Thermal Recovery and Stress-Strain Relation of Polycrystalline Zinc*

By Kichinosuke TANAKA** and Kinya OGAMA***

Thermal recovery and its effects on the stress-strain relations of polycrystalline zinc have been investigated experimentally. Specimens were pretrained in compression at a certain temperature and under several constant strain rates, and annealed isothermally. Results obtained are summarized as follows. (1) During both the static and the dynamic deformations at -195°C, no detectable thermal recovery occurs. (2) At -195°C, the stress-strain relation is able to be determined only by the strain rate at the time within the strain rate range of $10^{-4}/s$ to $10^{-3}/s$ and does not depend upon the strain rate history. (3) The activation energy obtained for thermal recovery is about $(10\pm12)$ kcal/mol and this value corresponds to the migration energy of vacancies produced during the plastic deformation.

1. Introduction

Temperature and strain rate effects upon the strength of polycrystalline zinc have been studied by many investigators. Seeger suggested that the flow stress of metals consists of the thermal and the athermal components. In general, there are various kinds of thermal mechanisms as well as the athermal ones. In fact, the steady state creep is rationalized in terms of competition of two kinds of thermal mechanisms, i.e., the work hardening due to the plastic deformation and the softening through the thermal recovery. Dorn et al. clarified that the diffusion process is a thermally activated mechanism and controls the strength of metals at high temperatures. When the work hardening and the thermal recovery operate simultaneously, the thermal components of the flow stress are affected by two kinds of thermally activated mechanisms, one being the thermal recovery and the other the work hardening.

Polycrystalline zinc can plastically deform by basal slip, non-basal slip and mechanical twinning. To discuss the stress-strain relations, it is necessary to clarify the temperature and the strain rate range where each mechanism takes place. The effect of the temperature on the strength of polycrystalline zinc must be rationalized in terms of the influences of the recovery and the work hardening.

From the metallurgical points of view, the thermal recovery has been investigated by the measurements of the stored energy using a calorimeter and of the change of the electrical resistivity. The correspondence of various kinds of thermal recovery processes to the annihilation and the rearrangement of point defects, dislocations and surface defects has been studied and the amounts of the activation energies for each process have been evaluated. The thermal recovery has been also examined by measurements of the changes of the hardness and the flow stress due to isothermal or isochronal annealing.

In the present paper, the thermal recovery and its effects upon the stress-strain relations of polycrystalline zinc are investigated and are discussed from the metallurgical point of view.

2. Material and Experimental Procedure

Cylindrical specimens of 40mm in length were cut from a cast dendritic zinc bar of 15mm in diameter. The chemical composition of the material is shown in Table 1. They were statically deformed in compression up to about 10% strain at 120°C, machined to specimens of 8mm in diameter and 6mm in length and annealed at 180°C for 30 minutes. Two kinds of average grain diameters shown in Table 2 were obtained by two different heating and cooling rates. Experimental conditions are also tabulated in Table 2.

By using an Instron testing machine and a Hopkinson split pressure bar apparatus, two kinds of compression tests were carried out at -195°C. The strain

<table>
<thead>
<tr>
<th>Table 1 Chemical composition of the material (%)</th>
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<tr>
<td>Sn</td>
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<td>99.99</td>
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rate is $10^7/\text{s}$ and $(3\times10^2)/\text{s}$, respectively. The stress-strain relations unaffected by thermal recovery - the reference stress-strain relations, were obtained. After plastically compressed at $-195^\circ\text{C}$ and at the strain rate of $10^7/\text{s}$ up to a true strain of about 8% or 1%, or compressed at $-195^\circ\text{C}$ and at $(3\times10^2)/\text{s}$ up to a true strain of about 7% or 12%, specimens were isothermally annealed in the range of temperatures from $-160^\circ\text{C}$ to $10^\circ\text{C}$, and were deformed again at the initial conditions. The required annealing temperature is usually attained after 10 seconds. On the other hand, it takes about 30-40 seconds to change the temperature from the annealing temperature to $-195^\circ\text{C}$. Annealing temperatures are measured with Alumel-Chromel thermocouples and are controlled to the required values within $\pm 1^\circ\text{C}$. The coolants used are tabulated in Table 3.

3. Experimental Results and Consideration

3.1. Definition of the amount of thermal recovery

It is assumed that the true stress-true strain relation which is unaffected by thermal recovery during the plastic deformation can be obtained at a given temperature $T_0$ at and at a given strain rate $\dot{\epsilon}_0$. As is shown in Fig.1, specimens are compressed up to the point A of the stress $\bar{\sigma}_m$ (the strain $\bar{\epsilon}_m$) on the $\bar{\sigma}$-$\bar{\epsilon}$ curve and are unloaded to the point B. The specimens are annealed isothermally at $T_0$ and then are deformed again at $T_0$ and $\dot{\epsilon}_0$.

With the stress-strain relations obtained before and after annealing, the apparent recovery ratio $P$ may be defined as follows:

$$P = (\bar{\sigma}_m - \bar{\sigma}_1)/(\bar{\sigma}_m - \bar{\sigma}_0) = 1 - (\bar{\sigma}_1 - \bar{\sigma}_0)/(\bar{\sigma}_m - \bar{\sigma}_0) \quad (1)$$

$\bar{\sigma}_0$ is the amount of true stress when the $\bar{\sigma}$-$\bar{\epsilon}$ curve is extrapolated to zero plastic strain and $\bar{\sigma}_1$ is the true stress corresponding to the nominal stress $\sigma_1$, which is obtained when the nominal stress-(nominal strain) relation obtained after annealing is extrapolated to the unloading line.

In general, the internal structure $St(\bar{\sigma}_m, \bar{\epsilon}_m)$ at the stress $\bar{\sigma}_m$ (the strain $\bar{\epsilon}_m$) may be different from other internal structures $St(\bar{\sigma}_1, \bar{\epsilon}_m)$ through the thermal recovery. When the internal structure $St(\bar{\sigma}_1, \bar{\epsilon}_m)$ coincides with $St(\bar{\sigma}_m, \bar{\epsilon}_m)$, it is supposed that the internal structure obtained by the thermal recovery can be also realized by the work hardening. This kind of recovery may be termed the true recovery. When the amounts of the stress $\bar{\sigma}$ and the work hardening rate $\bar{\sigma}/\bar{\epsilon}$ at a certain strain are the same as those obtained at a different strain under the same temperature and the same strain rate, two internal structures at these points are assumed to be identical. The assumption that the identical internal structure may be realized at a different strain means that the whole amount of the plastic strain does not contribute to the internal structure. In this paper we assume that the plastic strain consists of the effective strain which contributes to the internal structure and of the strain which does not contribute to the internal structure.

The thermal recovery is a thermally activated process and the rate of the recovery ratio is expressed as follows:

$$d\bar{\sigma}/dt = f(\bar{\sigma}) \exp(-Q_0/\kappa T) \quad (2)$$

<table>
<thead>
<tr>
<th>Grain Diameter</th>
<th>Experimental Condition</th>
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<tr>
<td>0.21 mm</td>
<td>Prestrain of 8% at $-195^\circ\text{C}$ and $10^7/\text{s}$, Isothermal annealing, Deformed at $-195^\circ\text{C}$ and $10^7/\text{s}$</td>
</tr>
<tr>
<td>0.45 mm</td>
<td>Prestrain of 14% at $-195^\circ\text{C}$ and $3\times10^7/\text{s}$, Isothermal annealing, Deformed at $-195^\circ\text{C}$ and $3\times10^7/\text{s}$</td>
</tr>
</tbody>
</table>

Table 3 Coolants and annealing temperatures

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Liq. N₂</th>
<th>Liq. N₂</th>
<th>Liq. N₂</th>
<th>Dry ice, Ethyl alcohol</th>
<th>NaCl + CaCl₂ + Ice</th>
<th>NaCl + Ice</th>
<th>Ice Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$-195^\circ\text{C}$</td>
<td>$-190^\circ\text{C}$</td>
<td>$-110^\circ\text{C}$</td>
<td>$-70^\circ\text{C}$</td>
<td>$-10^\circ\text{C}$</td>
<td>$-10^\circ\text{C}$</td>
<td>$0^\circ\text{C}$</td>
</tr>
</tbody>
</table>
where $S$ is the true recovery ratio, $Q_s$ the activation energy of the true recovery, $k$ the Boltzmann constant, $T$ the annealing temperature in °K and $t$ the time. When the relation between $S$ and $P$ is given as

$$S = g(P),$$

the equation (2) is transformed as follows.

$$\frac{dS}{dt} = f(g(P)) \exp(-Q_s/kT)$$

$$\therefore \frac{dP}{dt} = \frac{1}{(dQ/dP)}f(g(P))\exp(-Q_s/kT)$$

$$= F(P)\exp(-Q_s/kT)$$

If $Q_s$ is independent of $P$, the following relation is obtained.

$$G(P) = \ln t - Q_s/kT$$

where

$$G(P) = \ln \left(1/F(P)\right)$$

Therefore, $Q_s$ is evaluated from the $t-(1/T)$ relation at a given value of $P$. $Q_s$ and $G(P)$ are functions of strain and strain rate and $Q_s$ may be a constant in the given temperature range.

When the same value of the work hardening rate $dS/dE$ is obtained both at $(G_1, E_1)$ and $(G_2, E_2)$, the apparent recovery ratio $P$ indicates the true recovery ratio $S$ and the equation (2) can be rewritten as

$$\frac{dP}{dt} = f(P)\exp(-Q_s/kT)$$

3.2. Experimental Results (In the case that the stress-strain relation at -195°C and at the strain rate of 10⁻⁷/s is adopted as the reference stress-strain relation)

Fig. 2 represents the behaviours of the stress-strain relations at -195°C and -72°C obtained by cyclic abrupt strain rate change where the strain rate is changed repeatedly from 10⁻⁷/s to 10⁻⁷/s and from 10⁻⁷/s to 10⁻⁷/s and from 10⁻⁷/s to 10⁻⁷/s.

To evaluate the recovery ratio $P$ exactly, it is confirmed that when the specimens were compressed up to various amounts of the flow stress, unloaded to zero stress and kept at -195°C for 8 hours, they maintained the same flow stress to begin the proceeding deformation. Furthermore, it is also confirmed by the abrupt strain rate change tests at -195°C that the stress-strain relation is not affected by the thermal recovery as is shown in Fig. 2. The stress-strain relation is able to be determined only by the stress strain rate and the internal structure is independent of the strain rate history. Seeger suggested that the reversible stress change may be caused by a thermally activated mechanism. The thermal recovery may generally be caused by a decrease in the number of some kinds of defects which induce the work hardening. These defects may increase with an increase of the stress and the strain. The fact that the stress-strain relation at -195°C is independent of the strain rate history means that the internal structure is not influenced by the strain rate history even though the plastic deformation increases due to the increase of defects. It may be concluded that the thermal recovery does not occur at -195°C and at 10⁻⁷/s.

The stress-strain relation obtained at -72°C is affected by the strain rate history. The irreversible stress change may correspond to the change of the internal structure. In other words, if the number of defects changes with the time and the recovery rate depends upon the stress and the strain, the stress-strain relations are influenced by the softening due to the thermal recovery and the strain rate history produces a gradual change of the stress with the change of the strain rate.

Fig. 3 represents the residual recovery ratio (1-P) to the annealing temperature relation obtained by annealing for 10 minutes. It is interesting that the residual recovery ratio decreases linearly with an increase of the annealing temperature except at low temperatures.

Figs. 4 and 5 show the examples of the stress-strain curves obtained under the following condition. The specimens deformed up to 8% of true strain at -195°C were

![Fig. 2 The stress-strain relations with an abrupt strain rate change](image)

![Fig. 3 The relation between the residual recovery ratio and the annealing temperature (annealed for 10 minutes)](image)
annealed isothermally at -72°C and -19°C, respectively, and were deformed again at
-195°C. In these figures, the broken lines indicate the (nominal stress)-(nominal
strain) relation and the full lines indicate the (true stress)-(true strain) relation. Solid
circles represent the values of the nominal stress and the nominal
strain which are obtained by extrap-
olating the reloading (nominal stress)-(nominal
strain) relation to the unloading
line, and open circles represent the values of the true stress and the nominal strain.
Fig. 6 shows the stress-strain relations
when the specimens were prestrained up to
14% true strain and were annealed at -45°C.

In Figs. 4, 5, 6, it can be seen that the
work hardening rate obtained at the yield
stress on the reloading stress-strain curve coincides approximately with that at
the same stress on the reference stress-strain
curve. The stress-strain curves at -195°C
have a nearly constant work hardening rate of
up to about 10% strain and are not affected
by the thermal recovery, while at strain
more than about 10% the work hardening
rate decreases remarkably.

Dynamic recovery during the plastic
deformation may be caused by the cross-slip
of screw dislocations or by the climbing
of edge dislocations, and the cross-slip
mechanism is relatively sensitive to the
stress, but the climbing one is not so sen-
sic. Therefore, when the decrease in
the work hardening rate is due to the
dynamic recovery, the mechanism may be the
cross-slip of screw dislocations. There
is a possibility that the behaviour is
related to the operation of other slip
systems or different kinds of deformation
mechanisms. On the other hand, the ther-
mal recovery proceeding at the unloaded
state may be caused by the climbing of the
dislocations rather than the cross-
slip of the screw dislocations.

Figs. 7 and 8 show the relations be-
tween the residual recovery ratio and the
annealing time at 8% and 14% true strain,
respectively. For the basal slip of zinc
single crystals, it was demonstrated that
the thermal recovery occurred at higher
temperatures than -30°C, while in the pres-
ent experiment on polycrystalline zinc,
the thermal recovery is detected even at
-116°C for 8% strain and at -160°C for 14%
strain. Mashima et al. reported that
notable thermal recovery was detected in
the case of the operation of multiple slip
rather than of single slip. Therefore, it
is reasonable to consider that the thermal
recovery of polycrystalline zinc occurs
extensively rather than that of single
crystals, because multiple slip such as

\[
\frac{\sigma}{E} = \frac{\sigma}{E_0} \frac{T}{T_0} \quad \frac{\sigma}{E} = \frac{\sigma}{E_0} \frac{T}{T_0} 
\]

Fig. 4 The static stress-strain curves an-
nealed at 8% strain (annealed at
-72°C)

Fig. 5 The static stress-strain curves an-
nealed at 8% strain (annealed at
-19°C)

Fig. 6 The static stress-strain curves an-
nealed at 14% strain (annealed at
-45°C)

Fig. 7 The relations between the residual
recovery ratio at 8% strain and the
annealing time (static)
basal and non-basal slip may operate in the polycrystalline zinc.

From the results in Figs. 7 and 8, the relations between the reciprocal of annealing temperature and the logarithm of annealing time can be obtained with \(1-P\) as a parameter and are represented in Figs. 9 and 10. The values of the activation energy for the thermal recovery evaluated by using eq. (5) are also shown in the figures with the values of \(1-P\).

3.3. Experimental Results (In the case that the stress-strain relation at -195°C and at the strain rate of \((3\times 8)\times 10^2/s\) is adopted as the reference stress-strain relation)

Fig. 11 shows the stress-strain relations at room temperature and at high strain rate. The specimens dynamically pretrained were unloaded to zero stress and kept for a certain duration and were deformed again dynamically. The thermal recovery is perceived in the unloading for about 50 seconds, while the thermal recovery cannot be detected in the unloading for about 100ms. It is not unreasonable to consider that the thermal recovery does not occur in the dynamic deformation of 300μs (this duration corresponds to the time span when the specimen is strained up to 9% strain at the strain rate of \(3\times 10^2/s\)) and the stress-strain relation at -195°C and at the strain rate of \((3\times 8)\times 10^2/s\) can be also adopted as the reference stress-strain relation.

Figs. 12 and 13 show some examples of the stress-strain relations of the specimens which were annealed at the prestrains of 7% and 12%, respectively, and were deformed at -195°C. In Fig. 12 the work hardening rate at the yield stress on the reloading stress-strain curve coincides approximately with that at same amount of stress on the reference stress-strain curve. If the stress and the work hardening rate characterize the internal structure due to the thermal recovery may be closely related with the recovery of the effective strain.
In Fig.13 the work hardening rate at the yield stress on the reloading stress-strain curve is different from that at the same stress value on the reference stress-strain curve, and the specimen was crushed by reloading at strain less than 20%. Solid circles indicate the values of the stress and the strain where the specimens were crushed. The behaviour of crushing may be caused by the operation of latent cracks produced by the large prestrain. These cracks can not be annihilated by the thermal recovery and even through the yield stress on the reloading stress-strain curve decreases apparently, the cracks result in crushing the specimens with the subsequent deformation. The amount of prestrain may be sufficient to nucleate the cracks. The fact that at low temperatures the values of the strain rate sensitivities of the stress at larger strain than 10% are very small on the high strain rate range may be interpreted to have connection with the results shown in Fig.13.

The relations between the residual recovery ratio and the annealing time are represented in Fig.14 and 15 for 7% and 12% strains, respectively, taking the annealing temperature as a parameter. Both in Fig.7 and in Fig.14, there can be seen almost the same change of the residual recovery ratio and it may be concluded that the internal structure at (7-8)% strain depends little on the strain rate. The increase of the strain rate may cause an increase of the dislocation velocity, while it may scarcely produce a change of the internal structure. It is not unreasonable to consider that basal slip operates at small strain in polycrystalline zinc, and therefore that the internal structure produced by operation of the basal slip is scarcely affected by the strain rate history.

The relations between the annealing temperature and the logarithm of the time are shown in Figs.16 and 17, and the values of the activation energy are given taking the residual recovery ratio as a parameter.

3.4. Activation energy for thermal recovery

According to Drouard, the value of the activation energy for the thermal recovery was evaluated as 20kcal/mol for zinc single crystal. This value corresponds approximately to the value of (20±0.9)kcal/mol for self diffusion in the c-
axis direction. In the present experiment, the value of the activation energy for the thermal recovery is evaluated as (10–12) kcal/mol for (7±8)% prestrain both in the static and in the dynamic strain rate ranges.

It is well-known that the activation energy $H_d$ for self diffusion consists of the formation energy $H_f$ and the migration energy $H_m$ of vacancies. In the case of transition metals of a body centered cubic lattice structure, $H_f$ is estimated nearly equal to 0.88d and in the case of a more densely packed lattice structure, $H_f=0.68d$ holds. When the thermal recovery is controlled by the operation of vacancies such as the climbing of edge dislocations, the activation energy for the thermal recovery consists of the formation and the migration energy of vacancies. It is expected that when jogs produced by intersection of screw dislocations operating on basal and non-basal slip planes are forced to move, vacancies may be produced athermally. Thus, the plastic deformation produces a sufficient amount of vacancy concentration, then the activation energy for the thermal recovery controlled by vacancies corresponds to the migration energy of vacancies.

For zinc of a close packed hexagonal lattice structure, when $H_m=0.88d$ is adopted and the value of $H_d$ is estimated as 25 kcal/mol which corresponds to the average value of (20.4±22.5) kcal/mol and (23.9±31) kcal/mol, for the diffusion energy parallel and normal to the c-axis, respectively, the value of $H_m$ is evaluated as 10 kcal/mol which coincides satisfactorily with the experimental values of the activation energy.

In Fig.8 the increase of the thermal recovery is exhibited at early stage of the process with an increase of annealing temperature and slightly larger values of the activation energy are obtained than those in Fig.7. Activation energy for recrystallization is generally larger than that for recovery. When both the recovery and the recrystallization occur, the recovery predominates at relatively low temperatures and the recrystallization at relatively high temperatures. Therefore, the increase of the activation energy is due to the effect of the recrystallization in addition to the recovery. In fact, when the specimen prestrained up to 14% were annealed for a long time, fine grains were detected.

5.5. Thermal recovery effects on the stress-strain relations at room temperature and at high strain rate

The stress-strain curves at -195°C are not affected by the recovery under high strain rates and consequently the stress-strain relations at room temperature can be regarded as independent of the thermal recovery. Fig.18 shows the stress-strain relations obtained by repeated impacts at room temperature. The interval between each impact is about 5 minutes. The stress-strain relations are affected considerably by the thermal recovery proceeding in the interval.

![Fig.16 The relations between the logarithm of annealing time and the reciprocal of annealing temperature at 7% strain (dynamic)](image_url)

![Fig.17 The relations between the logarithm of annealing time and the reciprocal of annealing temperature at 12% strain (dynamic)](image_url)

![Fig.18 The stress-strain relations obtained by the repeated impacts](image_url)
4. Conclusion

Thermal recovery and its effects on the stress-strain relations of polycrystalline zinc have been investigated experimentally. After specimens were prestrained at -195°C in compression at several constant strain rates, they were annealed isothermally.

Results obtained are summarized as follows.

(1) During both the static (10^{-9}/s) and the dynamic ((3-8)x10^{3}/s) deformations at -195°C, no detectable thermal recovery occurs. At -195°C the stress-strain relation is able to be determined only by knowing the strain rate at that time within the strain rate range of 10^{-9}/s to 10^{3}/s and is not affected by the strain rate history.

(2) When the internal structure is determined by the stress and the work hardening rate, it may be supposed that at small strain less than 0%, the internal structure obtained by the thermal recovery can be also produced by the work hardening.

(3) The activation energy obtained for the thermal recovery is about (9x12) kca/mol at (7x3)% strain both in the static and in the dynamic deformations. These values correspond satisfactorily to the migration energy of vacancies produced athermally during the plastic deformation. The internal structure depends little upon the strain rate. The activation energy increases with an increase of the strain due to the superposition of the recrystallization on the thermal recovery.

(4) The specimen dynamically prestrained up to about 12% at -195°C can not recover thermally and is crushed by the subsequent deformation. The nucleation of cracks caused by the dynamic prestrain seems to lead to a fracture.

References