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## ANOMALY OF THE WORK HARDENING OF Zn-Cu SINGLE CRYSTALS ORIENTED FOR SLIP IN SECONDARY SYSTEMS

### ANOMALIA UMOCNIEŃIA ODKSZTAŁCENIOWEGO KRYSZTAŁÓW Zn-Cu ZORIENTOWANYCH DLA POŚLIZGU W SYSTEMACH WTÓRNYCH

The copper alloyed (up to 1.5%) zinc single crystals oriented for slip in non-basal systems (orientation close to  $\langle 11\bar{2}0 \rangle$ ) were subjected to compression test within a range of temperatures of 77-293K. It has been stated, that Zn-Cu crystals exhibit characteristic anomalies of the thermal dependence of yield stress and of the strain hardening exponent. Both of them are related to the change in type and sequence of active non-basal slip systems: pyramidal of the 1<sup>st</sup> order  $\{10\bar{1}1\} \langle \bar{1}\bar{1}23 \rangle$  (Py-1) and pyramidal of the 2<sup>nd</sup> order  $\{11\bar{2}2\} \langle \bar{1}\bar{1}23 \rangle$  (Py-2). The temperature anomaly of the yield stress results from the change of the slip from Py-2 systems to simultaneous slip in the Py-2 and Py-1 (Py-2 + Py-1) systems, occurring in the preyielding stage. On the other hand, sequential activation of pyramidal systems taking place in advanced plastic stage (i.e. the first Py-2 and next Py-2 + Py-1 systems) is responsible for temperature anomaly of strain hardening exponent. Increase in copper addition favors the activity of Py-2 systems at the expense of Py-1 slip, what leads to a drastic differences in plastic behavior of zinc single crystals.

*Keywords:* zinc, single crystal, compression, pyramidal slip

Kryształy cynku z dodatkiem miedzi (do 1.5%) zorientowane dla poślizgu w systemach wtórnych (orientacja bliska  $\langle 11\bar{2}0 \rangle$ ) poddano testowi ściskania w zakresie temperatur 77-293K. Stwierdzono, że kryształły te wykazują charakterystyczne anomalie temperaturowej zależności granicy plastyczności oraz wykładnika umocnienia odkształceniowego. Obie te anomalie są związane ze zmianą typu i sekwencji aktywności wtórnych systemów poślizgu: piramidального 1-go rzędu (Py-1)  $\{10\bar{1}1\} \langle \bar{1}\bar{1}23 \rangle$  oraz piramidального 2-go rzędu (Py-2)  $\{11\bar{2}2\} \langle \bar{1}\bar{1}23 \rangle$ . Temperaturowa anomalia granicy plastyczności jest wynikiem przejścia od poślizgu w systemach Py-2 do równoczesnego poślizgu w systemach Py-2 i Py-1 (Py-2 + Py-1), mającego miejsce w stadium quasi-sprężystym. Sekwencyjna aktywność systemów piramidalnych zachodząca w zaawansowanym stadium plastycznego płynięcia (tzn. przejście od poślizgu Py-2 do równoczesnego poślizgu Py-2 + Py-1) jest odpowiedzialna za temperaturową anomalię wykładnika umocnienia odkształceniowego. Wzrost koncentracji miedzi aktywizuje systemy Py-2 kosztem poślizgu Py-1, co prowadzi do drastycznego zróżnicowania plastycznych zachowań kryształów cynku.

## 1. Introduction

The temperature inversion effect of the yield stress dependence occurring at temperatures of about  $0.3 T_t$  (where:  $T_t$  – melting point) in Zn, Cd, Mg and Co crystals oriented for slip in secondary systems, is known for a long time [1-10] but, so far, it has found no rational explanation. As it seems, the proposed mechanisms was influenced by an excessive belief that the plastic flow of such crystals is realized by slip in 2<sup>nd</sup> order pyramidal (Py-2)  $\{11\bar{2}2\} \langle \bar{1}\bar{1}23 \rangle$  systems only and was based mainly on the results of etch pits investigations [10-22], and a few topographic [1, 23, 24] and TEM observations [18, 25, 26]. The anomaly of yield stress one associated with the kinetics of Py-2 dislocations movement and

activity of cross slip to the  $\{10\bar{1}1\}$  planes [21], the interactions of dislocations with vacancies and prismatic loops (by analogy to the phenomena accompanying the low temperature basal slip) [6], or with the activity of 'larger number' of Py-2 systems, which was to result in the wavy character of slip lines and athermal course of yield strength [2]. It was also suggested that this anomaly may be the result of 'specific' strengthening caused by the thermally activated dissociation of Py-2 dislocations on the partial dislocations [8] or dissociation on perfect dislocations (basal and pinned  $[0001]$ ), which immobilizes the Py-2 slip dislocations [3, 5, 6].

However, the mentioned, rather sophisticated concepts do not explain some other low-temperature behav-

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ior of Zn crystals, indicated by Gilman [1], such as: i) the drastic difference of the yield strengths of crystals with orientation  $\langle 11\bar{2}0 \rangle$  and  $\langle 10\bar{1}0 \rangle$ , greatly exceeding the differences in magnitude of Schmid orientation factors for the Py-2 systems, and ii) significant variation in the slope of the elastic parts of compression curves, not justified by the values of elastic constants of crystals. These features can be explained only with the assumption that plastic deformation takes place already in the preyielding stage (quasi-elastic stage), and that is realized by different amounts and / or by different types of pyramidal systems.

Such evidences were provided during systematic observations of slip traces carried out on Zn and Zn-Cu crystals, subjected to compression tests in the direction close to  $\langle 11\bar{2}0 \rangle$  in the temperature range 77-673K and 293-673K, respectively [27, 28]. They showed that the Py-2 systems may be accompanied by slip in the 1<sup>st</sup> order pyramidal systems (Py-1)  $\{10\bar{1}1\} \langle \bar{1}\bar{1}23 \rangle$ , and the simultaneous slip in both types of pyramidal systems (Py-2 + Py-1), occurring in the initial stage of plastic flow results in a strong strain hardening of the crystals. As a result, the compression curves present a stage of ‘quasi-elastic’ hardening (pre-yielding stage) and at certain range of temperatures there is an athermal dependence of macro-yielding stress (MYS) vs. deformation temperature. Moreover, it was found that the increase of Cu concentration strongly activates the Py-1 systems at elevated temperatures (up to 473K in ZnCu1.5%), while the transition from simultaneous slip Py-2 + Py-1 to the dominance of only two conjugate Py-2 systems leads to monotonic decrease of MYS with temperature [27].

The present work documents the influence of copper concentration on the plastic behavior of Zn-Cu crystals

at lower temperatures and proves the relationship of low temperature anomaly of work hardening with the changes in activity of two types pyramidal systems.

### 2. Experiment

The study was conducted on cylindrical ( $\varnothing 6$  mm x 9 mm) crystals of zinc with copper addition in amounts (in at.%) 0.11, 0.2, 0.5 0.9 and 1.5% obtained by Bridgman method at growth rate of  $0.85 \text{ cmh}^{-1}$ . Single crystals with initial orientation of  $\chi_o = 90^\circ$ ,  $\lambda_o = 3^\circ$  (where:  $\chi_o$ ,  $\lambda_o$  – the angle between the crystal axis and the directions  $[0001]$  and  $\langle 11\bar{2}0 \rangle$ , respectively) were used. All crystals were annealed at 623K for 10h and slowly cooled to ambient temperature. The crystals were chemically and electrolytically polished, and then compressed at initial rate of  $9 \times 10^{-4} \text{ s}^{-1}$  within the temperature range from 77K to 293K. Compression tests were carried out up to a total deformation of 10% on at least three crystals in any condition of deformation. Compression curves were fitted using parabolic dependence of compression stress vs. strain ( $\delta = k \varepsilon^n$ , where n – the strain hardening exponent). Identification of active slip systems was based on studies of topography of basal plane (0001) and close to prismatic ones  $\{10\bar{1}0\}$ . This allows for the determination of both the slip planes and shear vectors. Some results of slip markings observations carried out both at elevated temperatures (Zn and Zn-Cu crystals) and at lower temperatures (Zn crystals) were taken from the works [27, 28]. Figs. 1-3 show the compression curves, temperature dependence of flow stress and temperature dependence of the strain hardening exponent, respectively, while Figs. 4 and 5 contains the results of slip marking observations.

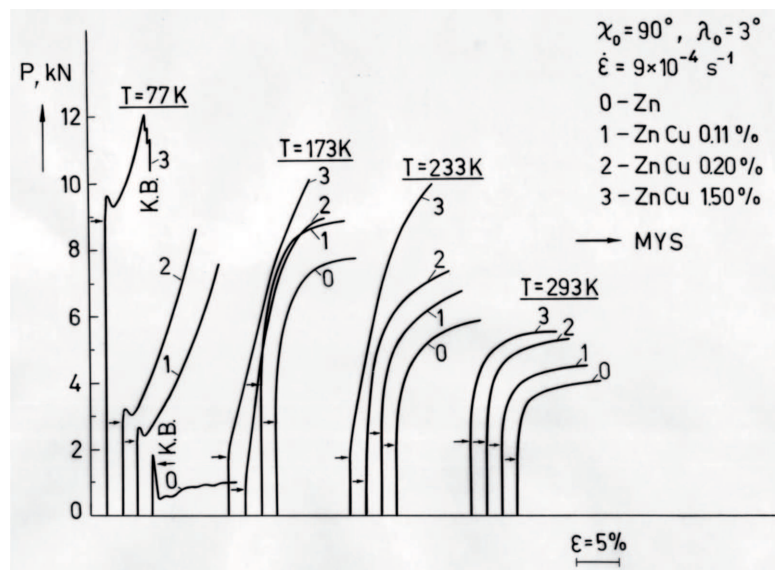


Fig. 1. Load-displacement curves for compressed Zn-Cu single crystals

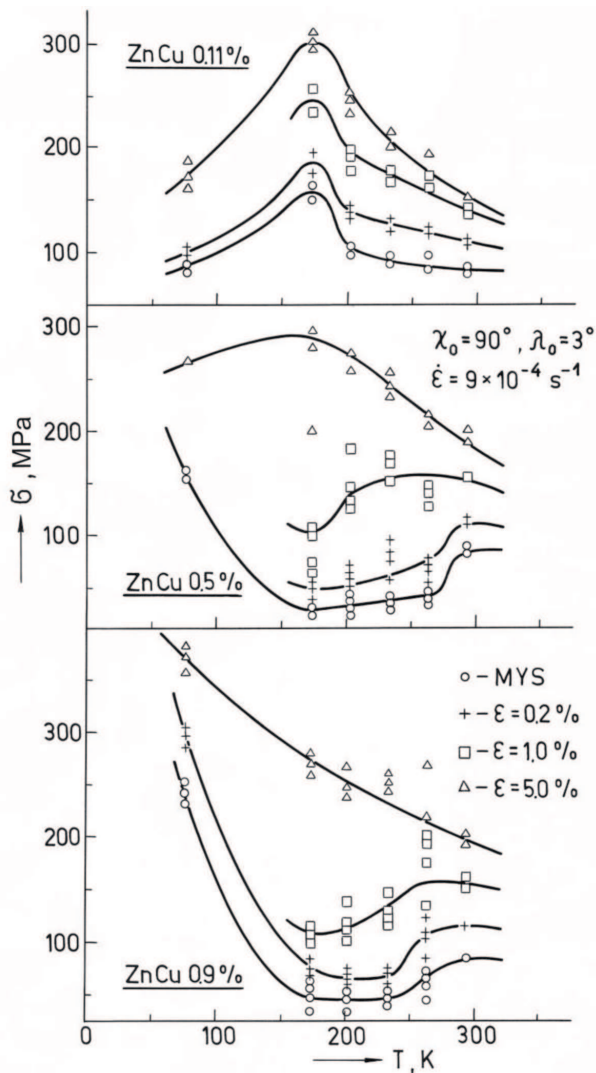


Fig. 2. Temperature dependence of the flow stress for compressed Zn-Cu single crystals

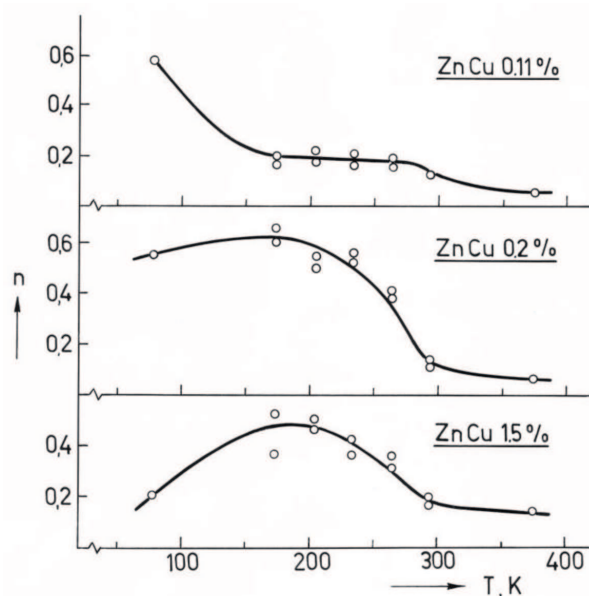


Fig. 3. Temperature dependence of the work hardening exponent for compressed Zn-Cu single crystals

### 3. Results

Surface observations of the compressed crystals showed that, as in previous works [27, 28], the plastic flow of crystals begins well below the macroscopic yield strength (MYS), corresponding to the end of the elastic range stress on compression curve and marked with arrows in Fig. 1. As a result, the magnitude of MYS is dependent on the amount and type of active slip systems in the quasi-elastic stage (preyielding stage) and is far overvalued in relation to the critical resolved shear stress for any nonbasal slip system.

Addition of copper causes a strong increase of MYS and flow stress of crystals at low temperatures (77K) and it has a relatively small effect, limited just to small concentrations of copper, at high temperatures (293K). At intermediate temperatures it diversifies both the course of the compression curves and the magnitude of MYS, as well as flow stress and the strain hardening exponent (Figs. 1-3).

#### 3.1. Temperature 77K

At the temperature 77K plastic deformation of all tested Zn-Cu single crystals is proceeded by slip in two conjugate Py-2 systems (Fig. 4, 5a,d). Propagation of Lüders-type slip bands front from the end faces of the crystal (contact surfaces with anvils) is accompanied by a 'yield point' (Fig. 1). It is worth to emphasize that along with the increase of copper concentration also the MYS of crystals strongly increases, while the strain hardening exponent of crystals in a homogeneous flow stage (the 'post-Lüders' stage) decreases drastically (Fig. 1-3). The latter effect was also observed in crystals deformed in Py-2 systems at high temperatures [28], but it is rather difficult to interpret physically. In case of highly alloyed crystals already after a few percent of strain (similarly as in pure zinc crystals in the preyielding stage [27]) there are significant load drops (Fig. 1), which are the result of the kink bands (K.B.) formation. Localized basal slip occurring within these bands is responsible for the formation and propagation of cracks along the basal planes, both in K.B. and in the matrix [27].

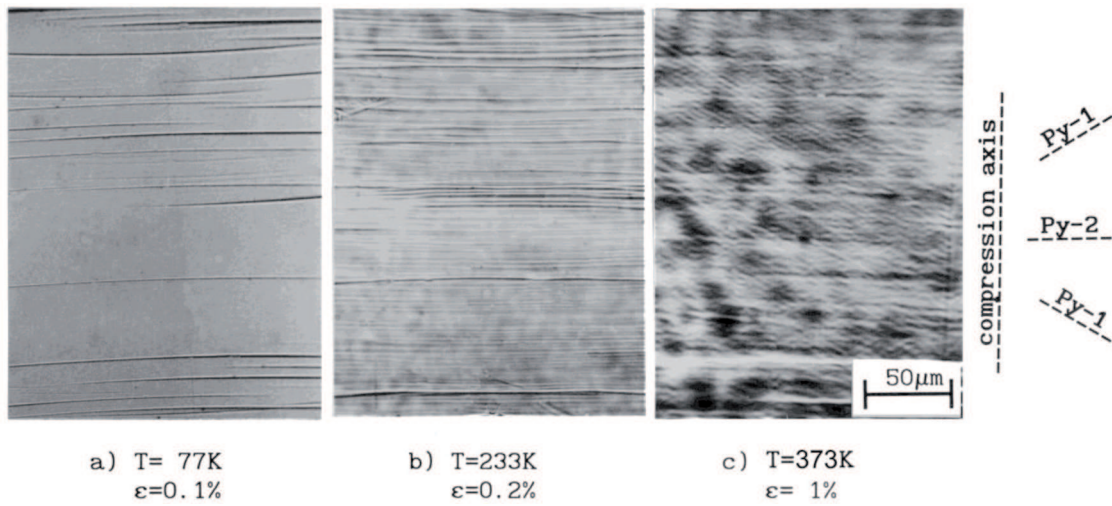


Fig. 4. Slip traces on (0001) planes for compressed ZnCu1.5% single crystals at early stage of deformation

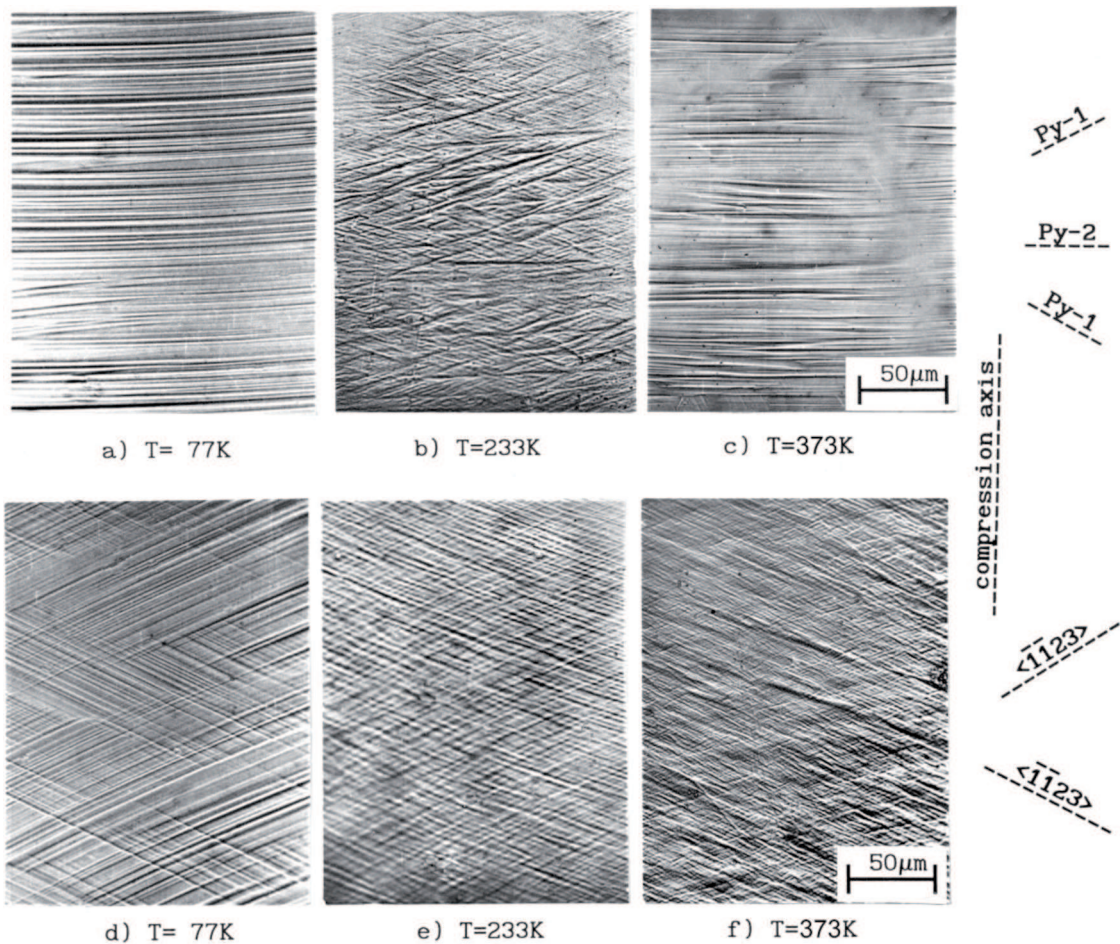


Fig. 5. Slip traces on (0001) (a-c) and on  $\sim\{10\bar{1}0\}$  (d-f) planes for ZnCu1.5% single crystals compressed up to  $\epsilon = 5\%$

**3.2. Temperature range from 173K to 203-233K**

Within this temperature range there is a drastic distinction of crystals deformation mechanism depending on copper concentration, temperature and strain.

Low-alloyed crystals (ZnCu0.11%) deform like pure Zn crystals, i.e. by simultaneous slip in the two types of pyramidal systems Py-2 + Py-1, and there are thick (especially at 173K) slip bands of the wavy character dominating in the structure [27]. MYS and the flow

stress shows a maximum at 173K and monotonically decreases with increasing deformation temperature. Strain hardening exponent of crystals is small ( $n \sim 0.2$ ) and almost independent of deformation temperature up to 293K (Figs. 2, 3). On the other hand, in crystals with higher copper concentrations the plastic flow in preyielding stage occurs (similarly as at 77K) by slip in two conjugate Py-2 systems. The higher copper addition the wider the temperature range of Py-2 systems activity is and for the ZnCu0.9-1.5% crystals reaches up to 233K (Fig. 4b). Slip in Py-2 systems is accompanied by a deep minimum of MYS vs. temperature dependence (Fig. 2). Activation of Py-1 systems occurs not earlier than at stresses above the MYS, in advanced plastic deformation stage (Fig. 5b,e) and causes a strong strain hardening of crystals (Fig. 3). Compression curves character is then almost linear (Fig. 1) and the exponent  $n$  has its maximum value at 173K and decreases monotonically with increasing copper concentration and temperature of deformation (Fig. 3).

### 3.3. Temperatures above 203-233K

At the temperatures above 203-233K just in preyielding stage the deformation of all crystals is carried out by slip in Py-2 systems accompanied by the activity of Py-1 systems (i.e. by Py-2 + Py-1 systems) (Fig. 4c) and then MYS of crystals with higher copper content than 0.11% gradually increases with deformation temperature to 293K and higher ones (Fig. 2) [28]. In advanced plastic stage the activity of Py-1 systems diminishes and the Py-2 systems are dominating (Fig. 5c,f). In low-alloyed crystals (like in crystals of pure Zn [27]) they are accompanied by the formation of fine K.B. in areas close to face of crystal, leading to buckling of samples, while the prevalence of one of these active Py-2 systems causes the obliquity of highly-alloyed crystals [28]. Both of these effects of shape instability are responsible for the apparent 'softening' of crystals at larger strains (Figs. 1, 3).

## 4. Analysis

Deformation temperature and the copper concentration control the plastic behavior of Zn-Cu single crystals in both the preyielding stage and the plastic stage by the type and sequence of activity of pyramidal slip systems. It was found that in the temperature range of 77K-293K plastic flow of compressed Zn-Cu crystals is realized by four mechanisms:

– slip in Py-2 systems, occurring in all crystals tested at 77K (Figs. 4a, 5a,d);

– simultaneous slip in two types pyramidal systems (Py-2 + Py-1) which is responsible for both the preyielding and the plastic stage of ZnCu0.11% crystals deformed in the temperature range of 173-293K;

– sequential slip (S-I) in pyramidal systems, i.e. Py-2 slip in preyielding stage and Py-2 + Py-1 slips in plastic stage only (ZnCu0.2-1.5% crystals in the temperature range from 173K to 203-233K) (Figs. 4b, 5b,e) and

– sequential slip (S-II), i.e. simultaneous slip in Py-2 + Py-1 systems in the preyielding stage and the subsequent domination of Py-2 systems in advanced plastic stage (all crystals tested at temperatures above 233K) (Figs. 4c, 5c,f).

Each of these mechanisms result in different plastic behaviour of tested crystals. The main features of the slip in Py-2 systems is that MYS is strongly dependent on the copper addition (at 77K) and temperature of deformation (especially for highly-alloyed crystals) and the strain hardening exponent drastically decreases with increasing of copper concentration. On the other hand, simultaneous slip in Py-2 + Py-1 systems which occurs in preyielding stage leads to high MYS. S-I sequential slip is characterized by low MYS and large strain hardening, and S-II sequential slip is accompanied by an increase of MYS and decrease of hardening (Figs. 1-3). Copper addition favors the activity of Py-2 systems and expands its temperature range of activity from 77K for ZnCu0.11% up to 233K for ZnCu1.5%. What is more, it causes that the activation of Py-1 systems occurs at higher strains and higher temperatures. This is the reason for the drastic variation of deformation mechanism of zinc crystals within the temperature range from 173K to 203-233K and consequently leads to the diversification of the compression curves and the course of MYS – deformation temperature dependence as well as of the strain hardening exponent (Figs. 1-3). When along with increase of deformation temperature the mechanism of plastic flow in preyielding stage changes from Py-2 slip to a slip in the two types (Py-2 + Py-1) pyramidal systems, an increase of yield stress and appearance of the anomaly of temperature dependence of MYS occurs. This change takes place in low-alloyed crystals in the temperature range of 77-173K, while in highly-alloyed crystals only above 233K (Fig. 2). The change of deformation mechanism in advanced plastic stage from the slip in Py-2 systems (at 77K) to a S-I sequential slip is responsible for the anomaly of temperature dependence of the strain hardening exponent (crystals containing at least 0.2% Cu) (Fig. 3). In case of low-alloyed crystals (ZnCu0.11%) the transition from Py-2 slip (at 77K) to Py-2 + Py-1 systems (at 173K and higher) leads to the anomaly of temperature dependence of flow stress (Fig. 2).

Obtained results provoke to ask a question about the source of different behaviors of alloyed zinc crystals, i.e. why is Cu so significantly changing the mechanism of plastic flow of Zn crystals at low temperatures, in particular, strongly favors the slip in the Py-2 systems and shifts the activation of Py-1 systems to higher temperatures.

It is known that the addition of Cu causes a significant increase of critical resolved shear stress in the basal system in Zn crystals ( $\sim 20$  times in ZnCu1.5% compared to pure Zn) [29]. For obvious reasons this feature may not be originated in the effect of solid solution strengthening (the difference of atomic radii of Zn and Cu does not exceed 4%). It has been proved that it is related to the strong influence of Cu concentration on the dislocation density in Zn crystals. For example, in ZnCu0.3% crystals the density of pyramidal screw dislocations was about two orders magnitude higher than in pure Zn [30].

A number of experiments carried out on carefully prepared pure Zn crystals indicated a very low density of Py-2 dislocations (of the order of  $10^3 \text{ cm}^{-2}$ ), for example: [12-19]. Moreover, with decreasing temperature the number of active sources of Py-2 dislocation as well as their mobility strongly decreases [19]. Thus it seems that it is these factors that may control the plastic behavior of Zn-Cu crystals in the initial stage of plastic flow. In such circumstances the plastic flow of pure Zn at 77K is at least difficult to be realized by pyramidal slip and in consequence it is achieved by the K.B. formation [27]. Gradual increase of density of pyramidal dislocations with increasing amount of Cu allows to realize the deformation by Py-2 systems for all tested crystals only at 77K, while for ones with higher concentration of Cu – also at 173K and at higher temperatures (up to 203-233K) in preyielding stage.

However, much more difficult to explain is the physical meaning of Py-1 systems in plastic flow of Zn-Cu crystals. In pure and low-alloyed (0.11%Cu) zinc crystals, its activity is present within wide range of temperatures (from 173K to 333-373K) in just preyielding stage [27, 28] and the increase of Cu concentration (increase of the pyramidal dislocations density) does not change this trend, but only moves the activity range of Py-1 system to higher temperatures. In each case the Py-1 slip accompanies the Py-2 systems, but its role changes with increase of deformation temperature and Cu addition. The wavy character of the thick slip lines observed in pure Zn (see Fig. 7 in [27]) and low-alloyed Zn crystals compressed at low temperatures suggests that the Py-1 slip systems are cross slip systems for the Py-2 dislocations (as suggested among others in [18]) or results from the 'pencil' glide in two type (Py-2 and Py-1) of

pyramidal systems. On the other hand, the straight, long and thin slip traces of Py-1 systems which one can see on surfaces of compressed pure Zn (Fig.7 in [27]) and Zn-Cu crystals (Fig. 4c) lead to the conclusion, that the Py-1 and Py-2 systems are then rather independent slip systems.

## 5. Conclusions

1. Copper concentration and deformation temperature determine the mechanism of plastic flow of zinc crystals by the type and sequence of activity of the 1<sup>st</sup> order  $\{10\bar{1}1\} < \bar{1}\bar{1}23 >$  (Py-1) and the 2<sup>nd</sup> order  $\{11\bar{2}2\} < \bar{1}\bar{1}23 >$  (Py-2) pyramidal slip systems.

2. The increase of copper concentration favors the slip in the Py-2 pyramidal systems, extends the temperature range of its activity and this leads to a strong diversification of the deformation mechanisms of zinc crystals.

3. The low-temperature plastic behaviour of compressed Zn-Cu single crystals is characterized by the appearance of the two anomalies: of the yield stress and of the work hardening exponent; both of them are connected with the change of deformation mechanisms.

4. The temperature anomaly of the yield stress is caused by transition from the Py-2 slip to simultaneous slip in two type pyramidal systems Py-2 + Py-1 occurring in the preyielding stage.

5. Anomaly of temperature dependence of the work hardening exponent (maximum at 173K) is a result of transition from Py-2 systems to Py-2 + Py-1 slips taking place in plastic stage.

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