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An Influence of Nitrogen Corrosion on Microstructural and Mechanical Features of the X5CrNi18-10 Steel

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Abstract

Corrosion-resistant steels form an important group of structural materials who's mechanical and corrosion-resistant properties are an irreplaceable part of the engineering industry. Despite their designation as "stainless steel", it is necessary to consider that even these steels can be subject to various types of corrosion attack under certain conditions. The article presents the effect of a controlled protective nitrogen atmosphere on X5CrNi18-10 steel, which is used to produce auxiliary components in the automotive industry. Steel X5CrNi18-10 is not only subject to corrosion after a short time (2hr) in a nitrogen atmosphere, at a temperature of 570 to 630°C, but at the same time the mechanical properties also change. Nitrogen atmosphere is used in heat treatment in automotive and X5CrNi18-10 steel is often used in these conditions as an auxiliary material, e.g. base grid. One test for X5CrNi18-10 steel was that the samples were exposed to a nitrogen atmosphere at various temperatures and then the agreed yield stress Rp0.2, hardness and microstructure were evaluated. The second test was the evaluation of the frame made of the given steel at 630 °C. The testing took place in a continuous furnace. Temperatures above 500 °C significantly changes the material's features.

Keywords: Protective atmosphere, Corrosion, Anti-corrosive steels

1. Introduction

The properties of materials are, in certain cases, fundamentally influenced by the effects of the environment to which the material is exposed. Among the most significant cases following materials applications the increase of temperature value and presence of corrosion environment may be indicated. Changes in temperature influences the properties of materials, for example, metals that have been strengthened by a certain heat treatment or forming technology may suddenly lose strength when heated [1, 2]. Increasing the temperature usually reduces the strength, stiffness and increases the plasticity of the material. During the heating of the metal, the surface of the material may be adversely affected by the environment in the furnace space. In shaft, chamber and wagon furnaces, an oxidizing atmosphere is usually used, which causes oxidation of the material surface, this case can lead to a decrease in surface quality [3, 4]. At elevated temperatures, the conditions for oxidation kinetics improve, for this reason most metals react with oxygen but also with other gases precisely at elevated temperatures [5, 6]. Oxidation of metals up to temperature value of 600-650 °C is almost negligible. At temperature value higher than 700 °C, a strong oxide layer forms on steels, and the surface under this layer is also significantly damaged. The thick oxidic layer formed during heating on the surfaces of steels is usually called scale. The chemical composition of this layer mainly depends on the heating temperature. Thicker oxidic layers, iron oxides, most often have an iron content of around 30%, the rest is oxygen, while the content of impurities is usually insignificant [7, 8, 9]. The oxidized layer is the reason for the different values of hardness, reduces the fatigue limit, etc. Oxidation of steel during heating also lowers of the weight of usable metal. These weight losses due to oxidation are called burn-through and are usually given in weight percentages, i.e. the ratio of the weight of the fittings to the total weight of the heated material [10].

Decarburization and oxidation are related because both processes take place in the surface layers of metals and are the result of chemical reactions between the environment and the heated material. Usually, decarburization precedes oxidation. However, the formation of an oxidation layer gradually prevents decarburization [11]. The more intense the oxidation, the slower the decarburization. The most suitable atmosphere would be neutral, i.e. one in which neither decarburization nor oxidation of the surface layers will take place. However, such a neutral state of the atmosphere is not achieved in natural furnace atmospheres. For the optimal state of the metal surface, we need to know how the metal interacts with the environment and determine the optimal heating parameters. In many cases, it is necessary to protect the surface of heated metals against environmental influences [12]. Protection against decarburization and oxidation can be implemented in two ways. By creating a protective layer on the surface of the part that separates the metal surface from the natural environment of the furnace. By replacing the natural environment in the furnace with an artificial one that does not react or reacts minimally with the heated material [13]. We can compare individual protective atmospheres from several points of view. A common feature of these atmospheres is that they protect the material against oxidation and decarburization. Each atmosphere is suitable for heat treatment of certain types of steel. The following table provides a brief overview of the use of individual protective atmospheres [14, 15]. Protective atmospheres can also be compared in terms of price. Exoatmospheres are cheap and suitable for use in almost all types of furnaces. Exomono atmospheres are also relatively cheap, but during their production, carbon dioxide must be removed, which means that the developers of these atmospheres are structurally more demanding. Endoatmospheres are among the better protective atmospheres. They are more expensive than exoatmospheres and exomonoatmospheres, because their production requires a significant input of energy. Nevertheless, their use in heat treatment is much more economical than heat treatment without the use of a protective atmosphere. Split ammonia and split methanol also have a high price, the disadvantage is their explosiveness [16, 17]. Protective atmospheres made of nitrogen and noble gases are too expensive for common practice. Industrially supplied nitrogen contains a certain amount of oxygen and moisture. These undesirable components must be reduced to some extent before use in order to avoid oxidation or decarburization [18]. This cleaning also increases the cost required to use a nitrogen shielding atmosphere. Industrially supplied nitrogen contains a certain proportion of oxygen and moisture. In order to prevent decarburization and oxidation, industrial nitrogen must be cleaned of this moisture before use. However, cleaning nitrogen from unwanted components is too expensive, because in real conditions it cannot be guaranteed that oxygen from the air will not enter the furnace [19]. It is more advantageous if the furnace atmosphere contains a certain proportion of gas that chemically binds oxygen to itself (e.g. hydrogen). Of the rare gases, argon and helium are particularly suitable, but the costs of their production and purification are also high for the area of heat treatment. Protective atmospheres are used in the engineering industry for various technological and chemical-technological processes, for example welding in a protective atmosphere. Protective atmospheres have the task of protecting the material from oxidation, corrosion and decarburization, respectively carburization [20].

2. Materials and Methods

The test material is steel X5CrNi18-10 (AlSI304). It is an austenitic steel with excellent corrosion resistance in a natural environment (atmosphere, atmosphere) without a significant concentration of chlorides or agents. It is easily weldable with and without filler metal. Heat treatment after welding is not necessary. Due to its high fracture toughness, it is necessary to pay attention to the correct cutting data during jet machining. Good malleability. Steel is used to make a variety of automotive parts such as exhaust systems, grilles and trim strips. With advancing technology, manufacturers prefer stainless steel for manufacturing structural components. Very good polishability, especially good face for deep drawing, edging and others. Since it is highly tough, it is therefore necessary to allow the correct cutting conditions during machining. It is used in the pharmaceutical, food and chemical industries in the production of beams, rod material, profiles or gratings [20]. Anti-corrosion steel are high-alloy materials used for parts working in an environment in which they have the usual steel with a minimum service life, that is, they have increased resistance to an aggressive environment. These environments can be oxidizing or non-oxidizing. Under certain conditions, the anti-corrosion layer must be used as a protective layer that slows down corrosion. The basic alloying element of anti-corrosion steels is chromium Cr. A minimum of 12% chromium concentration is required to ensure corrosion resistance in oxidizing environments when other alloying elements are not present [21, 22, 23]. Chromium ensures the formation of a protective passivation layer in an oxidizing environment, preventing corrosion of the material. In alloy steels of structures, with few exceptions, the same components as in carbon steels, namely ferrite, δ-ferrite, austenite, cementite, pearlite, bainite, martensite, ledeburite. The differences are only that individual solid solutions and cementite dissolve a number of alloying elements in a solid amount, and some elements form special carbides with carbon [24].

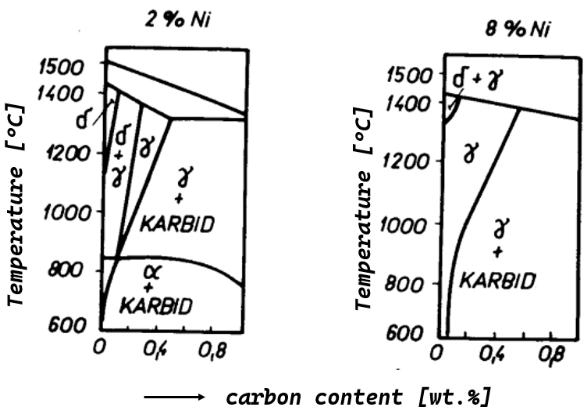

Fig. 1. Effect of nickel content in steel with 18% nickel content [25]

During alloying, the solubility of carbon in individual Fe modifications changes, as a result of which equilibrium lines in the Fe-C diagram shift. Therefore, alloying elements also affect the transformation temperatures α/γ and γ/δ in steel [25, 26]. The tool used for the preliminary determination of the resulting structure of stainless steels, which is based precisely on the graphic function of the chromium equivalent and the nickel equivalent, is called the Schäffler diagram (fig. 1).

In tab. 1 is the chemical composition of the tested material. Q2 ION spectrometer.

Table.1.

Chem. element	Wt. [%]		
	Sample	X5CrNi18-10	
		min.	max.
C	0,053	-	0,07
Si	0,205	-	1,00
Mn	2,059	-	2,00
S	< 0,010	-	0,03
P	< 0,010	-	0,045
Cr	18,240	18,00	20,00
Ni	7,656	8,00	10,00

We classify the X5CrNi18-10 steel among the austenitic, chrome-nickel steels. Nickel is an austenite-forming element that expands the austenite region in Fe alloys. Although chromium belongs to the ferrite-forming elements, with a suitable concentration of Cr and Ni, these steels have an austenitic structure at room temperature. Chromium-nickel steels are highly susceptible to intercrystalline corrosion if they are exposed to temperatures in the range of 425 - 870 °C for a long time. Then chromium carbides $Cr_{23}C_6$, which have a relatively high chromium content, are secreted at the grain boundaries, thus the grains are depleted of chromium. If the chromium concentration falls below 12%, intercrystalline corrosion occurs. This can be prevented by stabilization with elements Ti, Ta, Nb, or a low concentration of carbon in this steel. The microstructure of the basic materials before the test is shown in fig. 2.

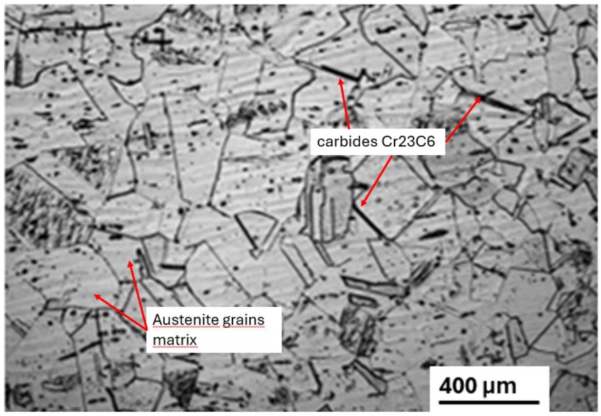

Fig. 2. Microstructure of X5CrNi18-10. Basic material

In Fig. 3 shows the microstructure of X5CrNi18-10, where intercrystalline corrosion can already be clearly seen along the material boundary. samples. We can observe the local exclusion of $M_{23}C_6$ carbides along the austenitic grain boundaries [27, 28, 29].

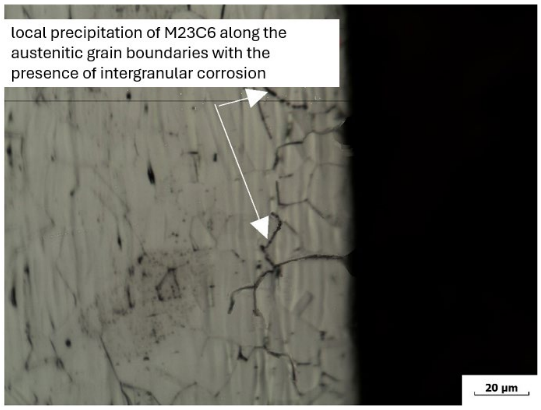

Fig. 3. Microstructure X5CrNi18-10

Since the test material in our case is used as a frame, welded from sheet metal, it has a characteristic structure after hot rolling. In Figure 4, we observe X5CrNi18-10 steel stretched in the form of forming.

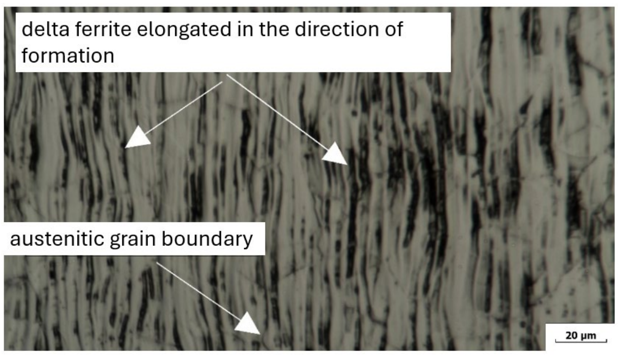

Fig. 4. Material microstructure elongated in the direction of forming

The service life of the material is very important in practice, especially from an economic point of view. The aim of the work was to analyse the effect of the nitrogen atmosphere on X5CrNi18-10 steel, which is used as a grate in automotive furnaces. The base on which the parts are placed, the whole set is subsequently placed in the furnace space, where it is exposed to a nitrogen atmosphere. The appearance of the frame can be found in fig. 5. In principle, the frame is a metal structure on which parts of the coolers are located placed. These frames were designed so that they could be stacked on top of each other, and also there was no damage to the individual parts of the coolers. The frames are then placed in a continuous furnace with a nitrogen atmosphere, where the process of soldering the individual parts of the aluminum coolers takes place. The soldering of the coolers itself takes place at temperatures T = 570-630 °C, which means that the frames are also subject to these demanding conditions. The testing process itself took place in such a way that the steel was in a nitrogen atmosphere at temperatures from 150 °C to 630 °C. The agreed yield stress, hardness, enamel layer and microstructure were evaluated. The material behaviour was always monitored after 2 hours in the continuous furnace.

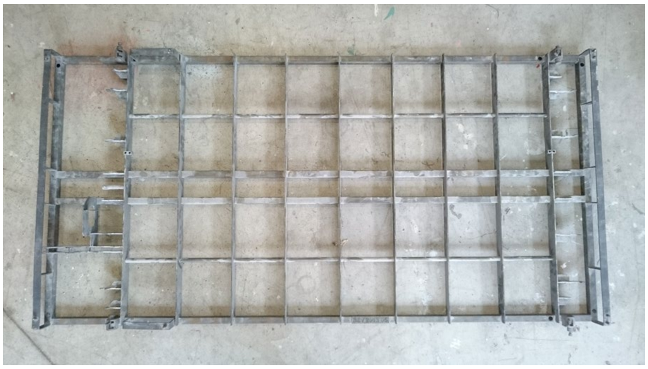

Fig. 5. The radiator frame before examining in the nitrogen atmosphere

3. Results

3.1. The frame

The nitrogen atmosphere at temperatures up to 150 °C has no effect on the degradation of X5CrNi18-10 steel grating, because nitrogen has a favorable effect on improving the quality of the mechanical properties of austenitic steels. However, the steel grade is long-term exposed to elevated temperatures, i.e. 570-630 °C, which results in local precipitation of chromium carbides at the austenitic grain boundaries. The steel became locally depleted of chromium and intergranular corrosion occurred.

Since the frame is made of X5CrNi18-10 steel, which is not heat-resistant, the frame corroded quite quickly. Since the grid is repeatedly placed in the continuous furnace and exposed to temperatures from 570 to 630 °C, the black color and the formed ironwork on the frame are a common phenomenon in the given working environment. Therefore, X5CrNi18-10 steel was not the most suitable choice for these frames. However, after a certain period of use, these frames turned black and showed significant elements of corrosion. Their condition can be seen in the following figure 6. Figure 7 presents the ironwork layer.

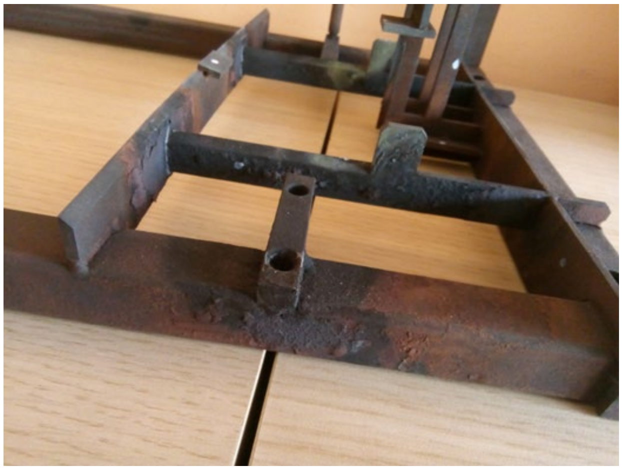

Fig. 6 The radiator frame after 6 hours in a nitrogen atmosphere at 630°C

Determining the thickness of the rust layer is one of the first verification methods. The thickest layer measured was 42 µm on a digital microscope.

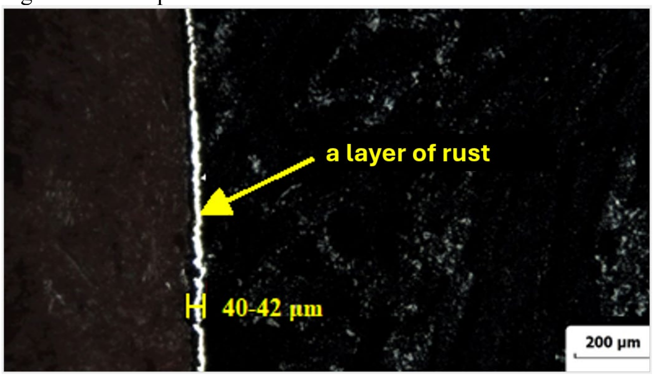

Fig. 7. Image of a layer of rust in a dark field

3.2. Sample research - agreed yield strength Rp0.2, hardness and nanohardness

The agreed yield stress was evaluated based on the comparison of tensile tests. For the tensile test, the specimens were made in a set of 5 pieces/10 sets. The steel specimens were in a nitrogen atmosphere at different temperatures for 6 hours. At the same time, Brinell hardness was measured on each tested object. The measurement values in the graph and in the picture are average values. By processing the results into a graphical dependence, it was clearly demonstrated that there are striking differences from the point of view of evaluating the agreed yield strength. The experiment shows a decrease in yield stress and hardness due to increasing temperature. The highest value of yield stress was noticed at 150 C. As the temperature increases, the yield stress decreases to 86 MPa at 650 °C.

Table.2

Temperature [°C]	Rp0.2 [MPa]	Hardness HBW 2.5/187.5	Indentational hardness HIT [MPa]
150	140	215	$7{,}1.10^3$
250	118	211	7.10^3
350	104	209	$6{,}2.10^3$
450	95	201	6.10^3
500	92	192	$5{,}9.10^3$
550	90	188	$5{,}7.10^3$
570	89	180	$5{,}4.10^3$
600	88	176	5.10^3
630	86	175	$4{,}5.10^3$
650	86	170	$4{,}3.10^3$

Depth-sensitive indentation - nanoindentation, is one of the methods of examining materials. Using nanoindentation, materials are examined in order to compare changes in mechanical properties over different periods of time. Low loading and displacement values are recorded. Using an analytical model, loading and displacement data can be used to determine hardness and other mechanical properties [20]. The results from the nanoidentification are shown in the graph (Fig. 6). Indentation parameters: Acquisition Rate: 10.0 [Hz], Approach speed: 3000 nm/min, Max load: 3.00 mN, Stiffness Threshold: 500 µN/µm. The average values of strength, hardness and nanohardness are shown in tab. 2.

4. Discussion

Production in the engineering industry is complicated and includes surface deformation processes. Surface damage is a phenomenon that affects the durability of the component. One of the main factors that affects the material in operation is the temperature and characteristics of the environment. Since X5CrNi18-10 steel shows significant signs of corrosion even at relatively low temperatures (from 500 °C), it does not appear to be a suitable material for acidic atmospheres and elevated temperatures. The lifetime assumption is low, and in practice this can translate into a high economic burden. When choosing a suitable material, it is important to take several factors into account, for example the chemical influence of the surrounding environment, the influence of temperature, operating conditions, the conditions under which the component will be exposed, etc. The structure (grain size, grain shape) and material preparation technology (casting, rolling...) are also important, as these also significantly affect the resulting properties of the materials. Finally, the price can also play a role in the choice of material. The choice of inappropriate material results in a decrease in the service life of the component, because of its dysfunction. Therefore, it is important to carefully evaluate all these factors when choosing a material. An important criterion for steels that are suitable for a nitrogen atmosphere is the chromium content min. 12%, as little as possible of carbon, which increases susceptibility to intercrystalline corrosion [30]. By alloying with the elements Ti, Nb, Ta, which have a higher affinity to C than to Cr, we can also prevent the occurrence of corrosion, because corrosion is a very undesirable phenomenon, it causes deterioration of the material and, in more advanced stages, dysfunction of parts and components, and other additional costs are closely related to this in operation. Stainless or anti-corrosion steels are largely resistant to aggressive corrosion environments.

Corrosion is usually minimized by coating. Coatings improve the surface of the tool, extend its life, and improve the quality of the manufactured parts. In the deep drawing industry, there is an effort to reduce sheet thicknesses, increase their strength and dynamic load capacity. Simply put, the sheets should be thin, strong, and well formable [31, 32], so that they show good resistance to corrosion.

Figure 8 presents a graphical evaluation of individual experimental tests. The mechanical properties have a decreasing character depending on the temperature in the nitrogen atmosphere. Knowledge of how the material reacts in the furnace atmosphere is important for practice. The obtained data show that X5CrNi18-10 steel is not suitable for working in a nitrogen atmosphere. High temperatures have a degrading effect on steel.

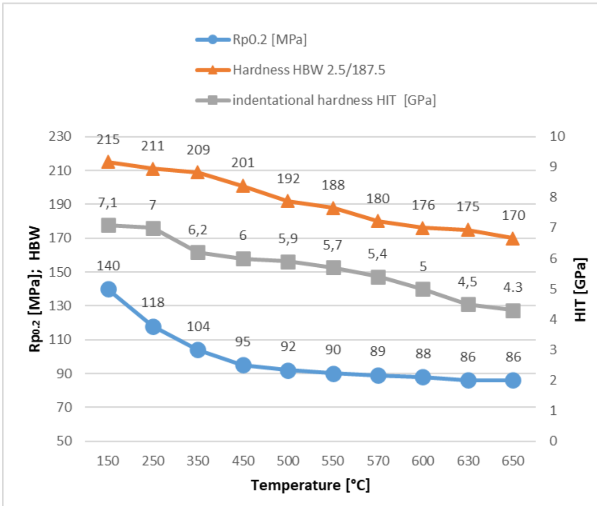

Fig. 8. Rp0.2 [MPa] – blue; Hardness HBW 2.5/187.5 – orange; HIT [GPa] – grey

5. Conclusions

- The first part of the experimental test represents a steel grade monitored in a nitrogen atmosphere in a continuous furnace at 630 °C. Cracks and extensive corrosion occurred after 6 hours.
- The second part follows the tested specimens. The formation of intercrystalline corrosion appears from 150 °C/ 2hr.
- The yield stress is highest at 150°C – 140 MPa and lowest after 650°C – 86 MPa.

- The hardness of HBW has a similar feature. The Highest at 150 °C – 215 HBW; the lowest at 650°C – 170 HBW.
- Indentational hardness HIT at 150 °C – $7.1.10^3$ MPa; the lowest at 650 °C – $4.3.10^3$ MPa.

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References

[1] Krajewski, S.J., Gutsche, W. & Urbanowicz, K. (2023). Analysis of X5CrNi18-10 (AISI 304) steel susceptibility to hot cracking in welded joints based on determining the range of high-temperature brittleness and the nil-strength temperature. *Metals*. 13(10), 1633, 1-19. https://doi.org/10.3390/met13101633.

[2] Zalecki, W., Wrozyna, A., Łapczynski, Z. & Molenda, R. (2016). Influence of Microstructure on Some Properties of AHSS Steels. *Journal of Matallic Materials*. 68, 19-25. (in Polish).

[3] Kurc-Lisiecka, A., Ozgowicz, W., Kalinowska-Ozgowicz, E. & Maziarz, W. (2016). The microstructure of metastable austenite in X5CrNi18- 10 steel after its strain-induced martensitic transformation. *Material in Technologije*. 50(6), 837-843.

[4] Vaško, A. (2014). Fatigue life of synthetic nodular cast irons at high frequency loading. *Scientific Papers of the University of Pardubice Series B*. 19, 121-128.

[5] Fojt-Dymara, G., Opiela, M. & Borek, W. (2022). Susceptibility of High-Manganese Steel to High-Temperature Cracking. *Materials*. 15(22), 8198, 1-12. https://doi.org/10.3390/ma15228198.

[6] Kawulok, R., Schindler, I., Navrátil, H., Ševčák, V., Sojka, J., Koneˇcná, K. & Chmiel, B. (2020). Hot formability of heat-resistant stainless steel X15CrNiSi20-12. *Archives of Metallurgy and Materials*. 65, 727-734. DOI: 10.24425/amm.2020.132812.

[7] Švec, P. (2010). *Construction materials*. STU Bratislava. ISBN 978-80-227-3386-1.

[8] Siddique, A.G., Vijaya, R.B., Elanchezhian, C., Siddhartha, D. & Ramanan, N. (2019). Analysis of the friction welding mechanism of low carbon steel–stainless steel and aluminium—copper. *Materials Today: Proceedings*. 16, 766-775. https://doi.org/10.1016/j.matpr.2019.05.157.

[9] Kawulok, P., Schindler, I., Smetana, B., Moravec, J., Mertová, A., Drozdová, L'., Kawulok, R., Opěla, P. & Rusz, S. (2020). The relationship between nil-strength temperature, zero strength temperature and solidus temperature of carbon steels. *Metals*. 10(3), 399, 1-14. https://doi.org/10.3390/met10030399.

[10] Skočovský, P., Bokuvka, O., Konečná, R. & Tillová, E (2014). *Material Science*. EDIS - vydavateľstvo Žilinskej univerzity, 349. ISBN 978-80-554-0871-2. (in Slovak).

[11] Macek, W., Pejkowski, Ł., Branco, R., Nejad, R.M. & Zak, K. (2022). Fatigue fracture surface metrology of thin-walled tubular austenitic ˙ steel specimens after asynchronous loadings. *Engineering Failure Analysis*. 138, 106354. https://doi.org/10.1016/j.engfailanal.2022.106354.

[12] Adamiec, J. (2023). Assessment of the hot-cracking susceptibility of welded joints of the 7CrMoVTiB10-10 bainitic steel used in heat exchangers. *Energies*. 16(1), 162, 1-21. https://doi.org/10.3390/en16010162.

[13] Dossett, J., Boyer, H. (2006). *Practical Heat Treating. Second Edition*. Ohio: ASM International. ISBN: 0-87170-829-9.

[14] Kocich, J., Tuleja, S. (1983). *Corrosion and protection of metals*. Bratislava: Alfa.

[15] Rajasekhara, S., Karjalainen, L.P., Kyröläinen, A. & Ferreira, P.J. (2010). Microstructure evolution in nano/submicron grained AISI 301LN stainless steel. *Materials Science and Engineering*. 527A, 1986–1996. DOI:10.1016/j.msea.2009.11.037. https://doi.org/10.1016/j.msea.2009.11.037.

[16] Blicharski, M. & Gorczyca, S. (1979). Structural inhomogeneity of deformed austenitic stainless steel. *Metal Science*. 12(7), 303-312. DOI:10.1179/msc.1978.12.7.303.

[17] Fabian, P., Kečková, E., Beták, P. (2007). *Heat treatment of metals*. Svidník: Tlačiareň svidnícka, s.r.o. ISBN 978-80-969592-7-3.

[18] Lee, W.S. & Lin, C.F. (2000). The morphologies and characteristics of impact-induced martensite in 304L stainless steel. *Scripta Materialia*. 43(8), 777–782. DOI:10.1016/S1359-6462(00)00487-5

[19] Das, A., Sivaprasad, S., Ghosh, M., Chakraborti, P.C. & Tarafder, S. (2008). Morphologies and characteristics of deformation induced martensite during tensile deformation of 304 LN stainless steel. *Materials Science and Engineering*. 486A (1-2), 283-286, DOI:10.1016/j.msea.2007.09.005.

[20] Skočovský, P., Durmis, I. (1984). *Technology of heat treatment of metals*. Bratislava: ALFA.

[21] Abid, M, Nash, D.H., Javed, S. & Wajid, H.A. (2018). Performance of a gasketed joint under bolt up and combined pressure, axial and thermal loading – FEA study. *International Journal of Pressure Vessels and Piping*. 168, 166-173. https://doi.org/10.1016/j.ijpvp.2018.10.014.

[22] Moravec, J., Jančušová, M., Kuba, J., Stroka, R. (2010). *Technology of forming technical materials*. Edis. ISBN 978-80-554-0220-9.

[23] Pfann, W.G. (1963). *Zone melting*. New York: John Wiley and sons.

[24] Tillová, E., Kucharikova, L., Belan, J. (2020). *Steels with special properties - anti-corrosion steels*. 2020. http://kmi2.uniza.sk/wp-content/uploads/2020/01/1_Obsah-%C3%9Avod-2.pdf.

[25] Dorazil, E. et.al. (1979). *Material science II*. Brno. ISBN: 55-600-79.

[26] Pluhar, J., Koritta, J. (1966). *Engineering materials*. SNTL Publishing house of technical literature. Praha.

[27] Albaharna, O.T., Argyropoulos, S.A. (1988). Artificial intelligence for materials processing and process control.

Journal of Metals. 40(10), 6-10. https://doi.org/10.1007/BF03257973.
[28] Davis, J.R. (1994). *Stainless steels*. Chagrin falls: ASM international. ISBN 0-87170-503-6
[29] Bernasovský, P. (2017). Atypical Cases of Welded Structure Failures. *Solid State Phenomena*. 270, 86-92.
[30] Martinec, J., Šveidler, Z., Janovec, J. (2014). *Corrosion-resistant materials - basic types of steel and recommendations for their weldability.* Retrieved Marcg, 8, 2023 from http://old.konstrukce.cz/clanek/korozivzdorne-materialy-zakladni/typy-oceli-a-doporuceni-pro-jejich-svaritelnost/
[31] Brenner, O. (2003). *Corrosion-resistant steels as structural materials.* Retrieved April, 2, 2023 from https://www.mmspektrum.com/clanek/korozivzdorne/oceli-jako-konstrukcni-materialy.
[32] Bahrami, A., Taheri, P. (2019). A study on the failure of AISI 304 stainless steel tubes in a gas heater unit. *Metals*. 9(9), 969. 1-7. https://doi.org/10.3390/met9090969.