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INFLUENCE OF PLASTIC DEFORMATION INHOMOGENEITY ON CORROSION RESISTANCE OF TIN PLATES

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Thin steel sheets are used in the production of food packaging, especially for long-term storage. Reducing the thickness of steel sheets and increasing the speed of the drawing process in the manufacture of packaging often decrements its plastic deformation stability. These changes bring about the need to use evaluation methods able to determine mechanical and plastic properties of steel sheets quickly and at a low cost. Two types of tin-plated steel sheets were used for experimental research into the influence of plastic deformation on their corrosion resistance. The paper compares the results of the uniaxial tension test and the biaxial tension test of tin-plated sheet properties.

Keywords: steel sheets, tin plates, corrosion, plastic deformation stability

INTRODUCTION

Thin steel sheets are among the most widely used materials in the production of packaging, especially for long-term food storage. In recent years, the development of these sheets has led to a significant reduction in thickness (from 0,26 mm to 0,24 mm thickness to 0,18 to 0,14 mm thickness) and a significant reduction in the thickness of the tin layer from the previous 11 g.m^{-2} (hot-dipped tin plating) to current 1-2 g.m^{-2} (electroplating) [1]. There has also been a significant change in the processing of thin sheets for packaging production [1,2]. During the drawing, considerable plastic deformations occur in the base material as well as on the coating [2,3].

Depending on their subsequent use, thin packaging sheets are produced by different rolling technologies (single rolling and double rolling – second reduction) and different annealing methods (batch and continuous annealing) [2,4,5]. The present packaging sheets, therefore, differ substantially in their strength and plastic properties. It is the method of production of the packaging sheets that has a considerable influence on the plastic properties which are required at their processing by drawing.

When evaluating the corrosion resistance of thin tin-plated sheets, the homogeneity of plastic deformation is important, which is manifested in the form of slip lines and bands. The corrosion resistance of thin steel sheets decreases significantly in the areas where the slip lines and bands originate – where the tin layer is thinned and micro-cracks develop [2,4,6]. When such a plastically deformed material is exposed to a corrosive environment, there is gradual intergranular corrosion of the steel sheet below the tin layer spreading along the grain boundaries of the base material. Intergranular corrosion is a form of non-uniform corrosion attack caused by the structural and chemical inhomogeneity of the metal at the grain boundaries. Well-chosen processes and manufacturing parameters provide the basis for proper anchoring of the coating, which results in proper surface morphology, uniform thickness, adhesion and integrity of the coating applied to the sheet in order to increase its corrosion resistance. Any damage to the coating compromises its protection function. [7,8,9,10,11] From the point of view of corrosion resistance, it is necessary to pay attention to the deformation and integrity of the tin coating of drawn tinplates, to identify changes, cracks and their size, to define their orientation and to predict their possible expansion. The authors want to stress that plastic deformation, its development and size significantly influence the corrosion resistance of thin tin-plated steel sheets.

MATERIALS AND METHODS

Two types of packaging sheets were used in the experiments, a once reduced continuously annealed plate labelled TH 435CA, 0,24 mm thick and twice reduced batch annealed plate labelled TS 550 BA, 0,16 mm thick. To compare the properties of the sheets, the sheets were evaluated using two different stress-strain techniques. Sheet properties were evaluated by the uniaxial tensile tests and biaxial tensile tests (bulge test). The uniaxial tensile test was performed according to STN EN 10002-1: 2002-11 on a TIRA Test 2300. The bulge test was performed on equipment developed and manufactured by our workplace. The stress-strain diagram is drawn from the pressure and height using custom software [6,12].

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Table 1 **Mechanical properties of experimental materials**

Material	Uniaxial test		
	R_{eh} / MPa	R_m / MPa	A_{50} / %
TH 435CA ⊥	468	447	28,1
TH 435CA÷÷	453	448	25,5
TS 550BA ⊥	525	534	2,6
TS 550BA ÷÷	523	531	3,1
	Biaxial test		
TH 435CA	342	506	14,6
TS 550BA	535	587	8,3

The measured results of the mechanical properties in both tests are shown in Table 1.

The chemical composition of the starting materials was provided by Belec Spectrometer. Both types of materials were chosen from the same heat. Its results are shown in Table 2. The composition and thickness of the tin layer were the same in all of the sheets used for experiments.

The steel sheets used for the experiments were made by progressive technology in oxygen converters in strict compliance with the required conditions. The steels are completely killed, cast continuously into slabs. The sheets are rolled on a five-stand tandem. After continuous or batch annealing, they are subjected to a single reduction (SR sheets) or a double reduction (DR sheets).

Table 2 **Chemical composition of both experimental materials / wt. %**

Fe	C	Si	Mn
99,52	0,075	0,022	0,130
P	S	Cu	Al
0,014	<0,002	0,030	0,065
Cr	Mo	Ni	V
0,009	0,013	0,005	0,009
Ti	Nb	Co	W
<0,002	0,018	0,036	0,048

The sheets have a tin coating deposited on both sides in a continuous electrolytic deposition. The manufacturer of the metal sheets used in the experiments indicates the weight of treatment of the two-sided tin layer 1 / 1 g.m^{-2}. The measured values of the test sheets were 1,1 / 1,1 g.m^{-2}. The roughness R_a of both sheets was in "Fine Stone" quality ranging from 0,25 to 0,45 μm. The packaging sheet produced by conventional rolling technology (single reduced) continuously annealed, has higher ductility and lower yield strength and tensile strength. The double-reduced sheet was batch annealed, which should ensure a more uniform structure and thus better properties.

However, a second reduction of the sheet significantly increased the yield strength, tensile strength and greatly reduced the ductility. The failure mode of the two types of plates examined after the tensile test is different and is shown in Figure 1.

RESULTS

Both materials used were deformed by bulge test to 3 % and 5 % deformation and deformation to failure. After these plastic deformations, the deformed samples were placed in a corrosion chamber with salt mist at 20 °C. The test was carried out according to ISO 9227: Corrosion tests in artificial atmospheres. Salt spray tests using 5 % wt. NaCl solution. This concentration is generally used in the NSS (Neutral Salt Spray, pH 6,5 to 7,1) methodology, which was also applied in this case. The exposure time was 240 h. The period of exposure to the corrosive environment corresponded to an average period of 3 years under real conditions. In case of loss of stability of plastic deformation (significant localization of plastic deformation) by the formation of slip zones, the porosity of the tin and lacquer layers increases in these areas.

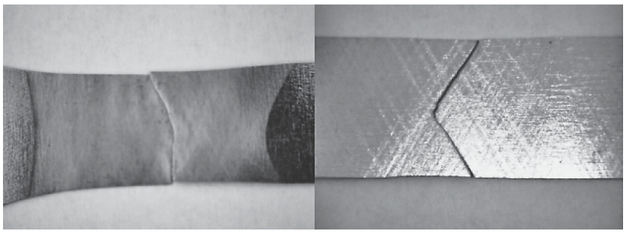

a) sheet TS 550BA b) sheet TH 435CA

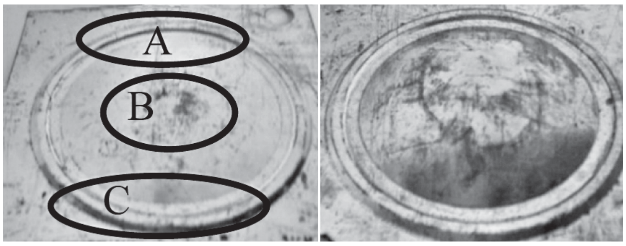
Figure 1 Sample after damage

The corrosion effect on the studied materials was evaluated visually and metallographically. Figures 2a), b) show sheets after plastic deformation with the bulge test. Figures 3 a), b) show sheets of TH 435CA grade after 5 % deformation and failure under corrosive environmental conditions in a corrosion chamber. In the case of continuously annealed TH 435CA sheet, higher elongation, lower yield strength and lower tensile strength were measured, but the sheet deformation showed considerable inhomogeneity in the form of significant slip planes.

From the analysis of the samples after corrosion, it is evident that significantly greater corrosion occurred in

a) after 3 % deformation b) after failure

Figure 2 TH 435CA sheet after bulge testing



a)after 5 % deformation b) after failure and corrosion

Figure 3 TH 435CA sheet

the sheets that were deformed to failure. In the case of the TH 435CA sheet with a 5 % deformation, a corrosion attack of the material is already evident in the area of the spherical canopy (Figure 3 area B). Both sheets showed significant corrosion attack at the edge of the spherical canopy (Figure 3 area A, C). Test samples, which were deformed by the bulge test until failure, showed an extensive corrosion attack on the spherical canopy of both sheets. This corrosion damaged the protective layer of tin and there was significant corrosion of the base material (Figure 3b).

The inhomogeneity of the plastic deformation of thin packaging sheets is also manifested in drawing the cans and lids from the packaging sheets. In places with significant localization of plastic deformation, the tin layer thinned, and its porosity increased. This problem was unclear because, according to the scientific literature, all authors classified meat and meat products into the category of the least aggressive fillings. Substantially more research was devoted to the cracking of cans with contents that released hydrogen sulfide (e.g. green beans). According to these sources, sulphides are effective accelerators of hydrogen diffusion in steel [13,14]. The hydrogen then accelerates the electrolytic corrosion. This occurs especially in the areas which are simultaneously deformed and have internal stresses. The effect of diffusing hydrogen on corrosion is a particularly large accelerator of non-metallic inclusions and carbides. In continuously cast steels, the influence of hydrogen is considerably lower [15]. Figure 4 a) shows the local deformation of the can lid at the bottom of the wall. The effect of such local deformation on reduced corrosion resistance and increasing of porosity in the tin layer is demonstrated in Figure 4 b), where it is precisely at these points that the material was subject to corrosion.

For meat cans, the interaction of the package with the contents is mostly associated only with the presence of dark iron and tin sulphides on the inner surface of the cans. The corrosion and cracking of meat cans is influenced by the quality of the meat contents, heat treatment by sterilization and the technology of meat can closing. In the case of meat can, both conditions were met. There were considerable residual tensile stresses at the lid and bottom rounding radii, and the contents for long-term storage contained significantly more chlorides. The above assumptions have been proven on a few meats can types that were had not been disturbed at the time of the investigation. An example of such a can seal with evident corrosion and local thinning at the lid radius is shown in Figure 4 a. Figure 4 b) shows an example where the lid was damaged by corrosion across nearly all of its thickness.

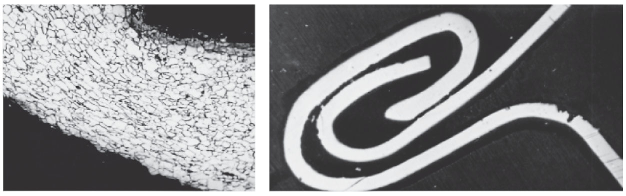

a) b)

Figure 4 a) Local deformation of a can´s lid
b) Can lid damaged by corrosion

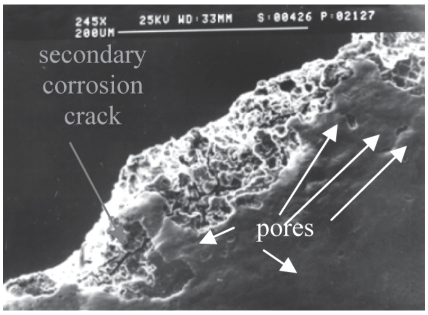


Figure 5 Missing tin layer in the breakage area and pores in the tin layer

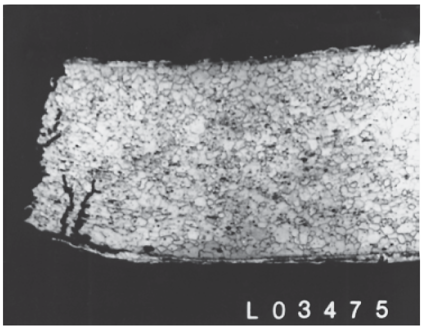


Figure 6 Secondary corrosion cracks

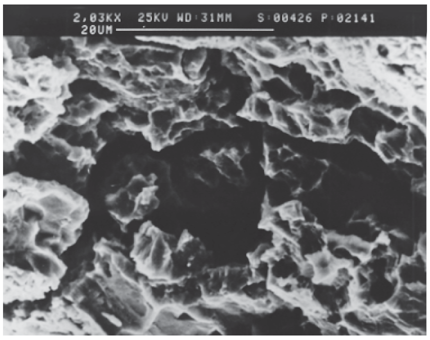


Figure 7 Local deformation of the can lid

These findings prove that the damage is not caused by the brittle failure of the material (base steel due to its high yield strength and low ductility).

It is obvious from Figures 5 and 6 that the protective tin layer was damaged by corrosion in the area of plastic deformation and intergranular corrosion occurred at several locations. The failure of the lid occurred in the area of primary corrosion.

Figure 6 clearly documents that in addition to primary corrosion, also areas of secondary intergranular corrosion are present. Figure 7 shows the intergranular corrosion in the area of the greatest deformation on the lid.

CONCLUSIONS

Based on the experiments we can conclude that the batch-annealed twice rolled sheets with lower plastic properties and higher yield strength and tensile strength develop uniform plastic deformation and lead to uniform thinning of the protective tin layer. The corrosion was even and did not interfere with the base material to a significant extent. Continuously annealed sheets were characterized by lower yield strength, lower tensile strength, and higher plasticity; however, their deformation under biaxial stress was characterized by inhomogeneity (significant slip strips). In the areas of significant slippage, the protective layer of tin was considerably thinned, its porosity increased and, as a result, the anti-corrosion protection was lost. Subsequent corrosion tests of the deformed sheets confirmed the assumption that corrosion occurs precisely in the areas where, due to high tensile stresses, slip zones arise and the porosity of the tin coating is increased significantly.

When using such sheets for the manufacturing of cans, the corrosion effect of the canned contents may lead to significant corrosion of the can lid and its subsequent failure. This phenomenon can be avoided by optimizing the conditions in the manufacture of can lids by drawing. Particular attention should be paid to the friction conditions and to the optimization of the holding pressures during the drawing process. The drawing process should be carried out in such a way as to avoid significant local deformations on the drawn part.

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