

## EFFECTS OF HOT AND COLD ROLLING ON THE MICROSTRUCTURE OF LOW ALLOY Zn-CU AND Zn-Cu-Ti ZINC ALLOY WITH IMPROVED CORROSION RESISTANCE

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*The microstructure of three wrought zinc alloys with improved corrosion resistance has been investigated by optical and scanning electron microscopy in as-cast condition as well as in hot and cold rolled condition. Important structural modifications such as shape and size changes of the crystalline grains, modifications in size non-uniformity, twinning and recrystallization, orientation changes of slip systems, have been put in evidence both in the binary Zn-0.19Cu alloy and in the ternary Zn-0.09Cu-0.19Ti and Zn-0.22Cu-0.61Ti alloys. The structural modifications have been corroborated with important changes in the mechanical properties that have accompanied the transformations.*

*A fost studiată prin microscopie optică și prin microscopie electronică prin baleiaj microstructura a trei aliaje de zinc deformabile cu rezistență sporită la coroziune atât în stare turnată cât și după deformare plastică la cald și la rece. Atât în aliajul binar Zn-0.19Cu cât și în aliajele ternare Zn-0.09Cu-0.19Ti și Zn-0.22Cu-0.61Ti au fost puse în evidență importante modificări structurale privind forma și dimensiunea grăunților cristalini, uniformitatea mărimii grăunților, maclarea și recristalizarea, reorientarea sistemelor de alunecare. Modificările structurale au fost coroborate cu schimbările importante în proprietățile mecanice care s-au produs în cursul transformărilor.*

**Keywords:** binary and ternary Zn alloys, cast structures, hot rolled structures, cold rolled structures

### Introduction

From a metallurgical point of view, there are two characteristics that confer to zinc a certain specificity: the melting temperature and the crystal lattice.

The melting temperature of 419<sup>0</sup>C determines the development of zinc recrystallization process at temperatures between 50-100<sup>0</sup>C. Its HCP (hexagonal close packed) crystal lattice has several consequences such as the specific behavior of zinc during the process of plastic deformation, the anisotropy of its

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mechanical-physical characteristics and the generation of solid solutions with very low concentrations of associate elements.

In the process of plastic deformation of zinc, the deformation takes place by slip and twinning. The important role of twinning doesn't result from the dimension of the deformation, but from the fact that the changes in orientation of the crystal lattice obtained after this kind of deformation lead to new slip systems with preferential orientation depending on the direction of applied stress. The preferential orientation the zinc crystalline grains in the plastic grains deformation process results in the anisotropy of the mechanical-physical characteristics, especially the yield point and the ultimate tensile strength and is greatly influenced by the method used for hot rolling. The hot rolling in bars decreases the anisotropy of the deformation and this fact is due to the factors that characterize this procedure: the heat accumulated in the rolling mill, the rolling character of the metal in the deformation area and the presence of the stress in the bar, [2-6].

The thermal effect resulted in the plastic deformation of zinc is stronger in comparison with other metals. This thermal effect causes the raise of the rolling bar temperature, in direct proportion to the degree of applied reduction and in reverse proportion to the rolling temperature, thus increasing deformation and the characteristics of the mechanical strength.

The process of zinc recrystallization includes a wide variety of structural transformations and, in the end, provides the total removal of the cold-hardening of the metallic material. The presence of impurities and alloying elements, in small concentrations, causes the raise of zinc recrystallization temperature and increases its mechanical characteristics.

The degree of cold-hardening, after cold deformation is influenced by the purity of zinc, temperature, degree of deformation and it is eliminated through an annealing heat treatment. So, the zinc sheets rolled on cold cylinders with small reductions for every passage, have a typical deformation structure until reheating. After reheating, even at temperatures of 100°C zinc undergoes the recrystallization. For the rolled sheets with high degree of deformation, the large heat effect results in a recrystallized structure, [1, 2, 4].

## **1. Experimental**

The effect of plastic deformation on the microstructure of three zinc alloys has been followed by optical and electron microscopy. The chemical composition of the investigated alloys is indicated in Table 1. The alloying elements, Cu and Ti, and their content have been selected in view of improving the corrosion behaviour of zinc. Further details on the best Cu/Ti ratio will be given in a next to

come paper intended to be published in this journal, in which the corrosion results will be presented.

In this paper a thorough investigation of the microstructure of the three alloys in Table 1 will be carried out both in cast condition and in hot and cold rolled condition. This previous structural investigation was considered a prerequisite to better enlighten the corrosion results in the next to come paper.

Table 1

Chemical composition of the investigated Zn alloys

CODE	Element %									Zn%
	Pb	Cd	Fe	Cu	Ti	Sn	Sb	As	Al	
B	0.0018	0.0009	0.005	0.1950	-	0.0007	0.0006	0.0007	<0.0003	balance
C	0.0019	0.008	0.005	0.0923	0.193	0.004	0.0006	0.0007	<0.0003	balance
D	0.0026	0.0016	0.004	0.2180	0.610	0.0020	0.0007	0.0007	<0.0003	balance

## 2. Results

The *as-cast structures* of the three alloys have been taken as a reference for the further investigation of the effect of plastic deformation on the microstructure. Fig. 1, Fig.2 and Fig. 3 show the microstructure of the three alloy safter casting.

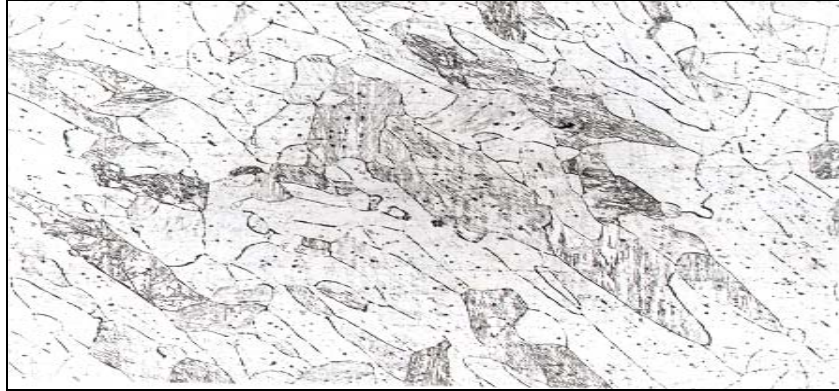


Fig.1. Optical micrograph of the binary alloy Zn-0.19Cu (alloy B) in cast conditions, x 200; etchant: CrO<sub>3</sub> 10%

As seen in Fig.1 the binary alloy Zn-0.19Cu has a cast structure typical for a single phase alloy. This was to be expected from the solid state solubility data of Cu in Zn. Actually the phase equilibrium diagram of the Cu-Zn system [7] indicates the following solid state solubilities of Cu in the terminal  $\eta$  solid solution (in weight per cent): 0.3 at 100°C; 0.9 at 200°C; 1.65 at 300°C; 2.5 at 400°C. As far as the morphology of the grains is concerned, the central area has an equiaxed structure, while the outer zone of the cast product exhibits a columnar structure. A

certain non-uniformity of the grain size was manifest, with an average grain diameter of about 0.2mm.



Fig. 2. Optical micrograph of the ternary alloy Zn-0.09Cu-0.19Ti (alloy C) in cast conditions, x 200; etchant: CrO<sub>3</sub> 10%

The structure of the low alloyed Zn-0.09Cu-0.19Ti alloy (Fig.2) shows a coarse (average grain size  $D_{av} \cong 0.035\text{mm}$ ) dendritic morphology in the outer zone and a fine dendritic morphology in the central zone ( $D_{av} \cong 0.025\text{mm}$ ). A second phase is visible as small dark particles located between the  $\eta$  solid solution dendrite arms. This is to be expected if the very low solid solubility values of Ti in Zn are considered [7] namely 0.007-0.0015 weight percent Ti at 300<sup>0</sup>C.

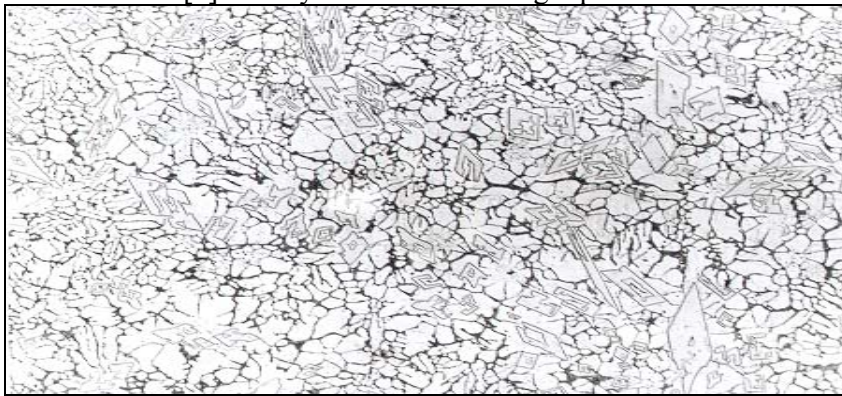


Fig. 3. Optical micrograph of the ternary alloy Zn-0.22Cu and 0.61Ti (alloy D) in cast conditions, x 200; etchant: CrO<sub>3</sub> 10%

When the copper and titanium content is increased up to 0.22Cu and 0.61Ti, respectively (alloy D in Fig.3) the dendritic morphology of the  $\eta$  solid solution becomes more uniform in grain size ( $D_{av} \cong 0.025\text{mm}$ ) and the amount of the dark particles of the secondary phase becomes larger. In the central area the

dark interdendritic regions comprising the secondary phase may be considered as representing an eutectic whose titanium content is 0.12Ti according to the binary Zn-Ti phase equilibrium diagram [7].

*The hot rolled structures* (rolling temperature 150-180°C) have been examined on flat bars of 5mm thickness. The structures appear to be completely recrystallized. In the binary Zn-0.19Cu single phase alloy the average size of the recrystallized grains is about 45  $\mu\text{m}$ , but there is a large grain size non-uniformity. In the ternary Zn-Cu-Ti alloys the recrystallized  $\eta$  grains are finer ( $D_{\text{av}} \cong 10\mu\text{m}$ ) and their size is more uniform on account of the grain refiner action of the secondary phase. The latter is distributed as lines about 10 $\mu\text{m}$  apart in the low alloy Zn-0.09Cu-0.19Ti and as lines and equidistant lamellae in the high alloy Zn-0.22Cu-0.61Ti.

*The cold rolled structures* of all three investigated alloys have been examined on the previously hot rolled bars on which a cold rolling with small reduction degrees has been applied at room temperature on water cooled rolls. All structures obtained in these conditions appear to have undergone the recrystallization process during cold rolling. This was true for the binary alloy (alloy B) as well as for the ternary alloys (alloy C and alloy D), as clearly put in evidence in Fig. 4, Fig.5 and Fig.6.

What makes a distinction between the cold rolled structure of the binary alloy and the ternary alloys is the volume fraction of the twins, that represented  $\cong 30\%$  in the binary alloy B (Fig. 4) and  $\cong 10\%$  in the ternary alloys C and D (Fig.5 and Fig 6). As pointed in the Introduction of this paper, the importance of the twinning process during cold plastic deformation lies not in the contribution of twinning to the overall plastic deformation but in the fact that by changing the crystallographic orientation, new slip planes are brought in the proper orientation for plastic deformation.



Fig. 4 Optical micrograph of the binary alloy Zn-0,19Cu (alloy B) in cold rolled condition, x 200; etchant: CrO<sub>3</sub> 10%

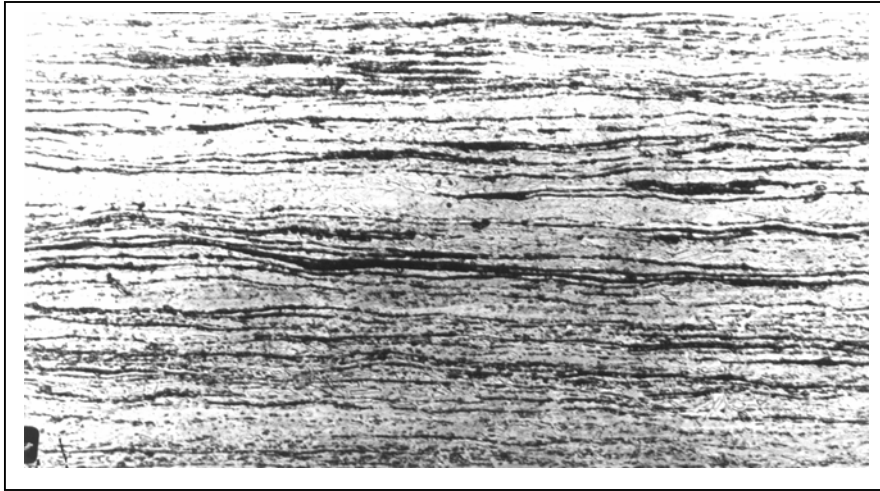


Fig. 5. Optical micrograph of the binary alloy Zn-0.09Cu-0.019Ti (alloy C) in cold rolled condition; x 200; etchant: CrO<sub>3</sub> 10%



Fig. 6. Optical micrograph of the binary alloy Zn-0.22Cu-0.61Ti (alloy C) in cold rolled condition; x 200; etchant: CrO<sub>3</sub> 10%

In order to elucidate the nature of the secondary phase in the ternary alloys we have performed an EDAX analysis on the dark regions of the scanning electron micrograph in Fig 7a. The obtained EDS spectrum is reproduced in Fig 7.b and the results of the EDAX analysis are presented in Fig 7c. The composition

of the secondary phase was thus confirmed to be (in the limits of the experimental errors) in agreement with the intermetallic compound  $TiZn_{15}$ .

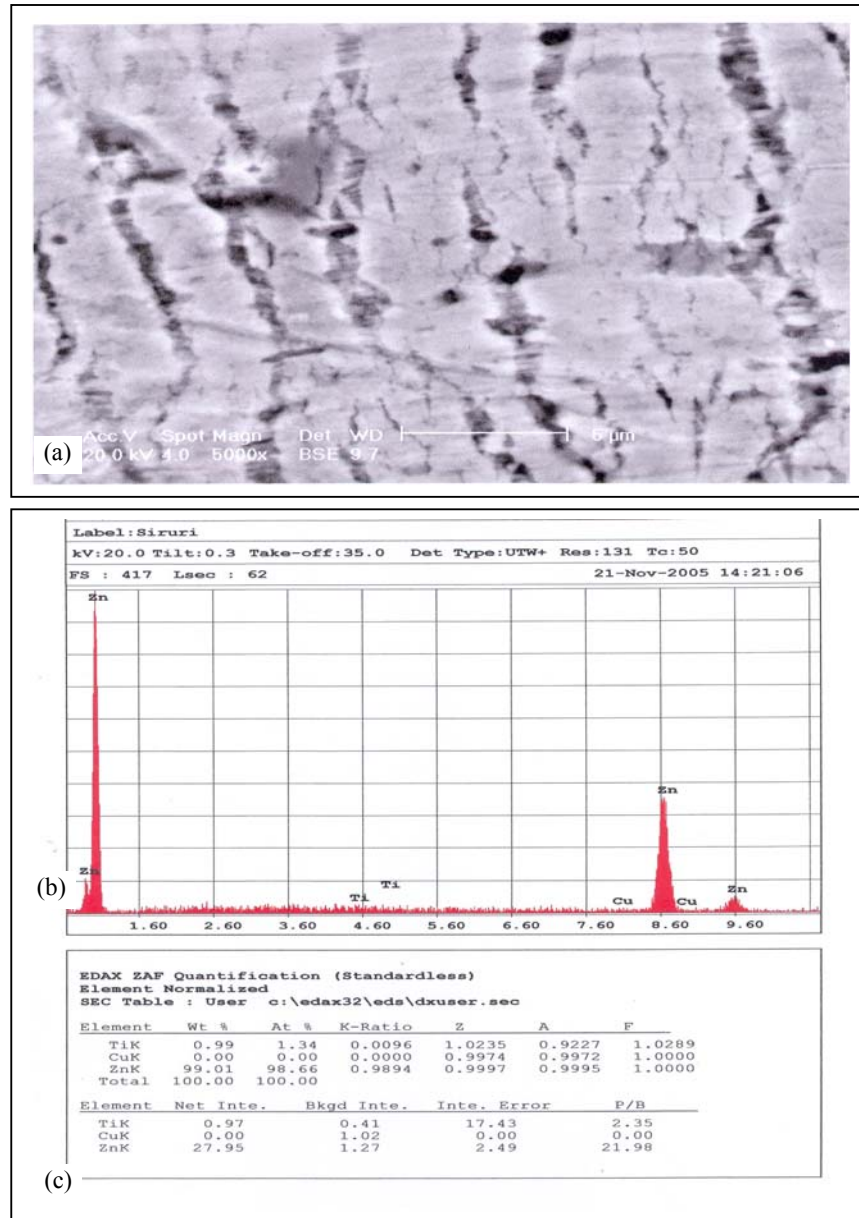


Fig. 7. Scanning electron examination and EDS analysis of the secondary phase in the ternary Zn-0.09Cu-0.19Ti alloy

- a. SEM composition image
- b. X-ray emitted spectrum by the dark arrays in image (a)
- c. EDS analysis results

## Discussion and Conclusions

The results obtained by optical microscopic analysis and scanning electron microscopical examination have pointed to important structural transformations induced by applying hot and cold rolling to the cast binary and ternary low alloyed zinc based alloys in the Zn-Cu and Zn-Cu-Ti systems. These structural changes can be associated with the modification of the mechanical properties brought about by plastic deformation as follows:

1. In the case of the binary Zn-0.19Cu alloy there is an intensive growth of the crystalline grains during cold rolling promoted by the deformation twins that served as preferential sites for recrystallization. On this account the mechanical strength was decreased by cold rolling reaching the following values: yield strength  $\sigma_y=107\text{MPa}$ , ultimate tensile strength  $\sigma_u=154\text{MPa}$  and the elongation at fracture 26%.

2. In the case of the ternary alloy Zn-0.09Cu-0.19Ti, by lowering the copper content and by introducing titanium the volume fraction of the deformation twins was decreased to ~8% and on this account the recrystallization process during cold rolling played a less important role. As a result the ultimate tensile strength  $\sigma_u$  was increased by ~18% and the elongation at fracture by ~42%

3. In the case of the higher alloyed ternary alloy Zn-0.22Cu-0.61Ti several structural phenomena were brought about in the cold rolled structure, namely the absence of deformation twins and the increase of the amount of the grain refiner secondary phase TiZn15. As a result a finer grain size was obtained that promoted an increase in the elongation at fracture by 35%. Concomitantly an increase in yield strength by 22% was promoted by solution hardening.

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