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THE BRITTLENESS OF Zn-Cu-Ti SHEET ALLOYS

KRUCHOŚĆ BLACH CYNKOWYCH Zn-Cu-Ti

At temperatures below 5°C, the ductility of ZnCuTi alloy sheets is observed to suffer a drastic drop in direction transverse to the rolling direction. Studies have shown that the critical temperature at which this phenomenon occurs is strongly dependent on the alloy structure and parameters of the sheet metal production process. Quite important is also the role of micro-inhomogeneity arising in the chemical composition of the alloy matrix, directly related with the structure of intermetallic precipitates containing Cu and Ti.

Keywords: Brittleness, Micro-segregation, Mechanical properties

W blachach wykonanych z cynku stopowego ZnCuTi w temperaturach poniżej 5°C obserwowane jest zjawisko spadku plastyczności w kierunku poprzecznym do kierunku walcowania. Badania wykazały, że temperatura krytyczna dla występowania zjawiska jest silnie uzależniona od struktury stopu oraz parametrów technologicznych produkcji blach. Duże znaczenie odgrywają także mikroniejednorodności składu chemicznego osnowy, co związane jest bezpośrednio ze strukturą wydzieleń faz międzymetalicznych z udziałem Cu oraz Ti.

1. Introduction

Zinc alloys containing as main alloying elements copper and titanium are widely used in the manufacture of roofing sheets. The addition of Cu results in the solution hardening of alloy and allows obtaining a satisfactory creep resistance by inhibiting the self-healing process typical for pure zinc at room temperature. The addition of Ti causes strong precipitation hardening of alloy with particles of the $Zn_{16}Ti$ phase [1-4]. ZnCuTi alloys are also prone to the formation of copper-titanium phases coherent with the alloy matrix (Cu_4Ti) [5].

Zinc has a hexagonal structure. With this phenomenon is associated the strong anisotropy of properties which, in combination with the anisotropy forced by plastic working (texture), results in the differentiation of product characteristics, depending on the rolling direction. This, in turn, has a decisive influence on the mechanical properties of finished zinc alloy sheet metal [6-9].

An important factor is the amount of the introduced alloying additions. Zinc alloys containing less than 0.1 wt.% Ti and approximately 0.1 wt.% Cu pose serious technological problems when the required and repetitive functional properties are to be obtained [6-9]. The currently produced sheets have a Cu content of 0.2 wt.% and Ti close to 0.1 wt.%. Higher content of alloying elements allows obtaining satisfactory properties in the final product. These alloys are also more heat treatable than alloys with a low content of alloying elements.

ZnCuTi alloy sheets are produced from the 8 mm thick cast strips obtained by a continuous casting process (contrary to the manufacture of ingots), and then rolled. The cast strip can be preheated and then rolled in a number of passages to a final thickness of 0.65-0.70 mm. Another option is to subject the cast strip to an additional heat treatment before or after the rolling process.

Unfortunately, despite positive results of the tensile test, some batches of thus produced ZnCuTi sheets may not meet the conditions of the technological bending test at 5°C, and if they do not, such sheet metal is not suitable for use as a roofing material.

Based on the results of structure examinations using electron microscopy, an attempt was made to clarify the reason for the decrease of the ZnCuTi sheet metal plastic properties at temperatures below 5°C.

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2. Research methodology

Studies were carried out on a 0.70 mm thick sheet made of the ZnCuTi alloy containing 0.15% Cu and 0.075% Ti, obtained from a strip of 8 mm thickness annealed and rolled to 10 passages.

In the above mentioned technological process of the sheet manufacture, three variants of the heat treatment (annealing) were applied to the cast strip prior to rolling:

Variant A; annealed at 180°C for 3 h, cooled in air and then rolled,

Variant B; annealed at 340°C for 0.5 h, cooled in air and then rolled,

Variant C; annealed at 390°C for 0.5 h, cooled in air and then rolled.

Structure of sheets after three variants of the heat treatment (A, B and C) and rolling was examined under a Jeol JEM-2010 ARP transmission electron microscope.

The mechanical properties of the examined sheet metal were determined from the results of the tensile test at room temperature. They were calculated by averaging the results obtained on seven samples taken for each variant of the sheet metal tested. The specimens for testing of the mechanical properties were cut out in direction parallel to the rolling direction. To test these properties, the strain rate of $\varepsilon = 1.7\times10^{-3}$ s^{-1} was applied.

The test sheets prepared in three variants (variants A, B and C) had satisfactory mechanical properties in accordance with the standard for zinc metal used in the construction industry ($R_{0.2\ min} = 100$ MPa, $R_{m,\ min} = 150$ MPa, $A_{50,\ min} = 35\%$ (Table 1).

Bending test was made on sheet metal samples 10 mm wide and 100 mm long. The test was performed in direction transverse to the rolling direction and consisted in complete forward bending of the sheet metal at a bending radius $r = 0$, followed by backward bending of the sheet until a characteristic “vee-shaped bend” was formed. The bend edge was parallel to the test sheet rolling direction. The surface of the sheet bend edge was subjected to visual examination. In the case of cracks or heterogeneous structure displayed on the bend edge, the test result was considered negative. The bending tests were performed at 5°C.

TABLE 1

Mechanical properties of the investigated sheets

Variant	Thickness [mm]	$Rp_{0,2}$ [MPa]	Rm [MPa]	A_{50mm} [%]
A	0,70	131,1	165,0	59,8
B	0,70	123,3	162.5	37,2
C	0,65	146,2	173,0	67,5

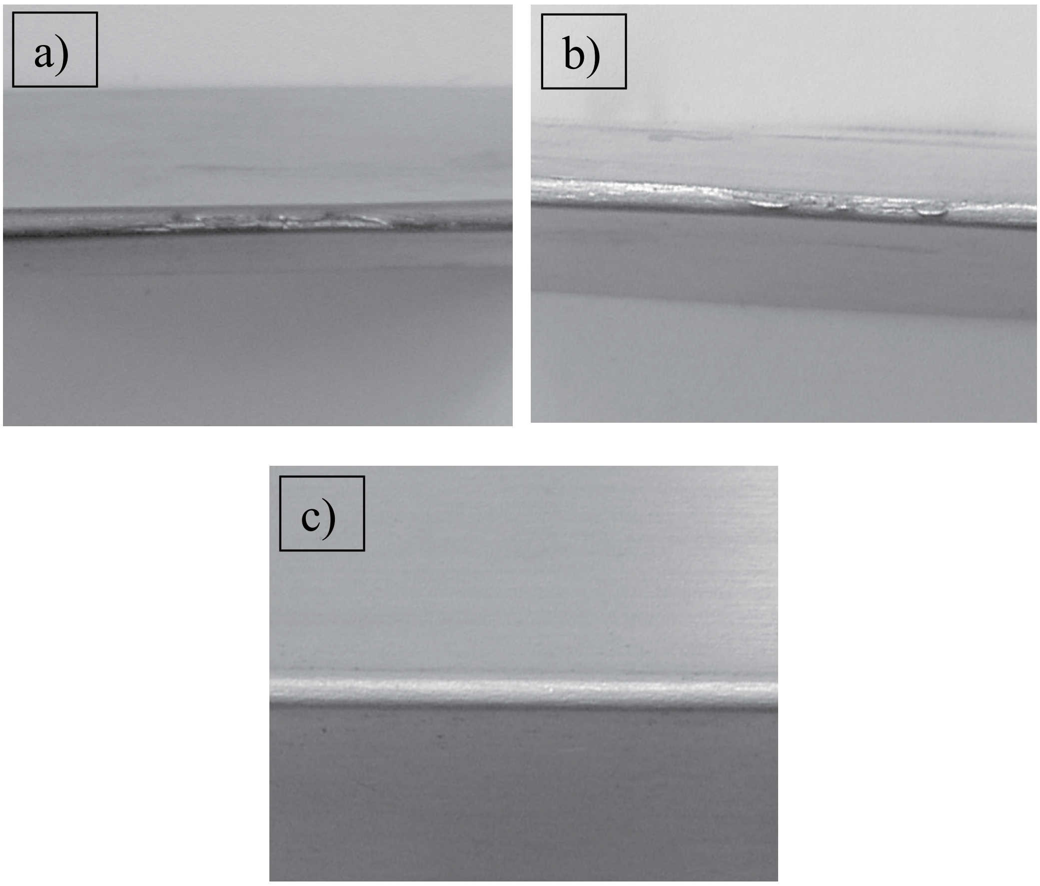

Fig. 1. Examples of bend edges obtained in various sheet metals after the backward bending test; a – (variant A and variant B) – negative results, c – (variant C) – positive result

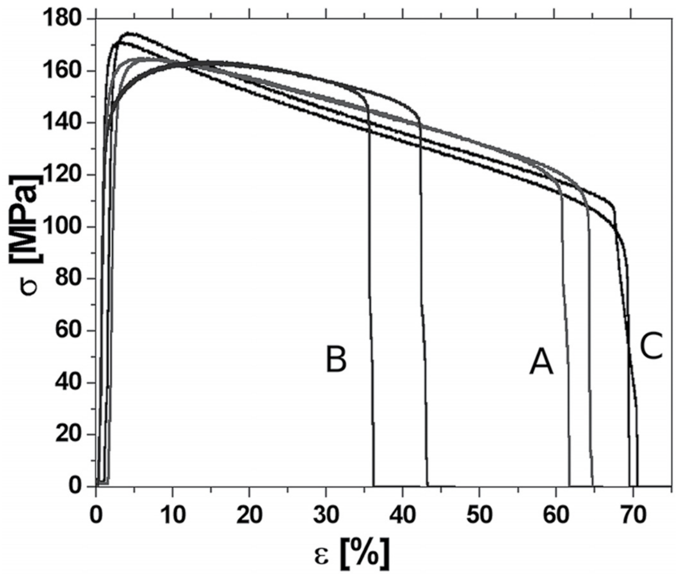

Fig. 2. Tensile test characteristics for the specified samples

3. Discussion of results and conclusions

The tested ZnCuTi alloy sheets showed a strong dependence of structure, and thus of mechanical properties (Table 1, Fig. 2), on the type of selected technological variant. The hardenability due to small amounts of alloying elements is a common feature observed in zinc alloys and other metals with a hexagonal structure. Another feature of alloys containing small amounts of alloying elements is the micro-inhomogeneity of the chemical composition [2,4,9]. Low content of alloying elements causes difficulties when repeatable mechanical properties are to be obtained in each batch of the material subjected to a heat treatment process. Then, to obtain the required repeatability of parameters in the ZnCuTi alloy, it is necessary to ensure the presence of alloying elements at a level of 0.2 wt.% Cu and 0.1 wt.% Ti.

Full understanding of processes affecting the hardening behavior of ZnCuTi alloys requires in-depth studies of the copper impact on alloy structure and of the impact of various phases formed by this element. Copper causes strong solution hardening of alloys, and together with titanium, promotes in the investigated ZnCuTi alloys the formation of numerous copper-titanium phases (Cu_2Ti, Cu_4Ti, Cu_7Ti_2, CuTi). Most of these phases are of a metastable character. The only stable phase is Cu_4Ti. Structure shaped by this phase is largely dependent on the annealing time and temperature (aging) [5].

The impact of micro-inhomogeneity arising in the chemical composition of alloy matrix was studied in [9]. Studies have shown that anomalies observed in the mechanical properties of single zinc crystals with alloying additions are most pronounced at the small growth rates. This is due to the strong segregation of alloying elements ahead of the crystallization front. The problem of concentration of alloying elements in the growth zone examined by Bridgman method was also analyzed numerically [10-14].Tests carried out on single crystals showed strong correlation between the resulting structure and crystallization rate. Likewise, the phenomenon of brittle fracture (anomalies) observed in single crystal zinc alloy samples has revealed a strong correlation between the structure and micro-segregation of alloying elements in the alloy matrix [9].

All test sheets obtained according to variants A, B and C have acquired the level of $Rp_{0.2}$, R_m and A_{50mm} demanded by respective standards, but not all passed the bending test with positive results. One of the important methods to evaluate the metal susceptibility to reverse bending is analysis of the hardening curve (Fig. 2). Sheets labelled as variant A and variant B showed the highest elongation A_{50mm} and high value of R_m but the results of bending tests were negative. The reason for this was too rapid hardening in the initial stage of deformation and too rapid achievement of R_m. As follows from the tests carried out on sheets in variants A and B, the deformation that took place when the material reached the tensile stress equal to R_m was accompanied by the formation of surface micro-cracks distributed along grain boundaries, parallel to the rolling direction, at sites where the precipitates of intermetallic phases have occurred (Figs. 3 and 4), leading next to the formation of cracks in bending test.

Further deformation generates cracks on the surface of the bend edge, which may lead to delamination of the sheet.

C-type variant of the sheets have a flatter hardening curve. The deformation of the surface of these sheets accompanying the bending test does not cause exceeding the tensile stress level equal to R_m. Owing to this, the surface of the bend edge is smooth and without cracks (Fig.1c).

It is therefore recommended to select the technological parameters of the sheet metal manufacturing process such that hardening in the initial stage of deformation during the tensile test does not result in the rapid achievement of stress corresponding to the value of R_m. The optimum hardening curve should have a low and positive strain hardening exponent, which in the initial range of deformation assumes the value of at least several percent of the total strain, before the value of R_m is achieved (e.g. the tensile curve obtained for variant C, Fig. 2).

High mechanical properties complying with standards valid for the ZnCuTi alloys and a positive result of the bending test were obtained for variant C. As shown by structure examinations (Fig. 4), the grain boundaries in these sheets are free from any precipitates of the intermetallic phases. The annealing temperature for this technological variant was 390°C, which made these phases dissolve in alloy matrix, thus preventing the formation of cracks along grain boundaries.

The results of structure examinations, mechanical tests and bending tests carried out on the ZnCuTi sheets produced according to the three different technological variants (A, B and C) enabled drawing of the following conclusions:

a. the structure of the sheet metal with inadequate resistance to the forward and backward bending test at 5°C (variants A and B) contains copper and titanium precipitates distributed along grain boundaries,
b. precipitates of this type do not occur at the grain boundaries in sheets produced from the plates subjected to high-temperature annealing (variant C),

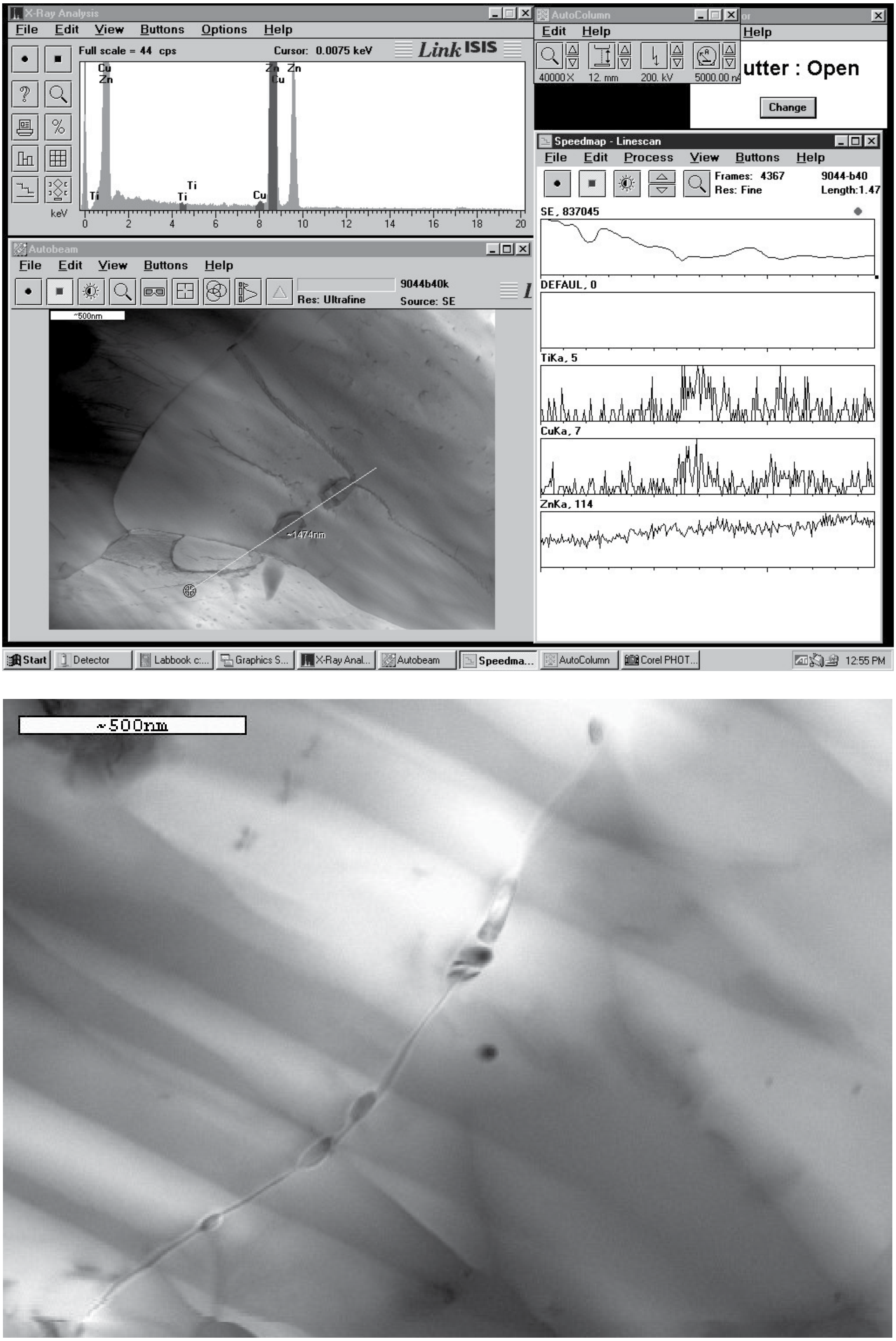

Fig. 3a, b. Precipitates of intermetallic phases observed on the inter-granular boundary. Sheet metal – variant A, negative result of the bending test

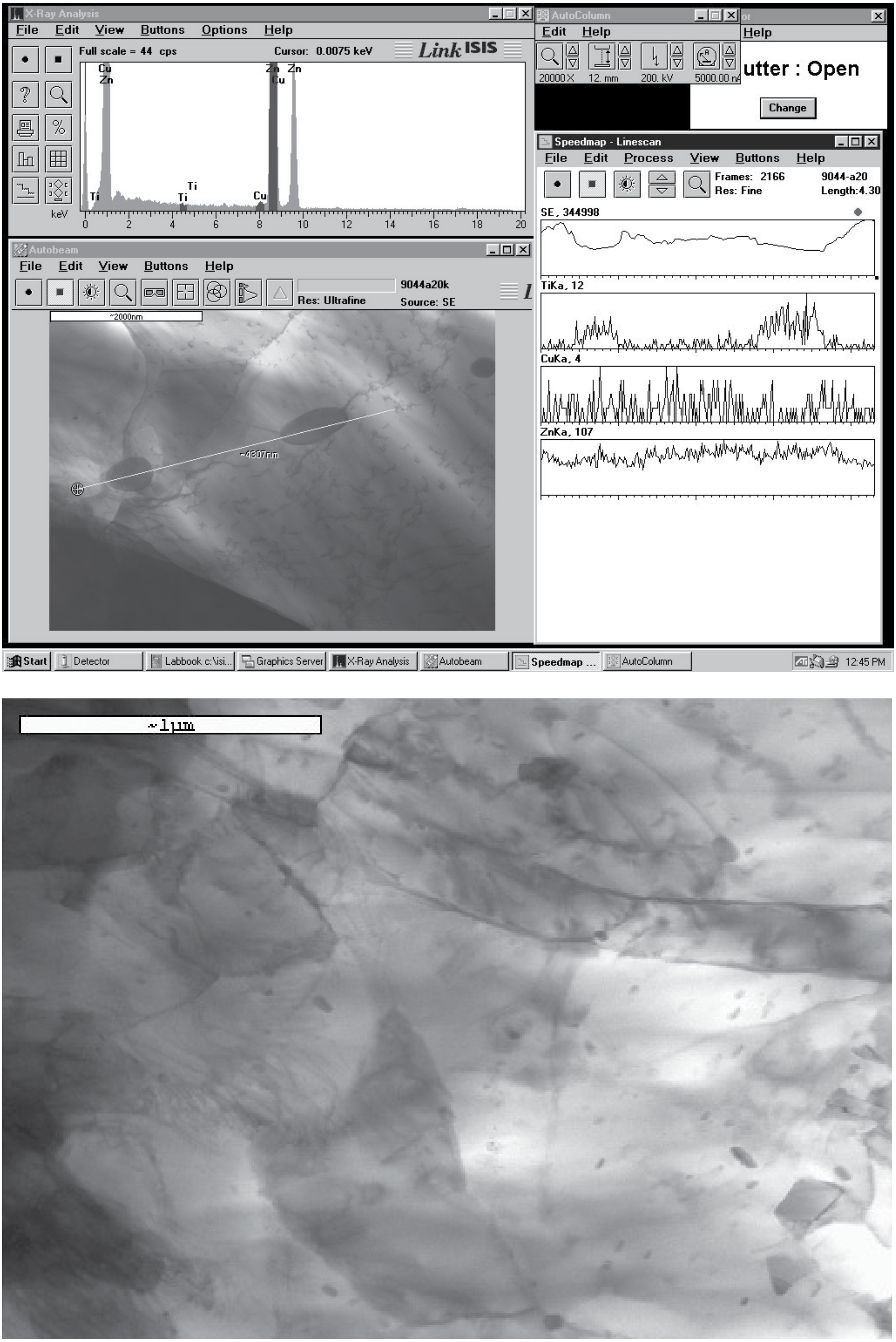

Fig. 4a, b. Precipitates of intermetallic phases observed in the entire sample volume. Sheet metal – variant C, positive result of the bending test

c. the precipitates of intermetallic phases rich in Cu and Ti are distributed along grain boundaries and are responsible for the drop of ductility in direction transverse to the rolling direction; they are also the main cause of the negative result of a bending test,

d. there is an additional factor contributing to the brittleness of the examined sheet metal, and these are the micro-inhomogeneity in the distribution of alloying elements in the matrix areas surrounding microscopic particles of the $Zn_{16}Ti$ phase.

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REFERENCES

[1] M. Saillard, G. Develey, C. Becle, J.M. Moreau, D. Paccard, The Structure of $ZnTi_{16}$, Acta Crystallographica Section B **37B**, 224-226 (1981).

[2] G. Boczkal, Structure and Properties of Zn-Ti0.2-Cu0.15 Single Crystal Containing Eutectic Precipitates, Archives of Metallurgy and Materials **58**, 4, 1019-1022 (2013).

[3] G. Boczkal, B. Mikułowski, W. Wołczyński, Oscillatory Structure of The Zn-Cu-Ti Single Crystals, Materials Science Forum **649**, 113-118 (2010).

[4] G. Boczkal, Second Phase Morphology in the Zn-Ti0.1-Cu0.1 Single Crystals obtained at different Growth Rates, Archives of Metallurgy and Materials **57**, 479-484 (2012).

[5] K.V. Chuistov, Copper–Titanium Solid Solutions are New Generation of High Strength Age-Hardening Alloys, Usp. Fiz. Met. **6**, 1001-1055 (2005).

[6] H.L. Plawer, Titanzinc im Bauwesen, Woeste Druck+Verlag, Essen (1992).

[7] G. Boczkal, B. Mikulowski, I. Hunsche, C.G. Oertel, W. Skrotzki, Precipitation of Intermetallic phase in Zn-Ti alloy single crystals, Crystal Research Technology **43**, 2, 135-140 (2008).

[8] G. Boczkal, B. Mikulowski, C.G. Oertel, W. Skrotzki, Work Hardening Characteristics of Zn-Ti Alloy Single Crystals, Crystal Research Technology **45**, 2, 111-114 (2010).

[9] G. Boczkal, The Influence of Growth Rate on Mechanical and Thermodynamical Properties of the Zn-Ti0.075-Cu0.15 Single Crystals Deformed at (0001)<11-20> System, Materials Science Forum **674**, 245-249 (2011).

[10] W. Wołczyński, Lamella / Rod Transformation as described by the Criterion of Minimum Entropy Production, International Journal of Thermodynamics **13**, 35-42 (2010).

[11] W. Wołczyński, G. Sibiga, P. Musielak, B. Mikułowski, G. Boczkal, Thermodynamic Justification for the Intermetallic Layers Formation within the Hexagonal Single Crystal, Inżynieria Materiałowa **182**, 789-792 (2011).

[12] W. Wołczyński, G. Boczkal, P. Musielak, G. Sibiga, B. Mikułowski, Control of the Structural Parameters in the (Zn) – Zn16Ti Single Crystal Growth, Archives of Foundry Engineering **11**, 149-156 (2011).

[13] W. Wołczyński, G. Boczkal, Pattern Selection within the Stripes Strengthening the Hexagonal (Zn)-Single Crystal, Inżynieria Materiałowa **189**, 349-352 (2012).

[14] W. Wołczyński, Thermodynamic Pattern Selection in the Stripes Generated Periodically during the (Zn) – Single Crystal Growth, Archives of Metallurgy and Materials **58**, 309-313 (2013).

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