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Elastic shape memory effect in In-Pb alloys in the temperature range 0.48–180 K

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Abstract: Pseudoelasticity caused by pseudotwinning in short-range ordered In-Pb alloys (6, 8 and 11.6 at. % Pb) is studied in the temperature range 0.48–180 K. The mechanical hysteresis parameters, namely, the thermodynamic stress τ_T which provides the reversibility of plastic deformation and the frictional stress τ_f which characterizes the resistance offered by crystal lattice and its defects to twin boundaries motion are estimated. It is found that athermal processes determine the reversible deformation: the mechanical parameters τ_T and τ_f do not depend on temperature and strain rate. The stress τ_T increases and the stress τ_f decreases with increasing Pb content. One of the main conditions of the exhibition of superelasticity is the fulfillment of the inequality $\tau_T > \tau_f$.

Keywords: In-Pb alloys, pseudoelasticity, pseudotwinning, mechanical hysteresis parameters, concentration dependence
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1 Introduction

In our previous studies [1] we found that single crystals of In-Pb alloys containing 6 and 8 at. % Pb at temperatures $T \leq 180$ K manifest the property of pseudoelasticity, i.e., reversibility of large plastic deformations. It was established that the pseudoelasticity effect in In-Pb alloys is unmistakably due to twinning and reversible motion of the boundaries of plane-parallel twin layers in them.

A preliminary study of diffuse X-ray scattering has indicated that these alloys are locally ordered solid solutions: a short-range order of the clusterization type is formed in

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them. As was shown by Cahn [2], twinning in ordered alloys, which occurs on systems which are characteristic for the disordered state, inevitably leads to the formation of pseudotwins having a crystal lattice structure different from that of the matrix. As a result, the chemical potential of a pseudotwin is higher than that of the matrix, and their difference determines the driving force — the thermodynamic stress τ_T that brings about the reverse process, untwinning, when the external load is removed.

Pseudotwinning is a special type of martensitic transformation taking place under stress. Hence, a pseudotwin can be considered as a stress-assisted martensite, and pseudoelasticity as an elastic shape memory effect. At the same time, pseudotwinning cannot be initiated with temperature change as in the usual martensitic transformation. Therefore, a shape memory effect is impossible to observe in In-Pb alloys.

The motion of twin boundaries both during twinning and during untwinning is resisted by a frictional force due to potential barriers created by the crystal lattice and its defects. On loading, the external stress τ is directed so as to overcome the thermodynamic stress τ_T and the frictional stress τ_f. During unloading, the reverse motion of the twin boundaries occurs under the influence of the thermodynamic stress, which counteracts the frictional stress and the external stress. It follows that the stresses for the onset of twinning τ_t and untwinning τ_u can be written in the known form [3, 4]

$$\tau_t = \tau_T + \tau_f, \tag{1}$$

$$\tau_u = \tau_T - \tau_f. \tag{2}$$

Relations (1) and (2) can be applied to describe the twinning and untwinning processes occurring in the absence of hardening. Fig. 1 shows a diagram of an idealized hysteresis

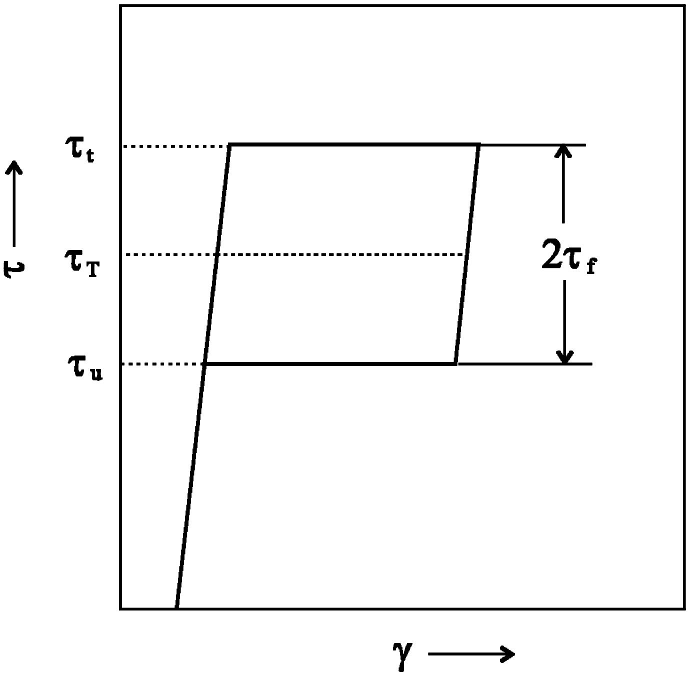

Fig. 1 Diagram of an idealized stress versus strain loop for a pseudoelastic crystal.

loop in coordinates "shear stress τ-shear strain "γ." According to (2), the reverse motion of the twin boundaries during unloading can occur only under the inequality

$$\tau_T > \tau_f. \qquad (3)$$

Apparently, it is condition (3) that is the criterion for the appearance of the pseudoelasticity effect in many alloys. In this paper we report a comprehensive study of deformation properties of In-Pb alloys for four values of the Pb concentration: 3.5, 6, 8, and 11.6 at. %. For each alloy the values of τ_T and τ_f are obtained, and the influence of temperature and strain rate on them is investigated. The temperature-concentration map of the deformation modes of the alloys is constructed, and the nature of the low-temperature pseudoelasticity of the alloys is discussed.

2 Experimental method

Four In-Pb alloys containing 3.5, 6, 8, and 11.6 at. % Pb (the maximum lead solubility is about 12 at. %) were prepared using 99.999 wt. % pure materials. Single crystals of size $5 \times 5 \times 50$ mm^3 were grown by a modified Bridgeman method in a knock-down graphite form. From these, samples of 15 mm height were prepared by acid sawing. Before experimentation, the ends and faces of the samples were polished chemically in a mixture of 30 percent hydroxide with nitric and hydrochloric acids.

The dislocation density was estimated by X-ray line broadening [5, 6]. In addition, an etching method was used [7]. Both methods showed that the average growth dislocation density in the crystals was about 10^7 cm^{-2}.

The crystal axis was [001] and the lateral faces were parallel to the crystallographic planes (100) and (010). The crystal orientation provided maximum shear stress with a Schmid factor of $S \backsim 0.5$ in four equivalent twinning systems of $(011)[01\bar{1}]$, $(1\bar{1}1)[0\bar{1}\bar{1}]$, $(101)[10\bar{1}]$, and $(\bar{1}01)[\bar{1}0\bar{1}]$ at uniaxial compression.

Compression tests were performed at the temperature 0.48 K with a special machine for the sub-Kelvin temperature range [8], and at temperatures between 1.7 K and 300 K on an MRK-1 strain-testing machine. Both machines were constructed at the B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, Kharkov. The experiments were conducted at a shear strain rate in the twinning system $\dot{\gamma}$ of between 10^{-5} s^{-1} and 10^{-2} s^{-1}.

The strain curves were recorded simultaneously on two chart recorders: a KSP-4 in load versus loading time coordinates, and a PDP-4 as load versus diplacement of the rod of the strain-testing machine.

The plastic deformation of the crystals occurred exclusively by twinning. Although all four of the twinning systems were equally loaded, usually one or two systems were actively operating. By contrast, specimens of In and In-Pb alloys with concentration less then 1 at. % Pb deformed primarily by slip everywhere over the temperature range [9].

3 Experimental results and discussion

3.1 Shape of the hysteresis loops

Fig. 2*a* shows a nearly ideal hysteresis loop for one of the highly perfect alloy samples with 8 at. % Pb at $T = 77$ K. For the given sample, $\tau_T = 0.62$ MPa and $\tau_f = 0.06$ MPa, so that inequality (3) holds.

Frictional stress is a structure-sensitive quantity. The lower the perfection of the initial structure of the sample, the greater the frictional stress, and it increases with increasing density of deformation defects (perfect dislocations, microtwins, twins, and so on). Fig. 2*b* shows a hysteresis loop for another alloy sample with the same Pb concentration, but less perfect in respect to its initial microstructure. The value of the stress τ_T did not change, but the frictional stress τ_f increased substantially: $\tau_T = 0.62$ MPa and $\tau_f = 0.22$ MPa.

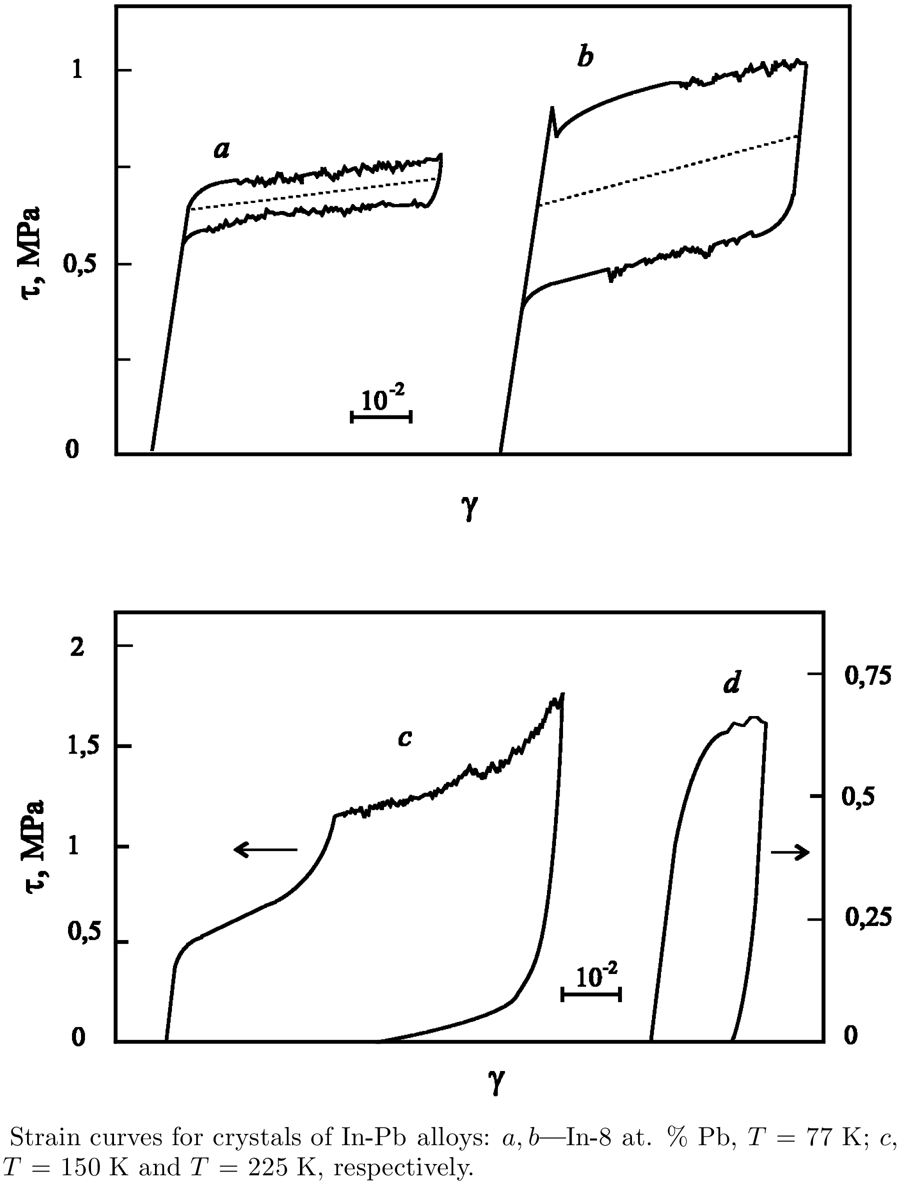

Fig. 2 Strain curves for crystals of In-Pb alloys: *a*, *b*—In-8 at. % Pb, $T = 77$ K; *c*, *d*—In-6 at. % Pb, $T = 150$ K and $T = 225$ K, respectively.

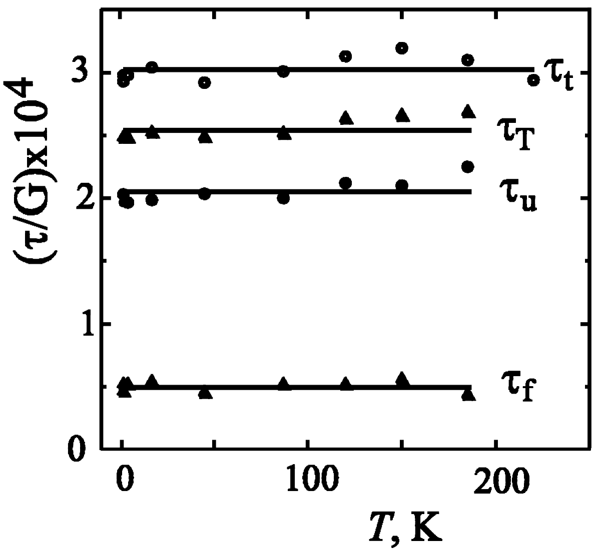

Fig. 3 Temperature dependence of the stresses τ_t, τ_u, τ_T, and τ_f, all normalized by shear modulus in the twinning system, for crystals of alloy In-8 at. % Pb.

The difference in the values of τ_f may be attributed to the different density of growth dislocations (see Section 3.5). Nevertheless, inequality (3) holds for the second sample too, so that the deformation remains completely reversible.

Fig. 2*c* shows an example of a hysteresis loop with a partially reversible deformation for a sample of the alloy In-6 at. % Pb which was subjected to multiple cyclic deformation. As a result of the cyclic deformation, the area of hysteresis loop increased greatly, and the shape of the loop was distorted. The large fraction of irreversible deformation indicates the violation of inequality (3).

3.2 Influence of temperature

Fig. 3 shows the temperature dependence of the stress (normalized by the shear modulus G) for the onset of twinning and untwinning for the In-8 at. % Pb alloy [10]. The values of τ_t and τ_u were obtained on the same sample by multiple loading and unloading at different temperatures. We see that for $T \leq 180$ K, the nucleation of twins and their emergence from the crystals are determined by factors which are insensitive to the testing temperature. Fig. 3 also shows the values of τ_T and τ_f calculated with the use of relations (1) and (2). The insensitivity of the stresses τ_t and τ_u to temperature is equivalent to the absence of temperature dependence in the quantities to be calculated, τ_T and τ_f. For the alloys In-6 at. % Pb [10] and In-11.6 at.% Pb, the values of the stresses τ_t and τ_u at $T \leq 180$ K are also independent of the testing temperature.

As we have said, the pseudoelastic behavior of In-Pb alloys is observed only for $T \leq 180$ K. At higher temperatures $T \geq 225$ K the twins remain in the crystal even after the load is removed, so that all of the deformation introduced in the crystal is irreversible (see Fig. 2*d*). The suppression of the pseudoelasticity effect at higher temperatures is due to the activation of diffusion processes, which promote the restoration of the equilibrium local atomic order that has been disrupted by the twinning shear: this results in a sharp decline in the thermodynamic stress τ_T with increasing temperature and increasing hold time of the sample under load.

In terms of the character of the influence of temperature on thermodynamic stress τ_T, the pseudoelasticity due to pseudotwinning is markedly different from the pseudoelasticity due to the formation of the stress-induced martensite. In the latter case, the stress of formation of the martensite and the matrix phase in the martensite and, hence, τ_T depend linearly on temperature and go to zero at temperatures at which the direct and inverse martensitic transformations begin [11]. The constancy of τ_T in In-Pb alloys for $T \leq 180$ K indicates that the phenomenon studied here does not belong to the class of ordinary martensitic transformation: the pseudotwinning discussed here is a special form of martensitic transformation which occurs only under an external load and cannot be caused by a change in temperature.

3.3 Influence of the strain rate

The jumplike change in the strain rate in the interval $10^{-5}\,\mathrm{s}^{-1} < \dot{\gamma} < 10^{-2}\,\mathrm{s}^{-1}$ during the deformation of samples of pseudoelastic In-Pb alloys at $T \leq 180$ K is not noticeably reflected on the $\tau - \gamma$ strain curve: neither the jumps nor the kinks characteristic of deformation by slip are observed. The parameters τ_t, τ_u, τ_T, and τ_f of the hysteresis loops likewise are insensitive to the strain rate. This finding agrees with the absence of temperature dependence of these parameters, with the presence of only an instantaneous creep during stepwise loading of the sample, and with the absence of stress relaxation when the strain testing machine is turned off [10]. The absence of rate dependence of the parameter τ_f means that the resistance to twinning deformation at low rates is of the nature of dry friction.

It is only in the region of pseudoelastic behaviour, i.e., for $T \leq 180$ K, that the strain rate does not have a noticeable influence on the deformation parameters of In-Pb alloys. For temperatures at which diffusion processes are activated, the strain rate can play a critical role in the appearance of the pseudoelasticity effect. For example, by going to shock loading, in which the sample is in the loaded state for approximately 30 μs, it has been possible to observe the pseudoelastic deformation at room temperature. The reason is that even at high temperature there is insufficient time during the brief loading for the equilibrium atomic order, disrupted by twinning, to be restored in the twin.

3.4 Influence of Pb concentration

The parameters of the mechanical hysteresis were found for alloys of three concentrations: 6, 8, and 11.6 at. % Pb; these data are presented in Fig. 4. We see that the thermodynamic stress increases linearly with increasing Pb concentration, while the frictional stress decreases. For the alloy with 3.5 at. % Pb, the thermodynamic stress was found by extrapolation of the $\tau_T(c)$ curve to the region of low concentrations (Fig. 4), while the frictional stress τ_f was determined as the difference between the stress for the onset of twinning and τ_T. It was found that for pseudoelastic In-Pb alloys with 6, 8, and 11.6 at. % Pb, inequality (3) is well satisfied, especially for the alloys with 8 and 11.6 at. % Pb. With decreasing lead concentration, the difference between these two stresses decreases because of a decrease in τ_T and an increase in τ_f. Finally for the alloy with 3.5 at.% Pb, there is approximate equality of τ_T and τ_f, leading to suppression of the pseudoelastic effect.

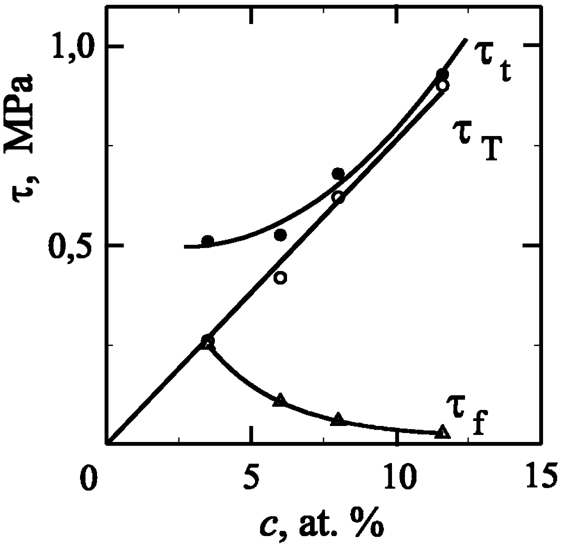

Fig. 4 Concentration dependence of the stresses τ_t, τ_T, and τ_f for In-Pb crystals at temperature $T = 77$ K.

In alloys with lead concentration $c \leq 3.5$ at. % Pb, twinning acquires the usual irreversible character, remaining the advantageous type of plastic deformation for favorably oriented crystals up to $c \simeq 1$ at. %. Further decrease in lead concentration brings about the transition from advantageous twinning to advantageous slip [9].

The results regarding the influence of temperature and lead concentration on the type and parameters of plastic deformation of In-Pb alloys obtained in this investigation and in [9] are summarized in Fig. 5 and Fig. 6. Fig. 5 shows the results obtained as a temperature-concentration map where the regions of the manifestation of a single type of deformation are indicated. The map was constructed for samples oriented favorably for twin shear and deformed at low strain rates of about 10^{-4} s^{-1} . The quantitative characteristics of the different deformation modes in relation to the Pb concentration are shwon in Fig. 6.

It should be noted that the region indicated as corresponding to pseudotwinning is fairly conventional. This region was identified as the region of manifestation of pseudoelasticity. Determination of this region from other evidence is impossible. Strictly speaking, in any ordered alloy, twin shear brings pseudotwin formation, but we can ignore this if the value of the thermodynamic stress τ_T is small and thus consider the deformation process as common simple twinning.

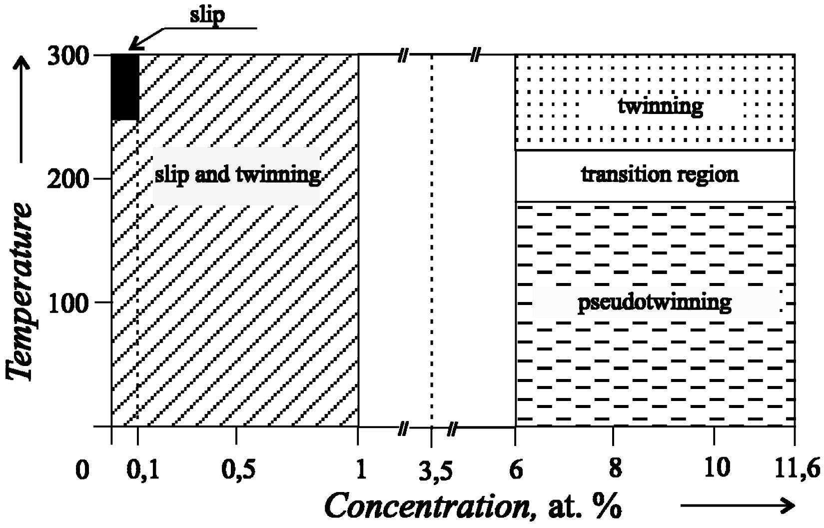

Fig. 5 Temperature-concentration map of the deformation modes for single crystals of In-Pb alloys. The compression axis is [001], and the unresolved strain rates are $\dot{\varepsilon} \leq 10^{-4}$ s^{-1}.

3.5 Nature of the athermality of low-temperature pseudoelastic deformation in In-Pb alloys

Undoubtedly, the question of origin for the two parameters of mechanical hysteresis, namely, thermodynamic stress and frictional stress, which determine the pseudoelastic behaviour of In-Pb alloys over a wide range of temperatures and concentrations is principal in discussion of the peculiar feature of plasticity of these alloys.

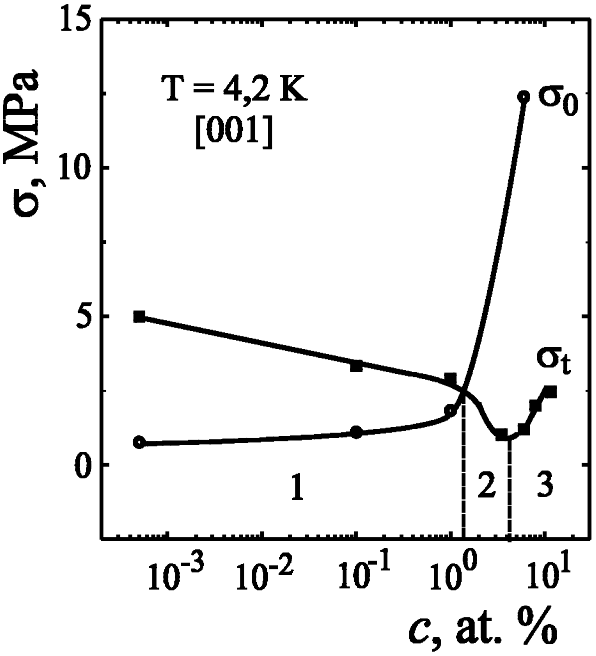

Fig. 6 Concentration dependencies of the yield stress by slip σ_0, and the stress of the onset of twinning σ_t for single crystals of In-Pb alloys with [001] compression axis and at temperature $T = 4.2$ K in semilogarithmic coordinates. Here σ is an unresolved compression stress; 1, 2, and 3 are the regions of the manifestation of slip, twinning, and pseudotwinning, respectively.

The thermodynamic stress generated by the disruption of the equilibrium atomic order as a result of a twinning shear in a locally ordered In-Pb alloy is uniquely determined by the degree of this order, which, as is shown by both theory and experiment, depends on the temperature. However, for many alloys, the degree of short-range order remains unchanged over a wide range of temperature. In the case of In-Pb alloys, the temperature independence of the thermodynamic stress may indicate either that the equilibrium order parameter is independent of temperature, or that the diffusion processes are frozen out. Below a certain temperature the diffusional relaxation time of the order parameter can turn out to be longer than the characteristic laboratory time, and a "frozen" order, established at higher temperatures, will be manifested in the low-temperature region.

In the absence of thermodynamic stress τ_T, the frictional stress τ_f will play the role of the yield stress for the twinning process. The frictional stress may be represented as a sum of two components: an athermal component due to the long-range internal stresses, and a temperature-dependent component due to resistance to the motion of the twin boundary by barriers of an atomic scale — Peierls relief, impurities, etc. It is natural to assume that the main component of the long-range internal stresses in the initial samples comes from perfect growth dislocations. This part of the athermal component of the frictional stress can be calculated by the formula [12]

$$\tau_{fd} = \alpha G b \rho^{1/2}, \tag{4}$$

where G is the shear modulus, b is the modulus of the Burgers vector, ρ is the density of growth dislocations, and α is a constant of the order of 0.2, the exact value of which depends on the specifics of the distribution of the dislocations. The stress τ_{fd} can increase substantially during cyclic deformation of a sample, as fresh dislocations arising in the cycling process accumulate in it.

The temperature-dependent component of the frictional stress has been calculated theoretically for the case when the expansion of the twin layer is governed by the motion of twinning dislocations [13]. The influence of temperature turned out to be different depending on the character of the motion of twinning dislocations. In the case of high-speed (above-barrier) motion of the boundaries, the frictional stress increases with increasing temperature in accordance with the temperature dependence of the coefficient of viscous drag of dislocations. In the thermally activated motion of twinning dislocations with extremely low velocities, the frictional stress to a first approximation varies in proportion to the temperature. Strong temperature dependence of the frictional force observed in the case of elastic twinning of perfect calcite crystals with a density of perfect dislocations $\rho \sim 10^2$ cm^{-2} is due to the overcoming of the Peierls potential relief by the twinning dislocations [14]. For fcc crystals, the Peierls stresses are typically low—hence for In-Pb crystals which have lattice close to fcc, this frictional component can apparently be neglected.

The twinning process consists primarily of the nucleation of twinning dislocations and their subsequent motion in the twinning plane. The fact that in the case of In-Pb alloys the frictional stress at $T \leq 180$ K turns out to be insensitive to temperature variations (see Fig. 3) and the strain rate means that under these conditions, the main part of τ_f is the long-range component, and the factor governing the twinning process is the athermal nucleation of twinning dislocations. An estimate of the frictional stress in In-Pb alloys according to formula (4) for $\alpha = 0.2$ and the typical density of growth dislocations for these alloys, $\rho \sim 10^7$ cm^{-2}, gives a value close to the measured value ($\tau_{fd} \simeq 0.06$ MPa, Fig. 4). A contribution of perfect growth dislocations to frictional stress has also been observed in calcite crystals with a high density of perfect dislocations, $\rho \sim 10^4$ cm^{-2} [14].

Analysis of the curves of $\tau_T(c)$ and $\tau_f(c)$ obtained for the In-Pb alloys affords the possibility of refining the microscopic nature of the parameters under study. The thermodynamic stress τ_T is determined by the degree of ordering of the alloy and for this reason depends on the concentration of the doping element. According to [15], the degree of short-range order increases linearly with increasing c in a certain interval of concentrations. This finds confirmation in our experiments (Fig. 4) if it is assumed that τ_T is to a first approximation proportional to the degree of local order. Moreover, with increasing lead concentration, the frictional stress τ_f decreases (Fig. 4). This means that impurity defects give an insignificant contribution to the frictional stress, but the presence of impurity complexes apparently promotes the nucleation of twinning dislocations.

As to the perfect dislocations, their initial density, and also the density of dislocations arising in the sample during the stage of microdeformation by slip, should decrease with increasing lead concentration together with the increase in the yield stress for deformation by slip. Thus the results obtained argue in favor of the hypothesis of a dislocation nature of the frictional force τ_f in the pseudotwinning of In-Pb single crystals.

In conclusion, it is worthy of note that the realization of the different types of plastic deformation (slip, twinning, and pseudotwinning) depending on Pb concentration, sample geometry, and external conditions makes In-Pb alloys particularly attractive in investigations of the mechanisms of plasticity of crystals.

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