INDENTATION RECOVERY PHENOMENA OF SOLID BODIES AT ROOM TEMPERATURE

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ABSTRACT

The recovery behavior of microindentations of metallic elements, Al and Ni, an intermetallic β'-NiAl phase, an amorphous fused-quartz, an ionic CaF₂, and an organic atactic polytetrafluoroethylene (teflon) has been studied. The indentations of all the solid bodies showed relaxations at room temperature regardless of type of bonding, structure and crystallinity. The recovery process could be expressed by the general transformation kinetic equation of Johnson-Mehl-Avrami-Ham (JMAH) type. The involved mechanism is considered to be the formation of volume elements of thermodynamically stable equilibrium normal state through atomic diffusion or a sort of pseudo-molecular diffusion within the plastically deformed local zone (PDLZ) around the local indentation.

I. INTRODUCTION

This paper is the extension of the previous work on microhardness after-effect [1]. The present work involves clarification of how to interpret room temperature indentation recovery phenomenon resulting from microhardness tests on a diverse range of solid materials such as amorphous (fused quartz), ionic (CaF₂) and organic (polytetrafluoroethylene: commonly known as PTFE, teflon or fluon) in addition to metals (Al and Ni) and intermetallic phase (β'-NiAl).

The existence of a local crater after unloading the indenter in a hardness test shows that a portion of the deformation under compression must be carried on plastically or by flow since a pure elastic deformation must rebound instantly. This hypothesis justifies the commonly observed indentation and hardness on polymers [2-4] and on brittle materials such as minerals, ceramics, glasses, carbides and intermetallics as well [2,3,5,15]. Since brittle materials are capable of ductile behavior under sufficiently high hydrostatic pressure [16,17], the plastically deformed zone is possible beneath a loaded small indenter because the stresses around the indenter are equivalent to a hydrostatic pressure (core in fig. 1) on which is superposed a shear stress that is sufficient enough to inhibit brittle failure [18]. The material response to local indentation while the indenter is still in place must thus be composed of plastic considering elastic simultaneous deformation [19,20], the plastically deformed local zone (PDLZ) close to the core area of contact with the indenter and the elastically deformed hinterland region (EDHR) between the PDLZ and the surrounding undeformed bulk matrix as presented in fig. 1 before that the indentation is frequently termed elastic-plastic [6,21,22] or elastoplastic [8,23] deformation.
Any solid body under positive or negative local pressure or stress yields or recovers its internal physical state in time as the general principle of thermodynamics demands: a system under a physicochemical constraint at a given temperature must proceed from a nonequilibrium state toward the state of equilibrium through a spontaneously occurring natural process known as irreversible process. The process appears in the form of relaxation, if not catastrophic, as a function of time with its typical relaxation time or times. The dimension of an indentation then ought to be a simultaneous function of temperature and time as is commonly observed [24-32]. At a given temperature, the dimension of an indentation must depend on time: the size grows with loading duration of indenter, the indentation creep, or it shrinks upon removing the indenter, the indentation recovery. As the indentation recovery is considered to be concurrent with relaxations of both stress and strain with time, it must consist of a cooperative or synergetic effect between them occurring in the PDLZ and the EDHR beneath the crater. The recovery process of a local indentation through the phenomenon of concurrent relaxation of the present sort is thus expected to be complex but is more simulative of natural process than those physically limited simple stress relaxations at constant strain and strain relaxation at constant stress encountered in common relaxation experiments. To explain the behavior of an after-effect of this nature occurring in diverse types of solid bodies in terms of responsible micromechanical processes ought to be a difficult and intriguing problem. Nevertheless, an indentation recovery technique is one of the experimentally simplest and cheapest methods in studying a behavior that is close to the natural relaxation phenomenon of a solid body under constraint and it may also be an interesting engineering problem.

Numerous literatures [1,2,8,24-28,32-46] show that a whole range of solid materials metallic, inorganic and organic in fact exhibit dimensional changes of indentation during loading and after removing the indenter. Studies on the indentation creep phenomena have been quite old and active [24-28,32-37] while studies on the indentation recovery phenomena are relatively new [39-46]. Detailed time-dependent interpretations on the recovery are, however, very few [1,4,44, 45]. Phillips et al [4] and Montmitonnet et al [44] studied indentation creep and recovery simultaneously and interpreted their data in terms of viscoelasticity. The former used a Rockwell hardness tester with a half-inch diameter steel ball indenter under the load of 60 kg on polymethylmethacrylate and polycarbonate plastics while the latter tested with a rigid tungsten carbides ball of 2 mm diameter.
indenter under 500g load on the compacted calcium stearate powders from room temperature up to 250°C. Chang and Li [45] have demonstrated that the recovery of indentation depth of a conical diamond indenter on atactic polystyrol near and above its glass transition temperature followed second order chemical kinetics.

The author [1], however, interpreted the recovery of Vickers indentation on intermetallic phase, β'-NiAl, at room temperature in terms of the kinetics of diffusion-controlled vacancy precipitation such as encountered in Ag-Zn solid solution [47], which is very similar to the second phase (solute) precipitation law which Wert [48], Zener [49] and Ham [50] observed in interstitial solid solutions. It was considered [1] that the recovery was related to formation of spherical vacancy cluster precipitates in the PDLZ under diffusion-controlled conditions so that the recovery was atomistically dominated by the concentration and movement of vacancies represented by the quantity \((C_{V}D)^{1/2}\) in and around the PDLZ, where \(C_{V}\) and D are respectively equilibrium vacancy concentration in the bulk and atomic diffusivity. This conclusion was based on the fact that

\[
(C_{V}D)^{1/2}_{\text{NiAl}} \gg (C_{V}D)^{1/2}_{\text{Ni}}
\]

as represented by the following ratio [1]:

\[
\frac{(C_{V}D)^{1/2}_{\text{NiAl}}}{(C_{V}D)^{1/2}_{\text{Ni}}} = 1.94 \times 10^{12}
\]

(C1)

Even though the extent and rate of recovery of the β'-NiAl phase is much larger than that of the Al. We concluded that the previous vacancy diffusion-controlled model was therefore false. We thus extended the work with the diverse range of solid materials in the hope of revealing a common ground for the indentation recovery phenomenon. Based on the present analysis, we arrived at the new conclusion that the indentation recovery is due to time-dependent formation of the thermodynamically stable volumes in the plastically-deformed nonequilibrium region.

II. MATERIAL AND EXPERIMENTAL

A small piece of aluminum of about 5mm cube was cut out from INLAB 99.999% Al rod and was normalized by keeping it at 500°C for 10h in argon gas flowing through tube furnace followed by slow cooling down to room temperature. The average cooling rate was
about 50°C/h. The Ni and β'-NiAl are the same specimens used in the previous report [1]. The details of their preparations and characteristics are reported in the paper. An ionic CaF₂ solid disk of about 5mm dia x 3mm height was cut out from a sintered pellet of double height. The pellet was prepared from analytical grade calcium fluoride powder (C-89) supplied by Fisher Scientific Company. The powder was sieved through a Sonic Sifter. The average size of the sieved powder measured by Fisher Sub-Sieve was 1.5 μ. The powder was dry-pressed to 35MPa (3500Kg/cm²) in the form of a cylinder by a hydraulic press. This pressed pellet was double-soak sintered [51] in an electric box furnace at 400°C for 1h followed by a second soak at 800°C for 1h in air. The fused-quartz used was a cut-out piece of about 5mm dia x 5mm height from a clear fused-quartz rod obtained from Quartz Scientific Inc. of Ohio. The teflon used was a white 5mm cube, which was cut out from a sheet obtained from a commercial source. Teflon is a non-cross-linking atactic polytetrafluoroethylene with a temperature of heat distortion at about 132°C and whose structure consists of about 90% crystallinity and 10% amorphous boundaries. This structural feature was confirmed by X-ray diffraction made with Ni-filtered Cu-Kα radiation in our laboratory. All the specimens were cold-mounted and polished to smooth surfaces through the same technique as revealed in Ref. 1. The indentation tests for the Al, Ni, β'-NiAl and CaF₂ were performed both on as-polish (not etched) and on etched surfaces. The etchant for all the metallic samples was a mixture of HCl-HNO₃-HF (45ml HCl, 15ml NO₃, 15 drops of HF and 25ml H₂O). The CaF₂ was etched with HCl solution.

The microindentations were made using a Leitz Durimet with a Vickers diamond Pyramid indenter. To minimize crack formation, as light a load as possible (p≤100g) but comfortable enough for dimensional measurement of an indent was employed in the present work. The loads applied for indentations, optical magnifications for the readings, and the initial microhardnesses Hᵥ⁰ of all the samples are presented in Table 1.

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<th>Material</th>
<th>Applied Load P(g)</th>
<th>Optical Magnification X times</th>
<th>Initial Microhardness Hᵥ⁰(Kg/mm²)</th>
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For the fused-quartz, a 50g load was used instead of 100g in order to avoid the development of microcracks. For teflon, X100 optical magnification instead of X400 was used because its indentation size was excessively larger than those of other specimens. In order to minimize random errors involved in the experiments, we have tried to maintain approximately constant duration of each touch of indenter (~5 sec) in making the initial indentation. The load was off allowing recovery. All the first readings done in the experiments were started 10 sec after the end of the unloading cycle.

The dimensional change of a diagonal length (chordal diameter) of each indentation \( d(t) \) was measured to a precision of 0.1\( \mu \)m as a function of time up to 2h. The optical resolving power of the Leitz Durimet at magnification X100 with its numerical aperture N.A. = 0.7 is approximately 0.5\( \mu \). It would, however, be feasible to appreciate a displacement of 0.1\( \mu \) although the minimum scale division of the eyepiece micrometer is 0.511 (see Brochure). The measured data are presented in Table 2 and are plotted in figs. 2A through 2F. All these figures are plotted on the same scale to disclose the differences in extent and velocity of the recovery processes occurring in different samples. Every data point in this paper except for fig. 2F represents the average of five individual test readings. Our experience demonstrated that a careful observation made it possible to perceive the displacement of even less than 0.1\( \mu \). Various of our laboratory members have tested and agreed on the fact. The observed indentation drops of about 0.02\( \mu \) on both etched and non etched CaF\(_2\) in fig.2F are thus definitely perceived by us, though the accuracy may be in question.
Fig. 2A. Aluminum

Fig. 2B. Nickel
Fig. 2C. $\beta'\text{-Ni Al}\\\\

Fig. 2D. Fused-Quartz
Fig. 2 The time dependent dimensional change of diagonal lengths $d(t)$ of Vickers indentations of the following solid materials:

(A) Al, (B) Ni, (C) $\beta'$-NiAl, (D) Fused-quartz, (E) Teflon, (F) $\text{CaF}_2$. All the figures are plotted on the same scale to disclose the difference in extent and velocity of the indentation recovery process occurring in different samples.
RESULT AND DISCUSSION

The experimental results, Table 2 and figs. 2A through 2F, clearly demonstrate that the deformed solid bodies in the form of microindentation in effect relax and recover in time toward the direction in reducing their stress constraints even at room temperature regardless of their type of bonding, structure and physical state.

The determined average indentation recovery rate of all materials based on the definition of Geach [31] and Roebuck and Almond [38]

\[
\frac{Dd(t)}{d_o} = \frac{1}{t} \left[1 - \frac{d(t)}{d_o}\right]
\]

are presented in Table 3, where \(\Delta d(t)\) is the extent of time variation of chordal diameter, and \(\Delta d(t)=d_o-d(t)\), and \(d(t)\) and \(d_o\) are respectively the diameters at time \(t\) and \(t=0\). If the indentation recovery was attributed to the previously proposed vacancy diffusion-controlled model [1], the recovery rate for those metallic solids, Al, Ni and the \(\beta^\prime\)-NiAl, should be roughly proportional to the source concentration of available vacancies and the diffusivity so that there must exist a relation between the rate and the magnitude of the quantity \((C_vD)^{1/2}\) presented in Table 4. The expected relation, however, does not exist as observed in Tables 3 and 4 as such:

\[
\frac{\Delta d(t)}{d_o t}: \text{NiAl} > \text{Ni} > \text{Al}
\]

\[(C_vD)^{1/2}: \text{Al} > \text{NiAl} > \text{Ni}\]

This negative result simply rules out the previously proposed model [1] even if the vacancies took part in the recovery process.

Table 2. Dimensional changes of diagonal length, \(d(t)\), of indentation with time.

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<th>t (sec)</th>
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### Dimensional change d(t) in μ

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<td>β'NiAl (*)</td>
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(*) Etched surface

---

### Table 3. Initial and instantaneous indentation diagonal lengths, \( d_0 \) and \( d(t) \) at \( t_1=10\text{min} \), \( t_2=60\text{min} \) and \( t_3=120\text{min} \), in \( \mu \text{m} \) and their corresponding average indentation recovery rates in \( \text{min}^{-1} \) in accord with equation (3).

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<tr>
<th>MATERIAL</th>
<th>( d_0 )</th>
<th>( d(t_1) )</th>
<th>( d(t_2) )</th>
<th>( d(t_3) )</th>
<th>( \frac{\Delta d(t_1)}{d_0 t_1} )</th>
<th>( \frac{\Delta d(t_2)}{d_0 t_2} )</th>
<th>( \frac{\Delta d(t_3)}{d_0 t_3} )</th>
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<td>104.46</td>
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Note: (*) Etched Surface, (+) Reference 1(500g load)

### Table 4. Vacancy and diffusion parameters and the quantity \( (\bar{C}_V)^{1/2} \)

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<th>MATERIAL</th>
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<th>( Q_D ) (cal/mol)</th>
<th>( D_0 ) (cm(^2)/sec)</th>
<th>( \frac{n}{N} )</th>
<th>( D ) (cm(^2)/sec)</th>
<th>( \left[ \frac{n}{N}, D \right] )</th>
<th>( (\bar{C}_V)^{1/2} )</th>
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<td>0.92*</td>
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</table>

(a) Ref. 52, (b) Ref. 53, (c) Ref. 54.

(*) Ref. 55 (these are interdiffusion values: \( \bar{Q}_D \) and \( \bar{D}_0 \)).
All the values in Table 4 are estimated as previously [1], where \( n/N \) represents the fraction of lattice sites vacant. We have approximated \( C_V \approx n/N \) in our discussion. All the estimated \( n/N \), \( D \) and \( [n/N\cdot D] \) values in the table are at 300°C. The \( \Delta H_f^V \) represents the enthalpy of formation of single vacancy for Al and Ni, and of vacancy pair for \( \beta'\)-NiAl. It should be noted here that the \( D \) value used for \( \beta'\)-NiAl in Table 4 is the inter-diffusion coefficient since it is this coefficient which represents the bulk diffusion behavior of this phase [55].

As a searching effort for a possible kinetics responsible for the indentation recovery process, we have plotted our data (except CaF_2) into various kinetic laws encountered in recovery processes of deformed solids [45, 56, 57] such as exponential decay of first order kinetics \( \log d \) Vs \( t \), as second order kinetics \( 1/d \) vs. \( t \), and as so-called logarithmic law \( d \) Vs log \( t \) in order to observe the best fit recovery behavior among those possible kinetic laws. The behavior of the curves varied at random and irregularly although a couple of them approximately fitted the given kinetic laws over a whole range, for example, the etched Al to the first order kinetic law and the fused-quartz to the logarithmic law within the experimental uncertainty. None of them fitted the second order kinetic law as was observed in the indentation recovery of atactic polystyrene [45] annealed above its glass transition temperature. All of them, however, appeared approximately to follow the logarithmic law with two slopes except for the fused-quartz, which had one slope. But it was premature to assign the behavior to this logarithmic kinetic equation without comparable basis for the responsible mechanism. We have thus replicated the same data into \( d(t) \) vs. \( \sqrt{t} \) to see if the recovery kinetics were still related to diffusion limited processes. Surprisingly enough, within experimental uncertainty, all the curves indeed follow straight lines over the whole range as shown in figs. 3A through 3E, which, accordingly, suggests the present indentation recoveries of those solids at room temperature are related to diffusion controlled mass flow process.
Fig. 3B Aluminum

Fig. 3B Nickel
Fig. 3C  \( \beta' \)-NiAl

Fig. 3D  Fused Quartz
The plots approximately follow straight lines over the whole range within the experimental uncertainties involved with the nature of the type of work.

To consider the kinetics of the indentation recovery, a further attempt is made to plot the data into \( \log[\ln(d_0/d(t))] \) vs. \( \log(t) \). Surprisingly again, all the data fit well with number of segments (segments) with breaking points as shown in Figs. 4A through 4E. All materials could be fitted with one break point \((i=1 \text{ and } 2 \text{ segments}) each. The fits yield the following relation

\[
\log \left[ \ln \left( \frac{d_0}{d(t)} \right) \right] = n \cdot \log(t) - n \cdot \log(\lambda) \tag{6}
\]

where \( n \) the slope and \( n \cdot \log(\lambda) \) the intercept of the fit line. The values of \( n_i \) and \( \lambda_i \) are obtained from the slopes and intercepts respectively. The results of this analysis of the data are presented in Table 5. Rearrangement of (6) gives the extent of relative time varying differential recovery of indentation diagonal

\[
\frac{\Delta d(t)}{d_0} \quad \frac{\Delta d(t)}{d_0} = \frac{d_0 - d(t)}{d_0} = 1 - \exp \left[ -\left( \frac{t}{\lambda} \right)^n \right] \tag{7}
\]

and the time varying \( d(t) \) for each segment \( i \):

\[
d(t)_i = d_0 \exp \left[ -\left( \frac{t}{\lambda_i} \right)^{n_i} \right] \tag{8}
\]
Fig. 4A Aluminum (etched)

Fig. 4A Aluminum (not etched)
Fig. 4B  Nickel (etched)

Fig. 4B  Nickel (not etched)
Fig. 4C  $\beta'$ - NiAl

Fig. 4D  Fused Quartz
**Fig. 4E** Teflon

The calculated recovery curves, \( d(t) \) values, from equation (8) and, \( n_i \) and \( \lambda_i \), fitted very well with the experiments. Formulation (7) appears equivalent to that of Johnson-Mehl-Avrami-Ham (JMAH)-type general transformation kinetic equation (9) for diffusion-limited process [58]; the Ham's theory of diffusion-limited precipitation kinetics and Johnson-Mehl-Avrami equation for a combined nucleation-growth involved phase transformation, if one relates the \( \Delta V(t)/d_0 \) to the differential volume fraction \( f(t) \), the extent of relative time varying transformation in volume:

\[
\Delta V(t)/V_0 = \frac{[V_0 - V(t)]}{V_0}
\]

\[
f(t) = \frac{\Delta V(t)}{V_0} = \left[ \frac{\Delta d(t)}{d_0} \right]^3 = 1 - \exp \left[ -\left( \frac{t}{\lambda} \right)^m \right]
\]

where the exponent \( m \) is a temperature insensitive geometrical factor as shape of precipitate or transformed phase and, \( \lambda \) is a temperature dependent relaxation time or times of the transformation process and is related to size and density of the precipitate. The \( \lambda \) is related to the specific rate of kinetics by \( k = \frac{1}{\lambda} \). For an observation in such a period \( t << \lambda \) as in our experimental range, (7) and (9) reduce [48] to:

\[
f(t) = \left( \frac{t}{\lambda} \right)^m = \left( \frac{t}{\lambda} \right)^{3n}
\]

\[ \text{(10)} \]
Table 5. Time exponents \( n_i (m_i = 3n_i) \), time constants \( \lambda_i \) and specific rates \( k_i \) for \( i=\text{stage} \) indentation recovery curves determined through equation (6):

\[
\log \left[ \ln \left( \frac{d_0}{d(t)} \right) \right] = n \cdot \log(t) - n \cdot \log(\lambda)
\]

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>( i=1 )-stage</th>
<th>( i=2 )-stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 90 \text{ sec} )</td>
<td>( t_2 = 90 \sim 7200 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 0.685 (m_1 = 2.05) )</td>
<td>( n_2 = 0.417 (m_2 = 1.25) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 2.80 \times 10^6 \text{ sec} )</td>
<td>( \lambda_2 = 2.13 \times 10^9 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 3.57 \times 10^{-7} \text{ sec}^{-1} )</td>
<td>( k_2 = 4.70 \times 10^{-10} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 1100 \text{ sec} )</td>
<td>( t_2 = 1100 \sim 7200 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 0.939 (m_1 = 2.82) )</td>
<td>( n_2 = 0.453 (m_2 = 1.36) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 1.02 \times 10^6 \text{ sec} )</td>
<td>( \lambda_2 = 1.53 \times 10^9 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 9.80 \times 10^{-7} \text{ sec}^{-1} )</td>
<td>( k_2 = 6.52 \times 10^{-10} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 130 \text{ sec} )</td>
<td>( t_2 = 130 \sim 7200 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 1.37 (m_1 = 4.10) )</td>
<td>( n_2 = 0.473 (m_2 = 1.42) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 1.52 \times 10^4 \text{ sec} )</td>
<td>( \lambda_2 = 1.20 \times 10^8 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 6.58 \times 10^{-5} \text{ sec}^{-1} )</td>
<td>( k_2 = 8.31 \times 10^{-9} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 100 \text{ sec} )</td>
<td>( t_2 = 100 \sim 7200 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 0.965 (m_1 = 2.90) )</td>
<td>( n_2 = 0.411 (m_2 = 1.23) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 8.28 \times 10^4 \text{ sec} )</td>
<td>( \lambda_2 = 7.13 \times 10^8 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.21 \times 10^{-5} \text{ sec}^{-1} )</td>
<td>( k_2 = 1.40 \times 10^{-9} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>(+)</td>
<td>( t = 0 \sim 3600 \text{ sec} )</td>
<td>( t = 3.83 \times 10^6 \text{ sec} )</td>
</tr>
<tr>
<td>( n = 0.486 (m = 1.46) )</td>
<td>( k = 1.46 \times 10^{-7} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 2000 \text{ sec} )</td>
<td>( t_2 = 2000 \sim 5600 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 0.658 (m_1 = 1.98) )</td>
<td>( n_2 = 0.382 (m_2 = 1.15) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 6.16 \times 10^5 \text{ sec} )</td>
<td>( \lambda_2 = 3.87 \times 10^7 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.62 \times 10^{-6} \text{ sec}^{-1} )</td>
<td>( k_2 = 2.58 \times 10^{-8} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Fused-Quartz</td>
<td>( t_1 = 0 \sim 90 \text{ sec} )</td>
<td>( t_2 = 90 \sim 7200 \text{ sec} )</td>
</tr>
<tr>
<td>( n_1 = 0.962 (m_1 = 2.89) )</td>
<td>( n_2 = 0.281 (m_2 = 0.844) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 8.18 \times 10^3 \text{ sec} )</td>
<td>( \lambda_2 = 3.26 \times 10^8 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 1.22 \times 10^{-4} \text{ sec}^{-1} )</td>
<td>( k_2 = 3.07 \times 10^{-9} \text{ sec}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( t_1 = 0 \sim 1100 \text{ sec} )</td>
<td>( t_2 = 1100 \sim 7200 \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( n_1 = 0.606 (m_1 = 1.82) )</td>
<td>( n_2 = 0.230 (m_2 = 0.690) )</td>
<td></td>
</tr>
<tr>
<td>( \lambda_1 = 3.44 \times 10^6 \text{ sec} )</td>
<td>( \lambda_2 = 1.58 \times 10^{12} \text{ sec} )</td>
<td></td>
</tr>
<tr>
<td>( k_1 = 2.91 \times 10^{-7} \text{ sec}^{-1} )</td>
<td>( k_2 = 6.31 \times 10^{-13} \text{ sec}^{-1} )</td>
<td></td>
</tr>
</tbody>
</table>

Note: (*) Etched surface, (+) Ref. 1 (500 g load).
The values, \( m_i = 3n_i \) and \( k_i = l/\lambda_i \), are also presented in Table 5.

The fact that the process of our indentation recovery is related with diffusion and that the recovery curves follow the JMAH-equation leads the author to imagine the analogy that the recovery phenomenon of indentation is considered to be equivalent to the time-dependent formation of thermodynamically stable volume elements at equilibrium normal state from the state of nonequilibrium in the region of PDLZ. The recovery process then corresponds to the accumulation of the stable volumes with time, which is equivalent to the time dependent increment of volume fraction of stress-free new material transformed within the plastically deformed nonequilibrium region. This thermodynamically irreversible process is substantiated by mass flow through diffusion.

The empirical JMAH-equation was successful, especially in studying the formation of cementite (Fe\(_3\)C) precipitates from the solid solution of C in \( \alpha\)-Fe by means of the internal friction peak associated with the stress-induced interstitial diffusion of the solute atoms [48]. In most circumstances, the equation valid with a few stages, the segments in our case, and numerous investigators have reported two or three stages in various transformation reactions such as in precipitation process of Fe\(_3\)C, Fe\(_4\)N and N-phase-I from solid solutions of C and N in \( \alpha\)-Fe [48], in tempering reaction of martensite in Fe(N) alloy [59], in crystallization process in Fe\(_{80}\)(B\(_{1-x}\)P\(_x\))\(_{20}\) amorphous alloys [60], and even in ordering kinetics of Fe\(_3\)Pt austenite [61].

On this basis, our \( n_i \) and \( \lambda_i \) values, in theory, ought to reflect the physical shape and size and density of the stress-free stable volumes formed in the PDLZ. The author also imagines that the change in slope of segment is related to the successive decrease of driving force during the recovery process, especially if we remember that the stress and strain relax concurrently in the indentation recovery. The decrease in the driving force with the progress of recovery should alter the rate of process at a certain stage where a sudden change of shape, size and density of the stable volumes might take place.

The implication that diffusion plays an important role in the process of indentation recovery suggests an involvement of defects of some sorts: Atomic movement in terms of vacancy in case of metallic phases, some pseudo-diffusion of molecules rather a molecular rotation, and relaxation of molecular forms aided by relevant defects in case of amorphous solids; fused-quartz and teflon, and diffusion assisted dislocation rearrangement in crystalline solids in general. The driving force responsible for this spontaneous process of the nonequilibrium state proceed the ward the initially undeformed equilibrium state comes from the imposed physicochemical constraint induced by the local damage by indentation. Three possible sources of driving force are conceivable: firstly, the stress released from elastic fields in the EDHR around the PDLZ, that is, the athermal springback toward the PDLZ or springpull toward the EDHR depending on the nature built-in local residual stress pattern [22] in the EDHR of a given solid;
secondly the stored energy of cold work of the PDLZ itself; thirdly, the force arisen from the difference in physical states between the affected PDLZ near surface and the unaffected bulk, that is, the gradient of degree of order and defect content of any kind point, line and plane defects pertaining to corresponding types of materials, including lattice distortion in crystalline solids and the possible bending, squeezing and disorientation of bonds in the case of amorphous solids. The related forces also may come from the gradients related to corresponding types of scalar point functions \( \phi_j \) of kinds \( j \) such as pressure \( P \) or stress \( \sigma \), density \( \rho \), temperature \( T \), or momentum \( M \). It is though uncertain which one of these sources plays a major role. It would be a difficult task to quantify the driving force even if a priori one knew the responsible one. The stiffness factor [46] defined by the ratio \( (Y/E) \) of yield stress \( Y \) to young's modules \( E \) seems relevant to the first category among the possible sources mentioned above and is as well quantifiable as follows.

The time dependency of the loading and unloading cycle in common hardness tests has the mode of constant displacement rate which operates at constant indenter speed. In this case, the stress field surrounding the indenter is considered quasistatic [62] and it exhibits a short-time indentation response after the indenter is withdrawn from diverse materials [8,40,42,46]. This early stage response, typically less than 10 sec [8,42] gives rise to a rebound which is considered effective during unloading period so that this recovery is termed various ways; elastic restitution [8], elastic recovery [40,42] and elastically driven recovery [46]. The post hardness reading after discount the elastic recovery is the recovered hardness [46,63], whose size of indentation is smaller than that of unrecovered one. In this context our initial chordal diameters of indentations do, are supposed to be the elastically recover-red ones because the initial readings at \( t = 0 \) are taken 10 sec after the end of full unloading cycle. The long-time indentation after-effect of the present work is thus termed here delayed indentation recovery or delayed reverse strain. This delayed recovery can be considered as plastic after-effect if one assumes that the elastic recovery is fully effected during the period before taking the initial read doing. Johnson [41] suggested the possibility of reversed plastic flow of indentation on metals by reverse yielding. Sargent et al [46] showed the elastically driven recovery in terms of the stiffness factor, \( (Y/E) \), on the ground that some fraction of the load on the indenter is supported by elastic deformation (EDHR) and this fraction is significant in stiff materials. On unloading, the material attempts to relax elastically by the relief of the elastic hinterland but will be prevented from entirely refilling the indentation by the plastically deformed material around the contact region (PDLZ). Unfortunately, however, both discussions are limited to the unloading period. There seems no reason why the above two possible reversed flows are confined to the unloading stage. The reversed flow may continue beyond the unloading period so long as the driving force responsible for the flow, say \( Y/E \), maintained. Provided that the aforementioned presumption is valid, that is, the elastic recovery is
already eliminated before taking the initial reading, the delayed indentation recovery of our case can be the result of the reversed flow, a plastic after-effect, operative by the residual stresses which are relieving simultaneously from both PDLZ and EDHR due to the persistent driving force. In this sense, the ratio $Y/E$ could be a good candidate for the major quantifiable driving force responsible for the delayed recovery among those possible driving forces mentioned earlier. It follows from the argument that the ratio $(PDLZ)/(EDHR)$, the volume ratio of plastically deformed to elastically deformed zones beneath the crater, are must be smaller the more the ratio $Y/E$ as a stiff material has a large $Y/E$ value as an elastic deformation is more significant in a stiff solid than that in a ductile one [46]. It then suggests absence of delayed recovery of indentation in an ideally elastic solid since plastic deformation is absent. The apparent absence of delayed recovery in CaF$_2$ may now be interpreted by applying the stiffness factor, $(Y/E)$, to Johnson's single parameter, $(E/Y)\tan\beta$ or $(Y/E)\cot\beta$, criterion in relation to deformation modes [64]; for values of $(E/Y)\tan\beta$ less than about 2 or $(Y/E)\cot\beta$ larger than about 0.5, the indentation deformation is almost entirely elastic. The estimated value of the parameter for CaF$_2$, from $E=10962$ kg/mm$^2$ [65], $Y=1500$ kg/mm$^2$ [66] and $\beta=19.7^\circ$ for Vickers [64], gives 2.6 or 0.38 respectively, which is close to the limiting value 2 or 0.5. This fact implies that the CaF$_2$ behaves strongly to pure elastic so that the ratio $(PDLZ)/(EDHR)$ must be small. This means the volume of plastically deformed zone is very small and the delayed recovery is then expected to be also very small. Even the existence of a small, recovered indentation on the CaF$_2$ may reflect the persistence of a small plastically deformed zone on it. The Hydrostatic core may have disappeared instantly on unloading even if it existed initially. In consequence, the small step drop of indentation size observed in our CaF$_2$ may constitute a genuine part of a long and slow delayed recovery curve and it may also be related to those discontinuities encountered in inhomogeneous deformations such as slips and twins commonly observed in many solid materials. However, direct evidence of the perceived size change of 0.02µ on CaF$_2$ is desirable and recommended through more precise experiments. The evidence could be realized perhaps either in the form of superimposed microphotographs or by dynamic on-the-run measurement with a tester armed with a precision sensor and recorder or even better it with a movie camera if attached to available.

On-the-run test indentation size vs. time records under condition of stepwise loading and unloading on polymers [4] and calcium stearate [44] showed instantaneous deformations, compressive and restitutive (spring back) elastic strains. Based on the resemblance of shapes of the resulting curves to those of viscoelastic behavior, the data have been interpreted in terms of theological models. In spite of the existence of time-independent instantaneous deformations, Phillips et al [4] applied irrelevant series of the Voigt-Kelvin model consisting of spring-dashpot two-parallel elements. They then approximated it with a single relaxation time so that the result of their analysis can be artificial. Montmitonnet et al [44], howe-
applying a plausible four-elements Burgers model which contains an instantaneous elasticity and two relaxation times. Because of the lack of instantaneous parts of elastic deformations together with the simultaneous presence of creep and recovery curves in the data, no attempt of our work to viscoelastic analysis has been made. Even the simple Voigt-Kelvin type analysis is not applicable since its form reduces to that of the first order kinetics, log d(t) vs. t, which, as mentioned before, did not represent our recovery behavior. Any physicochemical system under constraint exhibits either continuous or discontinuous dynamic reaction. We have demonstrated the Voigt-Kelvin type viscoelastic behavior in the magnetization and demagnetization of ferromagnetic materials [67-72]. We present a phenomenon of effect of concentration on time-dependent phase transformation, $\beta$-Hgl$_2 \rightarrow \alpha$-Hgl$_2$, in aqueous solutions [73] as well as in composite phenomena, relaxation and catastrophic, encountered in the electronic I-V switching process of diverse materials [74].

REFERENCES.


