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Determination of the Effect of Deformation on the Corrosion Resistance of Zn-Al-Mg Coated Sheets

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In the automotive industry, deep-drawn sheet metals are widely used and protective coatings are applied to its surfaces to improve certain performance properties (e.g. to increase corrosion resistance). Sheets with these coatings are stressed during the forming process of the part and cracking of the protective coating may occur. The main goal of this paper is to determine the resistance of a Zn-Al-Mg based protective coating to uniaxial and triaxial stresses, and also to determine how effective anticorrosion resistance the coating provides to the base steel matrix in the event that cracking occurs.

It has been shown that both uniaxial and triaxial loading leads to a failure of the Zn-Al-Mg coating integrity. Salt spray corrosion tests of 3 and 6 weeks were subsequently performed on both deformed and undeformed base material samples. These tests showed that a continuous Al_2O_3 layer is formed between the steel matrix and the coating, which, irrespective of the formation of cracks in the coating, is the main contributor to the increase in corrosion resistance of the sheet.

Keywords: corrosion resistance, deformation of sheets, Zn-Al-Mg coating

1 Introduction

Deep-drawn sheet metals are used for the production of body parts in the automotive industry. These sheets metals must meet a number of requirements. In addition to the requirements for seamless processing by various methods of forming, welding, bonding, painting and requirements for high mechanical properties, they must also have high corrosion resistance. For these reasons, coatings are applied to deep-drawn sheets to help meet these requirements. Metallic, inorganic (e.g. phosphated, chromated) and organic coatings (e.g. cathodic coating) are used for this purpose.

Of the metal coatings, zinc-based coatings are very often used in the automotive industry to increase corrosion resistance and provide cathodic protection to the steel [1]. Due to the fact that zinc has a lower electrode potential than iron, preferential oxidation of the zinc coating occurs, thus protecting the steel base from corrosion. In practice, zinc coatings are produced by two technologies, namely hot-dip galvanizing (HDG) and electrogalvanizing (EG) [2].

Zinc coating produced by hot-dip galvanizing is very widespread due to the simplicity and relatively cheap production with the possibility of automation. The production of zinc coating by this method starts with the mechanical removal of impurities (rust, scale), degreasing and pickling of the semi-finished product to ensure surface cleanliness. A flux is then applied to the material to prevent oxide formation and dissolve the oxides on the surface of the steel and zinc, bringing the two metals into the direct contact. These operations are followed by immersion of the blank in a bath of molten zinc at a temperature of 440-470 °C. In the bath, the zinc reacts with the steel to form an Fe-Zn alloy on the surface of the blank. This produces a coating consisting of several layers of Fe-Zn alloy phases, where the iron content decreases with distance from the steel base. It is possible to improve some of the properties of the resulting coating by adding alloying elements to the molten zinc bath [3].

In order to reduce friction during deep drawing of body parts, the surface of the semi-finished product is treated by fine dressing or blasting. This treatment enables the surface of the blank to accommodate a greater amount of lubricant and thus improve friction conditions. Another alternative surface treatment is the application of a coating with the trade name NIT (New Inorganic Treatment). A small amount of zinc sulphate ($ZnSO_4$) is added to the zinc bath. This crystallizes from its solutions as heptahydrate. It is a colourless crystalline substance that weathers in air. The addition of this substance to the zinc bath results in the formation of a thin layer on the surface of the zinc coating, which better absorbs the applied lubricant [2,3].

The corrosion resistance of the zinc coating can be improved by the addition of magnesium. The resulting coating, referred to as ZM, is formed by a Zn-Mg alloy. This type of coating has a higher corrosion resistance, better weldability and, due to its higher hardness, greater abrasion resistance compared to conventional zinc coating. The corrosion resistance can be further improved by adding of aluminium to Zn-Mg based coatings [4-6]. However, these types of coatings are not suitable for forming of complex parts due to the brittleness of the resulting layer [2,3]. In fact, when using high strength low alloyed steel (HSLA) body sheet as a substrate, the forming process results in significant surface roughening, which results in the formation of heterogeneous deformation in the coating and its cracking [7]. The resistance of coatings to cracking while maintaining the level of corrosion resistance can be partially improved by heat treatment [8] or by refining the microstructure of the primary zinc grains [9]. It was shown in [9], that a coating with a fine-grained microstructure has better ductility and fewer coarse strain twins, which serve as undesirable crack initiators. The microstructure character can be influenced by selection of the appropriate cooling rate during coating [10].

Another option to improve the corrosion resistance of the zinc coating is to alloy it with manganese (1.2 wt.%). This provides a 65% increase in corrosion resistance over the conventional zinc coating, while maintaining the formability and adhesion of the coating to the base material. A complication in the production of this coating is the high melting temperature of manganese (1 246 °C) compared to zinc (420 °C). A further problem in the production of this coating occurs when the blank is removed from the bath, when the manganese is immediately oxidised, resulting in the formation of unaesthetic stains. In order to eliminate this phenomenon, an admixture of aluminium (0.2 wt.%) is added to the Zn-Mn alloy. Aluminium has a greater negative electrode potential than zinc and manganese, thus preventing its initial oxidation and preventing the formation of stains [11].

The aim of the present study is to determine whether cracks form in the investigated protective coatings during the forming process of the part and whether these cracks affect the corrosion resistance of the sheet metal as a whole.

2 Material and experimental methods

The 0.7 mm thick plates with two types of coatings - designated ZM and NIT - were used for study of the effect of deformation on the corrosion resistance of the plates (Tab. 1 summarizes the nominal chemical composition of each coating). Both types of specimens were deformed by both uniaxial and multi-axial tension prior to corrosion tests.

The static test by uniaxial tension (ČSN EN ISO 6895-1) was carried out on a TIRA Test 2300 machine. The homogeneous tensile strength was determined from the test, which was 21.5% for the NIT coated sheet and 22.0 % for the ZM coated sheet. Taking into account the homogeneous tensile strength value, strain values of 10 % and 20 % were chosen for the experiment.

The multi-axial tension tests were carried out using the Nakazima test (ČSN EN ISO 12004-2) on a CBA 300 machine. The experiments performed again confirmed that the type of coating hardly influenced the amount of deformation of the sheet metal. The specimens used for the corrosion tests were again deformed to two strain values. The first strain value was chosen to match the strain caused by uniaxial deformation at 10 %. In this case, the height of the pulling of the test hat was 13 mm. The second strain value was chosen just before the cracks appeared on the surface of the hat, which corresponded to a pulling height of 35 mm.

The corrosion tests were carried out in the Liebisch chamber in repeated cycles consisting of:

- 4 h salt spray test according to DIN EN ISO 9227
- 4 h storage under normal climatic conditions according to ISO 554-23/50
- 16 h exposure to condensation water environment according to EN ISO 6270-2
- After 5 cycles 2 days resting phase under climatic conditions

Corrosion resistance was tested on two sets of specimens, one exposed to the corrosive environment for 3 weeks and the other for 6 weeks.

Metallographic samples were made from perpendicular sections of the examined samples to study of the corrosion products. The metallographic samples were studied by scanning electron microscopy (SEM) on a Tescan Mira 3 microscope. The local chemical composition of the resulting phases and the elemental distribution maps were determined using energy dispersive analysis (EDX) by an Oxford UltimMax 65 detector. The SEM Mira 3 was also used to study the surface of the sheets before and after deformation to determine the resistance of each coating to external deformation.

Tab. 1 *The nominal chemical composition of ZM and NIT coatings*

Sample	Zn [wt.%]	Al [wt.%]	Mg [wt.%]
ZM	**Balance**	**6.5**	**4.5**
NIT	**Balance**	**1.5**	**-**

3 Results and discussion

3.1 NIT and ZM samples before corrosion test

Fig. 1A and Fig. 1B show the coating surfaces of ZM and NIT samples without deformation. It can be seen from the figures that the ZM coating was smoother and more integral. Only the ZM coating showed cracks (Fig. 2A - after 10% deformation, Fig. 3A - after 20% deformation) after uniaxial tensile deformation (ZM – Fig. 2 and NIT – Fig. 3). The cracks had a width of 2 - 3 μm. A similar condition was also observed on specimens deformed by multi-axial tension (Figs. 4 and Fig. 5). Again, cracks were formed only in the ZM coating (Fig. 4A and Fig. 5A) and their width was 2 - 3 μm at a deformation height of 13 mm and 10 - 15 μm at a deformation height of 35 mm.

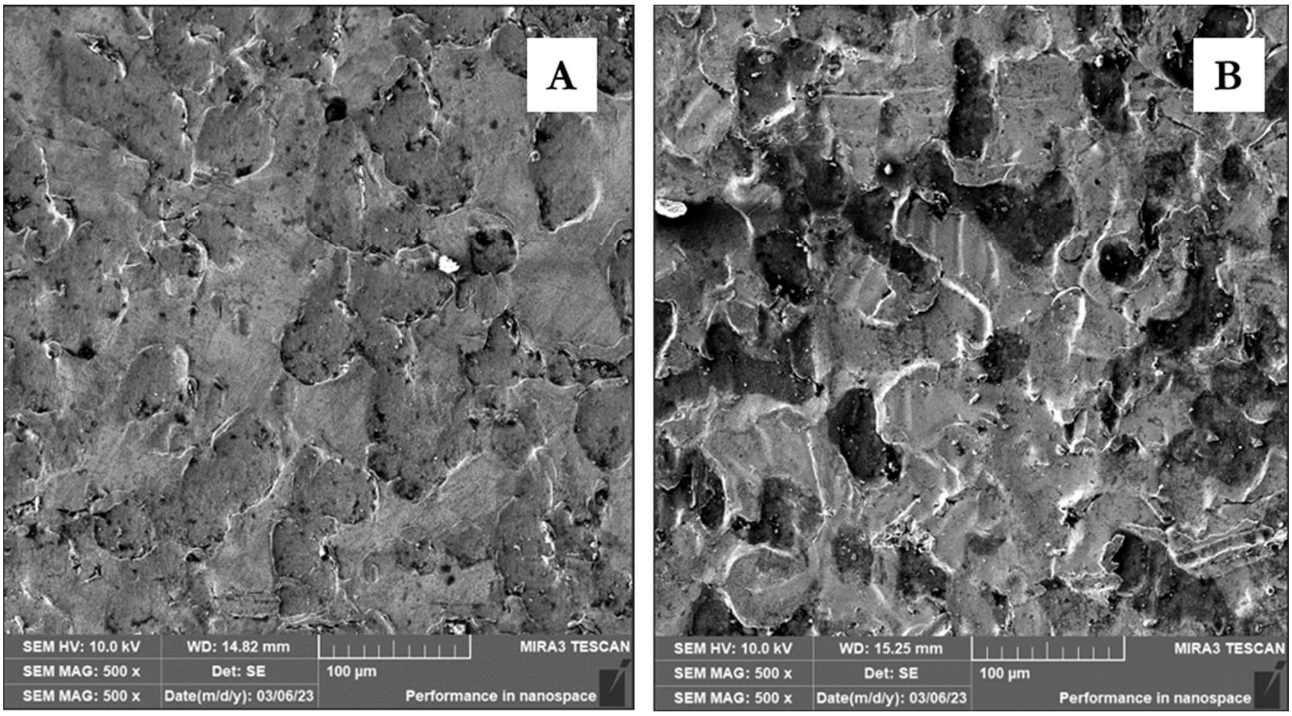


Fig. 1 *Surfaces of ZM (A) and NIT (B) coatings before deformation (SEM, HV 10kV, SE detector)*

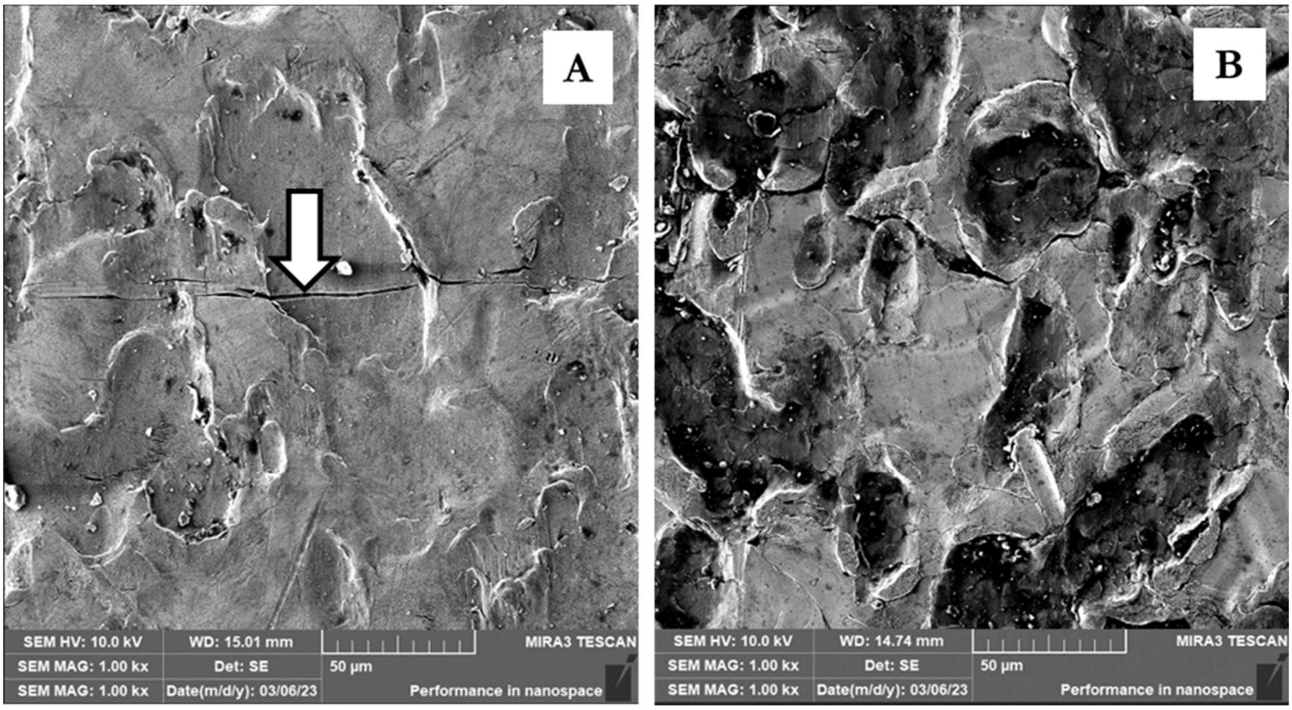


Fig. 2 *Surfaces of ZM (A) and NIT (B) coatings after 10% uniaxial tensile deformation (SEM, HV 10kV, SE detector), crack is indicated by arrow*

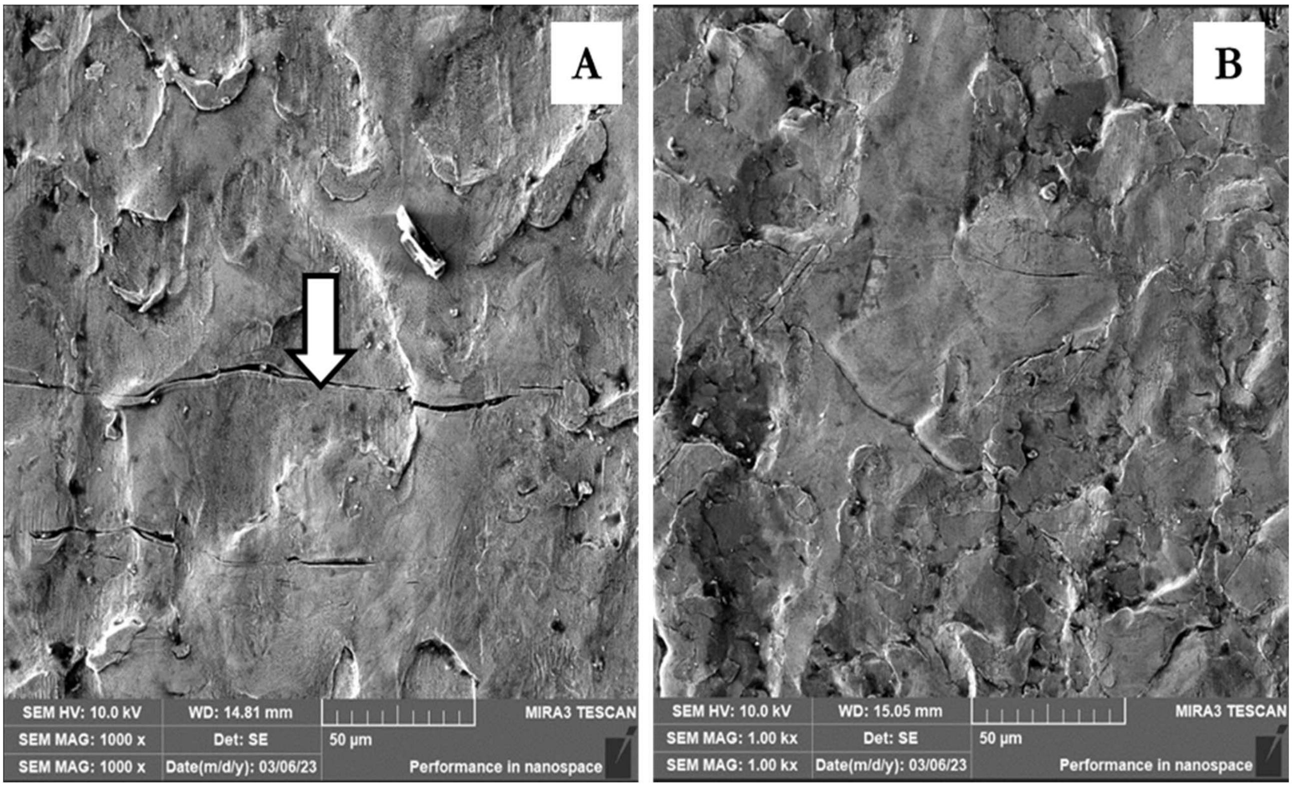


Fig. 3 *Surfaces of ZM (A) and NIT (B) coatings after 20% uniaxial tensile deformation (SEM, HV 10kV, SE detector), crack is indicated by arrow*

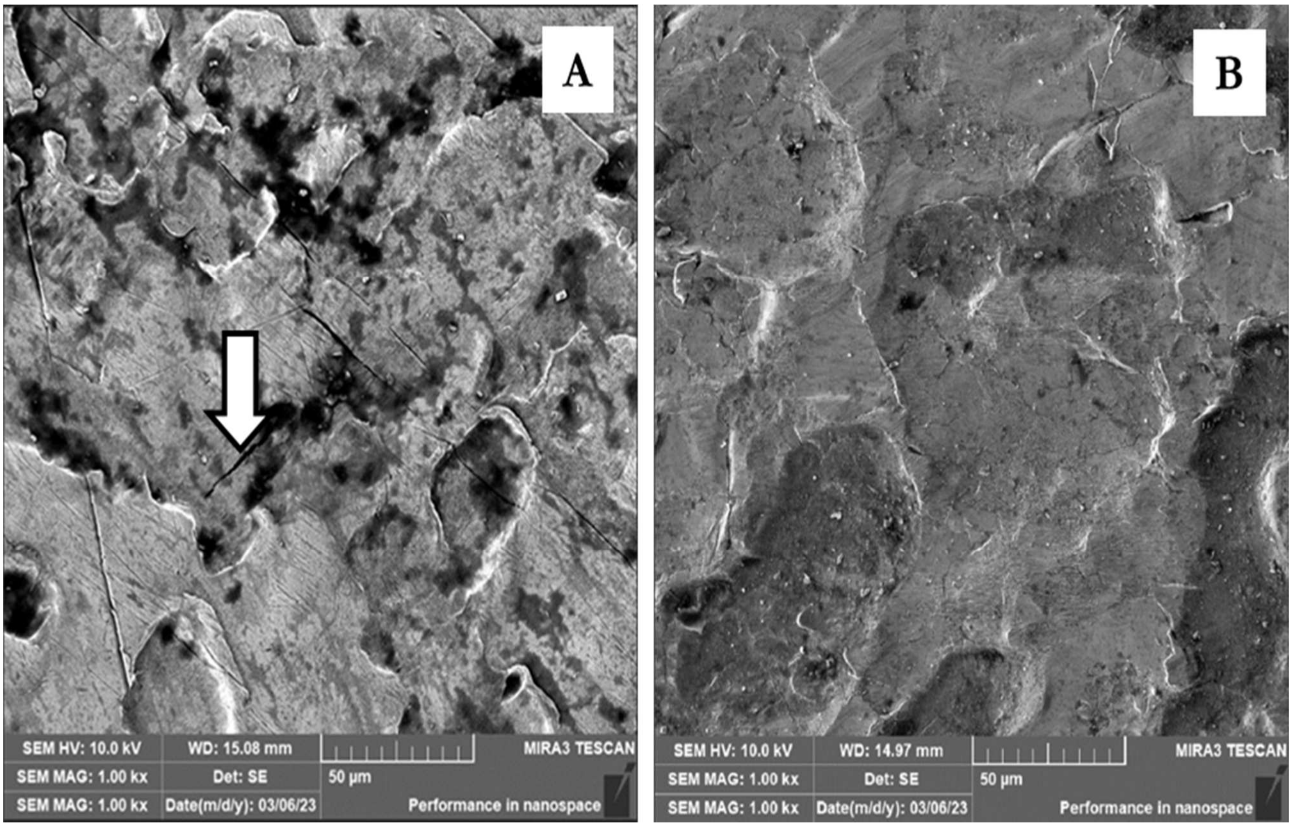


Fig. 4 *Surfaces of ZM (A) and NIT (B) coatings after multi-axial tensile deformation to a deformation height of 13mm (SEM, HV 10kV, SE detector), crack is indicated by arrow*

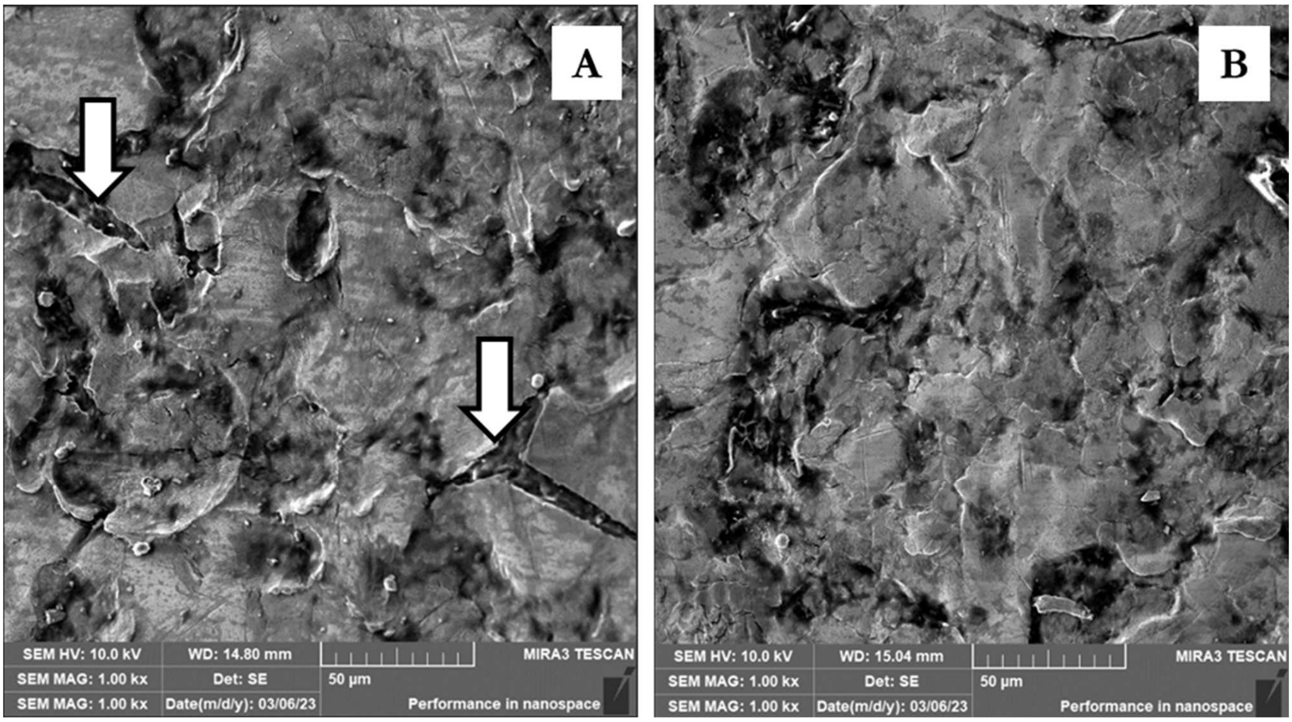


Fig. 5 *Surfaces of ZM (A) and NIT (B) coatings after multi-axial tensile deformation to a deformation height of 35mm (SEM, HV 10kV, SE detector), crack is indicated by arrow*

3.2 NIT and ZM samples after corrosion test of 3 weeks

The appearance of the specimens after a corrosion test of 3 weeks is shown in Fig. 6 (uniaxial deformation) and Fig. 7 (multi-axial deformation). It can be seen from the figures that all the studied samples have white rust (ZnO2 - see EDX analysis in Fig. 8) on the surface. Corrosion of the underlying steel matrix was observed only in the case of the NIT specimens deformed on the highest strain values (Fig. 6D - uniaxial strain of 20 % and Fig. 7D - multi-axial strain with 35 mm deformation height).

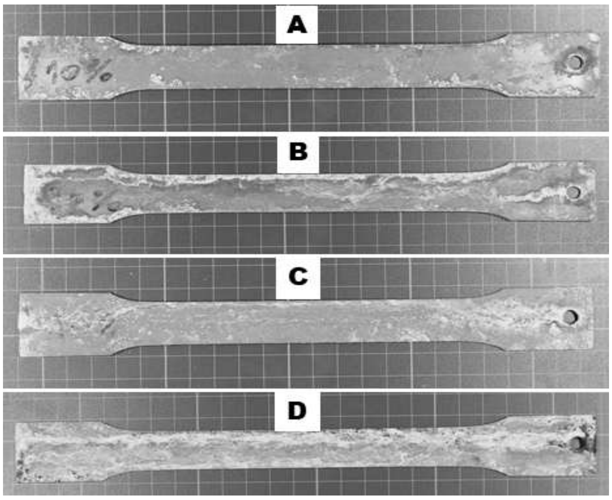


Fig. 6 *Appearance of the specimens deformed by uniaxial tension after corrosion test of 3 weeks (A - ZM deformation 10 %, B - ZM deformation 20 %, C - NIT deformation 10 %, D - NIT deformation 20 %)*

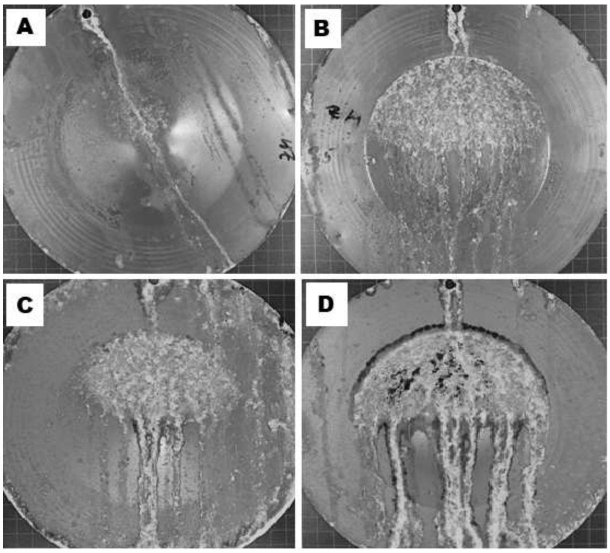
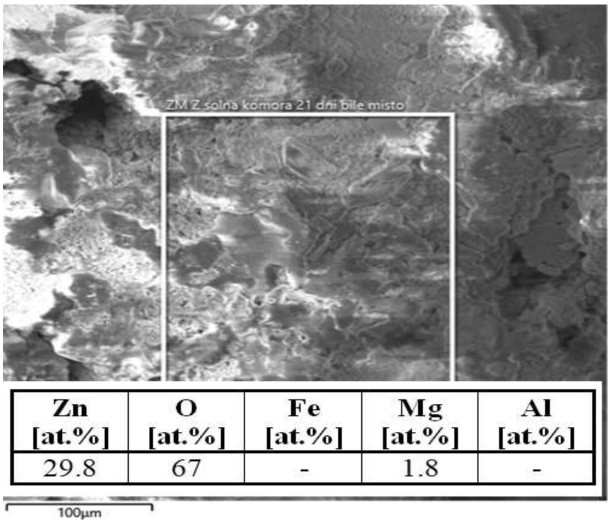


Fig. 7 *Appearance of the specimens deformed by multi-axial tension after corrosion test of 3 weeks (A - ZM deformation height 13 mm, B - ZM deformation height 35mm, C - NIT deformation height 13mm, D - NIT deformation height 35mm)*

Only the NIT specimens showed corrosion of the underlying steel matrix, although these specimens, unlike the ZM specimens, did not show any cracks in the coating. The study of the perpendicular metallographic sections of the samples by EDX analysis (Fig. 9) showed that a continuous layer of Al_2O_3 forms at the interface between the coating and the steel matrix in the case of ZM samples. This layer was also observed for the NIT samples, but it was much thinner and its integrity has been violated in many places, which is probably due to the more than 4 times lower aluminium content added to the NIT coatings. It can be inferred that this barrier layer of Al_2O_3 together with the addition of magnesium to the ZM coatings provides the high corrosion resistance of the ZM samples, even though cracks formed in the coating during deformation.



Zn [at.%]	O [at.%]	Fe [at.%]	Mg [at.%]	Al [at.%]
29.8	67	-	1.8	-

Fig. 8 *EDX analysis of the sample's surface after corrosion test (3 weeks) - white rust area*

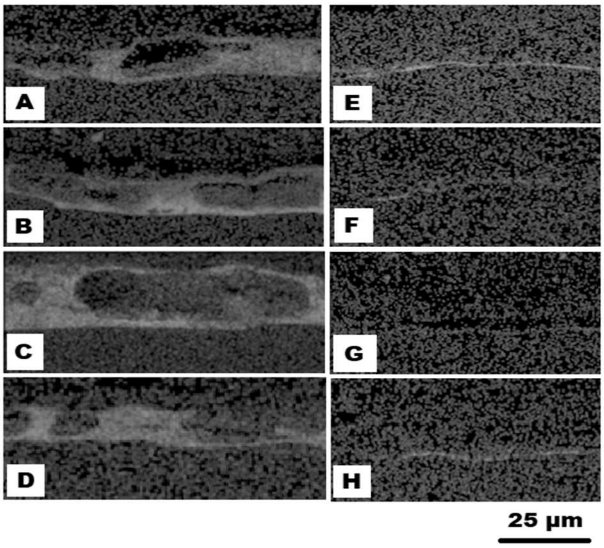


Fig. 9 *EDX map of aluminium at the interface between the coating and the steel matrix after a corrosion test of 3 weeks (A - ZM deformation 10 %, B - ZM deformation 20 %, C - ZM deformation height 13 mm, D - ZM deformation height 35 mm, E - NIT deformation 10 %, F - NIT deformation 20 %, G - NIT deformation height 13 mm, H - NIT deformation height 35 mm)*

3.3 NIT and ZM samples after corrosion test of 6 weeks

The appearance of the specimens after a corrosion test of 6 weeks is shown in Fig. 10 (uniaxial deformation) and Fig. 11 (multi-axial deformation). The underlying steel matrix did not corrode in the case of the ZM specimens even after the 6-week corrosion test (Fig. 10A and Fig. 10B for uniaxial strain and Fig. 11A and Fig.11B for multi-axial strain). Matrix corrosion was evident in the NIT specimens at all conditions and strain levels (Fig. 10C and Fig. 10D for uniaxial deformation and Fig. 11C and Fig. 11D for multi-axial deformation). Similar to the corrosion testing for 3 weeks, a continuous layer of Al2O3 at the interface between the coating and the steel matrix was observed on the perpendicular metallographic sections of the ZM samples after 6 weeks of corrosion testing (see EDX map for Al in Fig. 12). This layer was again absent or very thin in the case of NIT samples.

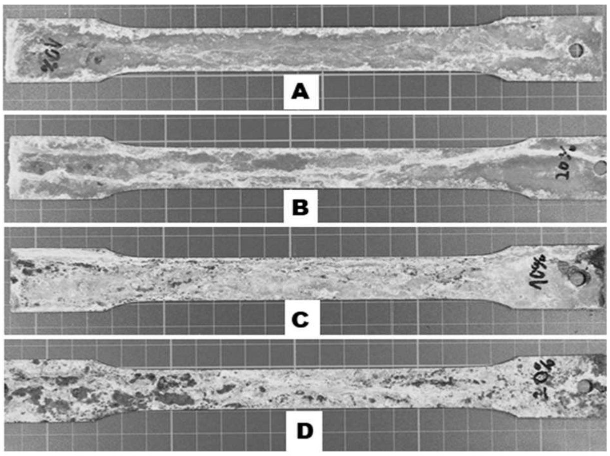


Fig. 10 *Appearance of the specimens deformed by uniaxial tension after a corrosion test of 6 weeks (A - ZM deformation 10 %, B - ZM deformation 20 %, C - NIT deformation 10 %, D - NIT deformation 20 %)*

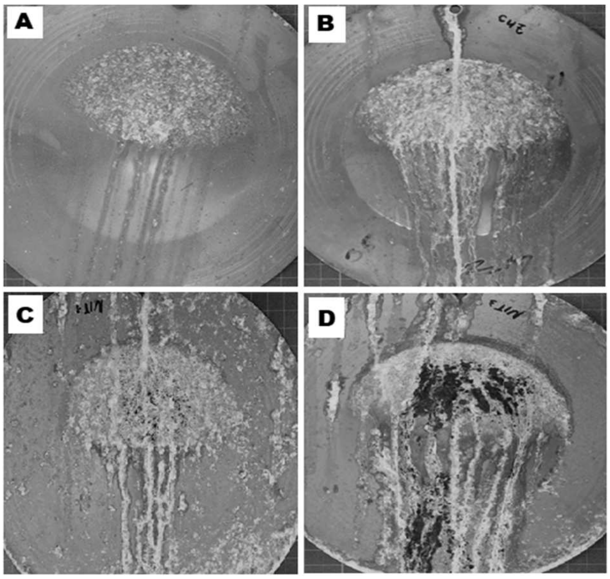


Fig. 11 *Appearance of the specimens deformed by multi-axial tension after corrosion test of 6 weeks (A - ZM deformation height 13 mm, B - ZM deformation height 35mm, C - NIT deformation height 13mm, D - NIT deformation height 35mm)*

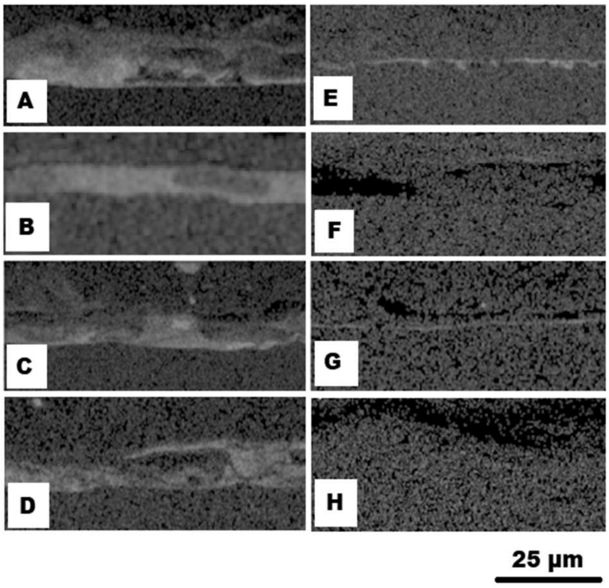


Fig. 12 *EDX map of aluminium at the interface between the coating and the steel matrix after a corrosion test of 6 weeks (A - ZM deformation 10 %, B - ZM deformation 20 %, C - ZM deformation height 13 mm, D - ZM deformation height 35 mm, E - NIT deformation 10 %, F - NIT deformation 20 %, G - NIT deformation height 13 mm, H - NIT deformation height 35 mm)*

4 Conclusion

- It was found that the ZM coated specimens exhibit coating cracks after deformation. The samples with NIT coating remained without damage.
- The NIT-coated specimens corroded after accelerated corrosion testing, although the protective coating remained intact after forming. The ZM coated samples did not corrode.
- After evaluation of the metallographic cross-sections of the samples, an interlayer based on aluminium oxides was observed in the samples with ZM coating, which was very thin or absent in the samples with NIT coating, which is probably due to the significantly lower aluminium content added to the NIT layer compared to the ZM layer. This aluminium interlayer will have a major effect on corrosion resistance regardless of the formation of cracks in the coating.
- ZM coatings are problematic in the production of body parts due to their brittleness and low plasticity, which often results in cracks of the base material and thus destruction of the parts. Therefore, the resulting aluminium interlayer has the potential to completely replace the brittle ZM coating while maintaining the plasticity of the sheet metal.

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