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INDOOR CONCENTRATION AND COMPOSITION OF FINE PARTICULATE MATTER (PM2.5) NEAR AN INTENSE CIRCULATED ROAD IN AN INDUSTRIAL CITY

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ABSTRACT

The purpose of the present work is to present results from a measuring campaign during February-March 2020, in Galati city, Romania, aiming the concentration of fine particulate matter ($PM_{2.5}$) in air and their heavy metal concentrations, then comparing the results with the air quality determined by the national monitoring system from the same city. Results show considerable differences concerning the air quality measured in this study compared with measurements of the national monitoring system that consist in four stations placed across the city. While values recorded in this study exceeded, in some situations, the maximum target from $PM_{2.5}$, the reports from the national monitoring system presented a good air quality, using a colour- and number-coding (maximum level 4 out of 6 was reported). Heavy metal concentrations of the fine particulate matters collected in this study was compared with other studies across the world, high Fe and Zn values being registered in agglomerated and industrialized cities, including the city considered in the present study, while in a study conducted in Beijing, China most higher values between all analysed heavy metals were recorded.

KEYWORDS: air quality, fine particulate maters, X-ray fluorescence

1. Introduction

The overall environmental situation in the world made air, water and soil quality monitoring to become compulsory in some situations. Air quality monitoring became compulsory in Romania, according to European Directives, for all urban agglomerations surpassing 100,000 inhabitants [1]. The pollutants taken into consideration and the way the air quality status is presented to the population was also standardized and included into Romanian legislation [2].

During air quality monitoring, two types of particulate matter (PM) dimensions are usually taken into consideration: $PM_{2.5}$ and PM_{10}, the later one being more frequently tracked, at least according to the Romanian legislation [2, 3]. This might be since this type of particle matter analysis also include the other, finer and more dangerous, PM dimensions: $PM_{2.5}$. The $PM_{2.5}$ quantitative analyses represent the determination of cumulative particulate matters mass for particle fraction with a 50% aerodynamic cutoff diameter of 2.5 µm in a known volume of analyzed atmospheric air [4-6]. The effect of this type of pollutant is well documented [7-8] and works are still emerging in the specialized literature, especially in Asia [9-12], where multiple great human agglomerations creates the premises [13] for extremely high values of particulate matters in the atmosphere (e.g.: a mean concentration of 102.45 µg/m^3 in Beijing, China, during 2015-2016 period, for $PM_{2.5}$) [14].

This type of pollutant was chosen for the present study since the finer share of particulate matters is considered most dangerous for the human health and although permanent monitoring stations already exist, articles from Eastern Europe are scarce and qualitative analysis of these particulates are even more so. While, as mentioned above, there are some hints regarding the effect of $PM_{2.5}$ on human health, the corroboration of qualitative analyses and health effect was not identified in the specialized literature and the possibility to do just that might emerge once a sufficient amount of data will be at hand. In this regard, this paper aims to present a comparation of air quality resulted from the local monitoring system and that registered in a residential apartment focused on the quantitative analysis of $PM_{2.5}$. Also, qualitative

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analysis (heavy metals concentration) was addressed, obtained data being compared with other studies around the world, most of them also focused on indoor $PM_{2.5}$ determination.

2. Materials and methods

The sampling campaign took place in Galati (an approx. 250,000 inhabitants city in south-east of Romania), in a building facing a four-line road with a fairly high traffic (Latitude: 45.433650, Longitude: 28.028543), during February and March 2020. The sampler was placed intermittently (24 hours for each filter) in a living room and inside its enclosed balcony (at all times with both balcony and living room windows being tilt-opened) of a residential apartment at the third floor. Against the pollution and noise from the road, as a green buffer (although during the sampling period the trees were without leaves), the building in discussion has a line of trees high enough to reach the fourth floor, situated between the road and the sidewalk near the building. The sampler was placed each time on the floor with its filter holder being situated at a height of 1.2 m.

2.1. Gravimetric analysis

In the present study, the same instruments and methodology as in [15] was used. Thus, for $PM_{2.5}$ collection an Automated Aerosol Sampling Device, type ISAP 1050e, was utilized (Figure 1-left). The flow rate of this device was equal to 2.3 m^3/h. Particulate matters were collected on a glass microfiber with 45 mm in diameter, a 0.30 mm in thickness and 0.7 μm in pores size (Figure 1-right), the support holder used this time being a specially $PM_{2.5}$ type one (Figure 1-middle). The filter was placed in the holder, between a rubber garniture and a metallic made mesh as a support. Before and after the aerosols collection, the filter was weighted using an analytical balance (type ALT 220-4NM, from KERN). The particulate matters collection time for each measurement was 24 hours, each time a new filter being used. The quantity of $PM_{2.5}$, expressed in $\mu g/m^3$, for one analysis was calculated based on the overall particles mass (gravimetrically analyzed), the volume of air filtered by the sampling device and the functioning time of this device (both values automatically calculated by the sampler and presented in a report and downloaded from the sampling device after each 24 hour functioning time).

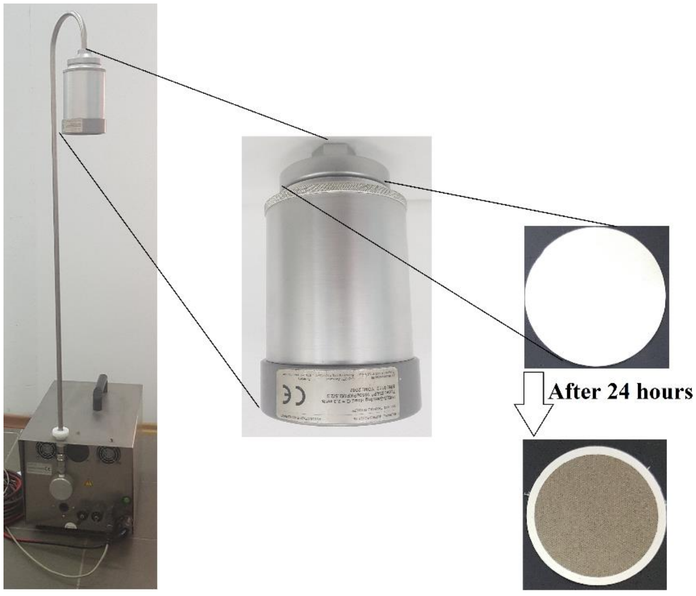

Fig. 1. *The Automated Aerosol Sampling Device, type ISAP 1050e, used for $PM_{2.5}$ collection (left) and the support holder (middle) for the glass microfiber filter (right-up), blackened by particulate matters after 24-hours utilization (right-down)*

2.2. Qualitative analysis of fine particulate matters

Before and after a 24-hour functioning of the sampling device, the filter was placed/extracted into/from the holder and weighted. Also, before and after the 24-hour functioning of the sampler, the side chosen to accumulate particulate matters was analyzed to determine the elemental composition using an INNOV-X type (α A-4000 series) X-ray fluorescence (XRF) spectrometer with an X-ray tube with acceleration tension of 40 kV, a Si-PiN<280 eV diode detector (thermoelectrically cooled), with 5.95 eV/K-α line. The values of XRF analyses represents an average of six separate readings, each reading being done on different surface of the same filter side. This way, most of the filter surface exposed to the intake air was analyzed before and after the sampling, increasing the obtained data solidity. As in [15], the concentration of heavy metals in retained $PM_{2.5}$ samples was calculated as described in [16]. Thus, the average value mentioned above (expressed in μg/cm^2) was multiplied with the exposed filter area (12.56 cm^2, smaller than the actual filter area of 15.89 cm^2), subtracting the value obtained the same way for the blank filter, then dividing by the air sample volume (55.2 m^3) and then multiplying with 1000 so the final data to be expressed in ng/m^3 (Equation 1).

$$HMC = \left(\frac{(Av_{UF} - Av_{BF}) \times EFA}{SV}\right) \times 1000, \text{ [ng/m}^3\text{]} \qquad (1)$$

where:

HMC - concentration of a certain heavy metal, [ng/m^3];

Av_{UF} - average value concentration of a certain heavy metal for a used filter, [μg/cm^2];

Av_{BF} - average value concentration of a certain heavy metal for a blank filter, [μg/cm^2];

EFA - exposed filter area (12.56 cm^2);

SV - air sample volume (55.2 m^3).

The values obtained after performing this analysis were then compared with those from the available literature, also aiming $PM_{2.5}$ qualitative measurements. The elements detected in this study (Ti, Ba, Cr, Mn, Fe, Zn, Rb and Sr) might not be mentioned in the legislation regarding their maximum permitted values, instead a comparison with other studies might offer an insight related to the fine particulate matters concentration from the elemental point of view.

3. Results and discussions

Results of this work, regarding the $PM_{2.5}$ concentration, were placed in contrast with results from the national monitoring system. The national monitoring system has 4 stations placed inside Galati city and the results are presented on the official website for each measured pollutant [17]. Also, to ease public information, an electric panel placed in a visible place inside the city presents in a color- and number-coded way the situation of air quality. Monthly reports are also available on the official website [18] and those issued for February and March periods were used for comparison in this study.

Since most of heavy metals concentrations in air are not regulated, a comparison was possible only with the available literature and various studies from numerous countries from different continents were selected.

3.1. Evolution of $PM_{2.5}$ concentration in the analyzed air samples

Results regarding the $PM_{2.5}$ concentration are presented in Figure 2, separately presented for living room and balcony sampling. Also, according to the national legislation, starting from 1st January 2020, the maximum annual exposure must not exceed 20 μg/m^3, and this value is represented as a constant in Figure 2. As expected, values inside the living room (average of 19.32 μg/m^3) are lower compared to those from the balcony (average of 37 μg/m^3). Nevertheless, it is worth mentioning that although the sampling from living room took place in a space separated from the outdoor atmosphere by two rounds of tilted windows, the maximum value recorded for this type of particle matters was 22 μg/m^3 and the minimum was not far behind. Furthermore, all values inside the balcony, thus separated only by one tilted window from the outside atmosphere, exceeded the annual maximum limit of 20 μg/m^3. The highest value, of 54 μg/m^3, represents almost three time the admissible value and the average for the balcony almost double. It must be mentioned that the weather was also monitored and no major differences were recorded. For the February-March 2020, the temperature varied between 5 and 20 °C, very few and brief showers, and the relative humidity varied between 45 and 81%.

For the same period, the reports for Galati city issued by the national agency presents a good air quality, using the beforementioned coding system. This coding system present 6 levels, based on each measured pollutant concentrations. If any of the five pollutants (SO_2, NO_2, O_3, CO and PM_{10}) measured by the monitoring station reaches a high level, the overall air quality is considered to be of that level. For the considered period, the air quality level varied between 1 and 3 for all four monitoring stations in February [19] and between 1 and 4 for all four monitoring stations in March [20], meaning that no exceeding of maximum values for PM_{10} was recorded. Although the monitoring stations measure PM_{10} and the present study presents values for $PM_{2.5}$,

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the overall quality of air samples might be compared since the PM_{10} fraction also incorporate fine particulate matters. However, as presented in [21], various methods or instrumentation used for measurements and different people or places involved, represent a big factor that might influence the outcome, especially regarding the fine fraction of the particulate matters. Also, in [22] data from a monitoring station in Galati city was used to demonstrate the dependence of particulate matter concentration from air on wind speed. All of these being considered, it can be stated that the air quality monitoring should continue in agglomerated cities and the national monitoring system could reevaluate the positioning of some monitoring stations or their supplementation, so that relevant data to create the premises for future actions in pollution mitigation. The city considered in this study is an industrial one, a steel company and a naval yard flanking it from west and east respectively. Also, a large number of vehicles (approx. 216,000, of all types [23]) ads as the major source of $PM_{2.5}$ pollution especially inside the city and mostly for locations near roads with high traffic, like the one selected for this study. More detailed and relevant information regarding the air pollution could in the end be the starting point for measures needed to obtain a less polluted air and consequently less pollution related diseases.

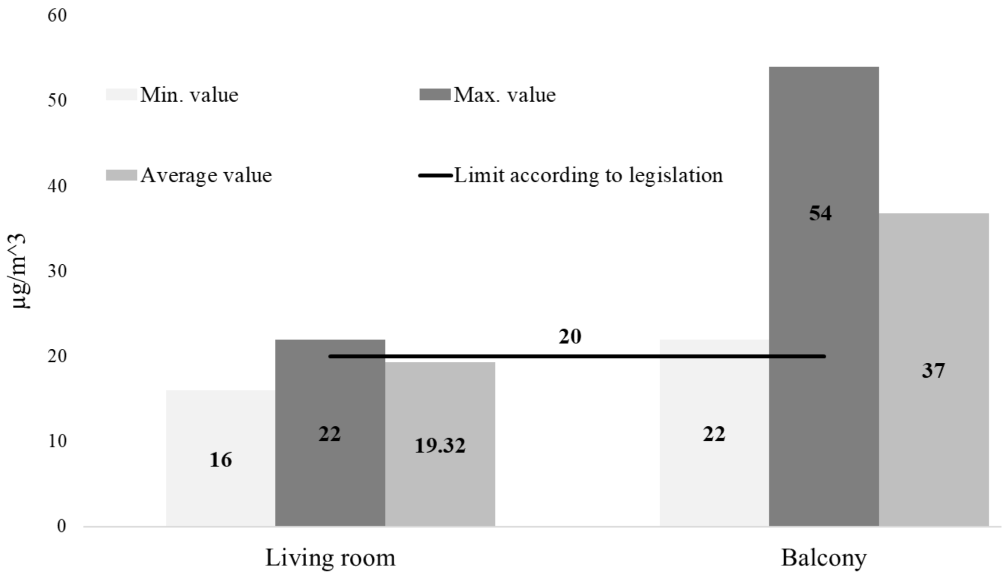

Fig. 2. *Results of $PM_{2.5}$ concentration in air: minimum, maximum and average for Living room and Balcony measurements, compared with the limit according to Romanian legislation*

3.2. Heavy metal concentration in collected $PM_{2.5}$

Particulate matters collected from the air samples contain different organic compounds or heavy metals that might negatively impact health population. Different studies around the world were focused on quantifying some of the possible heavy metals present in $PM_{2.5}$. Some results are offered in Table 1, and the majority of studies present results from indoor measurements. Also, Table 1 contains results from the present study for the living-room and for the balcony measurements. As expected, values of all elements considered were higher for balcony samples, except for Cr. One of the many possible explanations, for this unexpected result, might be the intermittence of sampling, the Automated Aerosol Sampling Device being moved from one measurement space to the other in different days. To overcome this drawback, a second device, running in tandem, could be used in future measurement campaigns. Nevertheless, compared to the former study conducted in Galati, in a different outdoor site [15], the values for Cr, Mn, Zn, Fe are comparable, lower for the present study, as expected, instead high values for Fe and Zn are again registered.

High values for Zn and Fe are also present in other studies conducted in cities with heavy industry, the highest value for Fe (1767,9 ng/m^3) being reported in Rooty Hill in Australia, and the highest value for Zn (950 ng/m^3) being reported in Beijing in China, while the lowest value for Fe (84.06 ng/m^3) was registered in the present study for living room measurements and the lowest value for Zn (34 ng/m^3) was registered in Córdoba, Argentina. High numbers were also registered for Ba, although fewer studies measured this type of heavy element. Again, for Ba, Beijing (China) registered the highest value (523,65

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ng/m^3), this city also presenting highest values, from all compared studies, for Mn (85 ng/m^3) and Sr (60 ng/m^3), while for Ti (167.5 ng/m^3) and Cr (121.7 ng/m^3) the highest values were registered in Istanbul in Turkey and for Rb (3 ng/m^3) in Cairo, Egypt. It is expected that high concentrations of heavy metals to be present in populous cities and even higher in industrialized ones, this is why this type of agglomerations should be better monitored from the air pollution point of view. From data presented in this paper it can be observed, when compared with the air quality national monitoring system, that big differences might occur between different areas of the same city, this is why a greater involvement in this respect and the subsequent measures should be applied in the near future.

Table 2. *Mean concentration of heavy elements in $PM_{2.5}$ from this study, compared to other studies (ng/m^3)*

City (Country)	Ti	Ba	Cr	Mn	Fe	Zn	Rb	Sr
This study (balcony), Galați (Romania)	22.12	157.88	4.80	71.16	415.25	574.27	1.64	17.69
This study (living room), Galați (Romania)	22.62	106.18	29.83	12.64	84.06	437.75	1.39	16.81
Cairo (Egypt) [24]	48	NA	NA	12	594	112	**3**	13
Beijing (China) [14]	NA	**523.65**	34.33	**85**	NA	**950**	NA	**60**
Xian (China) [25]	49	NA	5	50	806	587	NA	7
Chongqing (China) [25]	34	NA	4	41	408	152	NA	1
Córdoba, (Argentina) [26]	12	ND	4	14	325	34	NA	NA
Thessaloniki (Greece) [27]	45	125	23	35	426	110	NA	17
Oporto (Portugal) [28]	NA	2.65	4.01	3.54	NA	48.1	0.702	1.21
Shiprock, NM (USA) [29]	3.44	1.61	NA	0.93	44.7	1.22	0.1	0.37
Istanbul (Turkey) [30]	**167.5**	241.9	**121.7**	42.1	117.3	384.7	1.05	10
Jeddah (Saudi Arabia) [31]	55	34	2.1	19	590	41	1.2	4
Monterrey (Mexico) [32]	NA	NA	3.8	29.78	1026.18	39.19	NA	NA
Rooty Hill (Australia) [33]	8.9	NA	5.5	47.2	**1767.9**	284.4	NA	NA

4. Conclusions

As demonstrated by a large number of researches, the fine particulate matter in the breathable air is a major concern on public health. This is why the first obvious step is quantifying the extent of pollution with this type of pollutant. Numerous independent parties (e.g.: [34]) already started the monitoring of air in some big cities around the world and some surprising data already occurred, revealing that sometimes, the existing national monitoring system is unable to present the real extent of air pollution. Complementary to those situations, the present study demonstrates again this possibility, by comparing data regarding fine particulate matter concentration from an indoor site with data regarding the air quality from four monitoring stations of the national system during the same period (February-March 2020). While in the present study the legislative limit was exceeded by the measurements inside a balcony (a mean value of almost two times being registered), and the measurements inside a living-room almost reached the maximum admissible value, the four existing monitoring stations in the same city presented a maximum level of 4 out of 6 for the air quality. Although different types of measurement techniques and other influencing factors could be a reason for these differences, it is clear that reevaluation of monitoring sites positioning or supplementation could be a possibility worth considering. Meanwhile, independent measurements will continue, and the present study will be followed by others, monitoring particulate matters at the same time in different sites being one of the goals. Also, measuring this type of pollutant at the same time in the same site and at different heights might shed some light regarding the dispersion of particulate matters inside artificial canyons formed by roads flanked by high buildings.

Measurements of $PM_{2.5}$ concentration were completed by heavy metal concentration analyses. Data obtained this way were compared with results of other studies worldwide, most of them dealing with indoor $PM_{2.5}$ measurements. Of all heavy metals considered, highest values were registered for Fe and Zn in this study, compared with a former study conducted in an outdoor site from Galati city. Similar situations were also registered for all the other studies, higher values, as expected, being recorded in agglomerated and industrialized cities, the study conducted in Beijing being the one presenting the highest values for 4 out of 8 heavy metals considered (Ti, Ba, Cr, Mn, Fe, Zn, Rb and Sr). Results from the present study could be further supplemented in the future with data from other type of analysis methodologies, such as X-ray diffraction, for $PM_{2.5}$ mineralogical composition and scanning electron microscopy, for morphologic analysis purposes.

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STUDIES AND RESEARCH ON THE CONTROL OF THE RESIDUAL GAS LEAKS IN A CASTING METAL PARTS WORKSHOP

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ABSTRACT

The paper presents an analysis, regarding the control of the possible dangerous leaks of carbon monoxide, in this type of spaces, destined for the casting of the metal parts. These carbon monoxide leaks can occur mainly in the metal alloy making sector, which is to be cast into parts. The direct measurements were made especially in this working point, within the technological process, in different phases of the alloys elaboration process, but also during the time, when the workshop, was without production activity. The measurements were made with the help of the Fluke 975 Anemometer device, the results obtained being compared with the legislation in force, regarding safety and health at work.

KEYWORDS: dangerous gas leaks, alloy making, ventilation

1. Introduction

Environmental pollution is a reality today, it is found both in industrial areas and in urban settlements (to a lesser extent in rural areas). If natural pollution cannot be predicted, and in this context, only to a small extent can it be controlled, artificial pollution is induced by human activity (regardless of the type of activity undertaken), and depends only on us, to limiting the effects for the air - water - soil [1].

Steel is a ubiquitous material in our daily lives, it is a 100% durable and recyclable material. No matter how much steel is recycled, it remains just as strong and durable [2, 3].

There are a number of new, modern processes for the manufacture of steel, which are in operation in industrial practice. The technological advances made in recent years have had as their main goal, the minimization of electricity consumption, and maximize energy efficiency in the manufacturing process.

During these activities, greenhouse gas emissions occur due to the following causes:

- chemical processes that take place in the production of steel;

- burning fuel for technological purposes, or for heating workspaces.

The process of elaboration and casting of steels, in electric arc furnaces, is one of the determining factors for the formation of gas and dust emissions. The process of elaboration of steels in electric arc furnaces is based on physico-chemical processes, which take place at high temperatures, ensuring, based on specific technological instructions, the obtaining of steels, in the prescribed composition and quality.

The raw material used is scrap iron, and the main auxiliary materials are: iron ores, lime, dolomite, ferroalloys, coke, fluorine. The melting of the metal charge is done by means of the electric arc, formed between the electrodes of the electric furnace and the charge [4].

The process of making steel in electric arc furnaces includes several technological stages, characterized by technological operations which must be performed:

- adjustment (hot oven repairs - shotcreting);

- loading (operations of handling and loading of raw materials in these furnaces);

- melting (melting of the load, use of oxygen, oxy - gas burners);

- oxidation (insufflation of oxygen, evacuation of oxidizing slag);

- refining - deoxidation and alloying (addition of materials with deoxidizing action and alloying);

- evacuation (slag evacuation and steel evacuation, respectively).

In the current stage of technological development of the steel industry, the modernized electric furnace, transformed into a melting machine, transfers the refining - refining operations, in metallurgy aggregates in the pot, but here too, the

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mechanisms for forming gas and dust emissions are similar [5, 6].

Due to the physico-chemical processes, which take place at high temperatures, the elaboration is accompanied by the intense formation of gases, which contain an appreciable amount of dust.

The phenomenon is specific to all the mentioned technological stages, but especially to the melting and oxidation periods.

The amount of gas and dust emissions is directly proportional to the intensity of the physico-chemical processes, in the metal bath, and in the working space of the furnace, and depends on the specific periods of the elaboration process, presented below.

During the melting period:

- a brown smoke is emitted, due to the oxidation of metal vapours, which is emitted from the area of the electric arcs of the furnaces, where the temperature is much higher than their evaporation temperature;

- gas emissions are due to the oxidation of carbon in the area of the electric arc, where the temperature of the metal is maximum, and the burning of oils that contaminate the load, when during of the melting the load collapses.

Quantitatively, dust and gas emissions are variable, being influenced by two categories of factors:

a) technological factors:

- supply intensity and voltage of the furnace;

- how to intensify the melting (use of oxygen, oxy-gas burners);

- compactness of the load;

- the steel brand being developed;

b) random factors:

- unforeseen collapse of the load due to uneven melting;

- short circuits between the charge and the electrodes;

- damage to the electrodes.

During the oxidation period:

- gaseous emissions, in particular carbon oxides, because, due to the use of gaseous oxygen, decarburization occurs at high speed;

- a dense brown smoke is emitted, due to the vaporization of the metals, explainable by the fact that the decarburization process is accompanied by an intense release of heat, which determines the increase of the metal bath temperature, in the reaction zone, above the vaporization temperature of some metals dissolved in it; also, when the CO bubbles float and come out of the metal bath, on its entire surface, a mechanical extraction of the metal and slag particles takes place, which are entrained by the gas flow.

From a quantitative point of view, this is the stage in which the gas and dust emissions are maximum (usually the gas emissions from this period exceed by 20% the gas emissions from the melting period).

Taking samples for gas measurement can be performed either in the form of a network measurement or on point. Taking samples at a measuring point, in the measuring plane, means that the chosen measuring point is representative of the entire measuring cross section [7-9].

2. Experimental results

In the case of installations which operate in unchanging conditions, at least three discontinuous measurements are performed, in the case of a long-term normal operation, with maximum emission, and at least one more measurement, in the case of operating situations which repeats regularly, and aims at an oscillating emission behaviour.

In the case of installations whose operating conditions undergo temporal changes, sufficient measurements are made, but at least 6, in the case of operating conditions which can lead to maximum emissions.

The duration of a discontinuous measurement must not exceed half an hour; measured values are noted as values/half an hour. The appliance also determines the temperature in the combustion zone, where the measurements are made.

The verification is performed in two measurement plans, at the beginning and at the end of the elaboration. This device measures the percentage of heat by convection, and the heat of radiation is not taken into account.

Fig. 1. *Fluke 975 Anemometer*

The experimental determinations were made in a workshop for casting metal parts, in 2 working points, respectively in the steel making area, in the electric arc furnace (point 1), and in the non-ferrous alloy

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making area, in the flame furnace (point 2). Determinations were made, and while the production activity was interrupted. The measurements were made at 10 minutes, during the operation of the workshop, in a time interval of 8 hours, during a working day.

In order to be able to describe a gas flow as clearly as possible, it is necessary to follow the following parameters of waste gases, which can be considered marginal conditions for waste gases:

- waste gas density;
- humidity;
- flow rate and static pressure;
- temperature [10].

The inspection instrument, used for complete air quality testing, is the Fluke 975 Anemometer, which combines five air monitoring instruments into a single, robust and easy-to-use instrument. The Fluke 975 is used to verify the efficient operation of heating, ventilation and air conditioning systems, and to test for hazardous carbon monoxide leaks in all types of buildings (Fig. 1).

The determined values were centralized in table 1, and compare with the legislation in force, regarding the occupational exposure to chemical agents, according to GD. Nr. 1218/2006 [11-13].

Table 1. *Average values of the determined parameters*

Working point	Temperature °C	CO_2 ppm (average at 8 hours)	CO ppm (average at 8 hours)	RH %
1	122.3	866	1.03	28.5
2	222	736	2.02	12.8
3	20	18.3	0	9.4

*1-Electric arc oven; 2-Oven with flame; 3-Area without production activity

Concentrations of chemicals in the air are usually measured as the mass of chemicals (milligrams, micrograms, nanograms or picograms) per volume of air (cubic meters or cubic feet). Concentrations can also be expressed as parts per million (ppm) or parts per billion (ppb) by using a conversion factor. This conversion factor is based on the molecular weight of the chemical and it is different for every chemical. The temperature of the atmosphere also has an influence on the calculation.

To convert ppm to mg/m^3 the next formula was used: concentration (mg/m^3) = 0.0409 x concentration (ppm) x molecular weight.

Carbon monoxide [CO]: M = 28.01 g/mol.

Carbon dioxide [CO_2]: M = 44.01 g/mol.

Where-M represents Molecular Weight.

Mandatory national occupational exposure limit values for chemical agents, according to GD. No. 1218/2006 (Table 2).

Table 2. *Maximum allowable concentrations in the atmosphere of work areas according to the order of the Ministry of Health and Family no. 1218/2006*

Pollutant	**CMA mg/m³**		**The method used**
	Average (8 hours)	**Maximum (15 min)**	
Carbon monoxide (CO)	20	30	Analyzer
Carbon dioxide (CO_2)	9000	-	Titrimetric

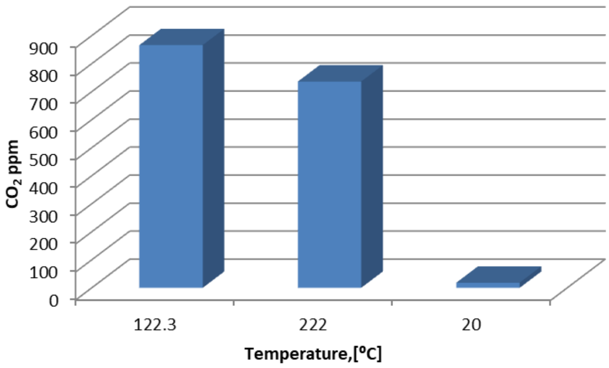

Fig. 2. *Average CO_2 values, determined in working points (1-Electric arc furnace; 2-Flame furnace; 3-Area without production activity)*

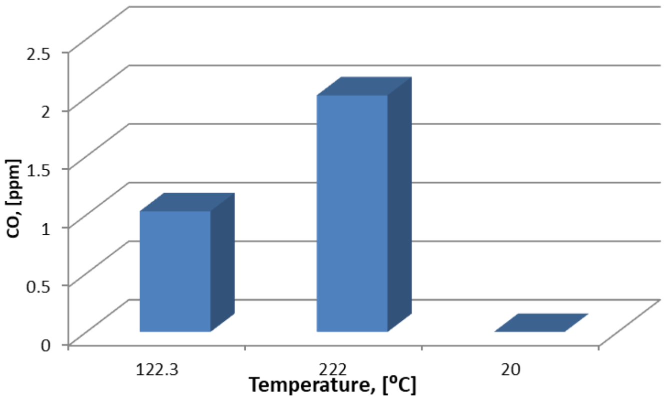

Fig. 3. *Average CO values, determined in working points (1-Electric arc furnace; 2-Flame furnace; 3-Area without production activity)*

As can be seen from the graphs above, the maximum values were determined in the flame furnace, especially during the melting and oxidation periods.

Although high values have been obtained, they fall within the limits prescribed by GD. No. 1218/2006, regarding professional exposure to chemical agents.

The carbon dioxide (CO_2) content of the air is an indicator of ambient air quality, assuming that human respiration is the main source of CO_2 emissions. Measuring instruments with CO_2 sensors allow you to reliably control this important value: because, due to the decrease in ambient air quality (increasing the CO_2 content in the air), performance decreases [11].

The highest determined value, for CO_2, was detected in the working area of the electric arc furnace. In the flame oven, we have a lower value of CO_2, determined at a higher temperature (Fig. 2).

When assessing ambient air quality by measuring the CO_2 concentration and other parameters, the CO_2 concentrations should not exceed 1000 ppm.

Carbon monoxide is colourless and odourless, and stops the absorption of oxygen by the blood, when inhaled too high a concentration. Breathing CO in a concentration of 700 ppm, in an enclosed space, leads to death in about 3 hours.

It is a suffocating, toxic gas, which arises from an incomplete combustion (oxidation) of carbon-containing substances. The most common sources of daily CO are: gasoline engines, gas ovens, heating systems, solid fuels such as wood and coal.

The maximum allowable concentration of carbon monoxide at work is 30 ppm (parts per million). Carbon monoxide can accumulate very quickly, to a life-threatening extent, in enclosed and semi-enclosed spaces. A carbon monoxide detector allows reliable detection of this insidious gas [12].

The average of the carbon monoxide determinations, in all the monitored working points, is inscribed in the allowed values, according to the norms in force, regarding the air quality in closed working spaces, obtaining a maximum, in the working point, the flame furnace (Fig. 3).

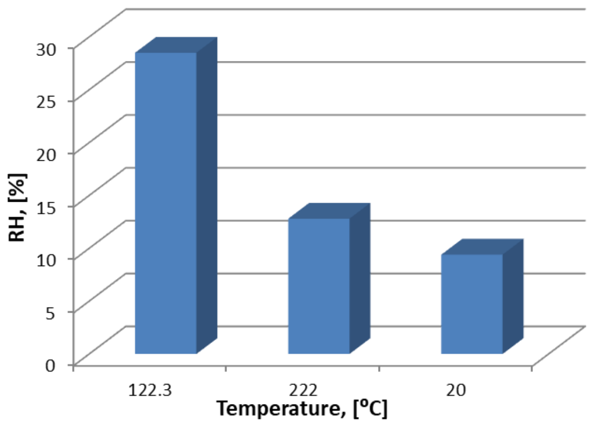

Fig. 4. *Average humidity values, determined in working points (1-Electric arc furnace; 2-Flame furnace; 3-Area without production activity)*

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The humidity formed in a room depends mainly on the following factors: moisture production in the room, air exchange with outside air, moisture absorption capacity by walls and furniture, transport of moisture by external construction components.

Parameters, air temperature, and relative humidity are important for planning, choosing, and installing ventilation systems, and air conditioning.

The humidity of the air decisively influences the feeling of comfort of the people in a room. The ideal ambient humidity is between 30 and 65%. Of course, in addition to this, the temperature is also decisive. High air humidity can be extremely annoying in high temperatures [13].

For this reason, humidity measuring devices are generally equipped with humidity and temperature sensors.

Humidity values, determined in all work points, as well as in the workshop, when we do not have production activity, are within the norms regarding air quality, in closed industrial workspaces (Fig. 4).

3. Conclusions

The paper presents the data necessary to investigate the occupational exposure to noxious pollution, regarding the control of hazardous waste gas leaks, in a workshop for casting metal parts.

The evaluation involves the investigation of the working environment conditions (knowledge of technological processes, choice of noxious substances, air sampling, method used, interpretation of results, etc.).

In order to create conditions appropriate to the working environment, a series of technical and organizational measures are required as follows:

Organizational measures:

- training on the need to use work-specific protective equipment;
- periodic medical control, with the theme of detecting diseases that are manifested, or are about to be installed, in the respiratory system;
- making determinations for the air quality in the workplace atmosphere, with the periodicity required by law;
- appropriate signalling of risks at workplaces.

Technical measures:

- Acquisition of E.I.P. corresponding to the activity to be carried out according to the regulations in force.
- Identification and design / redesign of the working conditions, in accordance with the legislation in force regarding the minimum safety and health requirements for the workplaces.

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EXPERIMENTS REGARDING THERMAL AND MECHANICAL DEFORMATIONS OF CONTINUOUS CAST STEEL WIRE

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ABSTRACT

During the casting process, the crust of the steel wire is permanently subjected to thermo mechanical stresses (temperature variations, pulling, bending and straightening forces, ferrostatic pressure), which, when exceeding the deformation capacity of the crust, can lead to cracks.

Therefore, it is necessary to know what kind of stresses act on the crust and how the steel behaves at high temperatures at certain process parameters (extraction speed, cooling intensity, etc.)

KEYWORDS: continuous casting, solidification, mechanical stresses

1. Introduction

In order to highlight the behaviour of the steel during the deformation that takes place during solidification, for straightening the wire or for its deformation in the continuous casting installation, it is necessary to know the mechanical properties of the cast steel at temperatures close to the solidification temperature. The experiments performed allow the simulation of the thermal and mechanical deformations to which the solidified crust of the steel wire is subjected in the continuous casting machine.

On the technological flow of manufacturing flat products, the sheet billets are casted and then hot rolled; these operations take place in a temperature range between the melting temperature and approx. 600 °C [7]. Due to the interaction of thermal, mechanical and chemical factors during the processes of solidification and plastic deformation, the plasticity shows an uneven variation as the temperature decreases. During the experiments we performed tensile tests on OL 37-4k steel samples (S235J2G4, according to EURONRM 10025) in the mentioned temperature range.

The cause of the formation of cracks that appear on the surface of continuously cast slabs is found in the fragility of steel corresponding to temperature ranges. These areas (characteristic for each type of steel) - in which the plasticity of the steel is reduced - were determined by tensile tests at different temperatures.

Knowing the deformation conditions of steel - at temperatures close to solidus temperature - leads to the possibility of finding technical solutions to reduce the risk of internal cracks appearance and technologies and equipment achievement that suggest the reduction of the continuous cast wire thickness on the incompletely solidified area [4].

There are two types of experimental methods: a method that involves measuring critical stresses (in which internal cracks appear) on laboratory stand in order to simulate the conditions of casting and plastic deformation, (e.g.: simulators Wumsi, Gleeble, etc. [5, 7]) and a method that involves determining the mechanical properties at high temperature, using tension test machines.

In order to simulate the deformation process of the continuously cast steel wire, we considered representative the thermal cycle through which the steel is brought into the molten state, being then cooled to the temperature at which the test is performed. During the experiments we followed the dynamics of steel deformation in the biphasic area, where the behavior of the liquid steel wire can be the cause of fragility and the premise of the development of internal cracks [4].

2. Experimental conditions

The tests were performed on an experimental stand for high temperature tensile tests, consisting of a universal hydraulic material testing machine, to which a high frequency generator (150 kHz, 25 kW) was attached for heating the samples, Figure 1.

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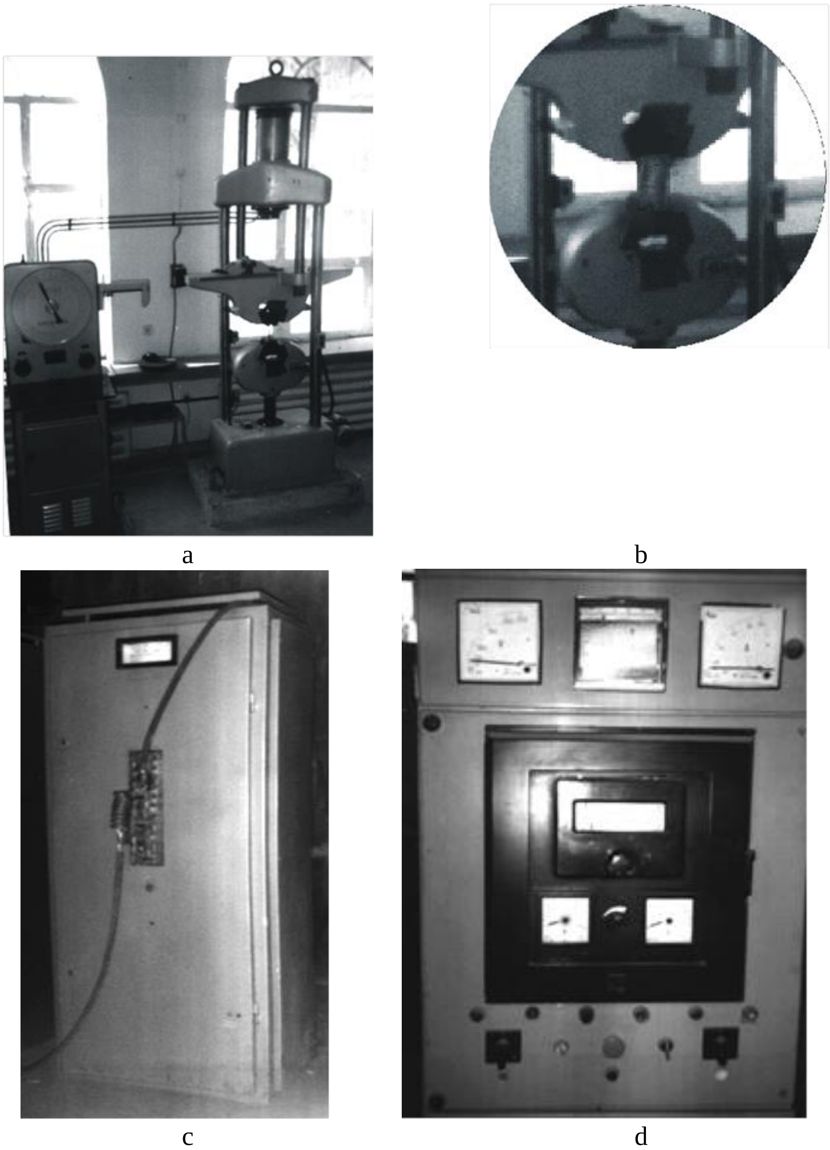

Fig. 1. *Experimental stand used to perform tensile tests at high temperatures: a. tension traction machine; b) detail; c. high frequency generator; d. control panel*

The dimensions of the samples used: diameter d = 20 mm; the area of the initial section S_0 = 314.2 mm^2; length of the calibrated portion L_c = 110 mm; length between marks L_0 = 100 mm ($L_0 = k \cdot \sqrt{S_0}$; k = 5.65, corresponding to proportional samples); length of the heated portion L_t = 30 mm.

The samples were heated to the melting temperature of the steel, respectively 1550 °C, cooled to 10 °C/s and, after maintaining the test temperature for 120 seconds, tensile tests were performed. The flow of steel in the molten area is stopped by its surface tension.

The chemical composition of the samples used (steel S235J2G4, according to EURONRM 10025) is given in Table 1.

Table 1. *The chemical composition of the samples used (steel S235J2G4)*

Chemical composition, [%]							
C	**Mn**	**P**	**S**	**Si**	**Al**	**Cr**	**Ni**
0.10	0.82	0.04	0.04	0.15	0.03	0.20	0.16

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The temperature was measured with two Pt/Pt Rd thermocouples, glued on the samples subjected to traction, at the upper and lower limit of the molten area, respectively (in order to follow its uniformity on the whole portion subjected to heating).

3. The behaviour of the steel wire at alternating stresses (on the route of the casting machine)

The structural transformations that take place in the continuously cast steel wire (grain finishing, ferrite fractionation, etc.) depend on the thermal cycles to which it is subjected. Transverse cracking is one of the biggest problems characteristic of continuous casting on vertical curved wire machine. This type of crack is generally formed along the oscillation traces, their propagation taking place due to the stresses that occur when straightening the steel wire, especially since this operation takes place in the temperature range of 1000-700 °C, which comprises two of the three fragility areas of the steel [1].

The thermal cycle to which the wire surface is subjected is produced by the alternating action: *cooling* (cooling water and contact with the rollers), *heating* (heat transfer inside the wire).

The concepts of simulation are relatively close to industrial conditions. In this regard, attention is paid to the fact that the surface layer, initially solidified (solidified crust), is periodically subjected to a cycle of tensile / compressive forces, as a result of cooling and reheating and as a result of swelling of the steel wire between the support-driving rolls of the continuous casting machine (due to the ferrostatic pressure of the steel).

During the experiments, the samples, cooled to ambient temperature, are subjected to alternative traction forces, the criterion for assessing the test being the number of cycles leading to their destruction. The purpose of the test is to determine the probability of surface cracks occurring, and, if they occur, to assess at what point in the process they occur.

The temperature ranges in which the solidified crust exhibits a low resistance capacity to alternating tension / compression stresses can be determined for each type (class) of steel.

Periodic forces can lead to the accumulation of stresses, the cyclic deformation produced having the effect of cracking the steel crust [1].

According to these premises, during the testing, we applied sinusoidal deformation cycles to the samples with a period of 15 seconds, at different temperatures, corresponding to those in the continuous casting process, the values of the deformation amplitude varying by 1%.

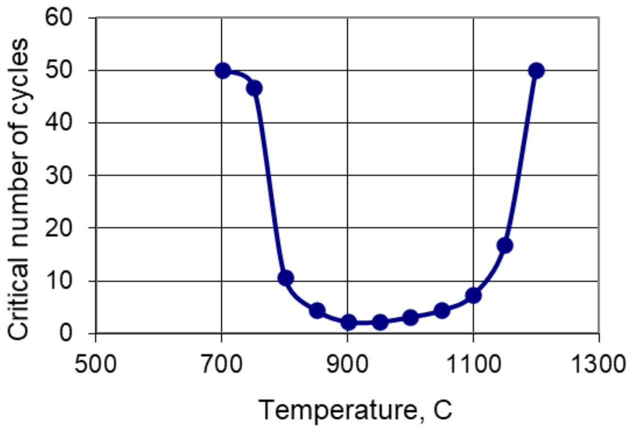

***Fig. 2.** The critical number of cycles at which cracks occur*

Figure 2 shows the results obtained when testing the steel. It can be noticed that the possibility of cracking occurs after only 3-4 cycles. Regarding the way in which the rupture occurred, an exclusively intercrystalline crack of minimum resistance is observed, the surfaces of the grain being covered with small depressions containing sulphur particles.

It is also noticeable the extension of the critical temperature range for the studied steel, at 750-1150 °C.

4. Conclusions

Sulphur precipitates at the grain limit: the ratio of Mn/S content is 8, in the case of the analysed steel. At the relative decrease of the manganese content in comparison with the sulphur content, smaller amounts of manganese sulphide precipitate during solidification. The solubility of sulphur decreases sharply in the lower austenitic zone while iron sulphide precipitate at the edges of the grain.

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Carbon content: to the extension of the critical temperature range also contributes the carbon content which is, for the analysed steel, in the critical range (0.12-0.14%).

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EXPERIMENTS REGARDING THE FABRICATION OF THE HIGHER STRENGTH STEELS PLATES

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ABSTRACT

The normalizing of ferritic-pearlitic steels is a heat treatment, which consist of reheating into the austenite and subsequent air-cooling. For greater thickness, e.g. 100 mm, variations in the requirements may be permitted or required for particular applications but a reduction of the required impact energy is not allowed. The most important cote of the cost can be eliminated if the process normalizing rolling is applied.

KEYWORDS: higher strength steels, normalizing, structural applications

1. Introduction

The normalizing of ferritic-pearlitic steels is a heat treatment, which consist of re-heating into the austenite and subsequent air-cooling. Its names derive from the fact that any micro-structural changes caused by the production process, by overheating during forming or by hardening, will be reversed resulting in a homogeneous microstructure. Normalizing is the standard technology for steel castings and is often applied for forging and heavy rolled products, when high processing temperatures are common. As a result, the coarse microstructure will become more homogeneous and grain refined, which guarantees both higher strength and better toughness.

In the "normalizing rolled" process, the rather high finish rolling temperature of 1050 ºC for normal processing of a 60 mm plate generates a rather coarse microstructure. If such a plate is processed in the lower austenite region at, for example, 880 ºC, its microstructure will be equivalent to that of steel in the normalized condition. Such finishing temperatures occur naturally with thinner gauges. For thicker material the rolling schedule has to be adjusted by introducing a delay time. In order to maintain the output of the mill, processing schedules have been developed, which allow for the simultaneous processing of more than one slab.

2. Experimental study

The LRS – E steel used for the structural applications is in conformity with LR Rules. The chemical analysis prescribed for the LRS-E steel sheets was tested and the results confirm equivalence with the LRS norms (Table 1).

The continuous cast slabs have been rolled at No. 2 heavy plate rolling mill and submitted to thermal treatment in the normalizing furnace. Subsequent to the normalizing treatment, the sheets were US controlled according to SEL 072-77 standard. The parameters of the casting are in Table 2.

The results obtain of the mechanic tests and at the micro-structural analysis are presented in Tables 3 and the Figures 1-3.

Table 1. *The chemical composition for the LRS-E steel*

C	Mn	Si	P	S	Al	Nb
[%]						
0.15-0.18	0.95-1.10	0.15-0.30	max. 0.025	max. 0.010	0.020-0.060	0.030-0.050

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Table 2. *The principal fabrication parameters for the LRS – E steel*

Tundish steel temperature		°C	1530
Casting time		minutes	59
Casting rate		m/min	0.74
Slab size		mm	250x1550
Slab heating temperature		°C	1280
Slab/plate rolling temperature	start	°C	1180
	end	°C	860
Plate thickness		mm	100
Normalizing temperature		°C	886

Table 3. *Steel grade: LRS E, sample 180-longitudinal tests, plate thickness 100 mm*

Sample	180-1 L	180-2 L	180-3 L	180-4 L
Section (mm)	Ǿ 14	Ǿ 14	Ǿ 14	Ǿ 14
Original gauge length Lo (mm)	70	70	70	70
Final gauge length Lo (mm)	91	91	91	90
Maximum force Fm (N)	84500	85500	83400	84500
Flow force F (N)	57500	60000	5500	58000
Proof stress at 0.2% (N/mm^2)	374	390	359	377
Tensile strength R_m (N/mm^2)	548	555	545	549
Total breaking elongation A (%)	30	30	30	28
Charpy V-Notch test 20 °C(J) Percentage crystallinity, % Lateral expansion (mm)	191-157-135 91-80-77 2.32-2.45-2.63	143-147-143 80-80-85 2.42-2.43-2.45	180-140-138 80-88-80 2.11-2.31-2.63	165-188-176 81-90-86 2.57-2.51-2.55
Charpy V-Notch test 0 °C(J) Percentage crystallinity, % Lateral expansion (mm)	141-149-136 85-85-77 2.29-2.32-2.32	151-166-164 85-81-80 2.30-2.52-2.40	150-142-145 851-80-85 2.18-2.25-2.34	159-153-180 80-85-88 2.37-2.31-2.23
Charpy V-Notch test -20 °C(J) Percentage crystallinity, % Lateral expansion (mm)	124-117-115 75-72-66 1.98-2.08-1.92	120-110-114 60-72-66 2.02-1.96-2.04	124-111-125 75-60-72 1.96-2.09-2.15	139-144-134 80-85-77 2.42-2.36-2.29
Charpy V-Notch test -40 °C(J) Percentage crystallinity, % Lateral expansion (mm)	43-62-70 21-33-38 1.56-1.39-1.34	62-72-43 33-38-21 1.39-1.56-0.87	51-47-51 26-26-27 0.62-0.65-1.10	47-52-81 26-26-44 0.55-0.65-0.92
Charpy V-Notch test -60 °C(J) Percentage crystallinity, % Lateral expansion (mm)	14-11-13 11-12-11 0.52-0.71-0.42	10-9-9 11-11-12 0.91-0.83-0.67	9-9-8 11-12-11 0.41-0.36-0.73	16-11-12 17-11-12 0.98-0.71-0.65
Strain age Charpy tests -40 °C(J)	8-7-6	6-6-8	7-18-10	8-8-8
Strain age Charpy tests -60 °C(J)	5-5-6	5-5-5	6-5-5	5-6-6
Bend Tests	satisfy	satisfy	satisfy	satisfy

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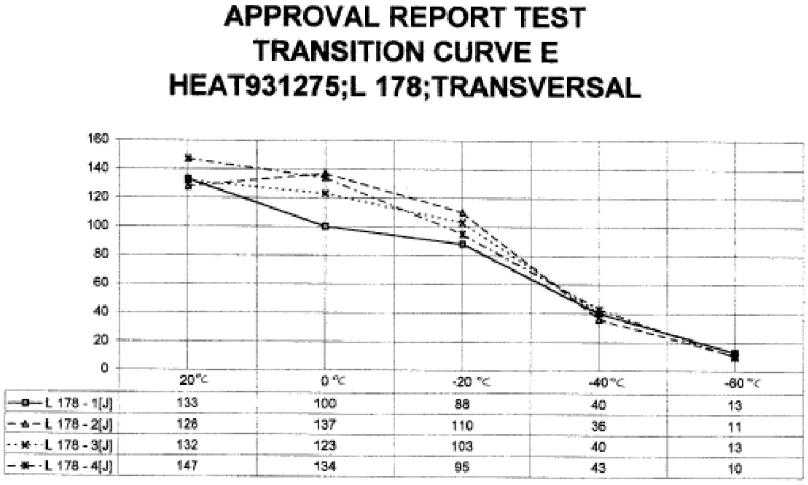

Fig. 1. *Approval report test transition curve – transversal position*

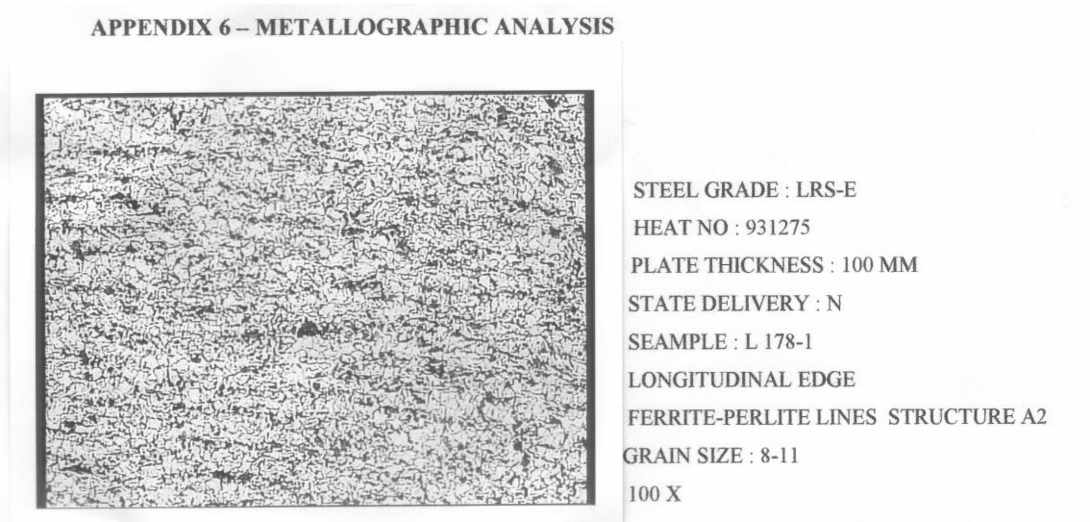

Fig. 2. *Metallographic analysis for longitudinal edge*

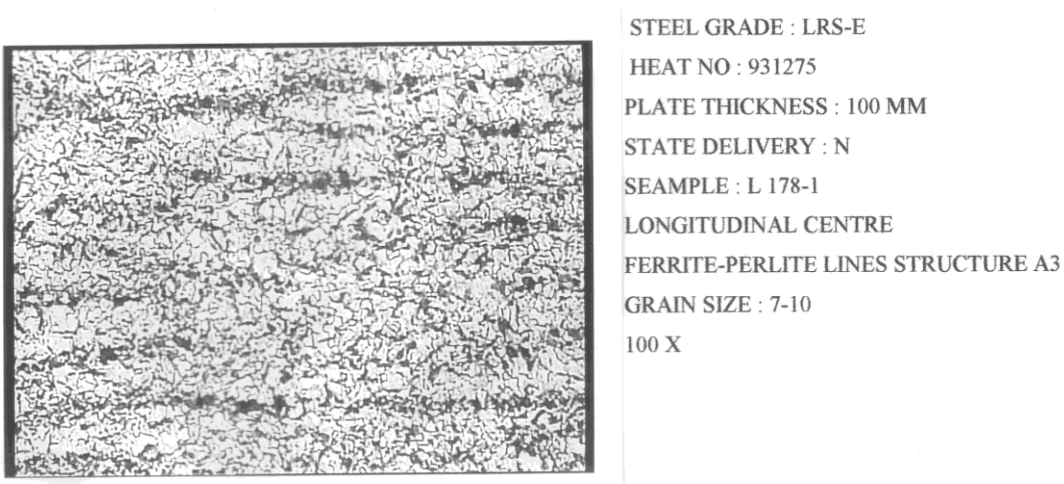

Fig. 3. *Metallographic analysis for longitudinal centre*

3. Conclusions

In order to realize a program for extended a fabrication authorization of the higher strength steels plates for ship or other structural applications Grades A, B, C, D and E, on effectuated an researches and experimental series which consists in:

- chemical analysis;
- Baumann sulphur print;
- metallographic analysis;
- ultrasonic control.

For this analysis we on refer to the Romanian standards for the grain size, microstructures and the sulphur print.

The results obtained lead to the conclusion that the fabrication of the higher strength steels plates for ship or other structural applications, LRS-E3 type, is accepted, because there are in conformity with the impose norms.

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THE ROLE OF FORMAL EDUCATION IN DEVELOPING CRITICAL THINKING SKILLS OF ENGINEERING STUDENTS

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ABSTRACT

The hereby paper intends to acknowledge and discuss the concept of critical thinking and the influence of this ability on engineering students. The purpose of this research is to establish the criteria according to which some students think more critically compared to other students in the same field of study. Logic is a term that seems simple, although very few know how to access that logical part of the human brain. This research has shown that the students' level of critical thinking is not related to the year of study. Therefore, there are no activities in faculties that have a significant influence on the development of critical thinking. Moreover, it has resulted that female participants think more critically than men participants, but on an insignificant level. Regarding satisfaction in life and its link to critical thinking, it has resulted that unfulfilled students obtained a level of critical thinking higher than the fulfilled ones, a difference that is not of significant relevance. The results of this research are based on two methods: online questioning and focus group.

KEYWORDS: critical thinking, gender, cumulative grade point average, life fulfilment

1. Introduction

The human brain is imperfect and prone to prejudice, irrationality, distortions and cognitive biases [1]. In most fields, the application of critical thinking is necessary, especially in areas such as engineering, medicine, law, entrepreneurship and journalism. Logical reasoning and the discipline of the mind are qualities that must be acquired through intellectual efforts [2]. This research aims to prove the importance of critical thinking in education as well as in personal life for a better understanding of problems and people.

The critical thinking process helps identifying the arguments that have no basis, no evidence and contain errors or absurdities in the statement. Having critical thinking as their starting point, people manage to be objective. By using critical thinking, people learn how to support their arguments with evidence in order to persuade an audience to agree with them or to support them [3]. In general, this process is very helpful in taking the best decisions as well as in solving various problems.

2. Setting the context

2.1. What is critical thinking

Dr. Richard Paul, Director of Research and Professional Development at the Center for Critical Thinking, believed that "critical thinking, properly conceptualized, entails understanding the ethical dimension of human life" [4]. This is what critical thinking means if you read behind the words and try to create an image inside your mind that helps you better understand the human behaviour and the empirical reality. Analysing an argument by using critical thinking intensively, guides you through the unknown of the human mind. Additionally, with the help of critical thinking, one has the ability to be able to ascertain another point of view so as to understand people's actions and beliefs. Critical thinking reveals you the path to one's subconscious part of the mind, helping you comprehend the reasons that determine people to act and react in certain ways [5].

Another definition stated by Robert H. Ennis acknowledges critical thinking as being: "the correct way of assessing statements" and "reasonable reflective thinking focused on deciding what to believe or do” [6]. Therefore, critical thinking not only develops the ability to identify other perspectives, but it also develops the ability to control their own decisions and actions.

2.2. Critical thinking in doing business

As far as business is concerned, critical thinking represents a very effective method in taking decisions, understanding the cause and effect of events and improving communication. When using critical thinking in business, a leader must think logically in order to find, synthesize, analyze, and solve problems [7]. However, acquiring it requires effort and a lot of practice in order to be applied correctly to streamlining product development [8]. In the workplace, critical thinking is in high demand [9], as most of the graduates who are hired fail to identify problems and generate solutions. They do not think logically, being most used to giving memorized answers to questions identified by someone else, but their process of digesting information can be changed through exercises and techniques to stimulate critical thinking [10].

As Bob Schoenberg stated in his book “Critical Thinking in Business: Revised and Expanded Second Edition”, the way managers analyze problems, determines the way in which their subordinates will manage the problems that might arise. Managers who use the critical thinking process, encourage the team not only to act likewise, but also to identify and evaluate problems, as well as to generate solutions [11].

2.3. Measuring methods

The measuring methods can be found in Professor’s William M. Bart paper [12]. There are five tests and each one of them targets the following skills:

(1) California Critical Thinking Skills Test (CCTST): analysis, inference, evaluation, deductive reasoning, inductive reasoning;

(2) Cornell Critical Thinking Test (CCTT): deduction, semantics, credibility, induction-judging conclusions, induction-planning, experiments, definition, assumption identification;

(3) Ennis-Weir Critical Thinking Essay (Ennis-Weir): analyzing arguments;

(4) University of Florida Critical Thinking Tests: interpretation, analysis, evaluation, inference, explanation, self-regulation;

(5) Watson Glaser Critical Thinking Appraisal (WGCTA): inference, recognition of assumptions, deduction, interpretation, evaluation of arguments.

2.4. Skills and competencies of successful people

Besides the profit that any business is willing to bring, moral values such as ethics, honesty, respect and courage of the one who runs it, define its ultimate success [13]. A true leader, serves his community through social contributions, values the quality of the products/services he offers, takes into account the needs of customers, teaches and encourages his employees, and above all, sets an example for them all.

Combining Noor’s Faris paper [14] with the results of “The Future of Jobs Report” [15], made by World Economic Forum, the skills of successful people are as follows: complex problem solving, critical thinking, creativity, people management, coordinating with others, emotional intelligence, judgement and decision making, service orientation, negotiation, cognitive flexibility and many other competencies such as: vision, initiative, optimism, leadership, motivation, and ethics.

3. Research methodology

3.1. Purpose of the research

In Romania, engineering students are always facing difficult problems regarding mechanics and other logical sciences [16]. They do not always find an answer to a problem, yet there may be a spark in their minds and critical thinking can help turn it into an idea.

This research, which is an exploratory study, aims to provide information on frequent questions or concerns regarding critical thinking.

Is critical thinking an innate talent or a skill that can be built and developed through exercise? Are there differences between thinking according to gender, age, occupation, education and people's mood? Do those who are happy or those who say that the feeling of fulfilment is not yet present in their lives think critically? Do all these criteria have anything in common with critical thinking? Here is the aim of this research: does the percentage of human’s logic have limits or can it be increased?

The purpose of this particular research is to find a relevant answer to the following question: does formal education in Romania have an impact on the development of critical thinking [17]?

3.2. Research hypotheses

This paper starts from research hypotheses that consist in reflecting critical thinking in academic performance.

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According to a study [18], it was found that critical thinking dispositions have a significant effect on entrepreneurship levels. There are also statistically significant differences in gender, high school and departmental variables with respect to CCTDI (California Critical Thinking Inventory).

Another research regarding the connection of critical thinking and life satisfaction [19], demonstrated that the meaning of life increases along with the dispositions of critical thinking in individuals.

Therefore, the hypotheses of this research are based on the aforementioned research:

I1. Critical thinking is reflected in academic performance.

I2. Critical thinking varies by gender.

I3. The feeling of fulfilment in life is to a greater extent present in the lives of those who think critically.

3.3. Instruments

For the first method of this research, the focus was on the score's analysis of ten participants chosen as a focus group. The participants had to solve various problems regarding critical thinking in order to make possible interpreting the level of critical thinking in a more practical way.

The second research method used to determine the level of critical thinking of students was the online questionnaire, which was composed of 25 questions regarding critical thinking and other 6 classification questions. To create and distribute it, the google forms platform was used by activating the option that displays to each participant, the score obtained at the end of the test - according to the grid proposed by those who developed the tool [20].

3.4. Sampling

The focus group, the first stage of this marketing research, consists of 10 students from secondary year, belonging to the specialisation of Economic Engineering in Mechanical Domain, Faculty of Engineering, "Lucian Blaga" University, Sibiu. The participants were chosen according to the principle of homogenization of groups based on the results in the admission contest.

The targeted group for the online questionnaire consists of 176 students. The number of students varies from one year of study to another, having in common the Faculty of Engineering, respectively the Economic Engineering in the Mechanical Domain specialization.

4. Results

The level of critical thinking is calculated based on the score obtained in the online questionnaire. The mathematical formula used by the tool developers consists in multiplying the obtained score by 100 and dividing the obtained result by the total number of questions. For example, the most obtained score by students was 13 out of 25 questions, which means a critical thinking level of 52%.

Figure 1 represents the level of critical thinking that was obtained by students according to their school's cumulative grade point average. Students with a cumulative grade point average between 9-10 scored the best level on the test, a 56.55% level out of 100%. Although the ones with a cumulative grade point average between 8-9 follow next as regards their level of critical thinking, one can notice an interruption with respect to the ascending order. Students with the cumulative grade point average below 7, scored better results than those with a cumulative grade point average between 7-8.

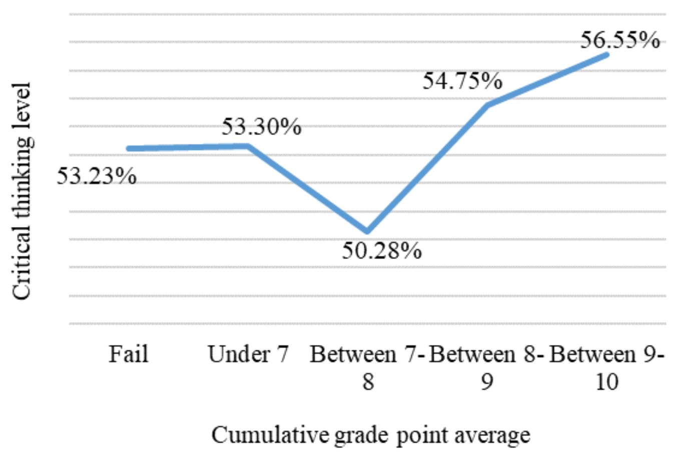

Fig. 1. *The level of critical thinking according to their cumulative grade point average*

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Figure 2 represents the level of critical thinking obtained on average by every year of study. With a level of 55.8%, the second year of study obtained the best score and the last year of study, the lowest score of 52.09%.

Figure 3 shows the level of critical thinking according to the feeling of fulfilment in the life of the students. As the figure shows, the unfulfilled students scored 54.75%, whereas those fulfilled scored 53.78%. There was a section for students who are not able to state whether they are fulfilled in life or not. This section scored the lowest level of 51.3%.

Table 1 contains information regarding the score of students per gender and per year of study. Besides the third year of study where male participants scored 54.24%, a level higher with 0.8% than the female participants, the scores of the females belonging to other years of study, outperformed the males' scores. The "total" row displays the average for all the four years of study according to gender. Females surpassed males, with a level of critical thinking of 55.28%, higher with 5.23% than the males' level.

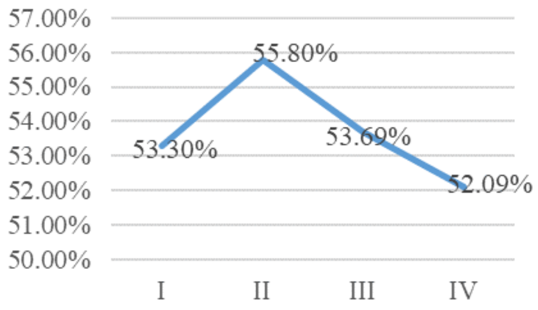

Fig. 2. *The level of critical thinking/ year of study*

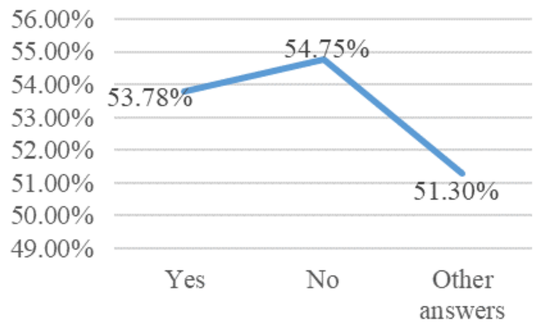

Fig. 3. *The level of critical thinking according to fulfilment in life*

Table 1. *Level of critical thinking/gender/year of study*

Year of study	Gender	
	Female	**Male**
I	56.56%	45.64%
II	56.32%	53.12%
III	53.44%	54.24%
IV	54.8%	47.2%
Total	55.28%	50.05%

5. Discussion

Following the analysis of the answers given by the focus group participants, the following observations resulted:

• the ability to distinguish a hypothesis from a concrete fact is quite low;

• on the part regarding frames of reference, 3/10 respondents did not understand what a perspective is, confusing it with a state / feeling; what is more, it can be seen that through the role play, good perspectives were found and related to the given situation;

• methodological thinking was one of the strengths of the participants, the arguments being largely strong and convincing;

• the metacognition part is the only one where everyone has found the right answer to the problem that requires teamwork;

• critical thinking games were the ones that stimulated the respondents the most, being much more receptive and curious due to the exposure of the problems in the form of images and diagrams.

Therefore, the participants do not know what critical thinking means and how to develop it, although some acquire it to a greater or lesser extent. Moreover, it has been observed that problems composed of images and text, stimulate critical thinking much more than problems composed only of text.

Regarding the interpretation of the results from the online questionnaire, the average score obtained by the sample of 176 students will be taken into account, this being 13/25 points, so a level of 52% of critical thinking.

In relation to the students' sense of accomplishment, the highest average level of critical thinking is that of respondents who do not consider themselves fulfilled, namely 54.75%, followed by a small difference from those fulfilled, of 53.78%.

According to statistics, the best results are those given by students whose cumulative grade point average is between 9-10, which means a percentage of 56.55% that exceeds the average level of critical thinking, followed by students with a cumulative grade point average between 8-9, with a percentage of 54.75%. Also, students with a cumulative grade point average below 7 obtained a higher level of critical thinking than those with a cumulative grade point average between 7-8.

The situation of the results for each year of study vary though the differences between the 4 years of study are insignificant, which shows that there are no teaching activities that have a significant impact on the development of critical thinking.

Regarding the interpretation of the results by gender, out of the 176 students, the female participants obtained on average a percentage of 55.28%, which is higher than that of the male participants with 5.32%. Considering the results belonging to each and every year of study, it is noticed that in the third year of study, males have a critical thinking level of 54.24%, surpassing females with 0.8%. In the other years of study, the female gender has a higher percentage than the male gender with:

- 10.92%, in the first year;
- 3.2, in the second year;
- 7.6%, in the fourth year.

Summarizing the statistics made by gender, the results of females are better compared to those obtained by males.

6. Research limitations

With regard to the limitations of the research, there have been identified the following:

- the online method can affect the respondents' way of answering because they can treat the questions with indifference;
- the surrounding conditions and stress may decrease the concentration of respondents at the time of the questionnaire;
- few classification questions relevant to creating a connection between critical thinking and performance in everyday life; questions related to hobbies, favourite activities, goals in life could be added;
- the small sample size cannot lead to the conclusion of general data;
- the sample's number of females and males is not balanced.

7. Conclusions and future research directions

Taking into account all that was mentioned above, two out of three hypotheses have been revealed as being partially true. On the one hand, the hereby research has managed to prove that the correlation between critical thinking and university performance is inexistent. The reason is merely the fact that the level of critical thinking according to the students' cumulative grade point average does not follow an ascending line. On the other hand, another partially true hypothesis has shown that depending on gender, students' critical thinking levels varies, but on an insignificant level.

Last but not the least, the third hypothesis regarding the feeling of fulfillment in life and its influence to critical thinking level has been unconfirmed for the tested sample. The difference between the two categories of people, fulfilled and unfulfilled is insignificant and a definitive statement cannot be made.

Considering the obtained results, the introduction in the academic schedule of activities related to the development of critical thinking through methods such as courses, project-based learning and workshops is highly recommended.

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CORROSION OF GALVANIZED STEEL IN VARIOUS AQUEOUS ENVIRONMENTS PRESENT IN NATURE

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ABSTRACT

Experimental research has focused on the corrosion behaviour of a widely used protective coating, respectively, galvanized sheet in various corrosive aqueous environments present in nature. In the laboratory experiments, the following were chosen as corrosive media: rainwater, domestic water, Danube water and sea water.

Galvanized sheet can interact with these environments due to its use in metal constructions, home appliances, car construction, food industry, others.

In order to assess the corrosion resistance, the mass loss was determined for a period of five weeks. The results showed a higher corrosion rate in rainwater compared to the other corrosive environments tested. The lowest corrosion rate was in sea water. In domestic water and Danube water the mass loss was comparable.

KEYWORDS: galvanized sheet, corrosion, rainwater, domestic water, Danube water

1. Introduction

Galvanized sheet is a product widely used in various fields such as construction, home appliances, car construction, food industry, others [1].

The corrosion resistance of the galvanized sheet is influenced by the following factors: the thickness of the zinc layer, the quality, purity and adhesion of the zinc layer, the composition of the corrosive environment [2].

Zinc corrosion is best controlled in the pH range of 5.5 to 12 and zinc can provide the steel protection for up to 25 years in rural areas and 5-12 years in urban areas [3, 4].

EN ISO 12944-2 specifies five categories of corrosion resistance (C1 to C5) for hot dip galvanized steel.

Table 1 presents the characteristics of these categories regarding the loss of mass and the reduction of the layer thickness at a one-year exposure to various corrosive atmospheric conditions [5].

Table 1. *Atmospheric corrosivity categories s of typical environments*

Corrosion category	**C1 very low**	**C2 low**	**C3 middle**	**C4 hig**	**C5 very hig**
Zinc mass loss [g/m^2 year]	< 0.7	>0.7-5	>5-15	>15-30	>30-60
Thickness reduction [µm/year]	<0.1	>0.1-0.7	>0.7-2.1	>2.1-4.2	>4.2-8.4
Corrosive environments	Rural areas	Atmospheres with low level of pollution	Urban and industrial atmospheres, moderate sulfur dioxide pollution. Coastal areas with low salinity	Industrial areas and coastal areas with moderate salinity	Industrial areas with high humidity and aggressive atmosphere

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The corrosion behaviour of galvanized steel in aqueous media, under conditions of immersion or exposure, is a less generalized case [6]. Moisture is highly corrosive to most metals, including steel and zinc [7].

EN ISO 12944-2 also contains three categories of corrosion for galvanized steel structures immersed in water (IM1, IM2) or buried in the ground (IM3) but no concrete values are indicated for mass loss (Table 2) [6].

Table 2. *Corrosion category for water and soil*

Corrosion category	Corrosion environment	Examples of environments and structures
IM1	Fresh water	River installations, hydro-electric power plants
IM2	Sea or brackish water	Harbor areas with structures like sluice gates, locks, jetties; offshore structures
IM3	Soil	Buried tanks, steel piles, steel pipes

Many parameters affect the corrosion of zinc in a water environment, such as pH, oxygen content, water temperature and other chemicals and dissolved elements.

For example, in distilled water, zinc may have a low corrosion rate, provided it is free of oxygen and carbon dioxide. Freshwater environments have a major component for classifying the corrosion potential respectively water hardness. Zinc is more resistant to hard water than water with low hardness.

Sea water has, at surface, pH of 8 due to excessive amounts of carbonates and the pH can drop to 7 in stagnant water. Also, the depth of the water has an influence on the pH level. Sea water temperature can vary greatly from negative values at the poles to 35 °C at the equator. The higher the temperature, the higher the corrosion of the zinc layer in the water. Tides and waves are also important considerations in determining the corrosion protection provided by galvanized steel [8, 9].

Determining the corrosion rate of zinc in water thus becomes a particular step necessary to assess the durability of galvanized products when used in an aqueous corrosive environment.

The present paper makes an analysis of the behaviour of galvanized sheet in rainwater, domestic water, sea water and Danube water, with the determination of mass loss in a period of five weeks.

2. Experimental research

The experimental researches aimed at the corrosion behaviour of some samples of hot-dip galvanized sheet with a layer thickness of 60 g/m^2 in four corrosive environments: rainwater, domestic water, Danube water and sea water.

Sea water was prepared in the laboratory and rainwater, domestic water and Danube water were collected from the environment.

The corrosion behaviour was assessed by determining the gravimetric index (I_g), respectively the mass loss, depending on the surface of the sample and the number of hours in which it was immersed in the corrosive environment [10].

$$I_g = m_0 - m_1 / 2S\,t\ [g/m^2h]$$

where:

m_0 = initial mass of the sample;
m_1 = mass of the sample after one week in a corrosive environment;
S = surface of the sample;
t = time.

The samples were individually immersed in separate containers containing the corrosive media tested. The testing was done at ambient temperature, static.

The samples were tested for 5 weeks, i.e. a number of 840 hours, with the measurement of mass variation every 7 days.

2.1. Behaviour of galvanized sheet in Danube water

Water was collected from the Danube River in the area of Galati. It was used after settling the impurities and had a pH of 8.71. Zinc corrosion in freshwater, such as Danube water, is a complex process largely controlled by water impurities [6].

Figure 1 shows the Ig variation for the analysed period. A close value of the gravimeter index is observed during the experiment except for the first week when the weight loss is lower.

Figure 2 shows the corrosion rate every week. It is observed that the corrosion rate is different depending on the analysed week, so in the second week the samples corrode at high speed, and in the next two weeks, the corrosion rate decreases substantially. The phenomenon is explained by the formation in the first two weeks of adherent corrosion products which does not clean off by applied

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washing, which ensures a passivation of the surface for the following weeks and a reduction of the corrosion rate to about one third. In the fifth week the corrosion rate increases again.

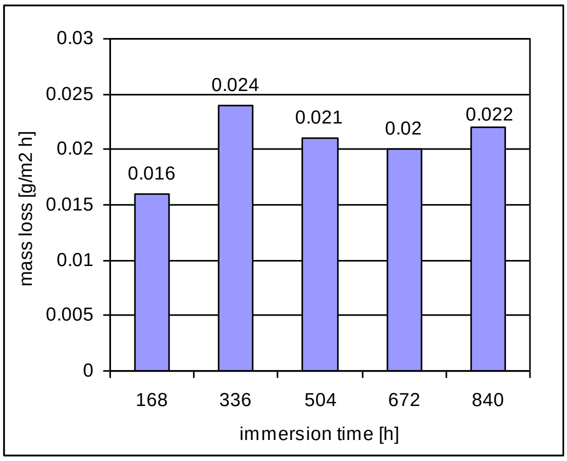

Fig. 1. *Mass loss in Danube water in time*

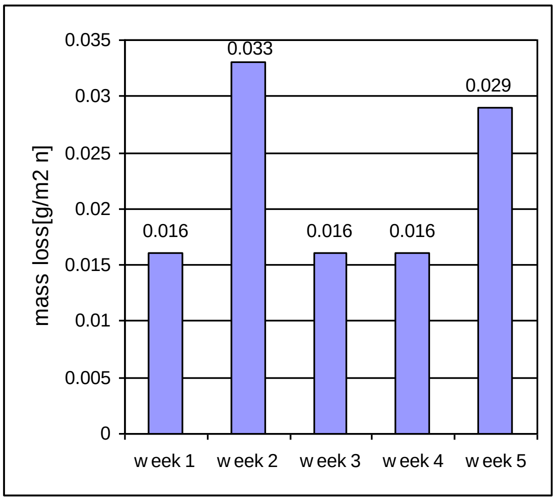

Fig. 2. *Weekly mass loss in Danube water*

2.2. Behaviour of galvanized sheet in rainwater

The rainwater had a pH of 7.04. Figure 3 shows the mass loss depending on the duration of the corrosion process in rainwater.

As can be seen and in Fig. 4, the highest corrosion rate is recorded in the first week (after 168 h). Continued maintenance of the galvanized sheet in the corrosive environment leads to a substantial decrease in the corrosion rate with a relatively constant maintenance over the next 4 weeks. However, we must keep in mind that, in practice, the galvanized sheet will be in contact with rainwater for a small number of hours and the exposure will be periodic. Rainwater is very corrosive to zinc coatings due to the presence of dissolved oxygen and carbon dioxide. Oxygen dissolved in pure water is five to ten times more aggressive than carbonic acid [6].

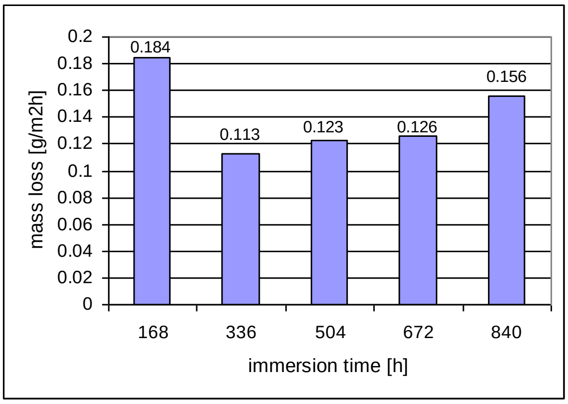

Fig. 3. *Mass loss in rainwater in time*

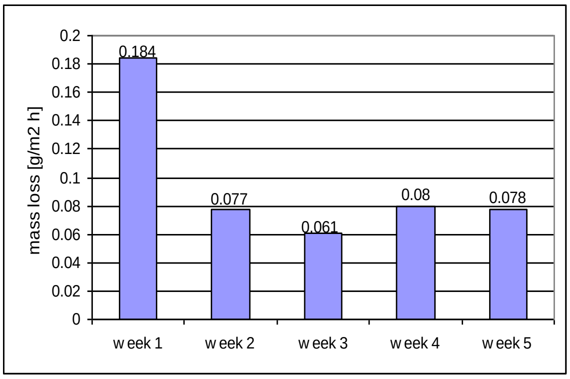

Fig. 4. *Weekly mass loss in rainwater*

2.3. Behaviour of galvanized sheet in domestic water

Domestic water was collected from a household. The solution presented, after settling the impurities, a pH of 6.56.

Figures 5 and 6 show the mass loss depending on the duration of the corrosion process in this corrosive environment, respectively, the weekly mass loss.

It is found that the galvanized sheet is progressively corroded over time in domestic water and the highest corrosion rate is observed in week 4.

2.4. Behaviour of galvanized sheet in sea water

Sea water was prepared in the laboratory by dissolving 3% sodium chloride, chemically reactive,

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in distilled water. The obtained solution had a pH of 9.18. The test results are shown in Figures 7 and 8.

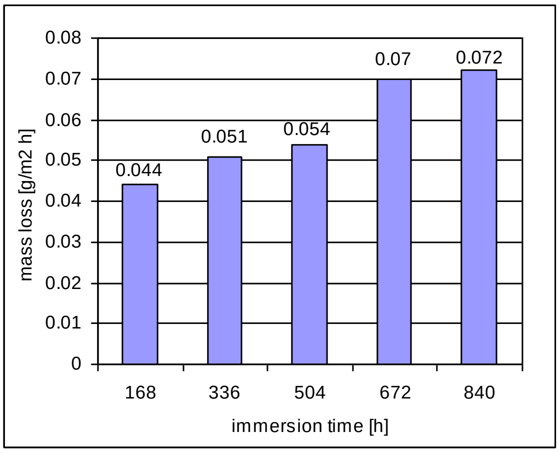

Fig. 5. *Mass loss in domestic water in time*

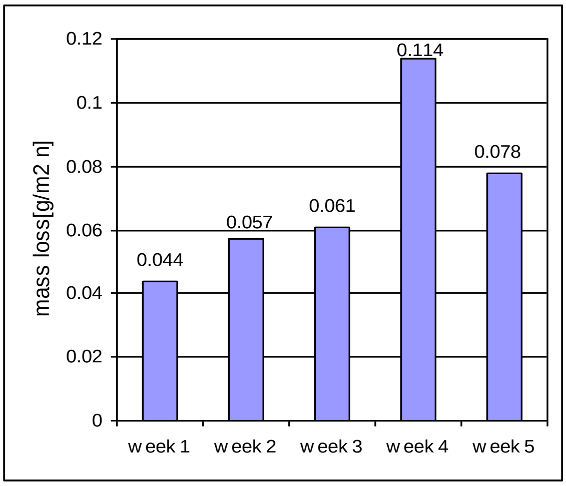

Fig. 6. *Weekly mass loss in domestic water*

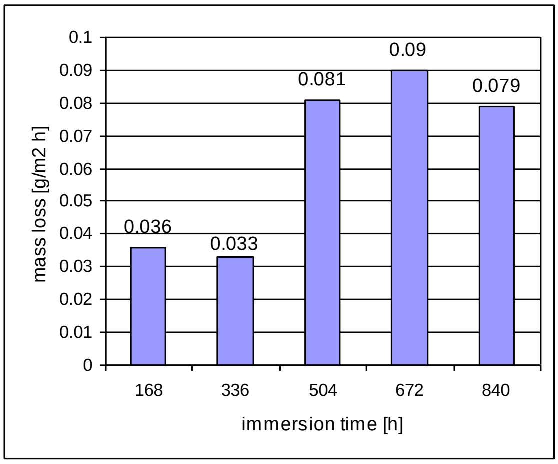

Fig. 7. *Mass loss in sea water in time*

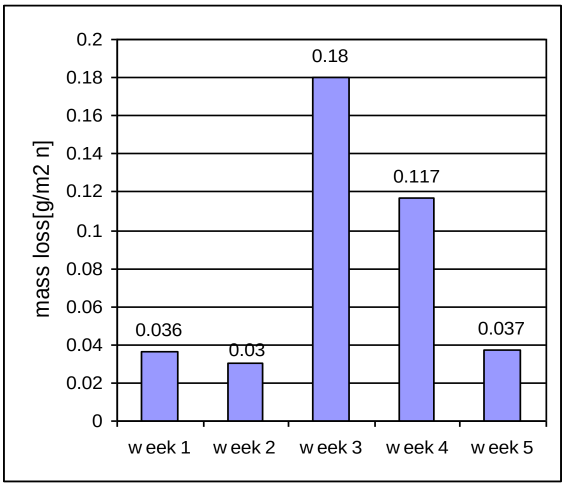

Fig. 8. *Weekly mass loss in sea water*

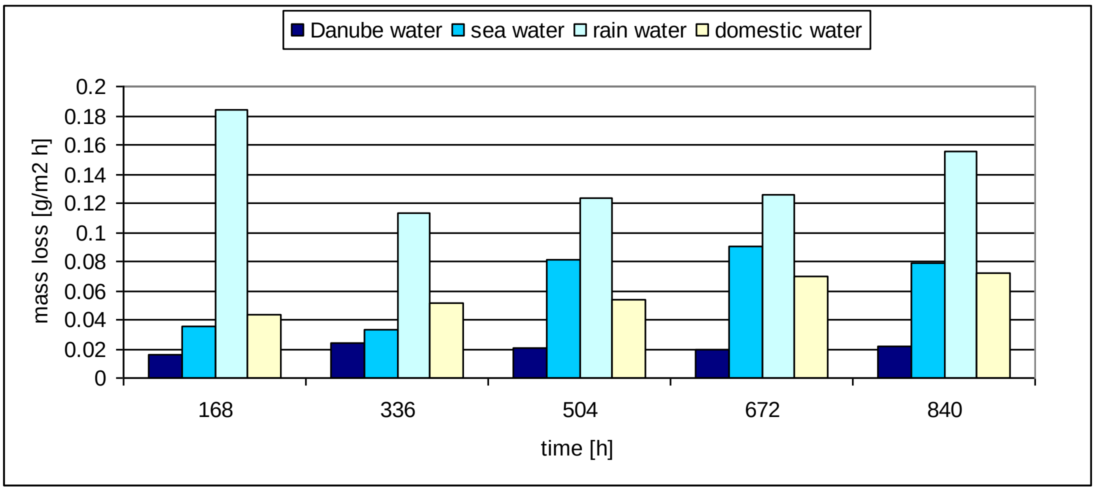

Fig. 9. *Comparatively, the mass loss over time, in the four corrosion environments tested*

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As can be seen, the corrosion process becomes significant after 504 hours of attack (Fig. 7), the highest mass loss being recorded in week 3 (Fig. 8). The formation of corrosion products slows down the corrosion rate in week 5.

Figure 9 shows, comparatively, the mass loss over time, in the four corrosion environments tested.

The best corrosion behaviour is observed in seawater and the weakest in rainwater. In Danube water and domestic water, the corrosion rate after 840 hours is comparable.

It is observed that in fresh water the corrosion rate of galvanized sheet is significantly higher than in sea water. It must be borne in mind that seawater was prepared containing only sodium chloride. The presence of other salts that are usually found in sea water can change the corrosion behaviour.

3. Conclusions

In Danube water a close value of the gravimeter index (0.022 g/m^2h) is observed during the experiment, except for the first week when the mass loss is lower (0.016 g/m^2h).

In the rainwater the highest corrosion rate is recorded in the first week (after 168 h) when the weight loss is 0.184 g/m^2h.

In domestic water the galvanized sheet is progressively corroded over time, and the highest corrosion rate is observed after 840 hours, respectively 0.072 g/m^2h.

The best corrosion behaviour for the galvanized sheet is observed in sea water and the weakest in rainwater. In Danube water and domestic water, the corrosion rate after 840 hours is comparable.

These results are strictly valid for the corrosive environments tested and cannot be generalized.

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EFFECTS OF NITRIDING SUBSEQUENT TITANALITING OF STEELS

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ABSTRACT

The paper presents the results of nitriding in partially dissociated ammonia of the pure technical iron, respectively 34CrAlMo5 steel after titanaliting in powdery solid medium, with direct reference on the growth kinetics of the layers, the phase composition and the morphology of the resulting layers. Thermodynamics was anticipated and experimentally demonstrated that the layers of titanium aluminide formed on the surfaces of the two metallic materials considered do not constitute barriers to nitrogen diffusion during the nitriding process, but actively participate in the formation of simple or complex nitrides of the two elements, titanium and aluminum. On the other hand, in the presence of these layers, the flux of nitrogen atoms is slightly diminished with repercussions on the dimensions of the structural components of the layer. The conclusion of the experimental research was that the role of titanaliting prior to nitriding is to increase the proportion of the hardening phases in the surface layers of thermochemically processed metal products after nitriding.

KEYWORDS: titanaliting; nitriding; thermodynamics of the conversion of aluminides to nitrides, formation of kinetic layer, optical microscopy, electronic microscopy

1. Introduction

The kinetics of nitrided layers formation, their phase composition and their properties are strongly influenced by the chemical composition of the matrix subjected to processing. The alloying elements, depending on their nature and properties, influence these aspects in different ways. The phase composition of the nitrided layers, depending on the temperature at which the thermochemical processing was performed, after slow cooling, varies from the average-metal matrix interface to their deep areas, as it follows: at temperatures below 590 °C: $\varepsilon+\gamma'\rightarrow\gamma'\rightarrow\alpha_N+\gamma'_{exc}\rightarrow\alpha$, and at temperatures above 590 °C: $\varepsilon+\gamma'\rightarrow\gamma'\rightarrow$eutectoid $(\alpha_N+\gamma')_{\rightarrow}\alpha_N+\gamma'_{exc}\rightarrow\alpha$.

It is observed that in the area adjacent to the surface (in the compounds area) appears a succession of nitride phases, in the case of iron and its alloys there order is ε-$Fe_{2-3}N$ and γ'-Fe_4N. Depending on the composition of the matrix, the type and the proportion of nitrides also change [1-4, 10]. Most alloying elements (Cr, Mo, Mn, etc.) except Al,Ti,Si, dissolve during the ε $(Fe,Me)_{2-3}N$, causing a decrease of size and nitrogen content of this phase. Aluminium, titanium and silicon favour the development of the γ'-$(Fe,Me)_4N$, phase, separated either continuously or in acicular / platelet form on the crystalline grains limit or on the sliding planes, a phenomenon that frequently determines, the fragility of this area. High values of nitrogen concentration in the nitride layer create the necessary conditions for the appearance of the ξ-(Fe_2N), phase, separated during cooling in those areas of the ε phase in which the nitrogen concentration reached values of 11-11.32% mass [4].

In the case of steel nitriding in ammonia atmosphere, a strong migration of carbon from the matrix to the surface is registered, which determines a carbon saturation of the ε phase and consequently the appearance of carbonitride $Fe_{2-3}(N,C)$ [5]. Nitriding at high nitrogen potential atmospheres can determine the fragility of the areas adjacent to this surface and the appearance of pores. The appearance of pores is

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related to the meta-stability of nitrides. Experimentally, it was demonstrated that the porosity of the ε- phase occurs at nitrogen concentrations higher than 8.15% [6]. After cooling this area remains single-phased. At nitrogen concentration values of 6.1-7.15%, the area of the layer characterized by the presence of the ε- phase will be free of porosity and also during this phase when slowly cooled, there will occur the separation of the excess γ' phase. With the increase of the technological maintenance period at the nitriding temperature, the size of the zone (ε+γ') does not change significantly, being registered only an increase the size of the phase ε porous area [6]. The increase in the carbon content of the steel determines a significant increase of the ε phase porous zone.

The diffusion zone (the "internal nitriding" zone) represents the multiple phase area under the (ε+γ') layer and consists of a solid solution of nitrogen in the base metal, its nitrides and the nitrides of the alloying elements (when they exist). Depending on the affinity for nitrogen of the alloying elements, the diffusion areas are of 1st and 2nd degree [4]; those of 1st degree appear in the case of pure metals and their alloys in which the alloying elements have a lower affinity for nitrogen compared to that of the basic element of the alloy, and on the contrary, those of 2nd degree have a higher affinity compared to it. In the first case, the diffusion area will consist of the solid solution and metal nitrides with the basic role of the alloy, and in the second case they consist of the solid solution, iron nitrides, γ' and also of nitrides of the alloying elements. 2nd degree diffusion areas appear in iron alloys with Ti, Cr, V alloying elements, nitralloy alloys and in refractory metal alloys. Simultaneously with the increase of the diffusion zone, the coagulation of separate nitrides takes place, a phenomenon which is possible only in the case of the simultaneous diffusion of both nitrogen atoms and those of alloying elements. These atoms have the maximum flux in the area of the metallic layer-matrix interface and consequently the strongest change of the separated nitrides size will be registered at the end of the diffusion area. The consequence of such phenomena / processes is that as the displacement in relation to the metal-average matrix interface, the degree of nitride dispersion decreases. From a thermodynamic point of view, in the case of allied matrices, the formation of nitrides in the diffusion area (internal nitriding area) is also possible due to the participation of the alloying elements carbides. Such a mechanism is triggered in the presence in the metal matrix subjected to nitriding of elements with high affinity for carbon, such as Ti, Zr, Hf, Cr, Mo, etc. For isomorphic crystalline networks the transition of carbides to nitrides becomes possible, and it can be described schematically as follows:

$$N+MeC \rightarrow Me(CN) \rightarrow MeN+C$$

The probability of the transition of carbides into different elements nitrides decreases in the following sequence: Zr→ Si→ Hf→ Ti→ V→ Nb→ Mn→ Cr→ Fe. [1, 4]. According to the information of the specialized literature, the increase of the metallic products exploitation performances can be rendered by a succession of thermochemical processing as titanaliting followed by classical or plasma nitriding [7, 8].

2. Materials and equipment used in research

The experimental research aimed at highlighting the effects of nitriding subsequent to the titanization of pure technical iron, respectively the alloying steel 34CrAlMo5 (chemical composition within the limits of W1.8507, respectively EN10085). The main aim was to highlight the extent to which titanium and aluminum contained in chemically defined Ti-Al compounds in the titanaliting layer influence the kinetics nitrided layer formed.

Samples with dimension 6X10X20 mm of both materials, after degreasing with isopropyl alcohol, they were titanaliting in a powdery solid medium followed by nitriding in partially dissociated ammonia. To have a reference element, some of the samples were in a simple nitrided variant; In this situation the samples from 34CrAlMo5 steel, prior to nitriding, were improved under the conditions: volumetric martensitic hardening with austenitization at 870 °C followed by cooling in oil and subsequently returning to 580 °C.

The powdery solid medium used for titanization was composed of: 30% made of (35% TiO_2 + 25% Al + 20CaF_2 + 20% Mg), 65% Al_2O_3 and 5% NH_4Cl. Titanaliting was made in refractory steel tin boxes, sealed with clay latches, in a 10KW electric chamber oven, with dimensions of chamber 300X180X180 mm, provided with automatic regulation and temperature control system. The processing was performed at 1050 °C, 2 hours of temperature maintenance, followed by slow cooling with the oven off. Nitriding was carried out in a vertical electric oven with the dimensions of the retort of Φ190X600 mm, of 8 KW installed power, provided with automatic system of regulation and temperature control. The temperature was varied in the range of 540-620 °C, below and above the eutectoid transformation temperature in the Fe-N system, and the degree of dissociation of ammonia (measured by titration) in the range of 40-70%, a range in which according to experimental findings the amount of adsorbed nitrogen decreases drastically [3].

The results obtained experimentally for both materials were investigated by optical metallography, using a Neophot 32 microscope equipped with Qimaging 01-MP5.0-RTC-CLR -10 color RTV 10 BIT camera connected to a software Struers SCENTIS V 5.6, electronic microscopy , using an FEI F50 Inspect SEM microscope, equipped with EDAX APEX 2i energy dispersion X-ray spectrometer with Apollo X SDD detector and X-ray diffraction using Rigaku Smart Lab X Ray Diffractometer. Note: In order to perform the metallographic investigations-phase composition, dimensions of the structural components, the samples were prepared metallographically and attacked with the nital reagent 3%.

3. Results of experimental research. Interpretations

The change of the nitriding medium activity by increasing the degree of ammonia dissociation has immediate repercussions on the kinetics of the layers growth, an aspect which can be observed both in the case of non-alloy matrices (Fig. 1-Fe-ARMCO), and in the case of alloy matrices (image 3-34CrAlMo5). Experimental research has shown that an increase in the degree of ammonia dissociation from 45% to 70% affects both the total size of the layer and the area of compounds. The explanation of this phenomenon is based on the behavior of ammonia during heating [11, 13], namely the ionic mechanism of adsorption [12].

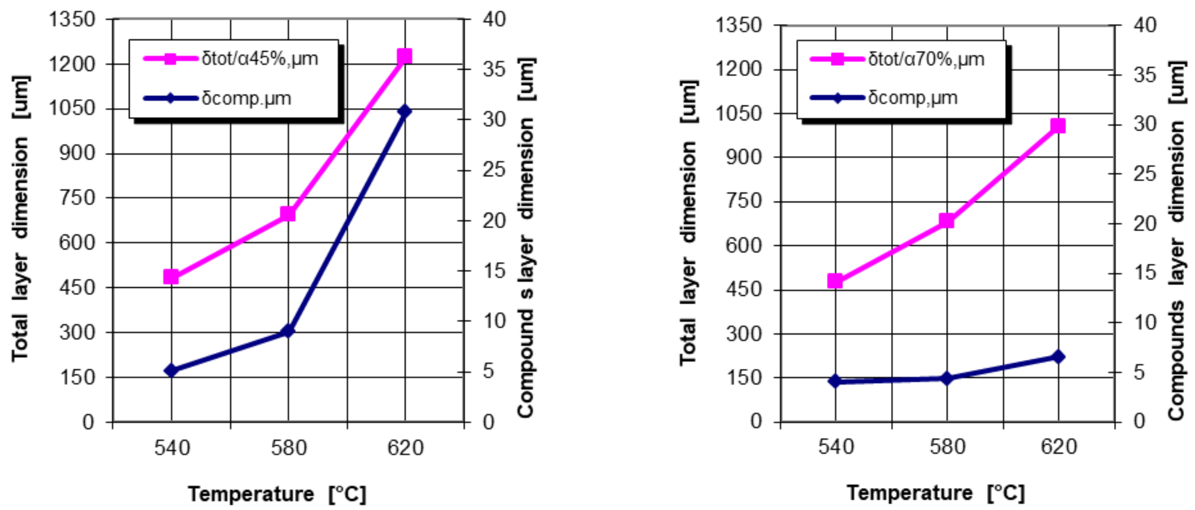

Fig. 1. *Kinetics growth of different components of nitride layer in technical pure iron depending by nitriding temperature and the degree of ammonia dissociation (tment-ct = 4 hours)*

Basically, with the increase of the ammonia dissociation degree there decreases the availability of ammonia molecules capable of ionizing by forming NH^{3-} anionic complexes, which by subsequent decomposition in adsorbed state to ensure the enrichment of the surface layers with nitrogen. The effects of changing the activity of the atmosphere as a result of increasing the degree of ammonia dissociation are highlighted by optical metallography images (Fig. 2) and are amplified by increasing the alloying degree of the metal matrix.

In the case of 34CrAlMo5 steel (1.12% Cr; 0.335% Mo; 0.92% Ti; 0.64% Mn) - (Fig 3, 4) the size of the structural components of the nitrided layer under the same conditions as pure technical iron are much lower, the presence of elements with affinity for nitrogen, capable of forming nitrides in the matrix of these steels obviously reduces the availability of nitrogen to contribute to the increase of the diffusion area and of the area of compounds, being more intense, as the ammonia dissociation degree is higher (beyond the optimal range, 20-45%).

The metallographic analysis of the nitrided layers obtained on the pure technical iron matrices (Fig. 2) at temperatures below the eutectoid transformation temperature of the Fe-N system, and different degrees of dissociation (45%; 70%), highlights the theoretically anticipated sequence of phases, $\varepsilon+\gamma' \rightarrow \gamma' \rightarrow \alpha_N+\gamma'_{exc} \rightarrow \alpha$, with slight differences in the size of the different structural components (Fig. 1-2).

In the case of the 34CrAlMo5 alloy improvement matrix, the phase sequence is the same as in the case of pure iron, but the morphological aspect is different and highlighted by the reaction with metallographic reagent (Image 4); the area of

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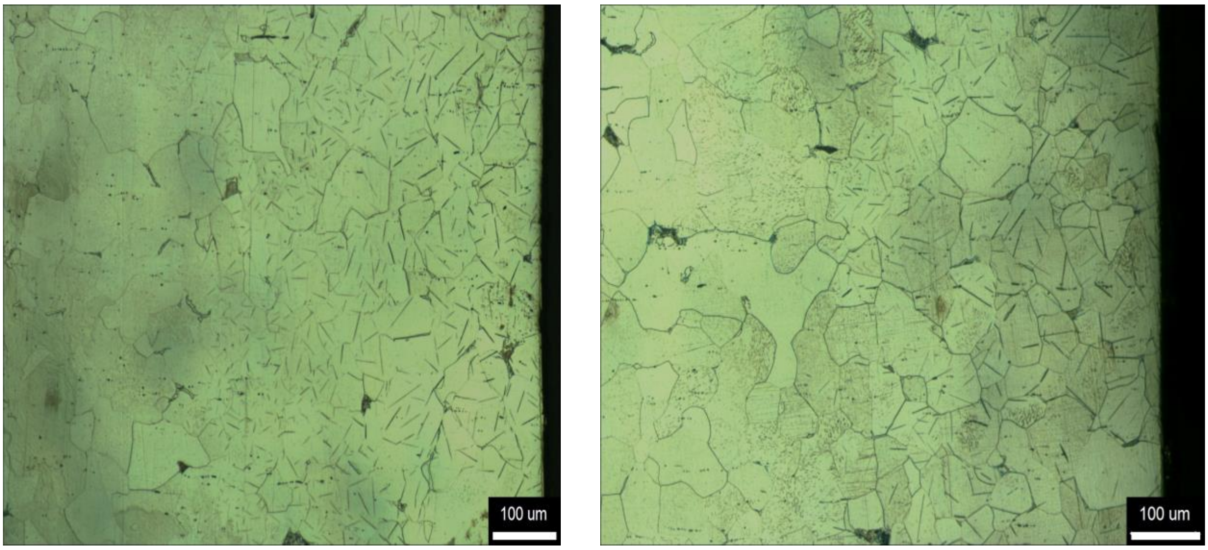
compounds appears clearly highlighted, and the diffusion area (internal nitriding) can be differentiated from the draw tempered sorbite mass by the chemical reaction differences (it appears to have a much more intense reaction): excess γ’ phase separations (Fe4N and nitrides of alloying elements CrN, Mo2N, AlN, highlighted by X-ray diffraction) are impossible to detect by optical metallography on the draw tempered sorbite background. Obviously, the size of the nitrided layers structural components obtained in the case of the improved 34CrAlMo5 alloy steel is much smaller compared to those made in the case of the nitrided matrix of the pure technical iron under the same conditions (Fig. 3 compared to Fig. 1), the causes being related the presence of alloying elements with affinity for nitrogen.



a) b)

Fig. 2. *Structure on the nitriding layer obtained in case of pure technical iron, nitriding in partially dissociation ammonia under conditions: T = 540 °C/4 ore; α_{NH3} = 45% (a); α_{NH3} = 70% (b). Attacked reagent: nital 3%*

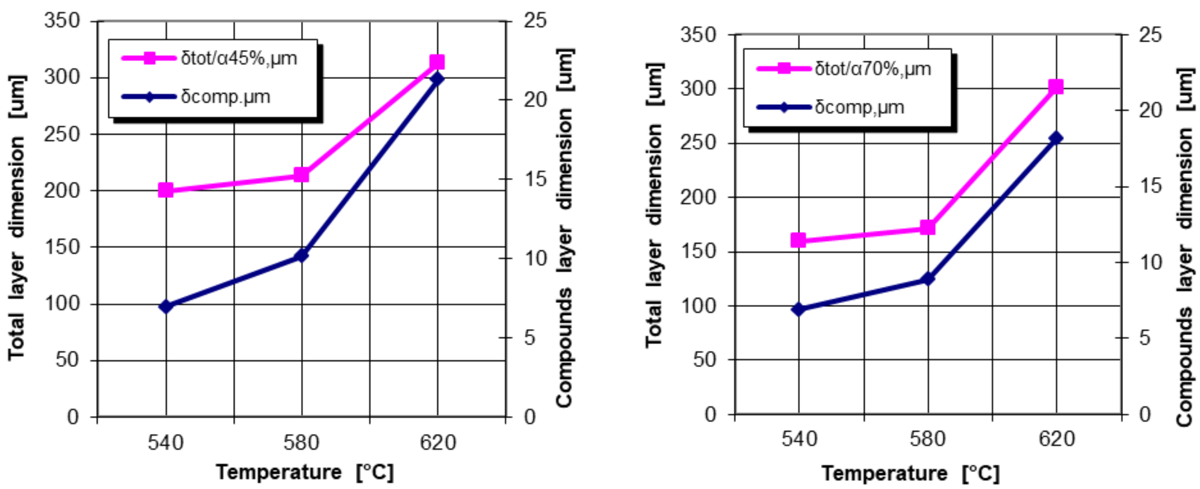


Fig. 3. *Kinetics growth of different components of the nitriding layer in the case of 34CrAlMo5 (tment-ct = 4 hours)*

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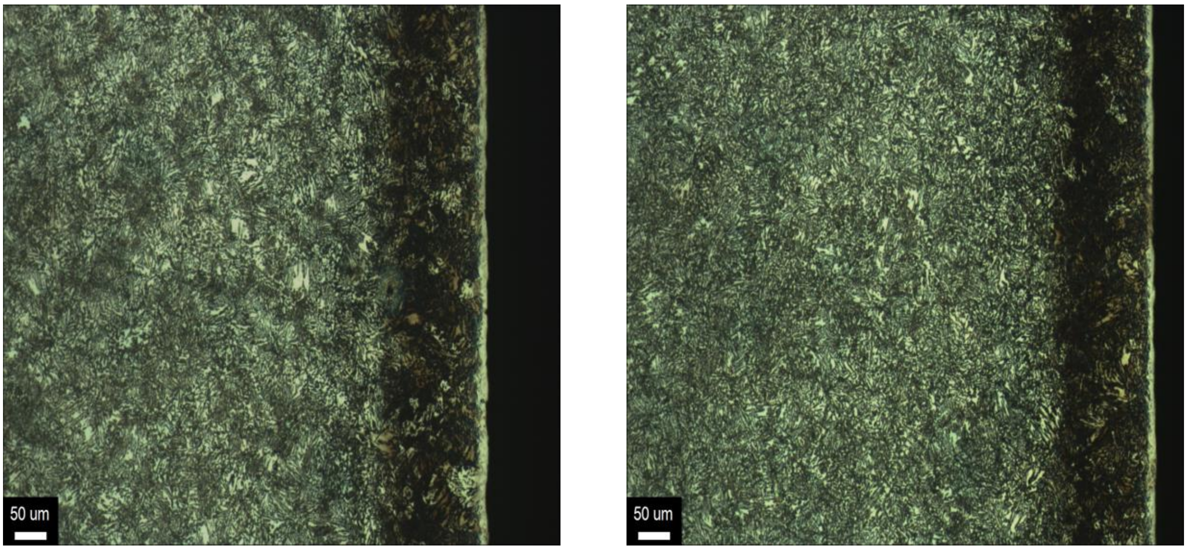

a) b)

Fig. 4. *Structure of nitriding layer obtained in the case of 34CrAlMo5 steel, nitriding in partially dissociated ammonia, under conditions: T = 540 °C/4 hours; α $_{NH3}$ = 45% (a); α $_{NH3}$ = 70% (b). Attacked reagent: nital 3%*

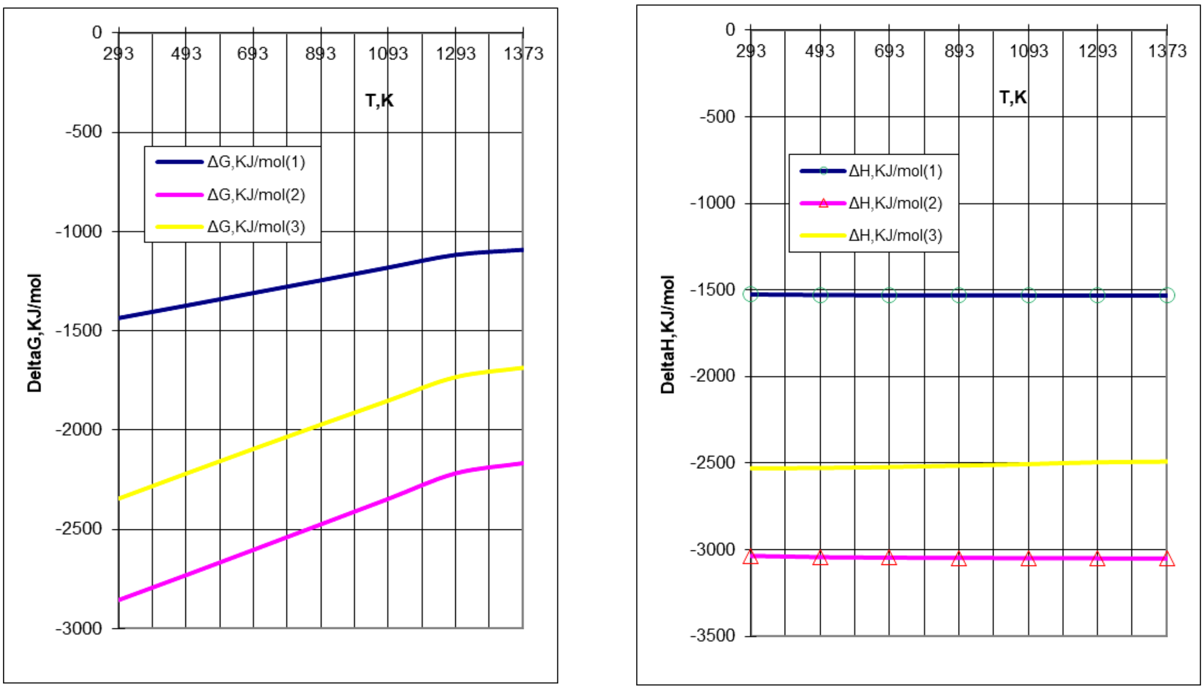

Fig. 5. *Temperature variation of the main thermodynamic measurements related to the synthesis reaction of the nitride of the elements initially in the state of chemical compounds defined by Al-Ti*
Note: Legends notes 1,2,3 correspond to chemical reactions 1-3

In the specialized literature there is information related to the association of chemical processes of titanating and nitriding [7] or nitriding and titanating [8, 9], the association of the two manners of thermochemical processing aiming to ensure special performances to the superficial layers of metallic products: microhardness close to 2000 μHV or more, special tribological behavior, corrosion resistance in aggressive environments, and others such performances. All these performances seem to be ensured according to the conclusions of various experimental researches by the presence in the superficial layers of the metallic products processed in this way of titanium, aluminum nitrides, or

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complex titanium and aluminum nitrides. Moreover, the nitriding of alloys with high titanium contents, for example of ferritic steels alloyed with titanium, ensures them a substantial increase in the hardness of the surface layers, especially if the Ti/C ratio of the steel is within the range 6.4-9.5 [1]. Our own experimental research has led to the conclusion that in the case of a simultaneous surface saturation with titanium and aluminum - titanization of metal matrices - and subsequent nitriding in partially dissociated ammonia, in the surface layers will be found in addition to iron aluminides, Fe3Al, iron nitrides and aluminum, molybdenum, etc. (Fe4N; AlN; TiN, etc.); in the case of matrices alloyed with alloying elements with affinity to nitrogen, after titanating and nitriding, in their layers will be found nitrides. Prior to nitriding titanium aluminides present in the titanium alloyed layer are characterized by high thermal stability, but from the thermodynamic point of view, in the presence of nitrogen the nitride synthesis reactions of the two elements are to be produced (ec. 1-3, Fig. 5), excess nitrogen further participating in the formation and growth of the diffusion area.

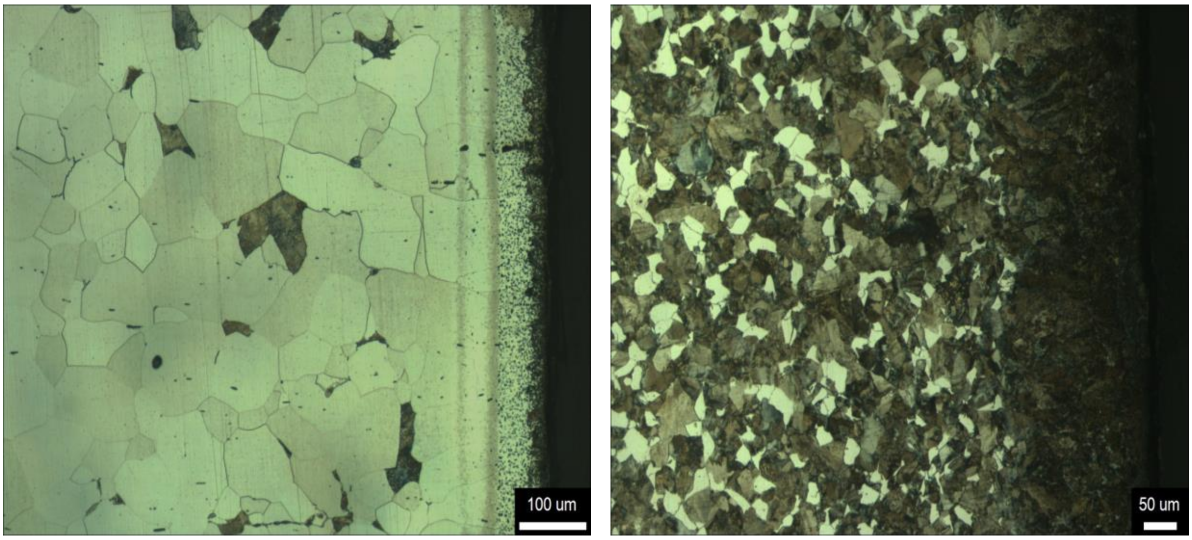
$$AlTi + 3N(g) = AlN + TiN + N\downarrow \quad (1)$$

$$Al_3Ti + 5N(g) = 3AlN + TiN + N\downarrow \quad (2)$$

$$2Fe_3Mo_2 + 6N(g) = 2Mo_2N + 3Fe_2N + N\downarrow \quad (3)$$

Note: The compound Fe2Ti, which can appear in the titanium alloyed layer, behaves in the presence of nitrogen in the nitriding medium similar to the other compounds (reactions 1-3), the free enthalpy of reactions by which it is converted into iron and titanium nitrides (Fe4N; TiN) being strongly negative in the range of 373K-873K and varying in the range -1822J / mol ÷ -1586 J/mol.

Therefore, the layer of aluminum compounds with titanium (titanium aluminides) formed as a result of the titanaliting process (Fig. 6) is not a barrier for the diffusion of nitrogen, but the reduction of the nitrogen atoms flow as a result of the synthesis reactions of aluminum and titanium nitrides (reactions 1-3 and not only) affects the formation kinetics of both the total layer and the area of compounds (stronger in the case of alloy matrices compared to pure metals).



a) b)

Fig. 6. *Optical microscopy images of Fe-ARMCO(a) and 34CrAlMo5-(b) after titanaliting in solid medium powder at 1050 °C/2 hours; Attacked reagent: nital 3%*

The titanium containing layers obtained in the case of the two metallic materials, Fe-ARMCO and 34CrAlMo5, have well-defined areas of aluminides; in the case of pure technical iron, the total layer affected by the diffusion of the two elements has sizes of 100 μm (Fig. 6a), contains aluminides of iron and titanium (Fe3Al; Fe2Ti; FeTi) and presents porosity in its extremities, phenomenon frequently encountered in titanating solid materials, in contrast to titanized steel 34 CrAlMo5 (Fig. 6b) for which the area of aluminides of iron and alloying elements, namely their titanium compounds, appears defined by the contrast generated by the reaction with the chemical reagent.

Note: Cooling from 1050 °C (temperature used for titanating) being done gradually in the oven, with the samples embedded in the powdery solid mixture used as a supplier of active elements, the structure of the 34CrAlMo5 steel matrix will become an annealing structure.

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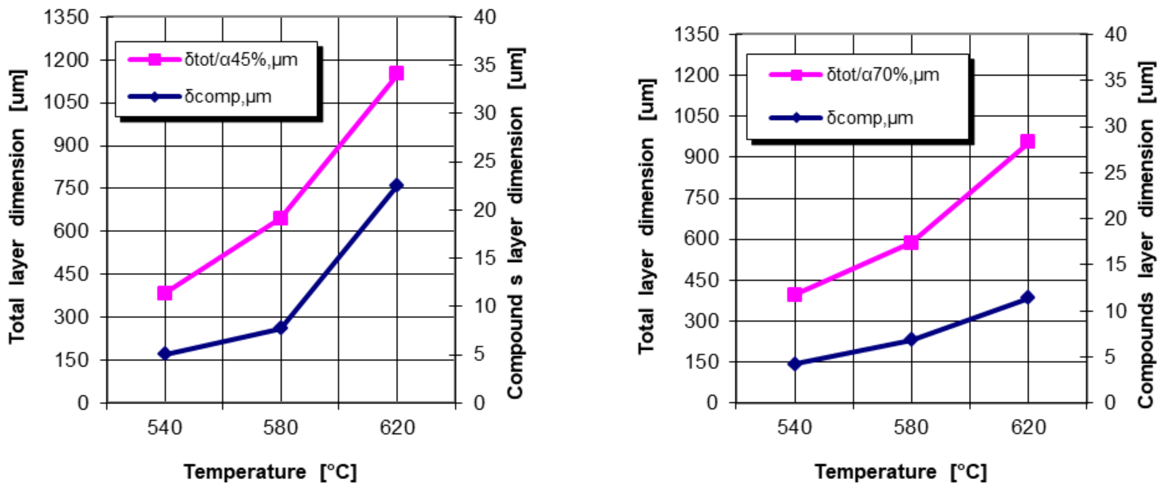
In order to ensure a level corresponding to the characteristics of the core of this steel, it is necessary to ensure an improvement of these areas before nitriding, in conditions that prevent cracking of the layer during cooling in order to harden the volumetric martensitic. The kinetics of the formation of nitrided layers, after titanating (Fig. 7, 10) is close to the one registered during processing in the absence of titanized layers (Fig. 1, 3), but slightly slower pursuant to the aforementioned reasons. From a morphological point of view, the structure of the layer obtained in the case of pure titanalized and subsequently nitrided technical iron (Fig. 8), is much more suggestive compared to that of the layer in the case of 34CrAlMo5 improvement steel (Fig. 11). The area formed during titanating, namely the diffusion zone (internal nitriding) appear clearly outlined, areas in which iron, titanium and aluminum nitrides were identified by X-ray diffraction, resulting from the interaction of aluminides with nitrogen, and by electron microscopy and quantitative chemical microanalysis (Fig. 13) in the superficial areas of the layer - the areas of compounds - there were identified high concentrations of aluminum (~6.3% compared to traces in the initial state) and titanium, namely (0.74% compared to traces in the initial state).



a) b)

Fig. 7. *Kinetics growth of different components on titanaliting layer in solid medium powder (1050 °C/2 ore) and subsequently nitrided in partially dissociated ammonia (α_{NH3} = 45%-**a**; α_{NH3} = 70%-**b**) case of technical pure iron*

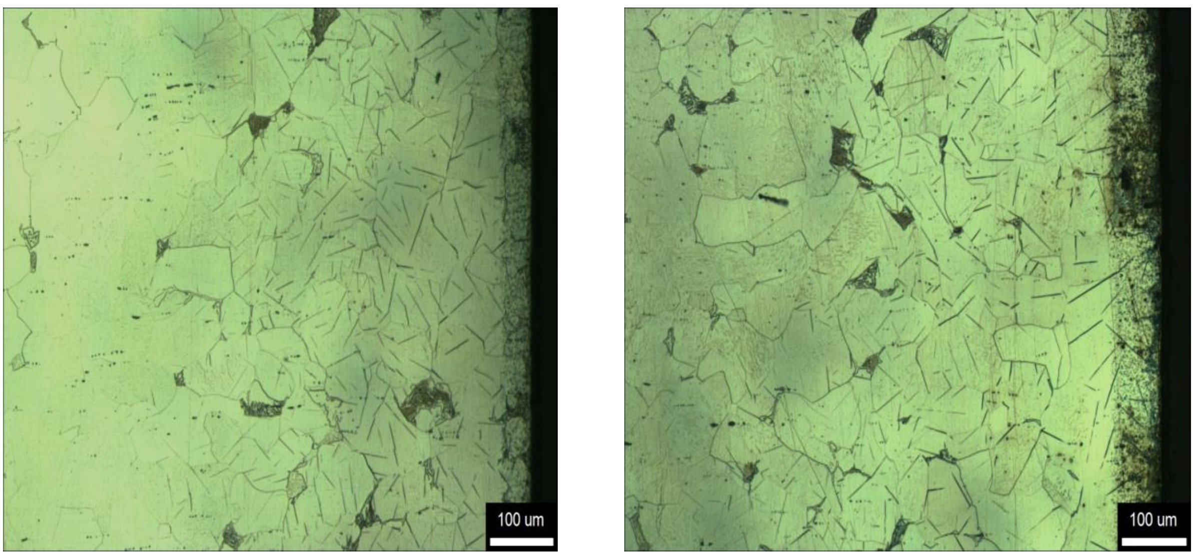


Fig. 8. *Optical microscopy of Fe-ARMCO titanaliting in solid medium powder (1050 °C/2 hours) and subsequently nitriding in partially dissociated ammonia-**a)** 540 °C/α_{NH3} = 45%; **b)** 540 °C/α_{NH3} = 70%; Attacked reagent: nital 3%*

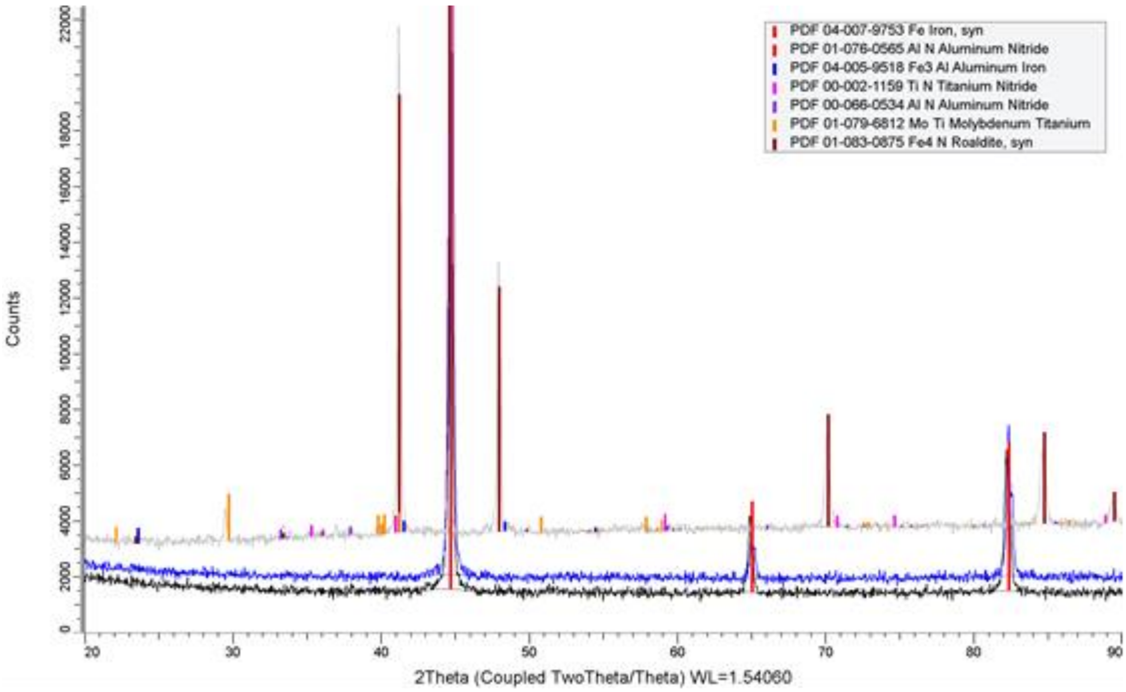
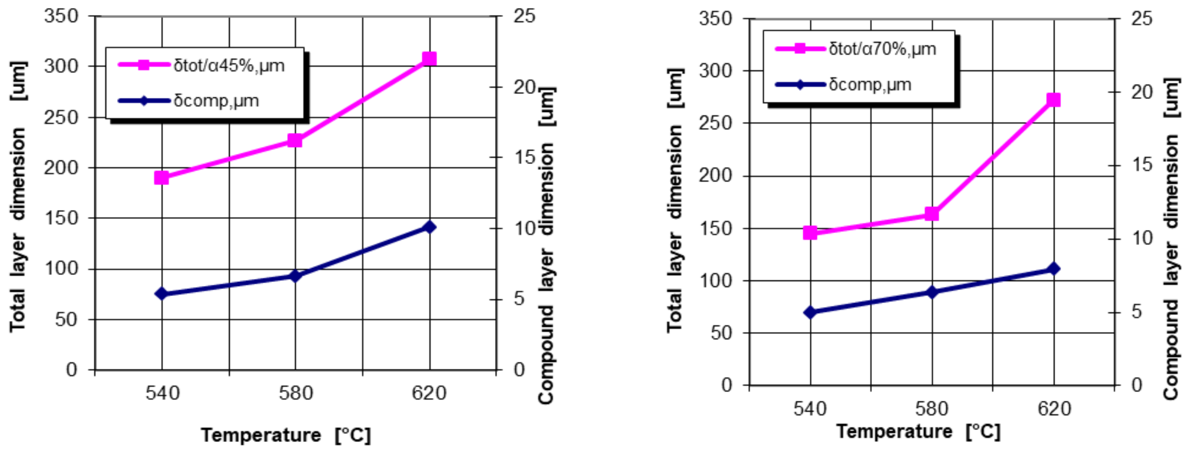


Fig. 9. *X-ray diffraction of technical pure iron in solid medium powder (1050 °C/2 hours) and subsequently nitriding in partially dissociated ammonia (580 °C/4 hours; α_{NH3} = 45%)*
Note: The two basic lines represent the diffraction lines of technical pure iron (reference)

The kinetics of layer formation after titanating and nitriding of the 34CrAlMo5 improvement alloy steel matrix (Fig. 10) is obviously much slower compared to that recorded in the case of pure technical iron (Fig. 7) and slightly slower compared to that recorded for nitriding performed directly to an improved matrix (Fig. 3).

The titanalized and subsequently nitrided layer (Fig. 11), in this case has a morphological aspect close to that following titanating, the differences being related to the phase composition of the layer: nitrides of aluminum, titanium, iron and molybdenum along with iron aluminide FeAl3 - Fig. 12, compared to the aluminides of iron, titanium, molybdenum or iron titanides of type Fe2Ti, according following titanating. The conversion of these types of compounds after following titanating of 34CrAlMo5 alloy matrix into nitrides during the nitriding process proved to be thermodynamically possible and was confirmed by X-ray diffraction (Fig. 12).



a) b)

Fig. 10. *Kinetics growth components of titanaliting layer in solid medium powder (1050 °C/2 hours) and subsequently nitriding in partially dissociated ammonia (α_{NH3} = 45%-**a**; α_{NH3} = 70%-**b**) in case of 34CrAlMo5 steel*

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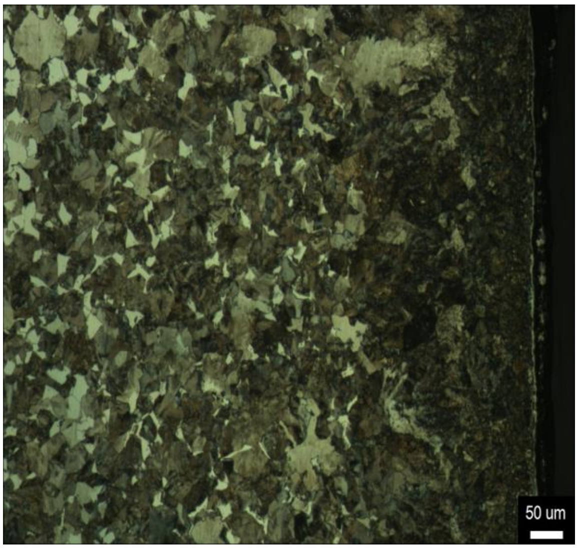
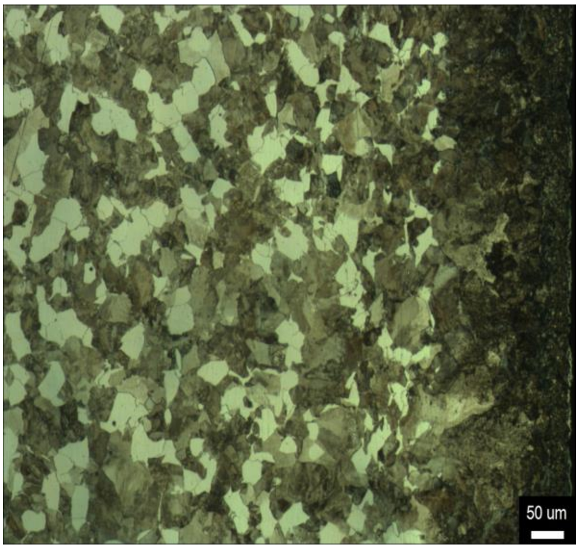


a)



b)

Fig. 11. *Optical microscopy of 34CrAlMo5 steel, titanaliting in solid medium powder (1050 °C/2 hours) and subsequently nitriding in partially dissociated ammonia -* ***a)*** *540 °C/α_{NH3} = 45%;* ***b)*** *540 °C/α_{NH3} = 70%; Attacked reagent: nital 3%*

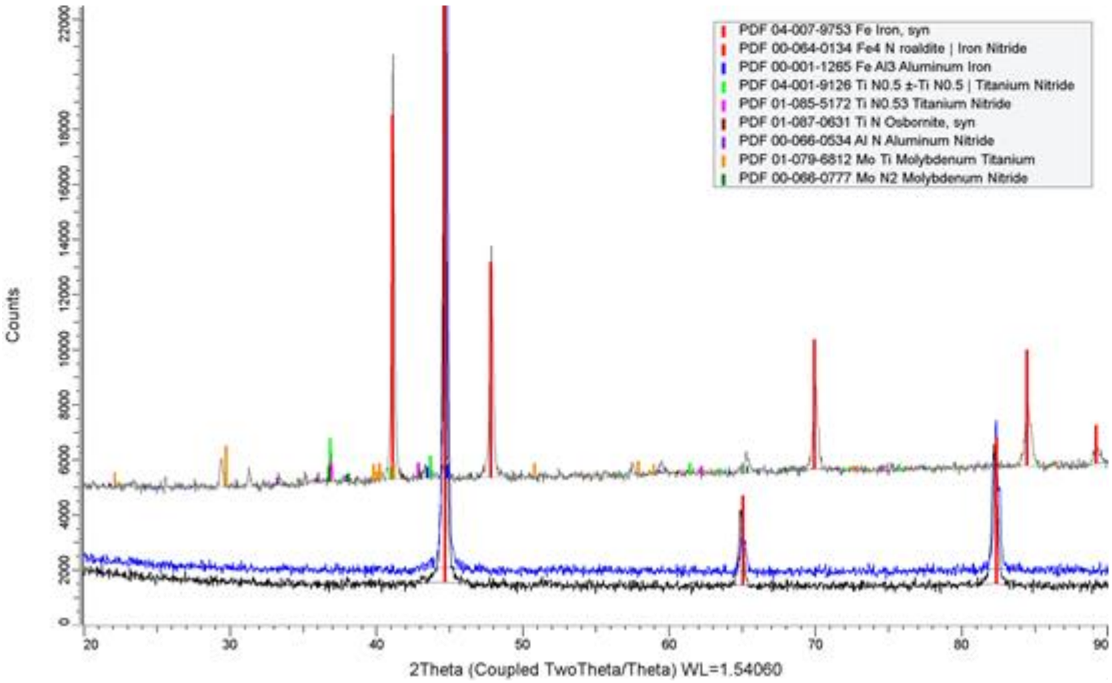


Fig. 12. *X-ray diffraction of titanaliting 34CrAlMo5 steel in solid medium powder (1050 °C/2 hours) and subsequently nitriding in partially dissociated ammonia (580 °C/4 hours; α_{NH3} = 45%)*
Note: The two basic lines represent the diffraction lines of technical pure iron (reference)

Electron microscopy research and quantitative chemical microanalysis (Fig. 1) highlighted the presence of aluminum in high concentrations in the surface areas of the layer (~15% compared to ~0.9% initially) and titanium (0.9% compared to 0.0005% in the initial state).

It should be noted that these elements are strictly compiled in the surface areas of the layer - the area of compounds, the variation (decrease) of their concentration on the layer thickness being much faster compared to that recorded in the case of pure technical iron.

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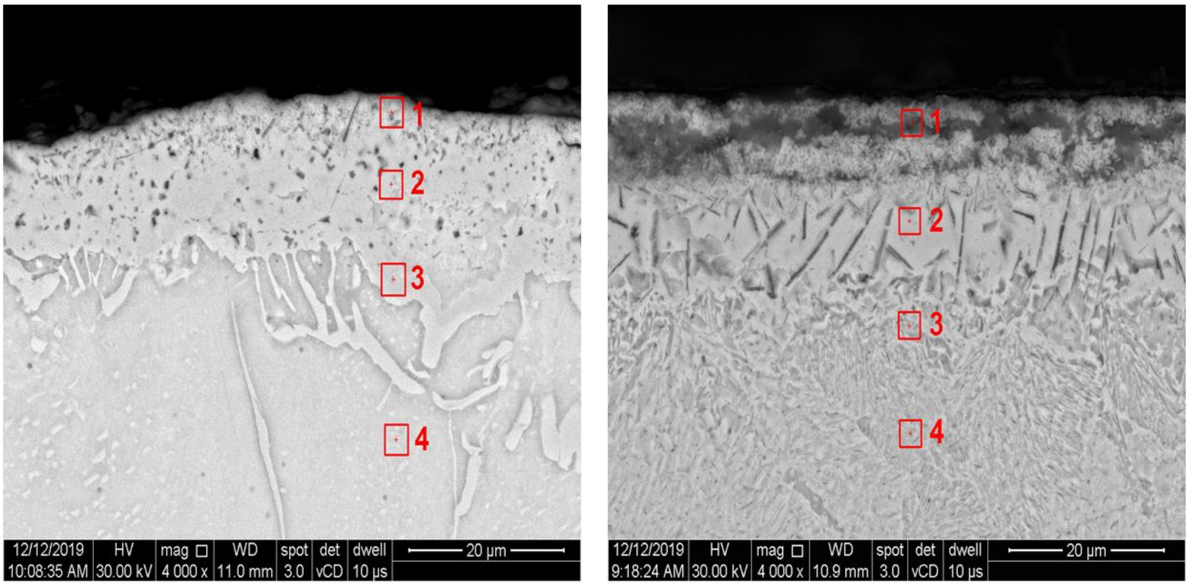
The differences regarding the aspect of the distribution of the two elements in the titanalized and subsequently nitrided layer of the two concerned materials, Fe-ARMCO and 34 CrAlMo5, are dictated by the very different values of the diffusion coefficients related to these elements in an unalloyed matrix, compared to an alloyed matrix.



Al=6.29%(Z1);4.69%(Z2);1.29%(Z3)……0.0%(Z4) Al=15.31%(Z1);2.63%(Z2);4.15%(Z3)…3.12%(Z4)
Ti=0.74%(Z1);0.75%(Z2);0.75%(Z3)…..0.0%(Z4) Ti=0.90%(Z1);0.0005%(Z2);0.0005%(Z3).0.0005%(Z4)

Fig. 13. *Electron microscopy of technical pure iron and 34CrAlMo5 steel, after titanaliting (1050 °C/2 hours) and nitriding in partially dissociated ammonia (580 °C/4 hours; α_{NH3} = 45%), with identification of the chemical composition in different microvolumes on depth layer*

The presence of FeAl3 type compounds in the titanalized and subsequently nitrided layer gives it high hardness (~8000 MN/m^2 [14]), wear resistance, as well as high values for the tensile strength and for compression limit [14]. The tribological characteristics of the titanalized and subsequently nitrided layers obtained on the 34CrAlMo5 matrices are substantially increased by the presence of aluminum, titanium, molybdenum and iron nitrides, as well as by the molybdenum titanide (MoTi).

4. Conclusions

Nitriding in a partially dissociated ammonia atmosphere after titanaliting in powder medium is an opportune variant for processing metallic matrices, pure metals or steels, in order to increase the operating performance of the products made from them.

The increase in the level of properties/performances is a direct consequence of the increase in the proportion of hardening phases in the superficial layers of metal products processed in this way, determined by the appearance after titanalitation of chemical compounds Al-Ti,Al-Fe,Fe-Ti etc. and their subsequent conversion into nitride in the nitriding stage. It is anticipated that tribological characteristics can be substantially increased in this way – hardness, wear resistance, but also corrosion resistance in some situations.

The presence of the titanium layer does not constitute a brake on nitrogen diffusion during nitriding after titanialitation, due to the behavior of the chemically defined compounds formed in the process of alitation in the presence of nitrogen. Thermodynamically it has been demonstrated and experimentally proven that the conversion reactions of these compounds in the presence of nitrogen from the nitride medium, be it titanium aluminids or titaniums of iron, in nitride of these elements, with nitrogen release, are extremely likely. In this way it is also justified the formation of a well-developed diffusion zone, close dimensionally to that obtained by simple nitride, but slightly less dimensional compared to it.

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EMISSIONS OF CARBON MONOXIDE AND SUSPENDED PARTICLES FROM THE STEEL FOUNDRY OF S.C. PROMEX S.A.

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ABSTRACT

The purpose of this article is to analyse the level of pollution of the installations related to the steel foundry operated by S.C. PROMEX S.A. Brăila, activity carried out on site and facilities put into operation, to assess the impact of these activities on the quality of environmental factors, potential risk and measures taken to prevent and reduce pollution. The determination of carbon monoxide (mg/m^3) and Suspended particles (mg/m^3) was done during 2016-2019.

KEYWORDS: air pollution, steel foundry, special steels, potential risk

1. Introduction

Environmental impact and usage of energy and equipment are significant issues in industry [1]. The iron and steel industry has an essential part by consuming extremely high materials and energy [2]. In this regard the air pollution is the fundamental significance. The iron and steel industry are the largest industrial sources of CO and furthermore, the foundry operations produce mineral ashes, acidifying mixtures, products of partial combustion, and volatile organic carbons.

Foundries are a significant component of the iron and steel industry and, consequently, are distinguished by the equivalent energy consumption and environmental issues [3].

Emissions resulting from the rough materials manipulation processes are fugitive particulates produced from receiving, discharging, stowage and transport all materials for the foundry. These emissions are directed by locking up the main pollution sources and directing the air from the chamber within the filter fabric. Emissions include hydrocarbons and contain smoke, organic substances, suspended particles and carbon monoxide (CO) [4].

Metal foundry functions at higher temperatures which has as effect the dispersion of gas into the atmosphere. To study the distinct processes in which pollution can prevail in the metal foundry, it is essential to understand the various processes that exist in the steel foundry [5]. The process executed by a steel foundry may be trippingly underlined as melting, casting and finishing [6].

According to [7] the atmospheric pollutants emitted from metal casting are those resulting mainly from analytical pyrolysis. Pollution control methods has an essential position in environmental protection. Filters, Wet scrubber and Cyclone technique are well known air pollution control methods that must be used in steel foundries to decrease the quantity of noxious emissions that can be dispersed into the atmosphere [8]. Worldwide is being considered air pollution control methods has a critical contribution in reducing the air pollutants [9].

2. Materials and methods

The Steel Foundry occupies an area of 28,080 sqm. The foundry is located in the north western part of Brăila (Figure 1). The Steel Foundry is located inside the S.C. PROMEX S.A. Brăila and is surrounded by other production sections: Loading Base, Auto base, Middle Forge and Excavator Factory (in conservation).

In the Steel Foundry section, cast steel semi-finished products are produced, from the simplest to the most complex, and the main activity is the processing of ferrous metals - smelters for ferrous metals, with a production capacity of more than 20 tons/day.

Operational processes of the Steel Foundry consist of: Unloading, storage and pneumatic transport of sand, preparation of mixtures for forming, preparing shapes according to patterns, elaboration of alloy and high alloy steels in electric

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arc furnaces, casting of steel molds, debating of forms, cleaning, sandblasting of semi-finished products, heat treatment in the oven with 40 sqm movable hearth, quality control and shipping of semi-finished products to the processing sections. The operational processes specific to the special foundry are: development of special steels and cast iron in induction furnaces of 250 kg each, nodulation and molding of steel. The formed parts reach the drum debater or the main debater, then enter the oxyacetylene cutting (weeding), enter the sandblasting machine with the belt, after which they are subjected to heat treatment in the oven with a fixed hearth of 2.5 sqm. The technological flow is presented schematically in Figure 2.

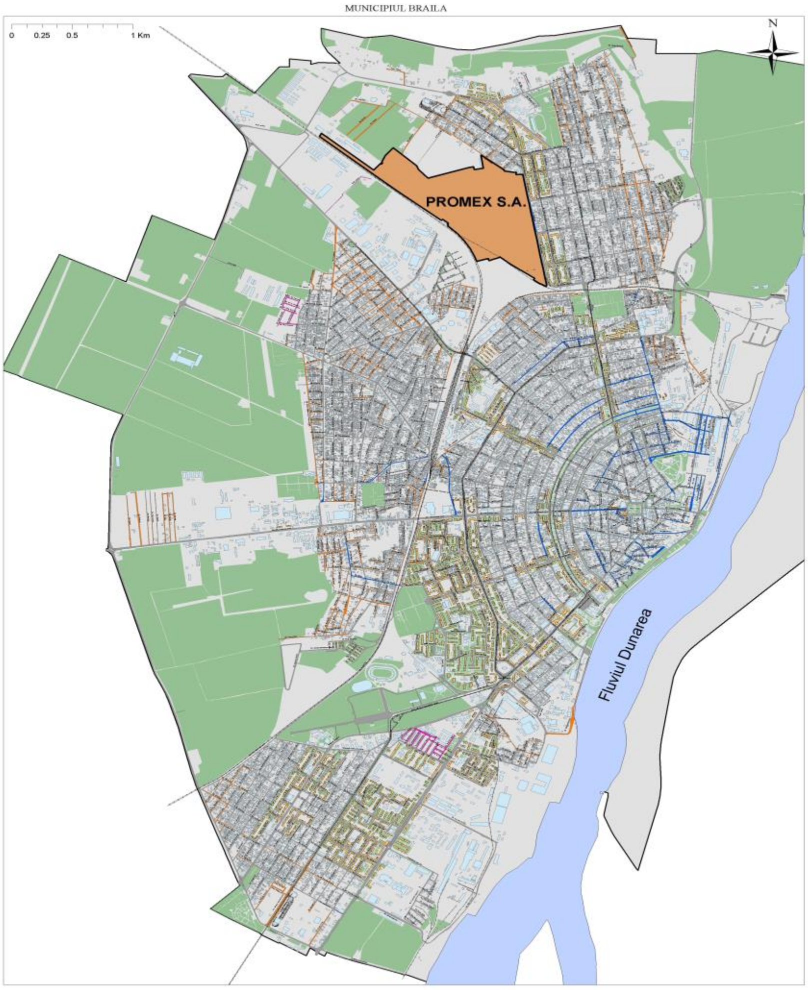

***Fig. 1**. Location of S.C. PROMEX S.A. Brăila*

***Table 1.** Organization of production*

Number	Industry sectors	Finished product
1.	Steel processing line: use fills in operation: 2 electric ovens with arc of 3 t/oven / charge and 1 oven of 5 t/charge	Liquid steel
2.	The casting line consists of 3 casting areas	Cast steel semi-finished products
3.	Debating area, cleaning, sandblasting	
4.	Heat treatment area installations in operation: 1 heat treatment furnace with movable hearth of 40 sqm and 1 furnace with fixed hearth of 2.5 sqm	
5.	Casting line for special parts - for special parts steel/cast iron is made in 3 electric induction furnaces, 250 kg each	Special steel/cast iron parts
6.	Shaping wood	Wooden models

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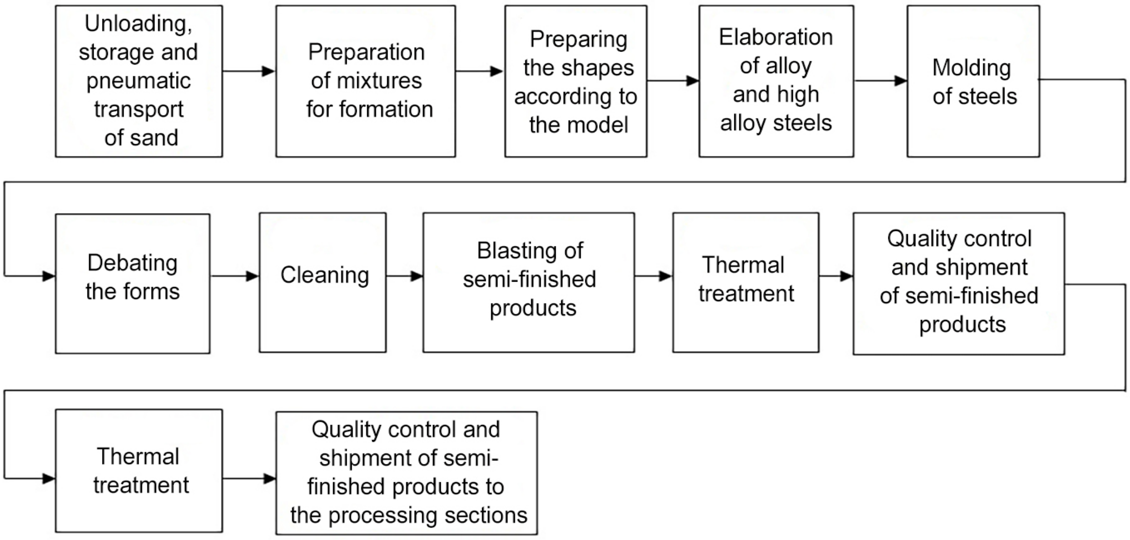

Fig. 2. *Technological flow - Steel foundry*

The activity of the Steel Foundry results in emissions in the form of sedimentable dusts, flue gases from combustion processes from heat treatment furnaces and flue gases from steel melting furnaces. Within the steel foundry, on the steel elaboration line are used 2 electric arc furnaces, each with a capacity of 3 t/charge and 1 furnace with a capacity of 5 t/charge. Each furnace is provided with a hood located above the respective furnace, which partially captures the gaseous emissions (NO_X, CO_2, CO) and the dust released as a result of the melting processes and from the evacuation of the molten steel. In the case of the special foundry, 3 electric induction furnaces of 250 kg each are used. The duration of a cold charge is about 1.5-2 h, after which the duration of the charges decreases to 1.5 h. As in the case of electric arc furnaces, induction furnaces are not used at the same time, due to the need to maintain a spare furnace.

Emissions in the form of sedimentable dust from the smelting of metals from the steel foundry and from electric furnaces (2 furnaces of 3 t/charge and 1 furnace of 5 t/charge) are captured by a hood located above each furnace. The 3 hoods are connected to a centrifugal fan, which flows directly into the filter, where the filtration takes place. For air protection the installations are provided with local and general ventilation installations.

The flue gases, containing CO resulting from the electric and heat treatment furnaces (operating with methane gas) are evacuated through individual chimneys provided with nozzles for measurements.

The Gas Probe IAQ analyser was used to determine the amount of CO. The Gas Probe is one of the most accurate portable gas detectors. Suspended particles were measured using the HUZ-DUST HD-1100 analyser. HAZ-DUST is a portable particle reader that uses infrared electromagnetic radiation to examine particles. The examination method is well known as light scattering.

Carbon monoxide (CO) and Suspended particles were determined between 2016-2019 at the following locations:

- Heat treatment oven 40 sqm;
- Electric oven 5 tons;
- Electric oven 3 tons;
- Special Foundry Line.

3. Results and discussions

In order to analyse the amounts of carbon monoxide and suspended dust, released into the atmosphere during 2016-2020, a set of measurements were performed annually. The monitoring of air pollutants has an essential role in the management of industrial emissions, including the choice of equipment and technologies.

The variation of the measured CO (mg/m^3) values was in the Heat treatment oven 40 sqm area between 38.75 (mg/m^3) and 11.11 mg/m^3, between 43.5 mg/m^3 and 7.12 mg/m^3 in the Electric oven area 5 tons. In the 3 Tons electric oven area the values varied between 40.33 mg/m^3 and 8.42 mg/m^3, compared to the Special Foundry Line area where the values varied between 58.25 mg/m^3 and 7.34 mg/m^3.

In Figure 3 in blue we represented the 20 values obtained by measuring the CO emission in the Heat treatment area 40 sqm and in red we presented the values obtained in the Electric oven area 5 tons.

The measurements in the 3 tons electric oven area were represented graphically in green and in

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orange the values in the Special Foundry Line area are represented. The measurements performed between 2016-2019 indicated the highest level of CO pollution in the area of Electric oven 5 tons and Special Foundry Line, at each data collection measurements were performed, after calibrating the device.

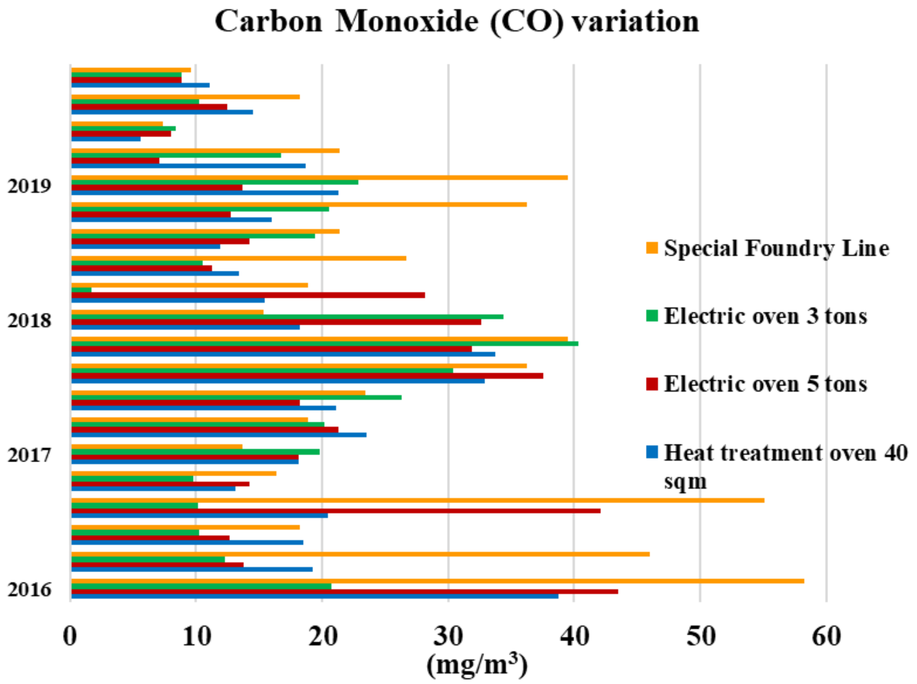

Fig. 3. *Carbon Monoxide variation*

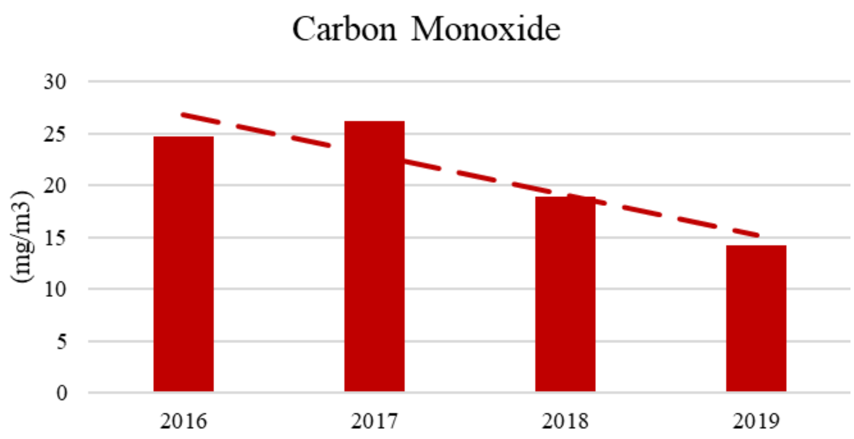

Fig. 4. *Carbon Monoxide yearly average*

The annual average of carbon monoxide for the four years, 2016-2019, was calculated in order to obtain a clear image of the pollutants emitted into the atmosphere by foundry steel sector of SC PROMEX SA.

It is obvious that the trend is decreasing (except for 2017), the quantities of carbon monoxide emitted varied from 24.67 mg/m^3 in 2016 to 26.25 mg/m^3 in 2017 and 14.22 mg/m^3 in 2019.

The measured values of the Suspended particles (mg/m^3) vary in the Heat Treatment Furnace area 40 sqm between 4.7 mg/m^3 and 0.7 mg/m^3, and between 6.05 mg/m^3 and 1.97 mg/m^3 in 5 tons Electric oven area. In the Electric Oven 3 tons area, were obtained values between 4.24 mg/m^3 and 0.8 mg/m^3, while in the Special Foundry Line area the values varied between 6.3 mg/m^3 and 2.96 mg/m^3.

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In Figure 5 the measured values for Suspended particles in the chimney, determined with the HUZ-DUST HD-1100 analyser, are presented. In purple we represented the values obtained after measuring the Suspended particles in the Heat treatment area 40 sqm, in red we presented the values obtained in the Electric oven area 5 tons. The measurements in the 3 tons electric oven area were represented graphically in blue and in green are represented the values in the Special Foundry Line area.

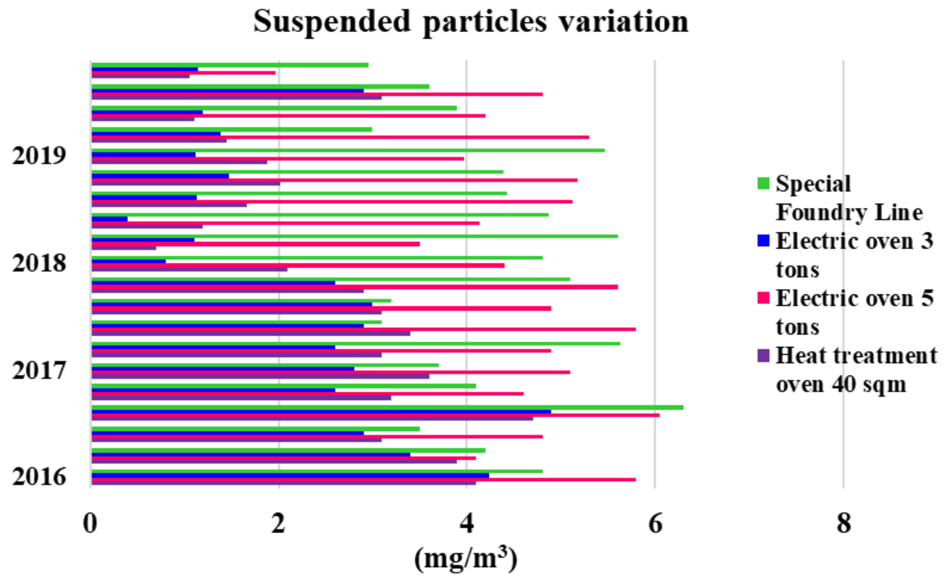

Fig. 5. *Suspended particles variation*

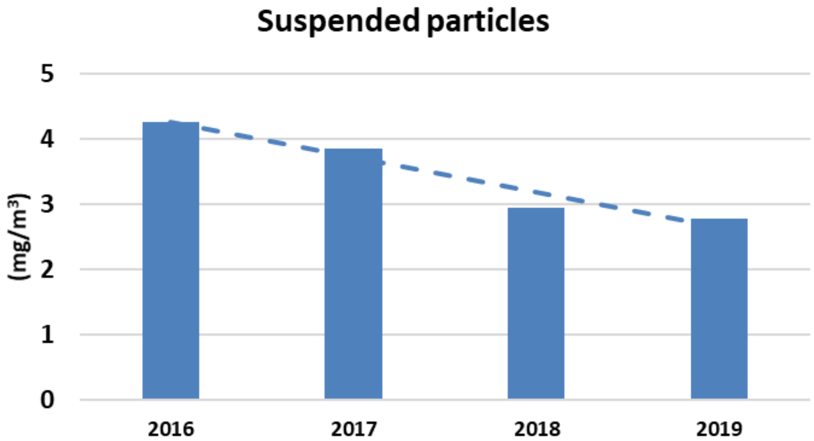

Fig. 6. *Suspended particles yearly average*

The yearly average of the amounts of suspended particles is a very precise method that allows us to observe the trend of variation of this pollutant.

As in the case of carbon monoxide and suspended powders, they also have a decreasing trend, with values ranging from 4.26 mg/m^3 in 2016 to 2.77 mg/m^3 in 2019.

4. Conclusions

If we analyse the variation of the two pollutants: carbon dioxide and suspended particles only from the point of view of environmental protection, we can say that the situation is a good one because the amounts of pollutants eliminated in the atmosphere are decreasing. More specifically, in the case of carbon monoxide emissions have been reduced with 12.03 mg/m^3 that represent 30%, comparing with suspended particles emissions that have decreased by 1.49 mg/m^3, which represents 22%.

In the analysis of the technological flow/process, no risks were identified that could generate environmental pollution. It is obvious that the pollution with suspended particles in the areas of

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Electric oven 5 tons and Special Foundry Line is higher compared to the area's Electric oven 3 tons and Heat treatment oven 40 sqm.

Unfortunately, if we talk about the quantities of materials produced, they have decreased significantly, so as a conclusion the decrease of the quantities of pollutants is the effect of the decrease of the production of this commercial company and not of the investments in high-performance equipment.

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MANUSCRISELE, CĂRŢILE ŞI REVISTELE PENTRU SCHIMB, PRECUM ŞI ORICE CORESPONDENŢE SE VOR TRIMITE PE ADRESA:

MANUSCRIPTS, REVIEWS AND BOOKS FOR EXCHANGE COOPERATION, AS WELL AS ANY CORRESPONDANCE WILL BE MAILED TO:

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