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Mapping Sulfides and Strength Properties of Bst420 and B500c Steel Bars Before and After Corrosion

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Влияние содержания сульфидов на прочностные свойства арматурной стали типов BSt420 и B500c до и после коррозии

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***Keywords**: corrosion of steel bars, mass loss, chloride induced corrosion, mechanical properties of steel rebars, sulfides in steel rebars.*

The aim of this study is to determine the occurrence of sulfides (MnS, FeS) in the cross section of two different reinforcing steel rebars, BSt420 and B500c Tempcore. The mechanical performance against chloride corrosion of steel bars was evaluated by means of mechanical tensile tests, before and after corrosion, and Scanning Electron Microscopy (SEM) techniques. In particular, the influence of corrosion of a set of reinforcement steels on the tensile strength of steel bars was studied. The experimental results showed that the steel type exhibiting the highest resistance, as far as chloride corrosion is concerned, was reinforcing steel BSt420. On the contrary, B500c Tempcore presents the minimal corrosion resistance, and this can be attributed to a higher sulfide content at least on the external surface of 500μm.

***Ключевые слова**: коррозия стального бруса, потеря массы, коррозия хлоридом, механические свойства арматурной стали, сульфиды в арматурной стали.*

Целью данного исследования является определение присутствия сульфидов (MnS, FeS) в поперечном сечении двух типов арматурной стали, BSt420 и B500c Tempcore. Проведена оценка механических свойств в присутствии коррозии хлоридом с помощью испытаний на растяжение до и после коррозии и методами электронной микроскопии. В частности, изучено влияние коррозии на предел прочности на разрыв для выборки арматурных сталей. Проведённые эксперименты показали, что самое высокое сопротивление с учетом влияния коррозии хлоридом показал тип стали BSt420. И напротив, тип B500c Tempcore показал минимальную устойчивость к коррозии, что объясняется высоким содержанием сульфидов, по крайней мере на внешней области толщиной 500 мкм.

1. Introduction

In Greece, from the early 1960s to the late 1990s, BStIII grade steel (according to the Hellenic Standard ELOT 959) was used as reinforcement in reinforced concrete structures (RC). It is equivalent to BSt420 grade steel according to the German Standard DIN 488. Despite its replacement since the late 1990s (mostly by BSt500s and B500c grade steels), BSt420 steel reinforcements can still be found in most RC structures now in Greece. Over the prolonged service time of these structures, damage has accumulated on their load-bearing elements. This damage, caused mainly by corrosion and earthquake loading, results in decreased residual strength bearing capacity.

The designing requirements based on new requirements and principles obliged the European Union to use dual high performance steel such as S500s and B500c. The upgraded mechanical performance of the dual-phase steel used in RC is achieved through the ideal combination of yield strength (R_p) and the ductility property (elongation at maximum load A_{gt}) of the material.

The dual-phase steels of RC show an outer high strength core (martensitic phase) and a softer core (ferrite-perlite phase). Beyond these two obvious phases, there is a transition zone called the bainite phase. The mechanical performance of B500c steel results from the combination of the mechanical properties in each of the individual phases, where the increased strength properties are credited to the presence of the outer martensitic zone and the increased ductility to the presence of the ferrite-pearlite core.

Most metals are found in nature in compounds with nonmetals such as oxygen and sulfur. For instance, iron exists as iron ore containing Fe_2O_3 and other oxides of iron. Corrosion, from this point of view, can be considered as the process of returning metals to their natural state (the ores from which they were originally obtained).

As it is well known, the serviceability of RC structures is deteriorated by reinforcement corrosion in a variety of ways. On the one hand, corrosion reduces the cross-sectional area of steel bars and results in a reduction of the load-bearing capacity and ductility of structures. On the other hand, the volumetric expansion of corrosion products leads to cracking or even spalling of the concrete cover, affecting the cohesion integrity of reinforced concrete members [1].

An important factor of steel corrosion is the existence of chemical sulfide compounds that are generated in steel at the stage of production. The existence of these non-metallic inclusions is mainly based on the desulfurization of steel.

The addition of Mn to steels dates from the early days of steel-making practice and its purpose is to segregate sulfur as MnS. This practice also includes the formation of FeS along grain boundaries that induce problems in the hot-rolling of steel [2]. Additionally, in structural steels, MnS (common sulfides) are appreciated as constituents for their beneficial role during machining. They also reduce machining costs [3, 4].

Moreover, the presence of chemical compounds of MnS and FeS or (Mn, Fe) S as components of steel has an influence on the microstructure of material. From the viewpoint of fracture mechanics, non-metallic inclusions are equivalent to small defects or cracks that can generate stresses within the surrounding matrix [3, 4]. The impact of this behavior of sulfides, as stress concentrators, depends on their size, position and shape, but also on their ability to bond with the matrix material [4]. In study [5], during the mechanical tensile tests, MnS sites host crack nucleation leading to sub-surface crack propagation. As such, the martensitic zone fractures following a semi-ductile appearance. The debonding of the martensitic zone is possible when the agglomeration of MnS inclusions / micro-cracks are positioned close to the interfacial zone. In this case, crack coalescence, being the result of crack growth, could lead to a crack of the interfacial circumference (appearing as debonding).

In this manuscript, the occurrence of sulfides (MnS, FeS) in the cross section of two different reinforcing steel rebars BSt420 and B500c, is to be determined. Based on the established quantity and density of sulfides, the degradation rate of the mechanical strength properties of specimens BSt420 and B500c, which will be exposed to the salt spray chamber, is to be examined. Additionally, this paper presents the results of mass loss calculations for the naturally corroded BSt420 steel bars of existing coastal structures.

2. Experimental Procedure

2.1. Materials BSt420, B500c

The experiments were conducted on BSt420 and B500c grades of reinforcing steel, specially produced for the needs of the current investigation by a Greek steel company. The materials were delivered in the form of 10 mm (Ø10) nominal diameter ribbed bars. According to ELOT 1421-1, the chemical composition of B500c steel in maximum by weight permissible values was C = 0,24, S = 0,055, P = 0,055, N = 0,014, and Cu = 0,85. The exact chemical composition of the alloys is given in Table 1.

Table 1

Chemical composition of BSt420 and B500c

Types of steel rebars	Chemical composition (%)											
	C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	Sn	Co
Hot-rolled (BSt420)	0,375	0,287	0,029	0,022	1,304	0,064	0,085	0,009	0,003	0,197	0,016	0,000
Tempcore (B500c)	0,219	0,193	0,047	0,015	0,870	0,106	0,082	0,014	0,001	0,261	0,016	0,010

2.2. Salt Spray (Fog) Corrosion

The selection of salt spray test relies on the fact that the salt spray test environment lies qualitatively closer to the natural coastal environment than other accelerated laboratory corrosion tests [6]. This being said, the laboratory environment is much more aggressive than the natural one and causes a severe corrosion in a short time. The selection of exposure duration was also made empirically so as to cause mass loss observed in existing structures [7]. The exposure times were 30, 45, 60 and 90 days.

Salt spray (fog) tests were conducted according to the ASTM B117-94 [8] specification. For the test, a special apparatus, SF 450 model made by Cand W. Specialist Equipment Ltd., was used. The salt solution was prepared by dissolving 5 parts by mass of sodium chloride (NaCl) in 95 parts of distilled water. The pH of the salt spray solution was such that when dissolved at 35 °C, the solution was in the pH range from 6,5 to 7,2. The pH measurements were made at 25 °C. The temperature in the zone of reinforcement material exposed inside the salt spray chamber was maintained at 35 ± 1,1 – 1,7 °C. After the exposure was complete, the specimens were washed with clean running water to remove any salt deposits from their surfaces and dried. Finally, the oxide layer was removed by means of a bristle brush according to the ASTM G1-90 specification

[9]. The specimens were then weighed in order to evaluate the mass loss due to corrosion exposure. The number of specimens treated was 5 for BSt420 and 6 for B500c per duration of exposure.

2.3. Gathering Specimens

Naturally corroded steel bars were obtained in the RC structures of existing buildings over 30 years old in the local area of the Gulf of Patras and Corinth. Some of the concrete cover blocks were removed to examine their chloride-ion content. Concrete and corroded steel bar samples were taken from several locations of the buildings. Not much chloride was found in the concrete, which implies that steel bar corrosion was mainly induced by carbonation. The diameter of the obtained rebars was Ø8 and Ø10 (8mm and 10mm), respectively. The chemical composition of the rebars is listed in Table 1.

According to the ASTM G1-90 specification, the specimens removed from the buildings were cleared from corrosion deposits by means of a non-metallic bristle brush, and then immersed in 3,5 g of hexamethylene tetramine diluted in 500 ml of hydrochloric acid (HCl, sp gr 1,19) [9]. The collected exposed rebars were classified according to the steel grades used in Greece over the last few decades. The collected steel specimens were of grades BSt III_S (according to DIN 488). The steel grades were confirmed mainly by civil engineering plans (where available) or, when this was not possible, by chemical analysis.

2.4. Tensile Tests BSt420 / B500c

Tensile tests were conducted on non-corroded and on artificially corroded BSt420 and B500c grade steels, respectively. The specimens treated for different durations in the accelerated salt spray environment were prepared in order to investigate their strength properties. Following that, the tensile tests were conducted according to the ISO 15630-1 [10] specification, at 24 °C, using a 2 mm/min strain rate. There were 25 mechanical tests performed for BSt420 (5 per each exposure level) grade and 30 for B500c (6 per each exposure level) grade steels.

2.5. SEM

In order to identify the quantity and density of sulfides in the two categories of steel rebars, microscopy and visual observation were used and micro-photos were taken. In respect to the steel category that displayed a higher density of sulfides, the corrosion product morphology of steel reinforcements through Scanning Electron Microscopy (SEM) in the external area was examined.

3. Results

3.1. SEM

In order to easily detect the presence of sulfides, the following preparation of specimens was made: BSt420 and B500c samples were ground and polished by a MinimetTM grinder polisher machine (Buehler Ltd.). Then, their surface was ground with SiC paper, diamond and SiO_2 polishing compounds for producing stress free surfaces. Finally, scanning electron microphotographs made records with a field emission scanning electron microscope (ZEISS, SUPRA 35VP), operating at 15 and 30 keV accelerating voltage. In addition, the microscope was equipped with a backscattered electron detector and an x-ray microanalysis system (QUANTA 200, BRUKER AXS) in order to get the required information from the surface structure of the cross-section area of the samples.

In Fig. 1 and 2, an indicative view of sulfides in the cross-section area of two grades of steel (BSt420, B500c) is presented. Figures 3 and 4 show some measurements, such as the quantity of BSt420, B500c, Ø10 sulfides, the area as a function of sulfide density in different distances from the surface (500μm and 5000mμ), and also the frequency as a function of sulfide area and max length.

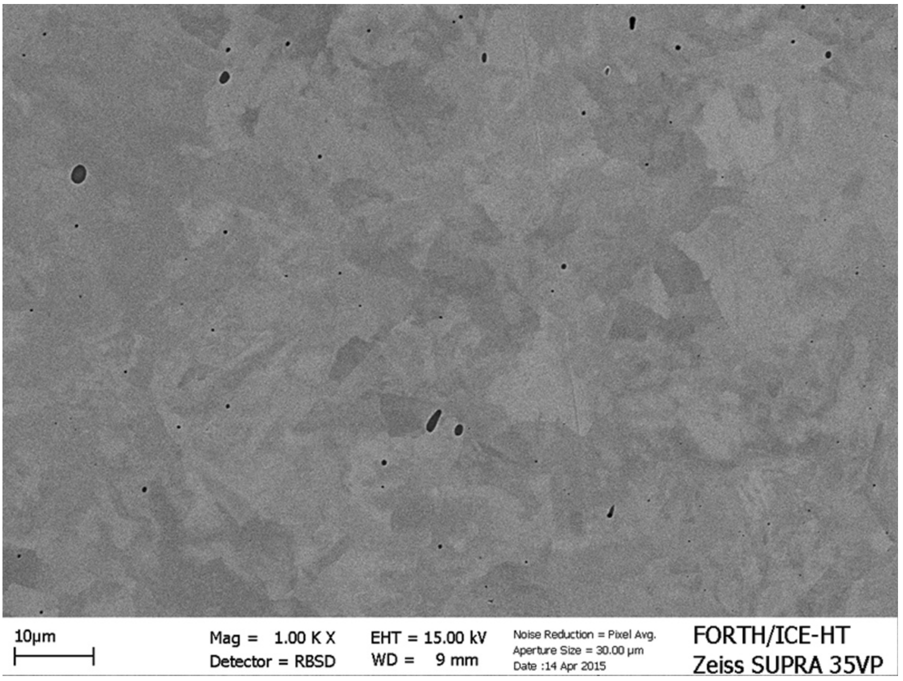

Fig. 1. View of sulfide density in 500μm, BSt420, Ø10 (05)

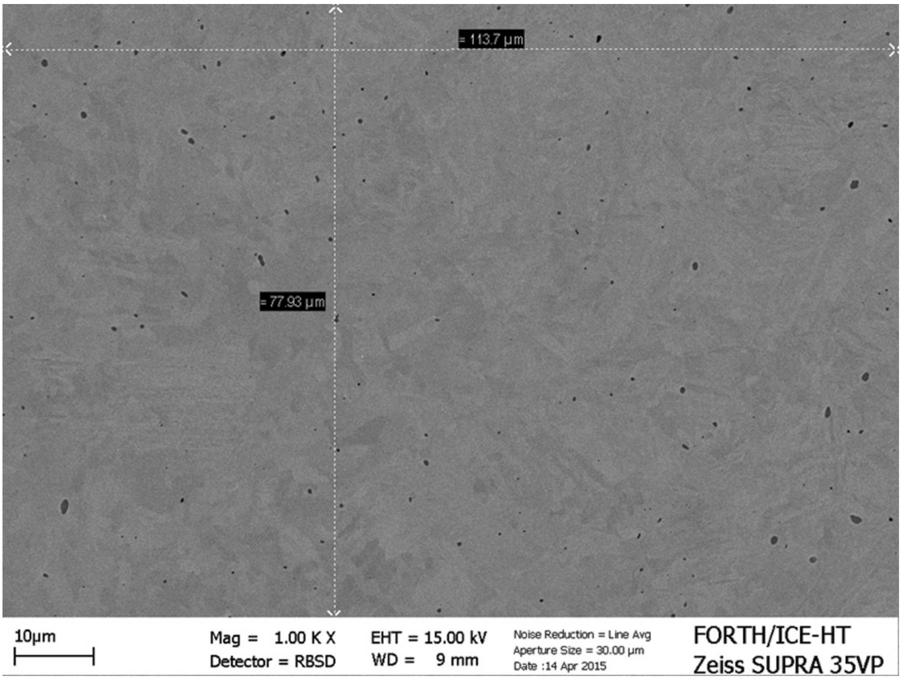

Fig. 2. View of sulfide density in 500μm, B500c, Ø10 (04)

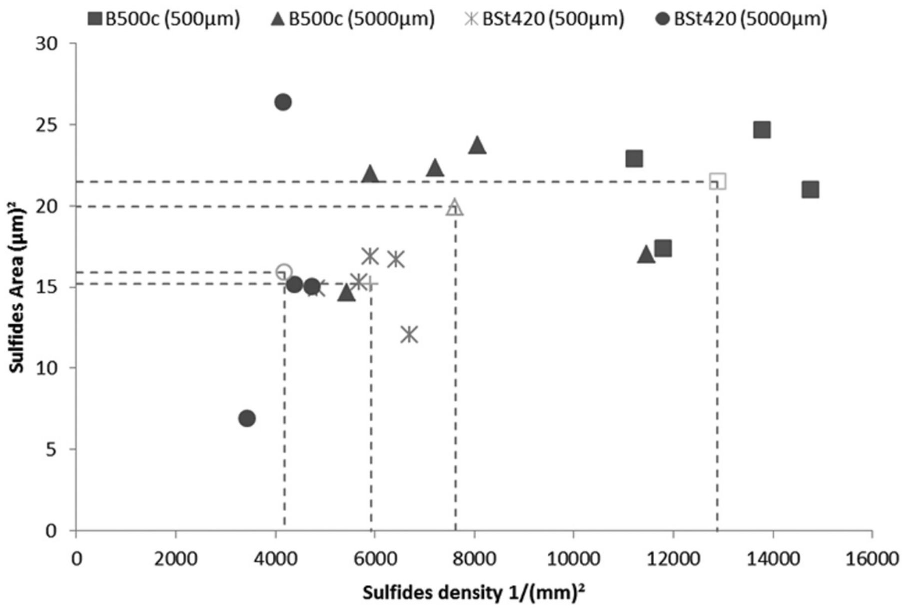

Fig. 3. Sulfide area as a function of sulfide density in different distances from the surface for B500c and BSt420 grade steels

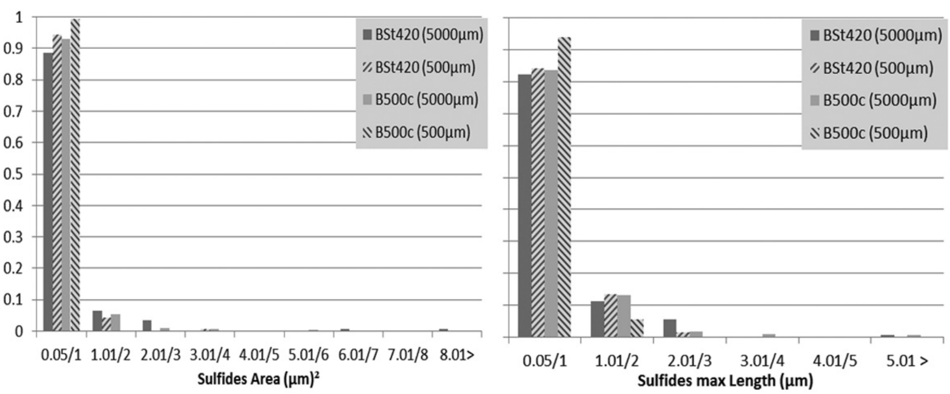

Fig. 4. Frequency as a function of sulfide area – max length for BSt420 and B500c grade steels

A high density of sulfides in dual-phase hot-rolled steel, especially at the external zone, triggered the investigation of the B500c surface subjected to damage through corrosion (Fig. 5).

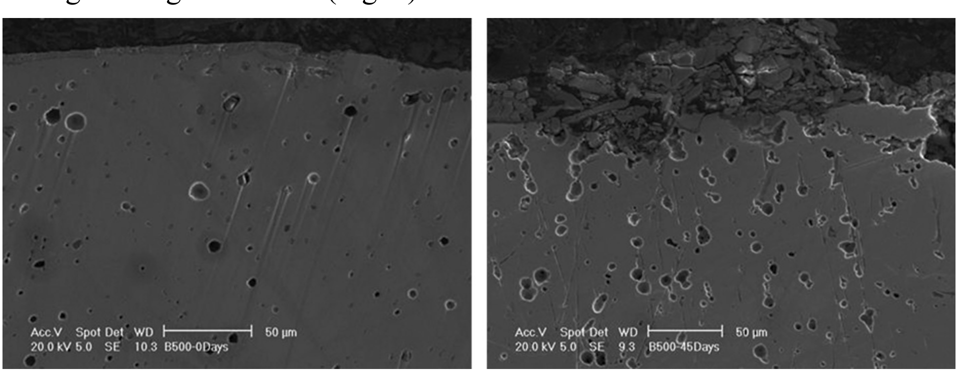

Fig. 5. View of the cross-section area of non-corroded and corroded B500c steel after 45-day exposure to the salt spray test

3.2 Mass Loss

In Table 2, the results of the mass loss of the artificially corroded specimens BSt420 and B500c are presented. In Fig. 6, the correlation between the mass loss of naturally corroded BSt420specimens and the age of the existing coastal structures is shown.

3.3 Mechanical Degradation

The degradation of the mechanical properties of two grades of steel (BSt420, B500c) after the exposure to the salt spray chamber is shown in Table 3.

Table 2

Mass loss of artificially corroded specimens

		Exposure to salt spray corrosion environment (days)		
	Grade	**30**	**60**	**90**
Mass Loss [%]	**BSt420**	3,77	7,23	8,48
	B500c	2,90	5,97	8,52

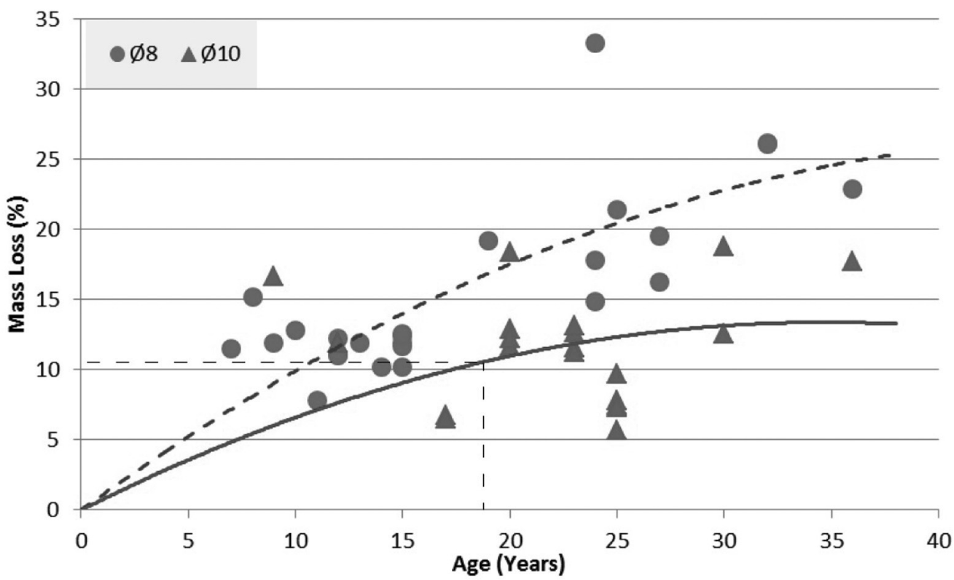

Fig. 6. Diagram of the correlation between mass loss and age for naturally corroded specimens

Table 3

Strength properties (Rp – Rm) in different exposure levels

Exposure Salt Spray (days)	Rp (MPa)	Rm (MPa)	Rp (MPa)	Rm (MPa)
	BSt420		**B500c**	
0	459,08	696,49	548,3	617,2
30	436,35	669,64	521,7	618,4
60	413,49	640,41	510,1	600,1
90	405,01	618,17	446,9	515,3

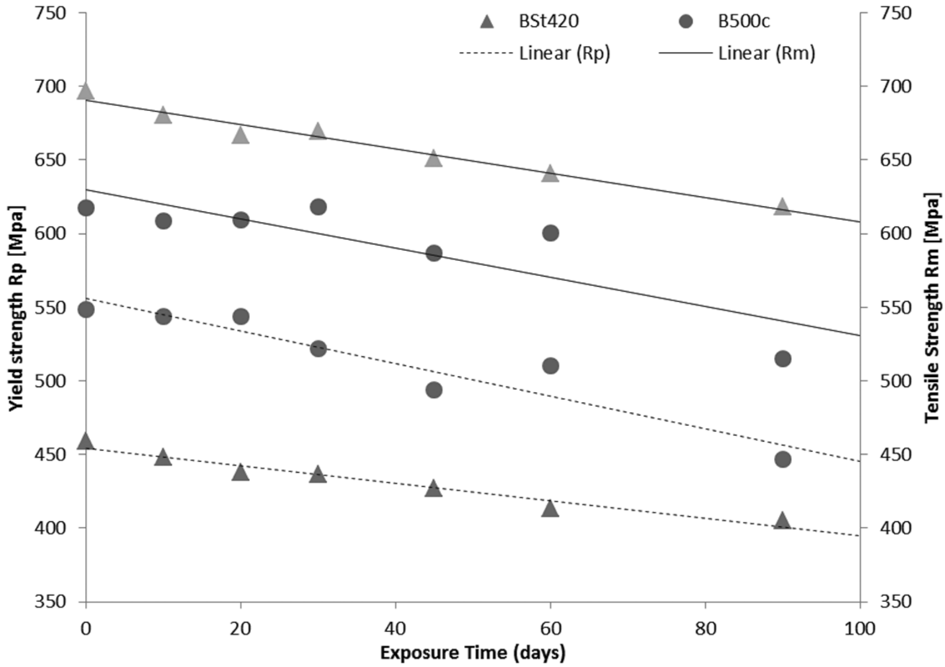

Fig. 7. Reduction of strength properties (Rp – Rm) at different exposure levels

4. Discussion

The corrosion level of the steel bars was quantified based on gravimetric mass loss, the average loss of the cross-sectional area of the corroded bars, and was calculated as the ratio of the difference between the mass of the bars before and after corrosion to the original mass of the bars before corrosion. The measurements of the naturally corroded rebars are listed in Fig. 6. As can be seen from Table 2, the accelerated salt spray test on bare BSt420 and B500c specimens with nominal diameter Ø10 induced an equivalent mass loss of approximately 8,50% to both types of material over a 90-day period.

According to study [11], by dividing the corrosion attack rates of the two similar steel grades and their diameters, it can be calculated that specimens of new rebars in the salt spray chamber corroded 74,5 times faster than the respective specimens of exposed rebars in their natural working environment. So, the mass loss (8,50%) of artificially corroded rebars equals 18–19 years of naturally corroded ones (Fig. 6). It was also found out that in terms of mass loss, artificially corroded bars were less affected by corrosion than naturally corroded ones, possibly due to the fact that the distribution of artificial corrosion along the length of the specimens was less variable (according to EN206, XS3).

According to the fact that the mechanical performance of steel is mainly determined by the mechanical behavior and structural integrity of the outer zone of material, it was considered appropriate to examine the presence of sulfides on B500c and BSt420 grades steel samples.

Sulfide inclusions (MnS, FeS) are known to accommodate galvanic corrosion due to their negative Gibbs free energy and lower oxidation reaction compared to Ferric ion [12]. More specifically, SEM analysis was conducted followed by a comparative study on two grades of non-corroded materials. The increased density of sulfides of non-corroded B500c grade steel over the respective ferrite-pearlite BSt420 corresponds to a rate equivalent to (195/127 = 1,53) 1,53.

These mean values are the result of all sulfide measurements in specific areas of the exterior zone of 500 μm in each category of steel. Measuring the number of sulfides on a surface larger than 0,05 μm^{-2} led to the creation of the corresponding diagrams.

As seen from the graphical depiction of the SEM results, hot rolled steel reinforcement, i.e. BSt420, displays a significantly lower number of MnS counts compared to Tempcore steel (B500c). Within the region near the surface (0–500 μm), BSt420 contains the average value of 128 counts while B500c has 166 counts. This can be attributed to a lower percentage of S with the average value of 0,029% traced in BSt420 compared to 0,047% in B500c .

Figure 3 demonstrates that the density of sulfides in B500c lies in the range from $5x10^3$ $(mm)^{-2}$ to 15×10^3 $(mm)^{-2}$, which is greater than the same indicator for BSt420 grade steel (3×10^3 to 7×10^3 $(mm)^{-2}$). Additionally, the average value of the surface area of sulfides for B500c shows an increase approximately 5 $(\mu m)^2$ greater than this for BSt420. Sulfide surface area: (20,7–15,5) $(\mu m)^2$ = 5,2 $(\mu m)^2$.

As can be seen from Table 3, the corrosion attack over 90 days of exposure to the salt spray environment caused a moderate tensile strength reduction that increased with increasing corrosion exposure time.

Furthermore, in contrast with BSt420, the values of the yield (R_p) and tensile (R_m) strength of B500c display a more significant deviation from the linear approximation throughout the gradually inflicted corrosion (Fig. 7). A possible explanation could be an intense and often random damage of the external martensitic zone caused by corrosion as well as the local delamination of the martensitic zone and ferrite-pearlite core along the cross-section area (Fig. 5) [13–15]. The dissolution rate of the FeS, MnS inclusions exposed to the salt spray environment has been identified to govern the reduction experienced in the mechanical properties of steel reinforcement with exposure time [15].

The results of the salt spray corrosion tests on the two grades of material with cross-section area Ø10 produced the equivalent rates of mass loss for both grades of steel. Despite this estimation, mass loss has a different impact on each of the two grades. For grade B500c, mass loss thereby corresponds to the martensitic zone that mechanically outweighs the ferrite-pearlite core. In contrast, the same rate of mass loss (8,50%) for grade BSt420 corresponds to the zone of a material named ferrite-pearlite as well as to the core. This fact in conjunction with an increased density of sulfides results in the reduction factor of strength properties for B500c exhibited for the yield strength ΔR_p = 548,3 – 446,9/548,3 = 18,49% and for the tensile strength ΔR_m = 617,2 – 515,3/617,2 = 16,51%. Therefore, the mean value of the strength-reduction factor for B500c is recorded close to 17,50%. For BSt420, the reduction factor is recorded for the yield strength ΔR_p = 459,08 – 405,01/459,08 = 11,78% and for the tensile strength ΔR_m = 696,49 – 618,17/696,49 = 11,23%. Thus, the mean value of the strength-reduction factor of dual-face B500c steel over ferrite-pearlite BSt420 corresponds to a ratio equal to 1,52. The coincidence of the ratio of sulfide density seems accidental although the density of voids has a significant influence on the mechanical performance of material under tensile loads.

The fact of inevitable martensite corrosion damage to B500c in combination with an increased density of sulfides, which is over 50% greater than ferrite-pearlite BSt420, triggered the SEM implementation and investigation of B500c. Figure 5 depicts SEM photographs of the samples of non-corroded and corroded steels after 45 days in the salt spray chamber. Herein is demonstrated the role of the porosity of as-received B500c rebars. In the case of a 45-day salt spray test, a newly formed condition with serious damage on the surface but also close to the surface and on the interior part of material acts in concert with the recognition of a high density of sulfides, which seems to have noticeably increased due to the presence of chloride ions, to improve the degradation rate of the mechanical performance of material.

Gathering naturally corroded BSt420 samples in coastal structures helped obtain the results of mass loss shown in diagram (Fig. 6). The results of experimental work make it possible to assume that should B500c samples be gathered, their mass loss can be expected to reach the levels equivalent to those reported in the diagram. However, as for the reduction factor of the mechanical strength properties of dual-face steel, it would be expected to present a decrease of about 50% more than the one of BSt420.

5. Conclusions

This study examines the correlation between the sulfides existing on the surface and in the core of two different sets of reinforcing steel bars, BSt420 and B500c Tempcore. In parallel, the mechanical strength properties of steel bars were examined and compared as well as the occurrence of sulfides before and after corrosion. The experimental results showed that:

- The corrosion resistance of BSt420 grade steel is higher than that of B500c.
- B500c Tempcore presents the minimal corrosion resistance, which can be attributed to a higher recording of sulfides (at least on the external surface of 500 μm).
- The results of mass loss of naturally corroded steel (BSt420) in structures of up to 36 years as well as the mechanical performance of dual phase steel B500c after a corresponding period in an adequate coastal environment (according to EN206, XS3) should become a major concern.

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