enhances the formation of austenite during welding. Lean duplex stainless steels shows similar pitting corrosion resistance number PREN = about 26, where $PREN = \% Cr + 3.3\% Mo + 16\% N$ (Pitting Resistance Equivalent Number - PREN) for austenitic stainless steel 1.4404 types, but are they yield strength is about twice (fig. 2). In the case of grade UNS S82441 (EN 1.4662) PREN equivalent value is even higher, equal to 33, which was achieved by increasing the concentration of molybdenum and made it stronger in terms of corrosion resistance than the austenitic Cr-Ni-Mo stainless steel, such as EN 1.4404. Group of lean duplex stainless steels is designed to compete with the austenitic stainless steel alloys in terms of corrosion resistance and price while maintaining the high mechanical properties of lean duplex stainless steel [1-7].

The most beneficial set of mechanical properties and corrosion resistance of duplex stainless steels is achieved when the austenite content is maintained in the range from 40 to 60% [8,9]. The high corrosion resistance of duplex stainless steels is due to the element concentrations that tend to increase the

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passivation of stainless steel (Cr and Mo), where corrosion resistance increases with the concentration of these elements. At a concentration of more than 18% of chromium the molybdenum addition is three times more effective than chromium in terms of increase of resistance to pitting and crevice corrosion in chloride-containing environments. However, the concentration of molybdenum is limited in duplex stainless steels to a maximum of 6%, which results from the high propensity of the element to accelerate the precipitation processes of intermetallic phases at elevated temperature. Duplex stainless steels are also enriched by the additions of Cu, W and Si, which increases corrosion resistance in oxidising environments, crevice corrosion and oxidation resistance. The concentration of carbon, as in all stainless steel grades except martensitic alloys is limited in the duplex steels to the level of 0.03%, which aims to reduce intergranular corrosion phenomena associated with chromium carbide precipitates in the heat-affected zone during welding.

Taking into consideration the pitting corrosion resistance equivalent PREN, the duplex stainless steels with PREN > 40 are considered the group of steels particularly resistant to pitting corrosion and are used in a very aggressive corrosive environments, such as in seawater, in the environment of diluted hydrochloric acid and sulphuric acid. The value of the equivalent is also the basis for the classification of duplex stainless steel into five groups: lean duplex steels, duplex 22%Cr, duplex 25%Cr, super-duplex and hyper-duplex stainless steels, where the PREN values in the range 40-45 stands for super-duplex stainless steels and for hyper-duplex stainless the PREN exceed 45 (fig. 1). Duplex stainless steels are characterized by a high resistance to pitting and stress corrosion cracking and have better anti-corrosion properties of austenitic phase stainless steels containing comparable concentrations of chromium and molybdenum [5,10].

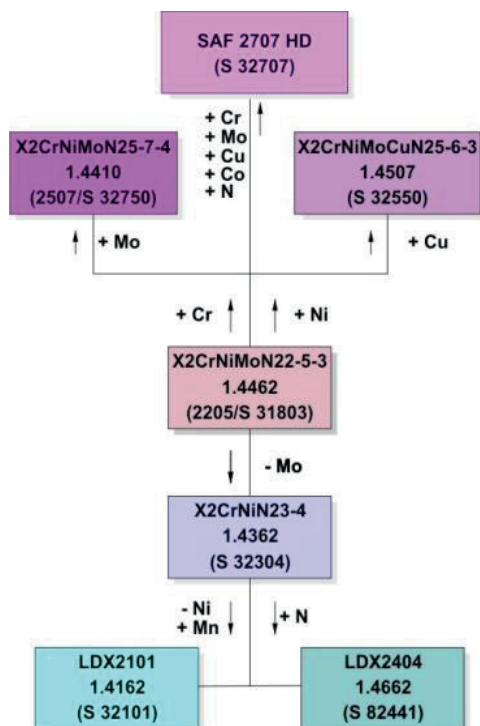


Fig. 1. Evolution of duplex stainless steel grades

Anti-corrosion properties of duplex stainless steels depend on their chemical composition, micro-structural composition and performed correctly heat treatment, that is solution annealing in the range of 1150-950°C, with subsequent cooling with water or in the air. The cooling rate of solution annealing temperature should be fast enough to prevent the precipitation of intermetallic phases adversely affecting its mechanical properties and corrosion resistance. Adjusting the cooling rate of solution annealing temperature allows to obtain a balance between two phases in steel microstructure. Too rapid cooling effect of the high ferrite fraction, a slower cooling leads to an increase of an austenite phase, which precipitates from the ferrite during cooling [11]. Balancing the share of the various phases in the structure gives the opportunity to influence the mechanical properties of steel, where the ferrite increases the tensile strength, yield strength and hardness, while the austenite provides high impact strength and elongation at break [3]. Modern duplex stainless steels have good mechanical properties in the temperature range from -50 to 280°C, together with good weldability and competitive price [5,8]. Operating temperature of duplex stainless steels at low temperatures is limited by the ductile–brittle transition temperature, which, due to the presence of ferrite in the steel is about -50°C. In an elevated temperature range the operating capabilities are limited by the precipitation of a number of intermetallic phases which appear above 280-300°C, with the separation of chromium-rich α' ferrite responsible for the effect of “the 475°C embrittlement”, M_7C_3 carbides, $M_{23}C_6$ Cr₂N nitrides, CrN, π and a number of intermetallic phases like the sigma phase σ , χ , R , τ , G , ϵ that affect the deterioration of corrosion resistance and decrease in the plastic properties of stainless steels [5,8,12,13].

Duplex stainless steels are characterized by higher mechanical properties compared to the single-phase austenitic and ferritic alloys as a result of the simultaneous occurrence in the steel microstructure of the two phases (ferrite α and austenite γ) and their fine-grained microstructure, solution-strengthening due to high proportion of the alloying elements Cr, Mo, Ni, and severe interstitial strengthening by nitrogen. Already addition of 0.2% N results in an increase in the strength of the austenite phase above the strength of ferritic phase. Duplex stainless steels are characterized by an elongation at break about 25%, which is half the ductility of single-phase austenitic alloys.

In order to obtain a fine-grained microstructure of the two-phase duplex steels, also known as micro-duplex, hot forged steel band with a characteristic coarse two-phase structure is subjected to strong deformation by cold rolling. After this step, the cold deformed material is annealed in the temperature range depending on the steel chemical composition. The use of this type of thermoplastic treatment provides ample opportunities to develop microstructure and thus the mechanical properties of duplex stainless steel.

An innovative method to increase formability of duplex stainless steel is to control the plasticity growth phenomenon due to stress - induced phase transformation, the TRIP effect (Transformation Induced Plasticity – TRIP). The plasticity growth due to phase transformation is obtained thanks to the presence of residual austenite in the steel microstructure, which as a result of plastic deformation is transformed into

the martensite. The transformation of austenite to martensite is usually carried out in accordance with the formula: austenite (γ) \rightarrow martensite (ϵ) \rightarrow deformation induced martensite (α'). In steels with controlled TRIP effect, gradually occurring martensitic transformation causes strong work hardening of the steel, which affects the delayed thinning of the metal during the stamping process and during stretching conditions slower formation of the neck in the sample. In the end, the increase in strength as well as high yield of finished products is achieved [14-16]. Adjusting the solution annealing temperature in the recommended range 900-1150°C makes it occurs austenite is more stable and transforms into martensite (ϵ) in a wider range of plastic deformation, which increases the plastic properties of the steel. Controlling the TRIP effect by adjusting the temperature of solution annealing in these steels can solve the problem of reduced yield of currently available duplex stainless steel. Steels with controlled TRIP effect, the approximate chemical composition of 0.3-1%Mo, 20-25% Cr, 1-3 %Ni allows increased plastic deformation to break from the value of 25% to 40-45% and in some grades up to 60%. Forming trials with pilot customers have already been done on plates for heat exchangers, where the same process parameters, same tools, same speed has been used. On this basis, there is possibility of using these steel for drawing components with required high plasticity during forming operations, such as flexible pipes, pump components, plate heat exchangers and beer kegs, where the use of duplex steels provides tangible results as a result of decreasing the weight of elements.

The next step in the development of applications of duplex stainless steel is an attempt to modify their surface layer by the surface engineering methods, especially laser techniques, which in recent years are gaining importance in the field for various highly alloyed steels [17,18] and as well for light metal alloys [19,20].

High mechanical properties in combination with the corrosion resistance of duplex stainless steels determine their application to components operating in an environment of sea water and in contact with many aggressive corrosive substances, including the construction of chemical tankers,

storage tanks and transport vessels, for the components in the paper, petrochemical, pharmaceutical industry, and many other applications, typically in construction [21]. An important issue apart from corrosion resistance of stainless steels are their mechanical properties of the base metal as well as of the welded joints. High mechanical properties and ability to maintain mechanical properties at elevated temperatures better than traditional low alloyed steel makes stainless steels beneficial for construction where fire resistance is crucial. The long-term service introduces the successive critical issue, the creep resistance is influenced by the welded joints microstructural characteristic and occurring mechanical stresses [22,23].

One of the most important features of virtually all high-alloy steels, including duplex stainless steel, which determine the success of their use in industrial practice is not only suitable corrosion resistance of the base material, but also of their welded joints. The lean duplex stainless steels like the duplex one shows good weldability. For lean duplex, as well as duplex grades it is essential to ensure that an adequate amount of austenite is formed in the weld metal and heat affected zone, in order to ensure adequate balance between austenite and ferrite phase. The second important factor that should be taken into consideration during welding of such alloys is to avoid the precipitation of detrimental phases such as intermetallic and nitrides [24-26]. Additionally, the proper post-welding cleaning should be performed to ensure good corrosion properties. Recently, the computer modelling and simulation techniques proven to be adequate for the prediction of material properties, like hardness related to microstructural changes in the material during thermal cycle of fabrication and processing [27].

The results of pitting corrosion resistance of the welded joints of lean duplex stainless steel S82441, according to ASTM G48, were presented. Studied welded joints were made using the TIG method and activated flux TIG method (A-TIG) with various shielding gases and different amounts of heat input. The comparative studies with welded lean duplex stainless steel S32101 were also presented.

TABLE 1

Chemical composition studied stainless steels

EN number	Trade name / UNS number	Thickness mm	Chemical composition, %							
			C	Si	Mn	Cr	Ni	Mo	Cu	N
1.4162	LDX 2101 /S32101	6.0	0.028	0.70	4.90	21.34	1.50	0.19	0.25	0.21
1.4662	LDX 2404 /S82441	6.0	0.025	0.36	3.00	23.92	3.66	1.61	0.39	0.279
1.4662	LDX 2404 / S82441	15.0	0.020	0.33	2.85	24.1	3.59	1.60	0.37	0.27
1.4401/ 1.4404	316/ 316L	6.0	0.020	0.48	1.31	17.10	10.27	2.08	0.36	0.042

TABLE 2

Chemical composition of applied filler metals

Welding wire grade	Diameter, mm	Chemical composition, %						
		C	Si	Mn	Cr	Mo	Ni	N
AVESTA LDX 2101	2.0	0.02	0.40	0.5	23.0	<0.5	7.0	0.14
LNT 4462	2.4	0.01	0.5	1.6	22.5	3.0	8.5	0.15

2. Studied materials

2.1. Base material, filler metal and shielding gases

The research was carried on using sheets of lean duplex stainless steel grade LDX 2101® (material EN number 1.4162 acc. PN-EN 10088-4 or S32101 acc. ASTM A240) and LDX 2404® (S82441 acc. ASTM A240 or 1.4662 acc. PN-EN 10088-4) of the thickness 6.0 and 15.0 mm made by Outokumpu, as well as a sheet of 6.0 mm thickness of AISI 316/316L (1.4401/1.4404) that was used for comparative tests. The chemical composition of applied grades is shown in Table 1. The TIG welded test joints of LDX 2101® (S32101) steel were made with filler metal of AVESTA LDX 2101® the 2.0 mm welding wire, while LDX 2404® (S82441) steel was welded using wire grade LNT 4462 of 2.4 mm diameter, with the composition presented in table 2.

During TIG welding appropriate shielding gases were applied: pure technical argon EN ISO 14175-I1-Ar, the mixes of argon and nitrogen (5, 10 and 15 %) with designations according to standard: EN ISO 14175-N2-ArN-5, EN ISO 14175-N3-ArN-10 and EN ISO 14175-N3-ArN-15, and also a mixture of Ar + He in the relation 50/50 with designation EN ISO 14175-I3-ArHe-50. The A-TIG welding was performed applying pure technical argon EN ISO 14175-I1-Ar and as the

activation flux the BC-31 preparation dedicated to welding of highly alloyed steels was applied. During all the tests of welding and melting the root of a weld was shielded with a technically pure argon EN ISO 14175-I1-Ar.

3. Experimental procedure

3.1. TIG autogenous welding

The tests of autogenous TIG welding (welding without filler) were performed on 6.0 mm sheet grade S82441 on TIG mechanized welding stand consisting of welding power source Lorch V40, a welding trolley DC20 Promotech with the precisely adjustable travel speed of torch and an attachment device to position welded pieces. The welding speed of all samples was constant and the current intensity was changed in the range from 50 to 300A (tab. 3). The A-TIG welds were made with BC-31 flux for highly alloyed steels. The welding speed for all test samples was 15 cm/min and variable arc length 1.5 mm was applied. The TIG welded steel S82441 with filler metal at 100% Ar shielding gas atmosphere and welding current 150A, in order to obtain a single and a multi-pass welds, were obtained with welding heat input of 0.39-0.40 kJ/mm.

TABLE 3

Parameters of autogenous TIG welded lean duplex stainless steel S82441, 6.0 mm thick

Current, A	Heat input, kJ/mm					
	Ar 100%	Ar+5%N2	Ar+10%N2	Ar+15%N2	Ar+He	A-TIG
50	0.11	-	-	-	-	-
100	0.27	0.26	0.26	0.26	-	0.29
150	0.45	0.42	0.44	0.43	-	0.48
200	0.65	0.65	0.65	0.65	0.72	0.68
250	0.89	-	-	-	-	-
300	1.17	-	-	-	-	-

TABLE 4

Parameters of TIG welded lean duplex stainless steel S82441

Sample designation	Welding position	Forming gas	Run	Current, A	Welding speed, cm/min	Heat input, kJ/mm
15DN10A	PA	Ar	root	100	3.43	0.98
			2	120	4.84	0.88
			3	120	6.10	0.71
			4-10	120	6.33	0.67
15DN16A	PA	Ar	root	160	6.58	0.95
			2	120	4.72	0.84
			3	120	6.29	0.69
			4-10	120	6.41	0.72
15DN10F	PF	Ar	root	100	4.03	1.11
			2	120	5.22	0.86
			3	120	5.40	0.97
			4-8	120	5.71	1.04
15DN10C	PC	Ar	root	100	3.91	0.88
			2	120	6.64	0.59
			3	120	6.25	0.74
			4-11	120	6.54	0.69

3.2. TIG welding with filler metal

The welded test joints of S82441 stainless steel were assembled on 15.0 mm thick sheets using specialised mounting device with the feeding of forming gas and welding equipment Lorch V40. The volume flow of the shielding gas during TIG welding was 8 to 10 l/min, and the forming gas - from 5 to 6 l/min. During welding the tungsten electrode type: Wth 20 acc. PN-EN ISO 6848 with the addition of approx. 2% m/m thorium oxide (ThO₂) with a diameter of 4.8 mm was applied. The welding with direct current and negative polarity (DC-) was used. When performing a root run of TIG welds the welding current was 100 and 160 A (tab. 4). The filling welds of multi-pass welds were performed using 120 A current. The welding speed was dependent on the current and the welding position and it was ranged 3.3-6.7 cm/min. The welded test joints were performed in positions: PA, PF and PC. Positions PF and the PC were selected based on the assumption that the weld root run will be obtained, respectively maximum and minimum welding heat input.

The welded butt joints of lean duplex stainless steel S82441 of 15 mm thickness were subjected to the following destructive tests: the impact test according to EN 875 at temperatures: -50, -40, -20 and +20 °C, tensile test according to EN 895 and bending test EN 910. The impact tests at various temperatures was also conducted for the base material (BM) – the sheet of lean duplex stainless steel S82441.

3.3. Corrosion resistance and mechanical properties testing

The study of corrosion resistance of welded S82441 and S32101 stainless steel was performed according to the requirements of ASTM G48 standard using method E [28], which concerns a test method to determine the critical pitting temperature (CPT) for stainless steel (Method E – Critical pitting temperature test for stainless steels). Test samples were prepared in accordance with the specifications in point 7 of the ASTM G48, and then exposed to a corrosive solution of the following composition: 68.72 g of FeCl₃ • 6H₂O, 16 ml of concentrated HCl; 600 ml of distillate H₂O. The exposure time was set to 24 h. The test was performed in a climatic chamber at three temperatures: 15, 25 and 35°C. The presence of pits at the weld start and crater on welds were not taken into account because in these areas the welding process was not stable.

Prepared welds were made in the manner that the beginning and the end did not go beyond the limits of the sample. Thus, during the corrosion testing according to ASTM G48 the ferric chloride solution affected only the face of welded joints. Applied samples dimensions are not in accordance with the standard ASTM G48, but their choice is explained by the fact that the use of standard samples with dimensions of 50x25 mm would require cutting them from the welded joint, and then during corrosion test the corrosive medium would affect both the joint surfaces and the surfaces of the weld cross section, which in the real conditions would never happen and could distort obtained results.

Testing of the weld microstructure was performed in the cross-section of welded samples using light microscopy

methods. Light microscope observations involved etching using Aqua Regia reagent and were performed at 400x and 1000x magnifications using a LEICA MEF4A microscope to evaluate phase content. The austenite and ferrite content, in studying welds was measured based on metallographic observations, according to ASTM E562 standard by systematic manual point count to determine the volume of observed phases. Microstructure observations and geometrical characteristics of weld bead were carried out in the light and scanning electron microscope. The scanning electron microscope (SEM) involved in the studies was a SUPRA 25 of ZEISS Company equipped with an EDS probe.

Moreover sample surface was treated in a variety of ways prior to corrosion testing and the following surface finish were created: 1) etching (abbreviation E) with a commercially available etching paste, 2) cleaning with a wire brush (abbreviation B+E), and then etched with the paste, 3) machining (abbreviation M) by milling surface layer removing material on depth 0.1 -0.3 mm (max. 0.5 mm) from the face of the weld. The milling was applied in aim to mechanically remove formed oxides and other surface contamination that might occur on the surface of the weld face and would not be removed by brushing and pickling treatment. The roughness of a surface worked in different ways was measured in terms of the surface roughness Ra parameter.

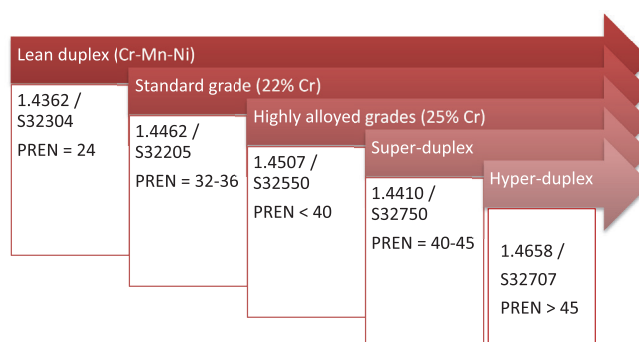


Fig. 2. The classification of duplex stainless steels according to the pitting corrosion resistance number and the concentration of alloying elements

4. Results and discussion

4.1. Phase content analysis

The phase content of the duplex microstructure was performed on a cross section of the weld joints, near the weld surface. The influence of the heat input increase with the austenite content is evident for TIG welded joints (tab. 5). Nitrogen presence in the shielding gas negligible influenced austenite content at low heat input (0.27 kJ/mm) and low nitrogen content (5%N₂), but its influence is evident for high heat input and high nitrogen content. The austenite content in welded joints varied from 20-25% for low heat input (0.11 kJ/mm) to 40-45% for high heat input 1.17 kJ/mm. TIG welding in Ar+He shielding gas mixture shows the same austenite content (30-35%) as for TIG welding for comparable heat input. The A-TIG weld joints compared to TIG welds shows higher austenite content (about 10%) when

comparing the same heat input. Figure 3 shows example of duplex stainless steel microstructure welded at different heat input and shielding gases.

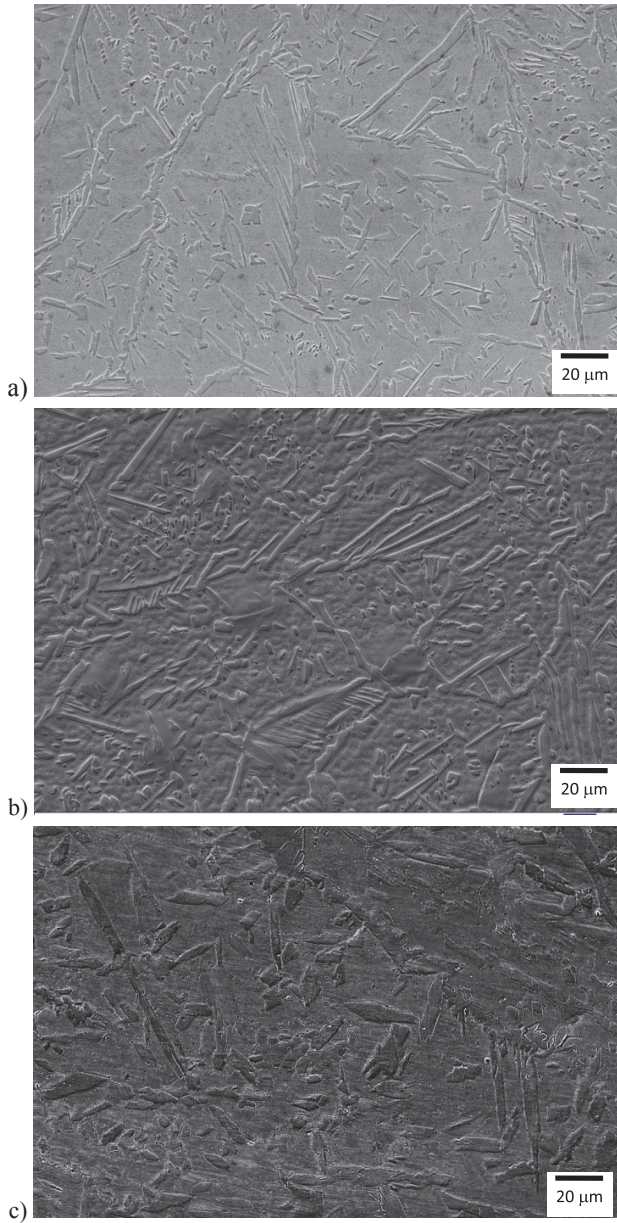


Fig. 3. The microstructure in the duplex stainless S82441 welded at heat input: a) 0.27kJ and shielding gas of 100% Ar, b) 0.43kJ and shielding gas of 85%Ar+15%N2, c) 0.72kJ and shielding gas of 50%Ar+50%He

4.2. Studies of autogenous TIG weld

Figure 4 shows a TIG weld surface of samples with surface runs in as welded condition made by TIG and A-TIG method and on figure 5 the TIG welds made with the filler metal. Single runs on sample surface were made to did not go outside their limits. Thanks that that the corrosive media was only affecting the face of the weld and had no contact with the interior material of the joints, which would be the case if the sample measuring 50x25 mm were cut from autogenous TIG welded joints. The impact of corrosive media only on the face of weld reflect the actual working conditions of such welded

joints, because the internal weld joint surfaces are never exposed to the corrosive environment because they are not cut and exposed.

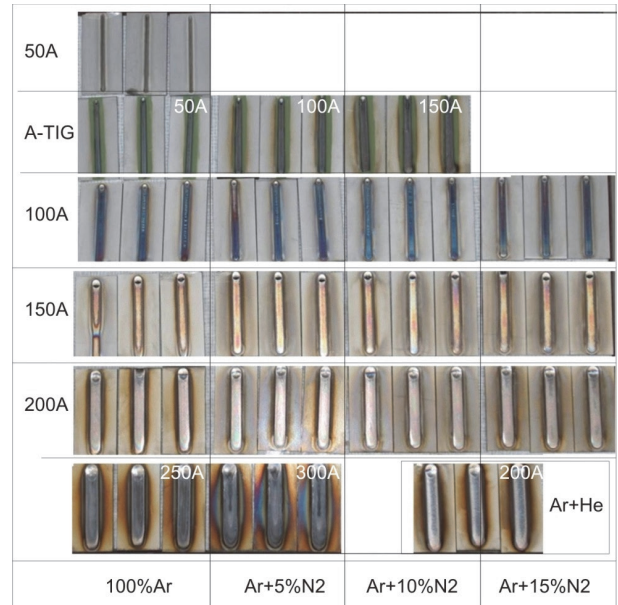


Fig. 4. The TIG welded surface of stainless steel S82441 (3 samples for each variant) in as welded condition

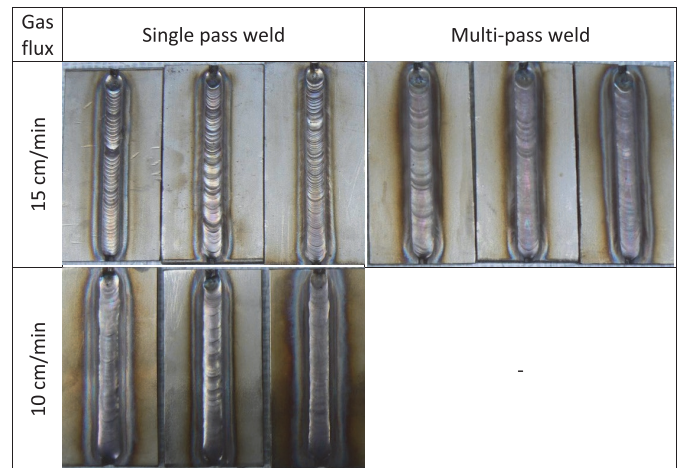


Fig. 5. The TIG welded surface of stainless steel S82441 with single pass weld and multi-pass weld made with filler metal (3 samples for each variant) in the 100% Ar shielding with flux 10 and 15 cm/min in as welded condition

Surface samples after welding is characterized by the presence of heat tint (discolorations), which is characteristic for TIG welding of stainless steel. Particularly strong discolorations were found when using Ar and a current of 250 and 300 A and also when welding with Ar + He mixture.

4.3. Corrosion resistance acc. ASTM G48 method

The weld joint surface prior corrosion test were cleaned by wire brushing and next etched (using dedicated surface etchant, the ANTOX composition), while the opposite end (the start of the weld) was the only chemical etched. The surface of welded joints in the centre area was mechanically

50A							
100A							
150A							
200A							
250A							
300A							
	Ar+He	100%Ar	Ar+5%N2	Ar+10%N2	Ar+15%N2	A-TIG	TIG+ filler metal, single and multi-pass weld

Fig. 6. The surface of studied welded joints of lean duplex stainless steel S82441 after corrosion test ASTM G48.

milled to remove material on the depth of 0.2 - 0.3mm (fig. 6). This surface preparation was intended to evaluate the post welding surface cleaning methods on the corrosion resistance at ASTM G48 test.

Corrosion test revealed (fig. 6) that corrosion pits are present in all test samples tested at temperatures 25 and 35 °C. The results of the critical pitting temperature (CPT) according to ASTM G48 shown in tables 6 provides data of the tests carried out at temperature of 15°C.

Corrosion test at a temperature of 15 °C revealed pitting in samples welded in a mixture of Ar + He and Ar shielding gas at a welding current of 200 and 250 A. On the surface of the other samples of lean duplex stainless steel S82441 corrosion pits occurred sporadically or they were not present at all (tab. 6). Detailed studies revealed that corrosion pits are present in welds made without addition of filler metal (fig. 7-9). The variation of welding current has no significant influence on quantity of forming pits (fig. 8 and 9), although when welding current of 250 A was applied the pits number increased, while at 300 A it was smaller. These results are difficult to explain at this stage of the research, because the surface of the welded joint when using the current intensity of 300A was clearly overheated and had traces of hard removable oxide layer, and nevertheless has not been attacked by corrosion. The appearance of the pits at a current intensity of 200A and 250A on both cleaned and milled surfaces is also understandable, because the joints have been made without a filler metal, but with the amount of heat input 0.65 and 0.89 kJ/mm respectively, which is within the recommended for the lean duplex stainless steel range 0.5-1.5 kJ/mm [6]. The addition of 5, 10 and 15 % nitrogen in the argon shielding gas that is strong austenite former element has no positive influence on the corrosion resistance of welded joints.

Studies of pitting corrosion resistance of welded joints at a test temperature of 25°C shows, that the pits are formed in almost all samples regardless applied welding parameters and shielding gases. The interesting thing is that after the removal from the weld surface a metal layer of the thickness 0.2-0.3

mm, the corrosion does not occur at all, although not machined weld surface is closely dotted with corrosion pits.

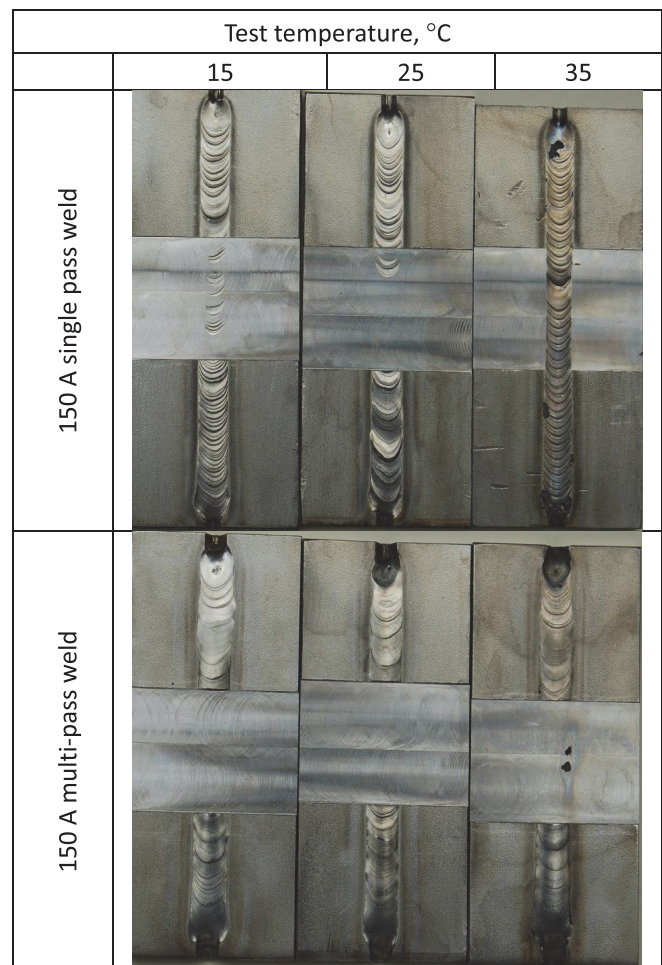


Fig. 7. The TIG welded joint of stainless steel S82441 made at 100% Ar shielding with filler metal after corrosion test ASTM G48 at temperatures 15, 25 and 35°C

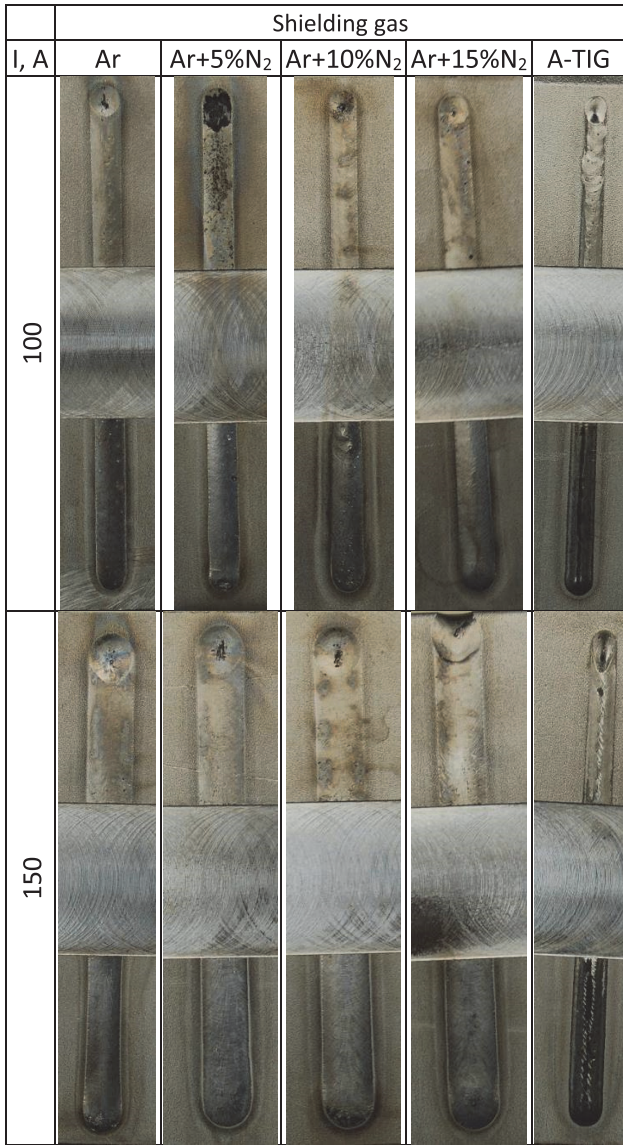


Fig. 9. The TIG and A-TIG welded joint of stainless steel S82441 made with current of 100A after corrosion test ASTM G48 at temperature 25°C

The surface of TIG welded joints without filler metal of all tested samples and test temperatures shows that corrosion pits are always found in the weld metal zone. There was no presence of pits outside the fusion line, and therefore there were no present either in the heat affected zone (HAZ) or in the base material. At current intensity levels of 50A and 100A, corrosion pits are uniformly distributed on the surface of the welded joints and have a shape close to circular. At a current intensity of 150A and higher, pitting mostly arranged in the vicinity of the fusion line and have an elongated shape mapping the weld shape during microstructure solidification (in the shape of a Christmas tree). This fact supports the assumption that the main cause of pitting corrosion is related to microstructural changes and formed surface oxides layers taking place during autogenous welding of lean duplex stainless steel S82441.

This can be supported by microstructure analysis of the welded joints welded at shielding of argon-nitrogen mixture (15%N₂) where along heat affected zone, inside coarse grained ferritic regions, the precipitates having morphology of Cr₂N nitrides type can be seen (fig. 10). Moreover, superficial corrosion

pits locates preferentially between the HAZ and the fusion line, where Cr₂N nitrides of rod-like or tetragonal shape can be observed (fig. 11, 12). The examination of corrosion pits surface revealed that preferentially is dissolved ferrite while austenite remain not attacked and thin needles of the secondary austenite of Widmanstatten type protrude from the ferrite matrix (fig. 13).

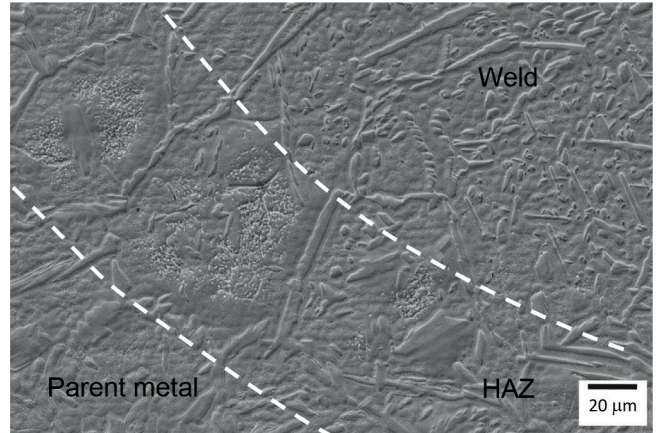


Fig. 10. The precipitations of chromium nitrides in the HAZ of duplex stainless S82441 welded at heat input of 0,43kJ and shielding gas of 85%Ar+15%N₂

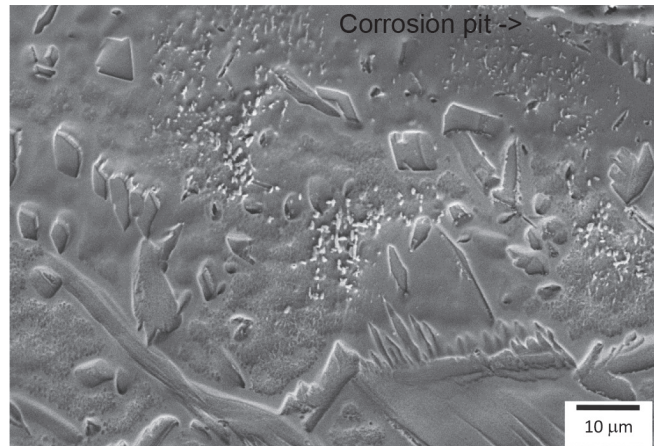


Fig. 11. The precipitations of chromium nitrides near the corrosion pit in the duplex stainless S82441 welded at heat input of 0,43kJ and shielding gas of 85%Ar+15%N₂

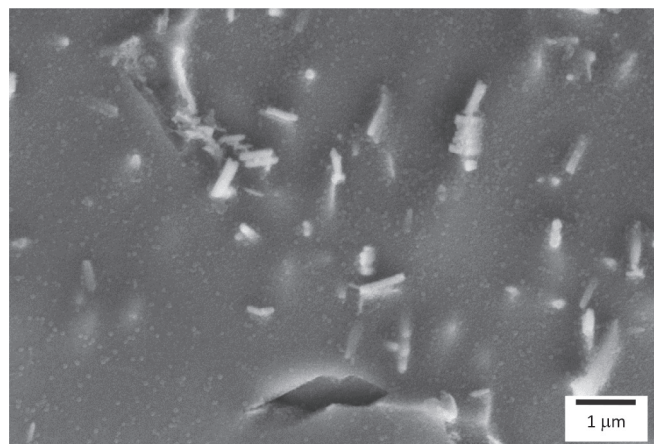


Fig. 12. The chromium nitrides precipitations near the corrosion pit in duplex stainless S82441 welded at heat input of 0,43kJ and shielding gas of 85%Ar+15%N₂

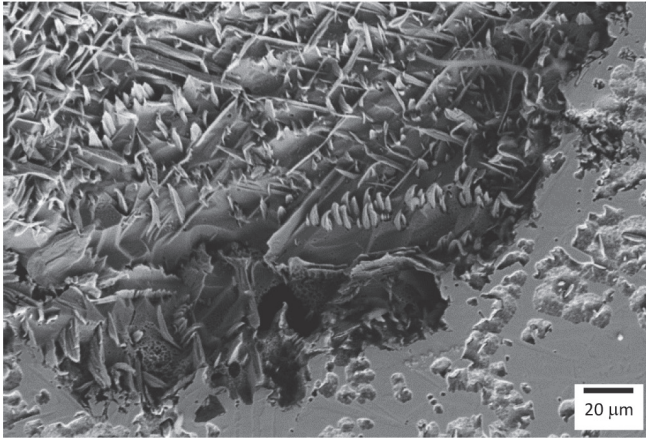


Fig. 13. The inside surface of corrosion pit in the duplex stainless S82441 welded at heat input of 0,43kJ and shielding gas of 85%Ar+15%N₂, where the net of non-dissolved needles of austenite protrude from ferritic matrix

The resistance to pitting corrosion was the highest for A-TIG welded joint which also not utilize the addition of filler metal during welding (fig. 8 and 9). Surface analysis of corroded A-TIG welds showed that rising welding current from 100 to 200 A the pitting corrosion resistance of welds is increased. It was also found that the corrosion resistance of welds made by A-TIG method is higher than traditional welds made by the TIG method (fig. 8). Therefore, the above results of corrosion tests indicate the possibility of A-TIG welding without the addition of filler metal, which can be explained by the advantageous thermal cycle for duplex stainless steels, which is the introduction of more heat than in conventional TIG welding and hence influencing on slower cooling and the formation of a higher amount of austenitic phase.

An interesting result was obtained for welds made under shielding of Ar + He mixture, where pitting already occurred at 15 °C (fig. 14). The addition of helium to the shielding gas is often recommended during welding of all duplex stainless steels, so such a high susceptibility to pitting corrosion of welded joints made with Ar + He mixture being quite surprising.

Next comparison of welded joints is focused on traditionally welded TIG joints with the addition of filler metal (fig. 5). This case shows that corrosion pits were only present at a temperature of 35 °C and was located on fusion line. That confirms the well-known recommendation of absolutely using an appropriate filler metal during welding of duplex stainless steels.

Comparative studies on resistance to pitting corrosion test according to ASTM G48 of lean duplex stainless S32101 and S82441 (fig. 15) shows much more susceptible to corrosion of lower magnesium alloyed lean duplex grade S32101, because pitting occurred already at corrosion test temperature of 0°C.

Even a quick look at the results of corrosion test acc. to ASTM G48 at 15, 25 and 35 °C of lean duplex stainless steel S82441 TIG welded joints with filler metal (fig. 7) shows that corrosive pits were formed only at temperature of 35°C, either on face and root of weld. It has been found that pitting occurs primarily in the fusion line zone. However It has been found, that their number is greater than on the face of weld side. It

is also noteworthy, that corrosion pits were practically absent both on the face and root side weld (just barely visible small pits) over a range of testing temperatures.

Analysis of the TIG welded joints on the root of weld side made at a current of 100 and 160 A showed that significant differences do not occur, and the pitting effects can be seen both in the near weld zone and on the fusion line, except that the pits on the fusion line are significantly smaller and in most cases not noticeable with an unarmed eye.

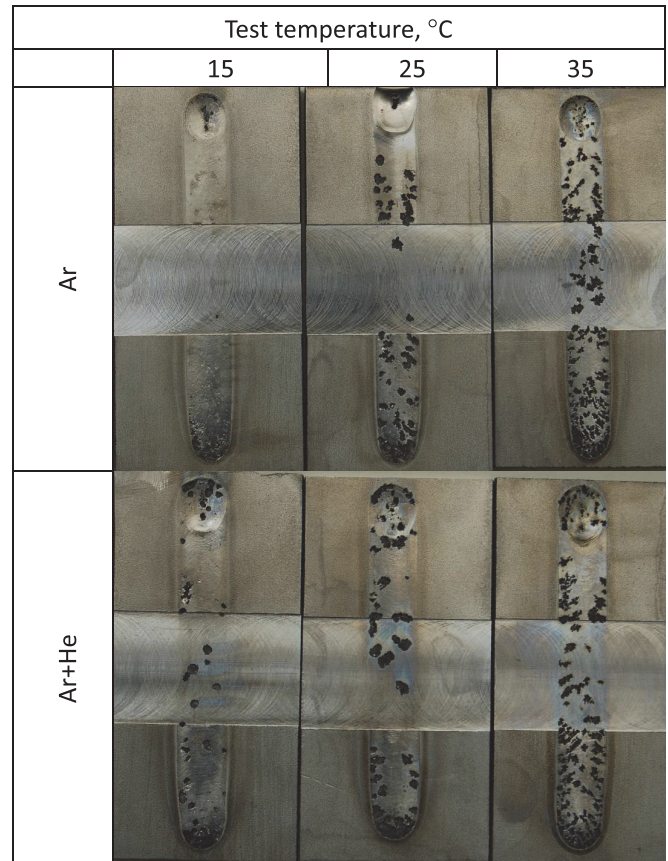


Fig. 14. The autogenous TIG welded joint of stainless steel S82441 made with Ar shielding and Ar+He mixture and welding current of 200A after corrosion test ASTM G48 at temperatures 15, 25 i 35 °C

4.4. Visual inspection of welded joints

The results of visual inspection of TIG welding with filler metal of lean duplex S82441 welds on the root of weld side shows bright metallic luster, and thus excellent surface purity in the root of weld side, obtained with argon as forming gas. It was also found that the welding root run using a current of 160A provides a smooth root of weld surface and the surface aspect have no elongated shape mapping the weld shape during microstructure solidification (in the shape of a Christmas tree), like in the case when 100A welding current was applied. The smoother root of weld surface is preferred because of the high corrosion resistance, as corrosive media are less able to attach to the smooth surface as compared to surface in the shape of a Christmas tree and rough one. However, performing welding at 160 A welding current requires more skill of the welder.

TABLE 5

The austenite content in the weld of TIG and A-TIG welded lean duplex stainless steel S82441

Current, A	Austenite content, % / Heat input, kJ/mm						
	Parent metal	TIG					A-TIG
		Ar	Ar+5%N2	Ar+10%N2	Ar+15%N2	Ar+He	
50	55/ -	20-25 / 0.11	-	-	-	-	-
100		20-25 / 0.27	25-30 / 0.26	30-35 / 0.26	35-40 / 0.26	-	40-45 / 0.29
150		25-30 / 0.45	30-35 / 0.42	30-35 / 0.44	40-45 / 0.43	-	40-45 / 0.48
200		30-35 / 0.65	30-35 / 0.65	35-40 / 0.65	40-45 / 0.65	30-35 / 0.72	45-55 / 0.68
250		35-40 / 0.89	-	-	-	-	-
300		40-45 / 1.17	-	-	-	-	-

TABLE 6

Results of corrosion test acc. to ASTM G48 in 15°C (surface treatment: E – etching, M – milling, B+E – brushing + etching)

Welding current, A	Surface treatment	Presence of pits after corrosion test at 15 °C				
		Ar	Ar + 5% N2	Ar + 10% N2	Ar + 15% N2	Ar + He
50	E	no	-	-	-	-
	M	no	-	-	-	-
	B+E	no	-	-	-	-
100	E	no	●	no	no	-
	M	no	no	no	no	-
	B+T	no	no	no	●	-
150	E	no	no	●	no	-
	M	no	no	no	no	-
	B+T	no	no	no	no	-
200	E	●	no	no	no	●●●
	M	●	no	no	no	●●●
	B+T	no	no	no	●●	●●
250	E	●	-	-	-	-
	M	●	-	-	-	-
	B+T	●	-	-	-	-
300	E	no	-	-	-	-
	M	no	-	-	-	-
	B+T	no	-	-	-	-

no – lack of pits, ● – single pits, ●● – medium amount of pits, ●●● – high amount of pits

TABLE 7

Mechanical properties of welded joints of lean duplex stainless steel S82441

Sample designation	Method	Position	Gas	Mechanical properties						
				Rm, MPa	Bending (180°)		Impact toughness HAZ, J at temperature, °C			
					face of weld	root of weld	+20	-20	-40	-50
BM				750 757	-	-	146-174 161	-	96-99 98	-
15DN10A	TIG	PA	Ar	744.2	lack of scratches and cracks		134	-	52-68 65	28-32 30
15DN16A	TIG	PA	Ar	738.4	lack of scratches and cracks		140	66-79 76	62-89 73	44-62 54
15DN10F	TIG	PF	Ar	747.9	lack of scratches and cracks		-	65-77 69	44-58 52	36-56 45
15DN10C	TIG	PC	Ar	743.2	lack of scratches and cracks		-	73-78 75	57-60 58	64-99 84

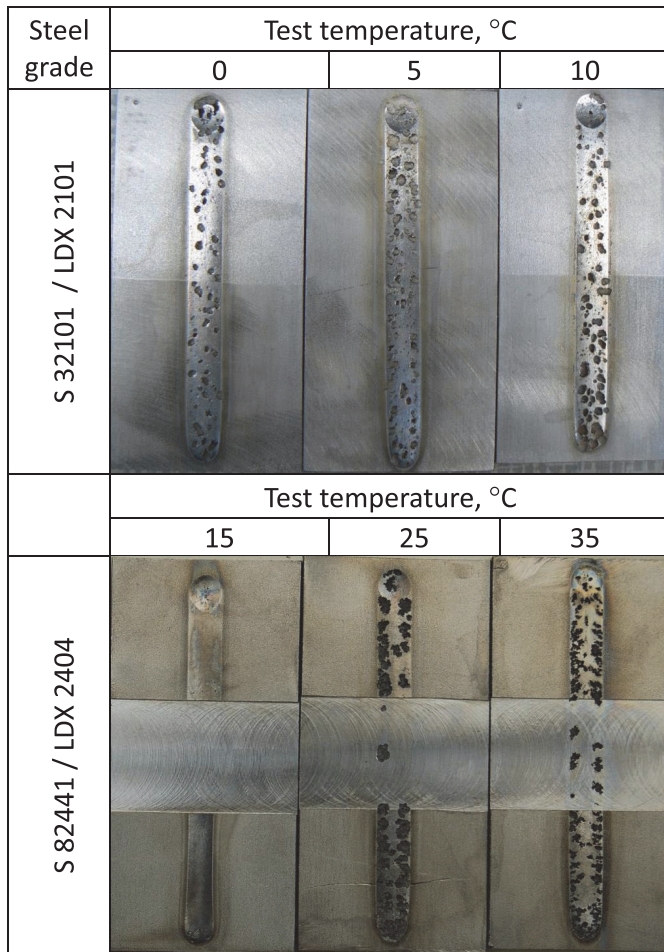


Fig. 15. The TIG welded joint of stainless steel S32101 and S82441 made with Ar shielding and welding current of 150A after corrosion test ASTM G48

4.5. Mechanical testing of welded joints

Studies of static tensile test, bending with tension of the face and root of weld as well as impact toughness test of Charpy-V of the base material (MP) and HAZ of welded joints were performed of lean duplex stainless steel S82441 at temperatures of +20, -20, -40 and -50 °C (table 7). As a criterion for evaluation a lean duplex stainless S82441 (LDX 2404®) the value $R_m = 680-900$ MPa according to ASTM A240 and EN 10088-2 was chosen.

The mechanical test results shows (tab. 7), that all welded joints meet the requirements of ASTM A240 and EN 1088-2 in terms of tensile strength. The minimum obtained value during the tests of ultimate tensile strength (R_m) was 738.4 MPa while the maximum one was 747.9 MPa, which is within the acceptable range of 680 to 900 MPa. The bending test (180°) of welded joints also was successful, none of the samples were found scratches and cracks on both sides the face and the root of the weld.

The separate issue is the evaluation of impact thoughts results. The lean duplex stainless steel S82441 is a new steel grade on the market, and its mechanical properties are not yet all been normalized. Regarding the absence of requirements for impact thoughts of steel in subzero temperatures, the requirements were assumed for welded steel pipes for pressure purposes made of duplex stainless steel grade 1.4462 where

the minimum value is 40 J at -40 °C acc. EN 10217-7.

Analysis of impact thoughts results on Charpy-V samples showed that the material of HAZ of all welded joints meets the required KV value of minimum 40 J at -40 °C (tab. 7). The lowest individual values measured during test were at the level of 44-52 J. Detailed analysis of impact thoughts performance showed that slightly lower test values and the average value of KV was found for the SWC welds made in the PF position, which arise from the most heat introduced in this welding position.

5. Discussion

The microstructural studies of welded joints of lean duplex stainless steel confirm that their phase composition depends on the amount of heat input during welding and chemical composition of applied shielding gas. Lean duplex stainless steels during cooling from welding temperature solidify as ferritic and the austenitic phase precipitate by diffusion at the ferrite grain boundaries. Adjusting the amount of heat input and hence rate of cooling allows control of participating phase. Too low heat input during welding affect high content of ferritic phase responsible for embrittlement, while too high content austenitic phase affects negatively the mechanical properties of welded joints. The lean duplex steels, particularly those modern like grade 1.4162 (S32101) and classic one 1.4462 (S32205), should be welded according to recommendations keeping the heat input in the range of 0.5 to 1.5 kJ/mm.

The welded joints of lean duplex stainless steel after corrosion test acc. ASTM G48 shows that almost all autogenous TIG welds made without filler metal shows lack of corrosion pits only at a test temperature of 15°C. The increase of corrosion test temperature to 25°C cause pitting corrosion on the TIG welded joints. The exemption from that have been found in the case of A-TIG joint and TIG joints welded with the filler metal. Detailed analysis revealed that corrosion pits have been present practically always in the weld zone. The interesting thing is that after removing from the welded joint surface a thin metal layer of 0.2-0.3µm, the corrosion does not occur at all, although not machined weld joint are closely covered with pitting corrosion. The reasons of such situation during welding of lean duplex stainless steel without filler metal maybe two: the presence of microstructural changes near the surface or the presence of hard to remove chemical compounds, such as manganese oxide formed during welding of Cr-Mn steels [31]. However, verification of these assumptions, requires more detailed study. At the present state of research, such behaviour can be attributed to the low surface roughness of milled surface $R_a=0.4-0.5\mu\text{m}$ in respect to not welded surface area, where etching increase the roughness to $R_a=3.0\text{mm}$ and the face of weld $R_a=1.0\mu\text{m}$. It is well known that lower surface roughness improve corrosion resistance of stainless steel, thus chloride ions difficultly accumulate and slowly destroy the passive film on the surface.

The studies phase composition of autogenous TIG welded joints shown that ferrite content in welds made at current 150-300A is included in the range 50-75%, which translates to a small number of welds, in which the ferrite content is outside the recommended range 35-65%. It follows that the presence

of corrosion pits after ASTM G48 test would be expected in less than a half of tested samples, especially when it comes to weld joint made using shielding gas with nitrogen addition (Ar+N₂ compositions). The ferrite measurements show that in these samples the upper limit of ferrite content is about 60%.

The nitrogen addition (5, 10 and 15 %) to argon shielding gas, that is a strong austenite former, did not reveal an expected strong increase of critical pitting temperature (CTP). In contrast to the results presented in the work [31], proving the increase of corrosion resistance of the welds made in Ar with 2% of HN₂. Too high addition of nitrogen to the shielding gas during lean duplex steel welding causes a wider near weld zone covered with a thin oxide layer of complex chemical composition, which favour the development of pitting corrosion phenomena. The above results of corrosion test acc. ASTM G48 of TIG welded joints put a question mark regarding appearing in the literature stating that plates or pipes of lean duplex of a thickness less than 3.0 mm can be welded without the addition of filler metal.

There were no observed differences in the corrosion resistance of the welded joint surface treated only with the pickling paste or wire brush and etching pastes. This shows that a properly used pickling paste provides the required surface cleanliness of the lean duplex stainless steel S82441 welded joints after TIG welding and the additional surface wire brushing is not necessary. Performed studies shows in most cases that removal of the weld surface layer by milling resulted in a strong increase in the resistance to the pitting corrosion. Depending on applied welding parameters the complete lack of pitting was observed or a significant reduction in their amount.

The resistance to pitting corrosion of A-TIG welded joints (without filler metal) shows, that increase of welding current from 100 to 200A results in increased weld corrosion resistance. The A-TIG welded joints shows higher corrosion resistance than traditional TIG welds (fig. 7). Results of corrosion tests indicate the possibility of A-TIG welding without addition of filler metal, due to advantageous thermal cycle for the duplex microstructure formation. The higher welding heat introduced during welding the slower cooling from welding temperature and thus formation of austenitic phase in higher amounts. This conclusion at the moment refers only to the face of weld and requires corrosion testing of samples with full penetration welds.

The TIG welded joints under shielding of Ar + He mixture, shows surprisingly lower pitting corrosion resistance, when pits were present already at test temperature of 15 °C (fig. 9). The addition of helium to the shielding gas is often recommended during welding of all duplex stainless steels, so such a high susceptibility to pitting corrosion of welded joints made with Ar + He mixture should be studied detailed. The helium addition to Ar shielding gas should produce a hotter arc and conduct more heat to the base metal to increase weld penetration and improve the weld puddle fluidity. The result of He addition is studied welds was non affecting on introduced welding heat and resulting cooling after welding.

The TIG welded joints with the addition of filler metal shows corrosion pits only at test temperature of 35 °C located on fusion line. This proves beneficial role of filler metal during welding of duplex stainless steels including studied lean duplex stainless steel.

The pitting corrosion resistance after ASTM G48 test of TIG welded joints with filler metal of lean duplex stainless S32101 and S82441 shows much more lower susceptibility to corrosion than highly alloyed steel S82441 that revealed pitting corrosion at test temperature 25°C, while welded grade S32101 started already at temperature 0°C.

Tests of pitting corrosion resistance according to ASTM G48 of autogenous TIG welds and ferrite content measurements shows that the susceptibility of welds to the pitting depends not only the ferrite content measured by the Feritscope or other image analysis method, but also on other factors, including ferrite grain size or presence of chromium nitride precipitates [29] that preferentially forms in the heat affected zone (HAZ) and the presence of oxide layers of complex composition depending on applied shielding gas and the base material.

Basing on the result of pitting corrosion resistance it also have been found that when using appropriate surface etchants after welding, more intense discoloration resulting from TIG welding with argon containing nitrogen or helium, does not increase the susceptibility to pitting corrosion of the welded zone. The level of pitting corrosion does not affect applied pre-cleaning before etching of weld surface with a wire brush. However a significant reduction of corrosion pits was visible when the surface of samples was mechanically milled to remove thin metal surface layers.

The results of visual inspection of lean duplex S82441 welds on the root of a weld side shows that increasing welding current from 100 to 160A results in smoother root of weld surface, and not scaly aspect, that is clearly visible on the root of weld welded at current 100A. The smoother and more regular root of the weld surface certainly increases corrosion resistance in the root of weld zone, due to lack of surface irregularity which could stop and accumulate corrosive media and accelerate pitting.

The macrostructure analysis of welded joints showed that the shape of the weld is dependent on the welding current intensity, welding position and the manual skills of the welder performing joints. The most correct shape of root of weld run was obtained when employing current of 100A. Increase the current intensity to 160A caused significant difficulties in ensuring a stable and uniform weld reinforcement on the root of weld side and require significant focus of the welder. Therefore, the majority of tested welds made using a current of 160 A is characterized by the irregular shape of the root of weld surface, caused mainly by excess weld metal, which generally fulfil acceptable limits (level B according to EN ISO 15614-1, point 7.5).

The mechanical test of TIG welded joints shows, that all tested joints meet the requirements in terms of tensile strength of lean duplex stainless steel S82441 (acc. ASTM A240 and EN 1088-2) and the differences between the various joints was very small. The bending test (180°) of welded joints was positive and not revealed to any surface scratches and cracks on the sample surface, on both sides the face and the root of the weld. The impact toughness results (Charpy-V samples) showed that the welded material of HAZ of all welded joints meets the requirements of minimal KV value of 40 J at temperature -40 °C required for standard duplex stainless steel grade 1.4462.

The analysis of welded joint mechanical properties

results indicates that regardless of the welding parameters and the welding positions, all welds meet the requirements of lean duplex stainless S82441. It should be noted that despite the change of welding current and welding speed, the amount of heat input in particular during the weld root run has not fallen below the critical value of 0.5 kJ/mm, which is the lower limit of the recommended range (0.5 to 2.5 kJ/mm) of introduced heat input during welding lean duplex stainless steel. On the other hand, the welding tests carried out with various welding parameters and conditions of prepared welded joints indicate that for a given stainless steel grade and used sheet thickness it is very difficult to obtain joints with unacceptable mechanical properties, which can be in contradiction with the not unusual cases of materials destruction of welded duplex stainless steel construction during operation.

Surface analysis of TIG welded joints with filler metal of lean duplex stainless steel S82441 after pitting corrosion tests according to ASTM G48 in test temperatures 15, 25 and 35 °C showed that pitting occurs only at the highest one 35 °C on both the face and root of weld sides. It was found that corrosion pits occur primarily on the fusion line. However, it has been found that their number is greater on the face of weld side. It is noteworthy to notice, that the surface of the welded material is practically free of pitting (just barely visible small pits) in both sides, the face and the root of weld sides over a range of a test temperature.

6. Conclusions

1. The pitting corrosion resistance test according to ASTM G48 of TIG welded joints without addition of filler metal (autogenous welding) with argon and argon with nitrogen mixtures of a shielding gas at test temperatures of 15, 25 and 35 °C showed a large number of pits formed in all samples at temperatures 25 and 35 °C. The corrosive pits were found only in the weld material. The addition of nitrogen to the shielding gas did not increase the corrosion resistance of studied welded joints.
2. The surface of A-TIG welded joints shows a much lower tendency to pitting corrosion than the welds made by conventional TIG welding. The resistance to pitting corrosion of the welds made by the A-TIG method increased with increasing welding current from 100 to 200 A.
3. Application of the shielding gas mixture of 50% helium and 50% argon to traditional TIG welding causes a decrease in resistance to pitting evaluated by ASTM G48 method, which is not in accordance with the well-known recommendation to use the additive helium during welding of duplex stainless steels.
4. The mechanical properties of butt welds of lean duplex stainless steel S82441, 15.0 mm thick made by the TIG method in various welding positions meet the requirements of standards ASTM A240 and EN 10217-7 for duplex stainless steels.
5. The pitting corrosion tests according to ASTM G48 at temperatures of 15, 25 and 35°C of welded joints showed that the pitting was formed in all samples from both side the face and the root of weld side, mainly on the fusion

line, only at test temperature of 35 °C. The corrosion pits were practically absent in the weld zone.

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