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CHAPTER 14

INVESTIGATION OF VARIOUS METHOD FOR STEEL SURFACE MODIFICATION

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CONTENTS

14.1 INTRODUCTION

The surface treatment of steel surface is often used, especially in an automotive industry, which creates the motive power for research, design, and production. New methods of surface treatment are also developed having major influence on improvement of the surface properties of steel sheets while keeping the price at reasonable level.[1–3]

The nitrooxidation is one of the nonconventional surface treatment methods, which combine the advantages of nitridation and oxidation processes. The improvement of the mechanical properties (tensile strength, yield strength) together with the corrosion resistance (up to level 10) can be achieved.[4–7] The fatigue characteristics of the nitrooxidized material can be also raised.[5]

Steel sheets with surface treatment are more often used, especially in an automotive industry that creates the motive power for research, design, and production. New methods of surface treatment are also developed having major influence on improvement of the surface properties of steel sheets while keeping the price at reasonable level.

Previous outcomes[1,3,8,4,10] dealt with the welding of steel sheets treated by the process of nitrooxidation by various arc and beam welding methods. Due to high oxygen and nitrogen content in the surface layer, problems with high level of porosity had occurred in every method. The best results were achieved by the solid-state laser beam welding, by which the defect-free joints were created. Due to high initial cost of the laser equipment, further research was directed to the joining method that has not been tested. Therefore, the adhesive bonding was chosen, because the joints are not thermally affected, they have uniform stress distribution and good corrosion resistance.

The goal of the paper is to review the adhesive bonding of steel sheets treated by nitrooxidation and to compare the acquired results to the nontreated steel.

14.2 EXPERIMENTAL

For the experiments, low-carbon deep-drawing steel DC 01 EN 10130/91 of 1 mm in thickness was used. The chemical composition of steel DC 01 is documented in Table 14.1.

TABLE 14.1 Chemical Composition of Steel DC 01 EN 10130/91.

EN designation	C (%)	Mn (%)	P (%)	S (%)	Si (%)	Al (%)
DC 01 10130/91	0.10	0.45	0.03	0.03	0.01	–

14.2.1 CHEMICAL MODIFICATION

The base material was consequently treated by the process of nitrooxidation in fluidized bed. The nitridation fluid environment consisted of the Al_2O_3 with granularity of 120 μm. The fluid environment was wafted by the gaseous ammonia. After the process of nitridation, the oxidation process started immediately. The oxidation itself was performed in the vapors of distilled water. Processes parameters are referred in Table 14.2.

TABLE 14.2 Process of Nitrooxidation Parameters.

	Nitridation	Oxidation
Time (min)	45	5
Temperature (°C)	580	380

14.2.2 ADHESIVES

In the experiments, four types of two-component epoxy adhesives made by Loctite Company (Hysol 9466, Hysol 9455, Hysol 9492, and Hysol 9497) were used. The properties of the adhesives are documented in Table 14.3.

TABLE 14.3 The Characterization of the Adhesives.

	Hysol 9466	Hysol 9455	Hysol 9492	Hysol 9497
Resin type	Epoxy	Epoxy	Epoxy	Epoxy
Hardener type	Amin	Methanethiol	Modified amin	
Mixing ratio (resin:hardener)	2:1	1:1	2:1	2:1
Elongation (%)	3	80	0.8	2.9
Shore hardness	60	50	80	83

14.2.3 METHODS

The experiments were done at the Faculty of Materials Science and Technology, Department of Welding and Foundry in Trnava. The adhesive bonding was applied on the grinded as well as non-grinded surfaces of the material to determine the grinding effect on total adhesion of the material so as on ultimate shear strength of the joints. The grinded material was prepared by grinding with silicone carbide paper up to 240 grit.

Before the adhesive bonding, the bonding surfaces (both grinded as well as non-grinded) were decreased with aerosol cleaner. The overlap area was 30 mm. To ensure the maximum strength of the joints, the continuous layer of the adhesive was coated on the overlap area of both bonded materials. The thickness of the adhesive layer was 0.1 mm and was measured by a calliper. The joints were cured under fixed stress for 48 h at the room temperature. The dimensions of the joints are referred in Figure 14.1.

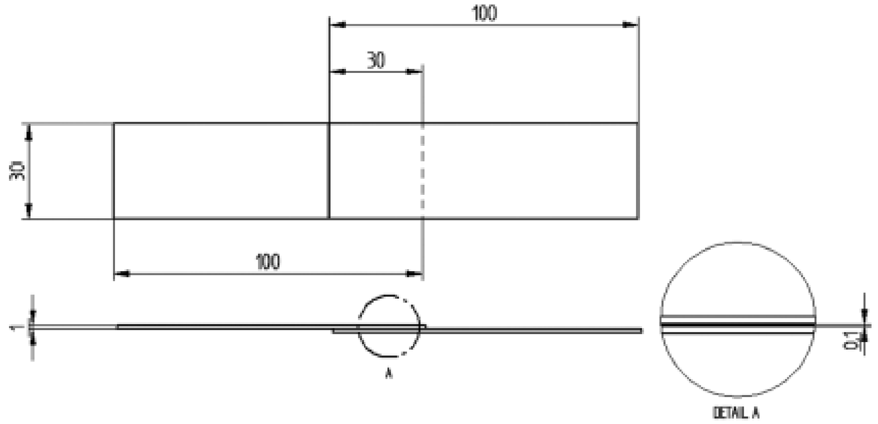

FIGURE 14.1 The dimension of the bonded joints.

The mechanical properties of the joints were examined by the static shear tests. As a device, the LaborTech LabTest SP1 was used. The conditions of the tests were set in accordance with STN EN 10002-1. The static shear tests were repeated on three separate samples and an average value was calculated.
The fracture areas were observed in order to obtain the fracture character of the joints. The JEOL JSM-7600F scanning electron microscope was used as a measuring device.
The differential scanning calorimetry (DSC) was performed on Netzsch STA 409 C/CD equipment. As the shielding gas, Helium with purity of 99.999% was used. The heating process starts at the room temperature and continued up to 400°C with heating rate 10°C/min. The DSC analysis on Hysol 9455 was done on Diamond DSC Perkin Elmer, capable of doing analyses from −70°C.

14.3 RESULTS AND DISCUSSION

The material analysis represents the first step of evaluation. There are many factors having an influence on the joint quality. The properties of the nitrooxidized material depends on the treatment process parameters. For the adhesive bonding, the surface layer properties are important because of that, the high adhesion is needed to ensure the high strength of the joint.

The overall view on the microstructure of the nitrooxidized material surface layer is referred in Figure 14.2a. On the top of the surface, the oxide layer (Fig. 14.2b) was created. This layer had a thickness of ~700 μm. Beneath the oxide layer, the continous layer of ε-phase, consisting of nitrides $Fe_{2-3}N$ and with the thickness of 8–10 μm was observed.

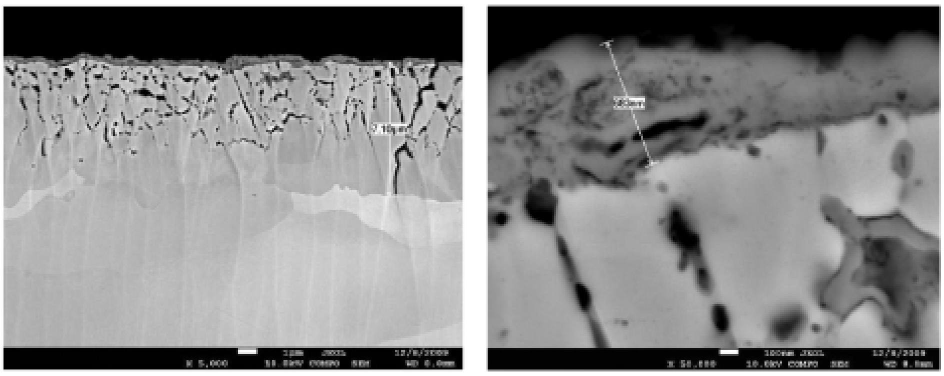

FIGURE 14.2 The microstructure of the surface layer. (a) Overall view and (b) detail view on the oxide layer.

The surface energy measurements were performed due to obtain the properties of the material, which are important for adhesive bonding. For observing the grinding effect on the total surface energy, the measurements were done on the base as well as on the grinded material.

To determine the surface energy, the portable computer-based instrument See-System was used. Four different liquids (distilled water, formamide, diiodomethan, and ethylene glycol) were instilled on the material surface and contact angle was measured. The Owens–Wendt regression model was used for the surface energy calculation. The total amount of six droplets were analyzed of each liquid. The results (Table 14.4) proved that the nitrooxidation treatment had a strong effect on material surface energy, where the decrease by 28% in comparison to non-nitrooxidized material had occurred. The surface energies of grinded and non-grinded material without nitrooxidation were very similar, while the increase of surface energy of grinded nitrooxidized material by 35% in comparison to non-grinded material was observed. In the case of barrier plasma-modified steel, the surface energy is higher than that of unmodified material and namely its polar component is significantly higher than polar component of surface energy for unmodified sample as well as for sample modified by nitrooxidation.

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TABLE 14.4 The Surface Energy of Materials.

Material type	Total surface energy (mJ/m²)	Dispersion component (mJ/m²)	Acid–base component (mJ/m²)
DC 01	38.20	35.62	2.58
DC 01 grinded	38.80	33.66	5.14
Nitrooxidized	27.60	25.79	1.80
Nitrooxidized grinded	37.31	32.54	4.77
Barrier plasma treated	39.99	33.69	6.30

The mechanical properties of the material were obtained by the static tensile test. Total amount of three measurements were done and the average values are documented in Table 14.5. Based on the results, it can be stated that after the process of nitrooxidation, the increase of yield strength by 55% and tensile strength by 40% were observed. The barrier plasma did not influence the mechanical properties after surface modification of steel, which remained the same as for unmodified sample.

TABLE 14.5 Mechanical Properties of the Base Materials.

	Yield strength (MPa)	Tensile strength (MPa)
DC 01	200	270
Nitrooxidized	310	380
Barrier plasma Treated	200	270

The tensile test of the adhesives were carried out on the specimens, which were created by curing of the adhesives in special designed polyethylene forms for 48 h. The results are shown in Table 14.6. In three of the adhesives (Hysol 9466, Hysol 9492, and Hysol 9497), very similar values were observed while in case of Hysol 9455, only tensile strength of 1 MPa was observed.

TABLE 14.6 The Mechanical Properties of the Adhesives.

	Hysol 9466	Hysol 9455	Hysol 9492	Hysol 9497
Tensile strength (MPa)	60	1	58	65

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The differential scanning calorimetry was performed due to obtain the glass transition temperature as well as the melting points of the adhesives. The results are shown in Table 14.7. To measure the glass transition temperature of Hysol 9455, the measurements had to be started from the cryogenic temperatures. The results of such a low glass transition temperature explained the low tensile strength of the Hysol 9455, where at the room temperature, the mechanical behavior changed from rigid to rubbery state. The results of DSC analyses are given in Figure 14.3–14.6.

TABLE 14.7 The Glass Transition Temperatures of Adhesives.

	Hysol 9466	Hysol 9455	Hysol 9492	Hysol 9497
Glass transition temperature (°C)	52.6	5.0	61.2	62.4
Melting point (°C)	315.7	337.0	351.8	327.3

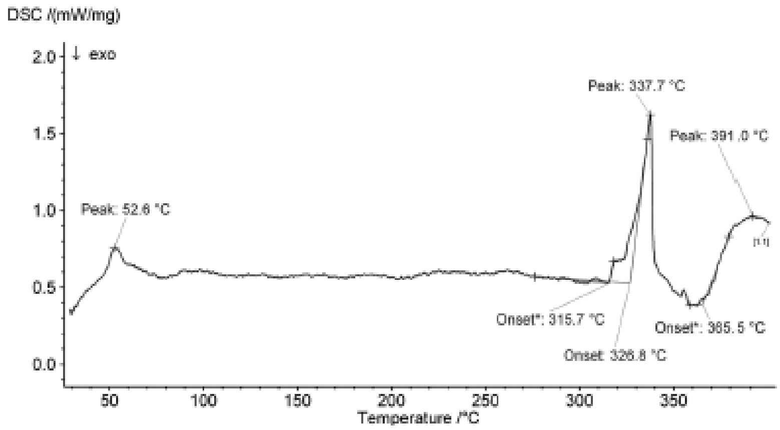

FIGURE 14.3 The DSC analysis of the Hysol 9466.

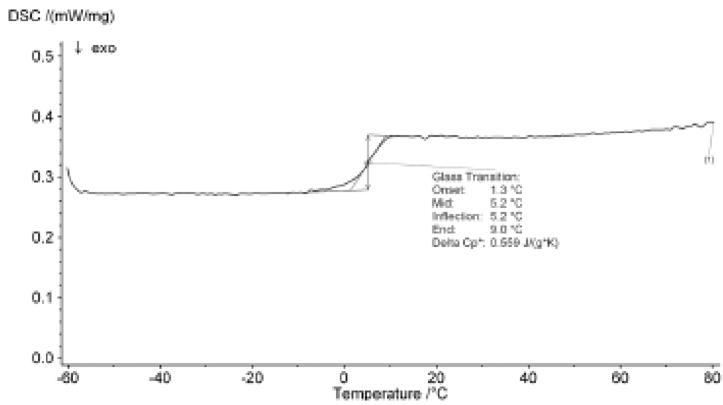

FIGURE 14.4 The DSC analysis of the Hysol 9455.

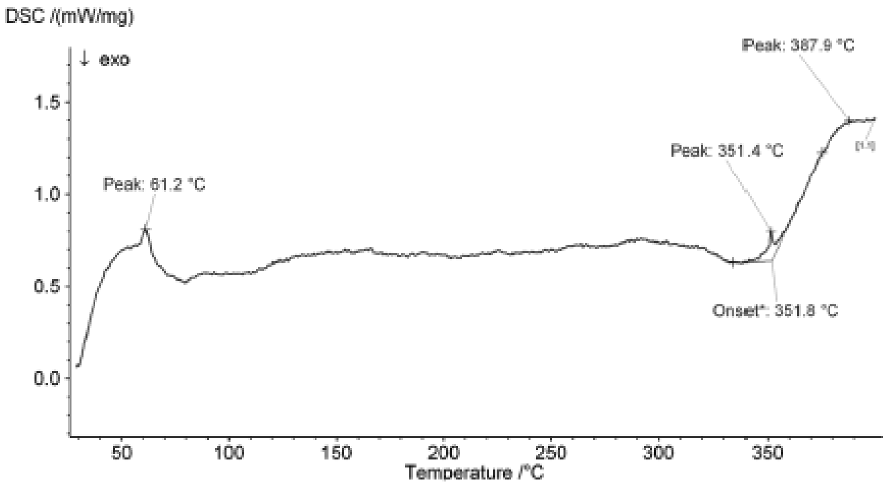

FIGURE 14.5 The DSC analysis of the Hysol 9492.

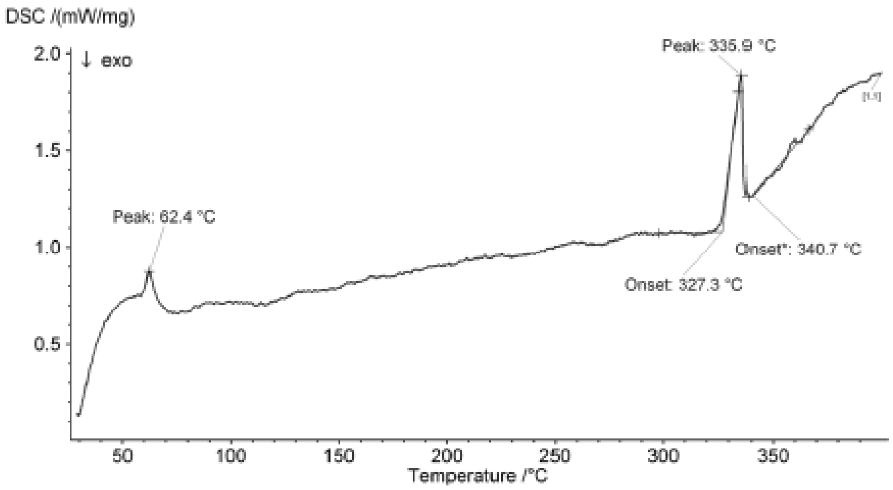

FIGURE 14.6 The DSC analysis of the Hysol 9497.

The adhesive joint evaluation consisted of observing the mechanical properties and fracture surface, respectively.

In order to obtain mechanical properties of the joints, the static shear tests were carried out. Results (Table 14.8) showed that the highest shear strength was observed in grinded nitrooxidized joints. The Hysol 9466 provided joints with the highest shear strength

TABLE 14.8 The Results of Shear Test of the Joints.

Material	Shear strength (MPa)			
	Hysol 9466	Hysol 9455	Hysol 9492	Hysol 9497
DC 01	9.0	2.8	7.1	6.0
DC 01 grinded	8.9	2.9	7.2	6.1
Nitrooxidized	12.9	3.1	7.8	5.4
Nitrooxidized grinded	12.9	5.9	12.7	7.0
Barier plasma treated	13.8	6.1	14.2	7.8

The mechanical properties of the joints made on non-nitrooxidized material did not depend on the surface grinding. The mechanical properties of the joints made on nitrooxidized material, in comparison to DC 01, were higher by 43% in case of Hysol 9466, 11% in case of Hysol 9455, and 10% in case of Hysol 9492. In the case of adhesive Hysol 9497, the decrease of the shear strength had occurred. The joints produced on grinded nitrooxidized material, in comparison to DC 01, had a higher shear strength by 43% in case of Hysol 9466, 110% in case of Hysol 9455, 79% in case of Hysol 9492, and 15% in case of Hysol 9497. The shear strength of adhesive joint was for barrier plasma-modified steel for all kinds of adhesive Hysol higher than unmodified and nitrooxidized steel.

Results of fracture morphology of the joints made of non-nitrooxidized material are shown in Figure 14.7a. Only the adhesive type of fracture morphology (Fig. 14.7b) was observed in every type of the adhesive. Cohesive and combined fracture type were not observed. It can be stated that the adhesion forces were not strong enough, hence, the joints were fractured between the material and adhesive.

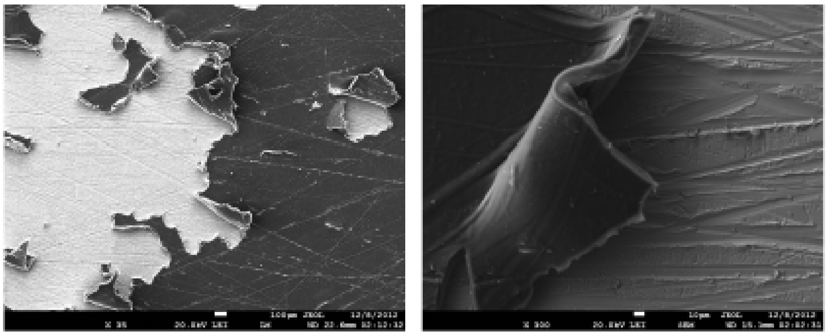

FIGURE 14.7 The fractographic analysis of the fractured adhesive joint of non-nitrooxidized material. (a) Overall view and (b) close-up view.

The results of the fractographic analysis of the non-grinded nitrooxidized steel are documented in Figure 14.8. No oxide layer peeling was observed. The cleavage fracture pattern as well as adhesive fracture morphology was observed. The close-up view on the cleavage fracture is shown in Figure 14.8b.

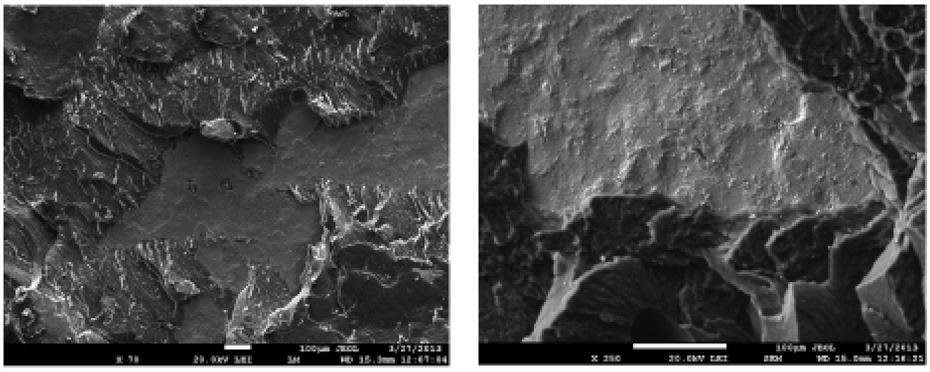

FIGURE 14.8 The fractographic analysis of the fractured adhesive joint of nitrooxidized material. (a) Overall view and (b) close-up view.

Differential scanning calorimetry revealed that three of the adhesives had a very similar glass transition temperature, so the meshing of the adhesives will start in the same way.

The results of mechanical properties evaluation of the joints proved that the material after the nitrooxidation process had a better adhesion to the epoxy adhesives than plain material DC01. Due to this fact, the higher shear strength was achieved. It can be explained by the surface oxide layer porosity, which helped the adhesive to leak in.

On the other hand, increase of mechanical properties of joints prepared from grinded nitrooxidized material can be explained by removing the surface oxide layer, and thus resulting into rapid increase of surface energy.

Only adhesive type of fracture was observed and the fractographic analysis showed that only cleavage type of fractures has been created. It can be stated that the surface energy of the materials was not appropriate for the cohesive fracture pattern.

14.4 CONCLUSION

Joining of steel sheets treated by the process of nitrooxidation represents an interesting technical as well as technological problem. The fusion welding methods with high-energy concentration, for example, laser beam welding are one of the possible options; however, even with high effort of minimizing the surface layer deterioration, it is not possible to completely avoid it.

Adhesive bonding of nitrooxidized steels presents, thus the second alternative, when the surface layer is not damaged and the adhesive joint keeps its properties after it has been cured. Adhesive bonding of metallic substrates often requires removing the surface oxide layer from the areas to be bonded. In case of materials treated by nitrooxidation, this is possible, however, the damage of the formed surface layer will occur. The goal of this paper was to review the effect of surface layer, created by the process of nitrooxidation and or by barrier discharge plasma treatment, on final mechanical properties of the joints, evaluation of fracture morphology, and results comparison for both treated and untreated material.

The acquired results have revealed that the presence of nitrooxidation surface layer caused decrease of free surface energy by 28%. The surface energy and namely its polar component were for barrier plasma-modified steel higher than for unmodified and nitrooxidized steel. On the other hand, this surface layer brings, on the joints, shear strength increase by 10–43% in dependence of the adhesive used. In case of Hysol 9497, the decrease of the joint shear strength by 10% was observed. In the case of barrier plasma-modified steel, the strength of adhesive joint were higher than unmodified and nitrooxidized material. We can presume that the increase of the shear strength was mainly due to porous structure of the surface layer, which enabled the adhesive to leak in.

The adhesive type of fracture morphology was observed during fractographic analysis. Regarding the characteristics of used adhesives, the cleavage fracture morphology of the joints had occurred.

Based on received results, it can be concluded that the epoxy adhesive bonding represents the suitable alternative of creating the high-quality joints of steel sheets treated by nitrooxidation as well as treated by barrier discharge plasma.

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KEYWORDS

- steel surface
- fracture character
- nitrooxidation
- adhesive bonding
- differential scanning calorimetry

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