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The Recovery Phenomena of the Cold Worked Pure Zirconium

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Abstract

In the present study, recovery behaviour of cold compressed pure zirconium was investigated by the measurement of X-ray line breadth and microhardness. By isochronal annealing, it was found that both hardness · and X-ray line breadth do not show remarkable decrease below 300°C. It was also found that at the same degree of cold work, the rate of recovery of X-ray line breadth is different from that of hardness, and that regardless of cold working degrees, activation energy for the recovery of X-ray line breadth is less than that of hardness.

Activation energies for recovery of X-ray line breadth in 8%, 19% and 28% cold worked zirconium were 64,800 cal/gram atom, 56,400 cal/gram atom and 48,500 cal/gram atom, respectively, and those of hardness were 72,800 cal/gram atom, 64,300 cal/gram atom and 58,600 cal/gram atom, respectively.

요 약

냉간 압축가공한 순수 지르코늄의 회복현상을 X-ray line broadening과 미소경도 (microhardness)를 측정하여 연구하였다.

Isochronal 소둔한 결과에서 경도나 X-ray line breadth가 300°C 이하에서는 감소하지 않는다는 것을 알 수 있었다. 같은 크기의 냉간가공도에서 X-ray line breadth의 회복속도는 경도의 회복속도와 다르게 나타났으며 가공도에 상관없이 X-ray line breadth의 회복에 필요한 활성화 에너지는 경도의 회복에 필요한 활성화 에너지보다 작은 것을 알 수 있었다.

8%, 19%, 28% 냉간가공한 지르코늄에서의 X-ray line breadth의 회복에 필요한 활성화 에너지는 각각 64,800cal/gram atom, 56,400 cal/gram atom, 48,500 cal/gram atom이었으며 경도의 회복에 필요한 활성화 에너지는 72,800 cal/gram atom, 64,300 cal/gram atom, 58,600 cal/gram atom인 것으로 나타났다.

1. Introduction

When a metal is plastically deformed, its physical and mechanical properties generally undergo considerable changes and by subsequent annealing these changes are partly or wholly annihilated.

Recovery may be defined as a gradual return of the mechanical and physical properties of strain-hardened material; an increase in annealing temperature increases the rate of recovery.

Changes which occur in a cold worked metal during deformation depend to a large extent upon the amount and type of deformation. Cold working of a metal usually causes a change in the existing dislocation network as well as an increase of the dislocation density, and point defects such as interstitials and vacancies produced due to various types of dislocation interactions. By annealing a cold worked metal the point defects and dislocation will interact in many ways and the modes by which they interact will in large part determine the rate of recovery and the extent of property restoration prior to recrystallization.

Much work has been done by various methods in order to clarify the kinetics and mechanism of recovery in many metals and alloys.[1-10] It was shown that the onset and rate of recovery of various properties such as hardness, electrical resistivity, X-ray line breadth and yield stress, etc. and the calculated activation energies differ one another. The reason for these differences are thought to be that those are not the properties which could truly reflect the state of cold work.

But the study of recovery behaviour of zirconium has been relatively scarece since most of the work has been more concerned with recrystallization and grain growth than recovery. Nevertheless some notable exceptions are the works of DeSalvo,[11] Treco[12] and Renucci *et al.*[13]

Boghen[14] observed pre-recrystallization softening in zirconium and zirconium alloys. Treco[12] noted the onset of recovery at various temperatures below 500°C by the sharpening of Debye rings in X-ray photograms. Renucci *et al.* measured the electrical resistivity ratio of cold worked iodine and sponge zirconium after annealing at various temperatures. It was shown for both materials that a considerable decrease in the resistivity ratio, $R_{20.4°K}/R_{293°K}$, occurred at temperatures up to 400°C. The recovery of 80% cold worked zirconium of different impurity contents has been studied by DeSalvo and Zignani[11] by electrical resistivity measurements. They showed that two regions were detected in 99.5% zirconium, the first stage extending from 20°C to 315°C and having a variable activation energy. This region exhibited recovery according to logarithmic kinetics. The second region of recovery was centred at 475°C and extended to 575°C. It was shown that the decrease in impurity contents caused the decrease in the activation energy for recovery.

The purpose of the present study is to investigate the recovery behaviour of hardness and X-ray line breadth in cold worked pure zirconium and the effect of the degree of cold work on the activation energy for recovery of these properties. For this study, microhardness and X-ray peak breadth of the isochronally and isothermally annealed zirconium were measured with Kentron microhardness tester and X-ray diffractometer.

2. Experimental Procedure

1) Material and fabrication

The high purity zirconium (99.9%) rods of 6.35mm diameter were cut into disk shape perpendicular to the drawing direction and prepared in three thicknesses. After grinding and polishing the specimens to the final thickness of 5.0mm, 5.68mm and 6.39mm, respectively, they were cheked if the upper and lower cross sections were parallel and both cross sections were perpendicular to the rod axis. Then the specimens were sealed in quartz glass evacuated to 10^{-4}mmHg and fully annealed for 24 hours at 835°C and then furnace cooled. These annealed specimens were uniaxially compressed at room temperature to the final thickness of 4.6mm, which resulted in 8%, 19% and 28% reduction in thickness. Then these specimens were sealed in pyrex glass and evacuated to 10^{-4}mmHg and filled with super-purity (99.999%) helium gas of about 1/8 atmosphere.

2) Annealing

The specimens were isothermally annealed for various length of time from 1 minute to 10,000 minutes at temperature range of 325°C to 525°C with 25C interval, using a electric muffle furnace equiped with a SCR type controller. The temperature of the furnace was controlled to ±2°C of set point throughout the work. Isochronal annealing was done at temperature range of 100°C-700°C with 25°C interval for one hour period.

The specimens were taken out by breaking the sealing glasses for the measurement of hardness and X-ray line breadth. Delay between taking out from the furnace and room temperature meaurement was about one hour. Before measuring the properties, the specimens were slightly polished in order to remove the possibly distorted surface.

3) Measurement of X-ray half-intensity breadth

X-ray diffraction measurements were made with a Shimadzu X-ray diffractometer. Copper radiation was used with the X-ray tube operating 50 KV and 10 mA. Diffraction profiles of the (105) K_α were determined by slow scans at 1/8 degree per minute. 0.6mm exit slit and 0.04mm entry slit were used. In any case, it was not necessary to separate the $K_{\alpha1}$ and the $K_{\alpha2}$ peaks since the overlap was very small.

Line broadening was measured from the half width at the half height of maximum intensity, B, as shown in Fig. 1. In determining B, the intensity peak was first divided by a vertical line drawn from I_{max}. The half width was measured on the low angle side of this line.

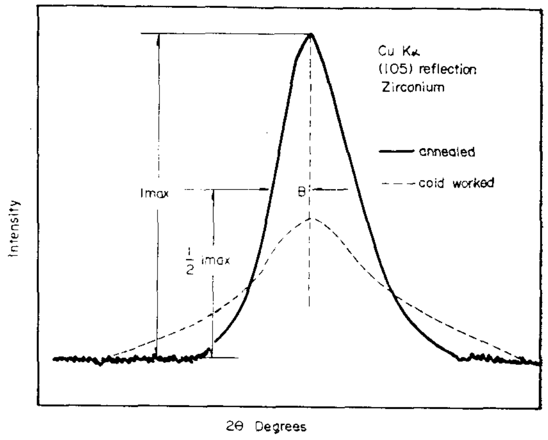

Fig. 1. Schematic curves of the diffraction intensities of cold worked and annealed zirconium as a function of diffraction angle.

4) Microhardness testing

Indentation by Kentron microhardness tester with Knoop indentor was made on the transverse cross section of each specimen after X-ray line measurement. Ten measurements were made on each specimen and an average microhardness reading with 500 gram load was taken for each specimen in order to screen out the inhomogeniety of compressed specimens.

3. Result and Discussion

For present study, the fractional change in property has been taken as a measure of the amount of recovery. This fractional change, R, is given by,

$$R=\frac{P_c-P_t}{P_c-P_o}$$

where,

P_c=the value of hardness or X-ray line breadth of cold worked specimen

P_c=the value annealed at a given condition of temperature and time after cold working

P_o=the fully annealed value

Fig. 2 and Fig. 3 are isochronal plots of fractional changes in hardness and X-ray line breadth with respect to annealing temperature from 100°C up to 700°C. The noteworthy feature of these figures is that both hardness and X-ray line breadth do not show remarkable decrease. below 300°C, and that there is an abrupt change in slope at the temperature range of 300°C to 600°C.

Even though the decrease in hardness and X-ray diffraction line breadth does not occur at low temperatures in cold worked zirconium, Bostrum and Kulin$^{15)}$ has found that there was a considerable decrease in electrical resistivity below 300°C.

And it was suggested that this decrease in electrical resistivity is attributed to the annihilation of point defects. Comparing Fig. 2 with Fig. 3, though it is shown that the rate of recovery in X-ray diffraction line broadening takes a similar trend to that in hardness, the former is somewhat faster than the latter. This phenomenon could be explained as two successive processes in recovery defined by Gray;$^{16)}$ first migration and annihilation of point defect and second, formation of subgrain due to dislocation rearrangement and subgrain growth. The former causes decrease mainly in electrical resistivity and slightly X-ray line breadth, and the latter causes decrease in hardness, X-ray line broadening and electrical resistivity. Even though X-ray line breadth does not show remarkable decrease below 300°C, it seems that point defect annihilation contributes to increase the rate of recovery in X-ray line broadening at higher temperatures.

Isothermal annealing data of fractional changes in hardness and X-ray line broadening obtained at the temperature range of 325°C to 525°C are shown in Fig. 4. Measurement were continued after much longer times up to 10,000 minutes than shown in figure.

In every case, the rate of recovery increases abruptly in early stage, then slowly increases at longer times.

Through the isothermal annealing curves, only part of the property increased due to cold work is recovered during low temperature annealing and the recovered amount increases gradually with temperature.

In order to determine the activation energy for recovery, Arrhenius rate equation was applied;

$$\frac{1}{\tau}=Ae^{-Q/RT}$$

Where, A is constant, R is gas constant, Q is activation energy for recovery, T is absolute temperature and τ is the time to reach a given recovery ratio.

By plotting the logarithmic scale of time for a given amount of recovery against the reciprocal of annealing temperature T°K, activation energy was calculated from the slop. Fig. 5 shows the temperature dependence of the time required to reach a given amount of recovery of X-ray diffraction line breadth in 19% cold worked zirconium.

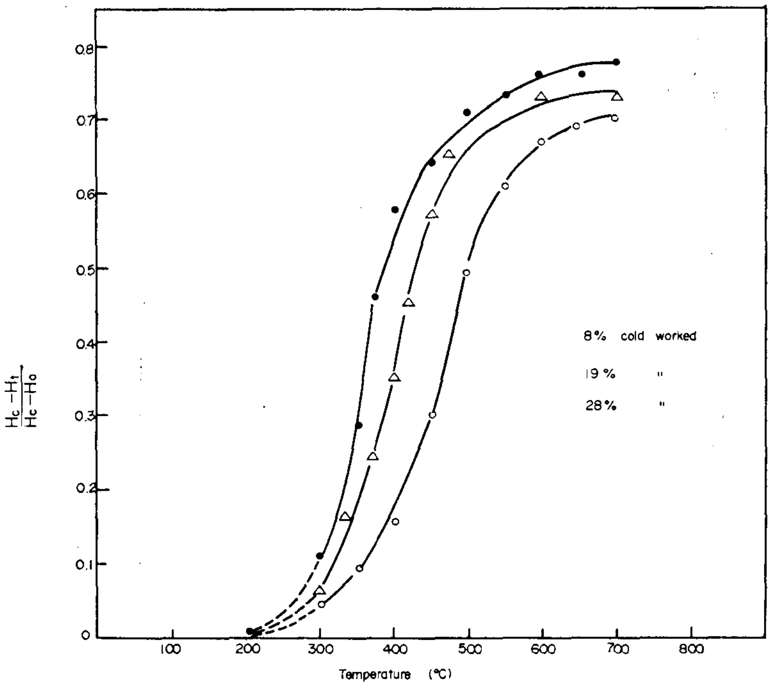

Fig. 2. Isochronal recovery curve of hardness for cold worked Zirconium: annealing time I hour

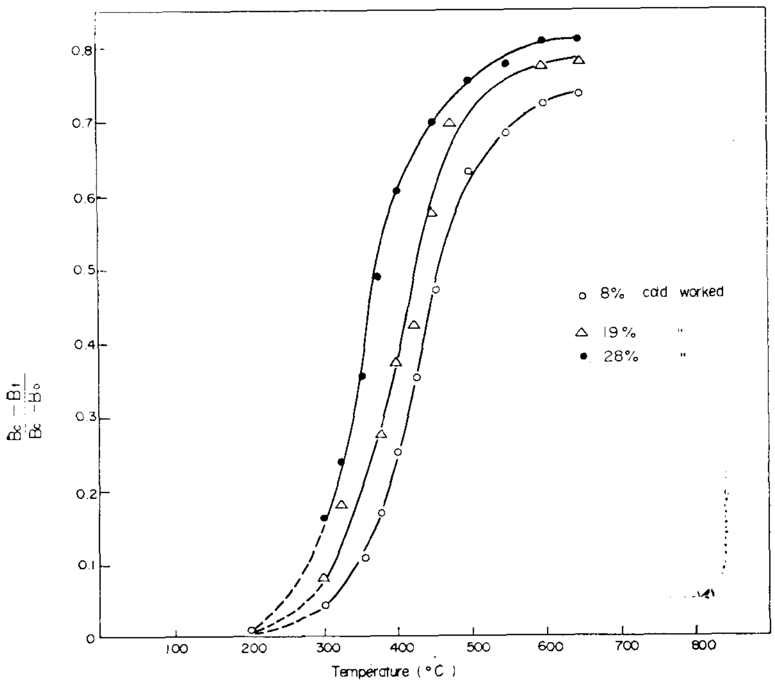

Fig. 3. Isochronal recovery curve of X-ray line breadth for cold worked zirconium; annealing time I hour

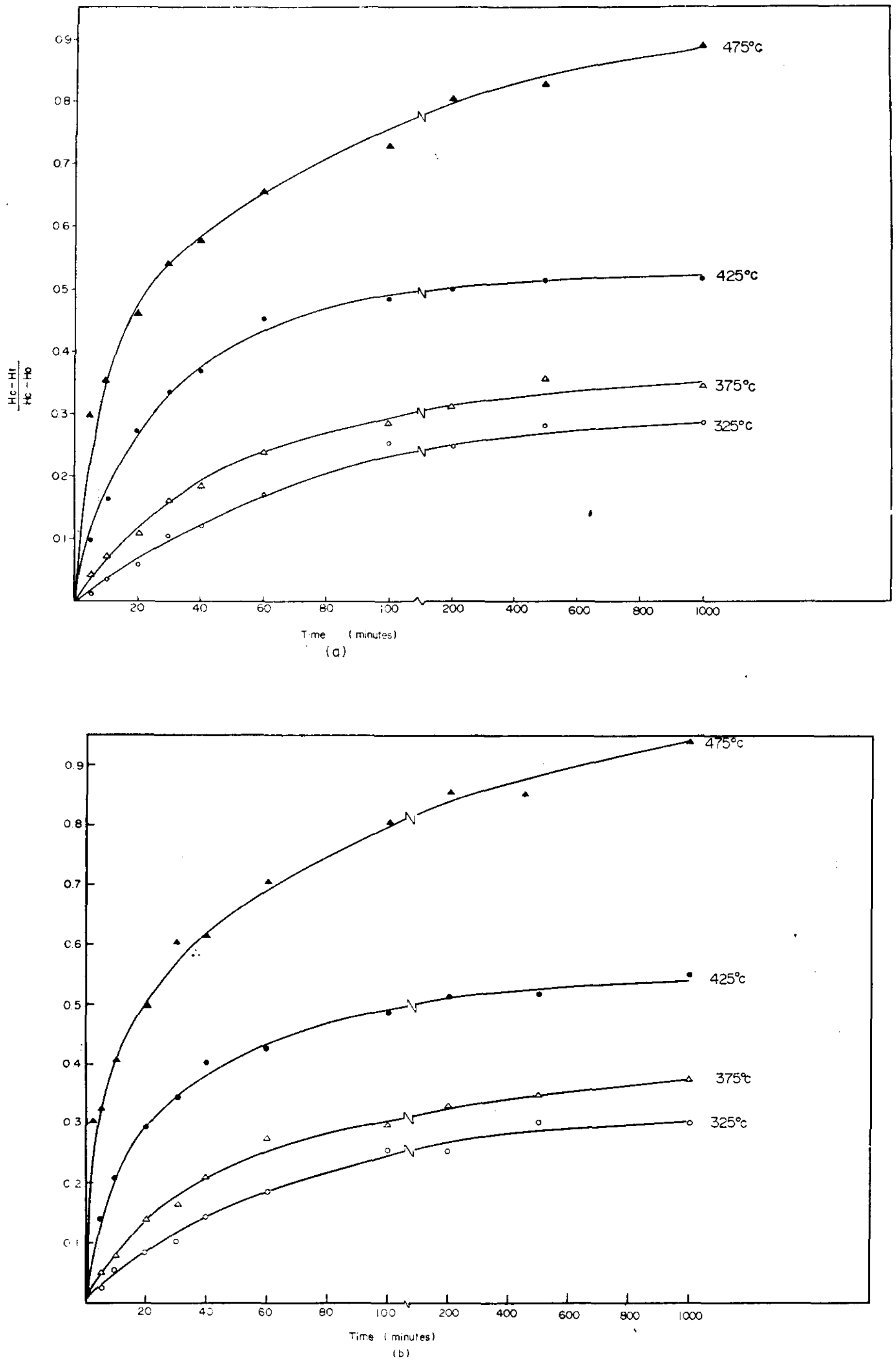

Fig. 4. Fractional change of hardness (a) and X-ray line breadth (b) is shown ar a function of annealing time for 19% cold worked zirconium.

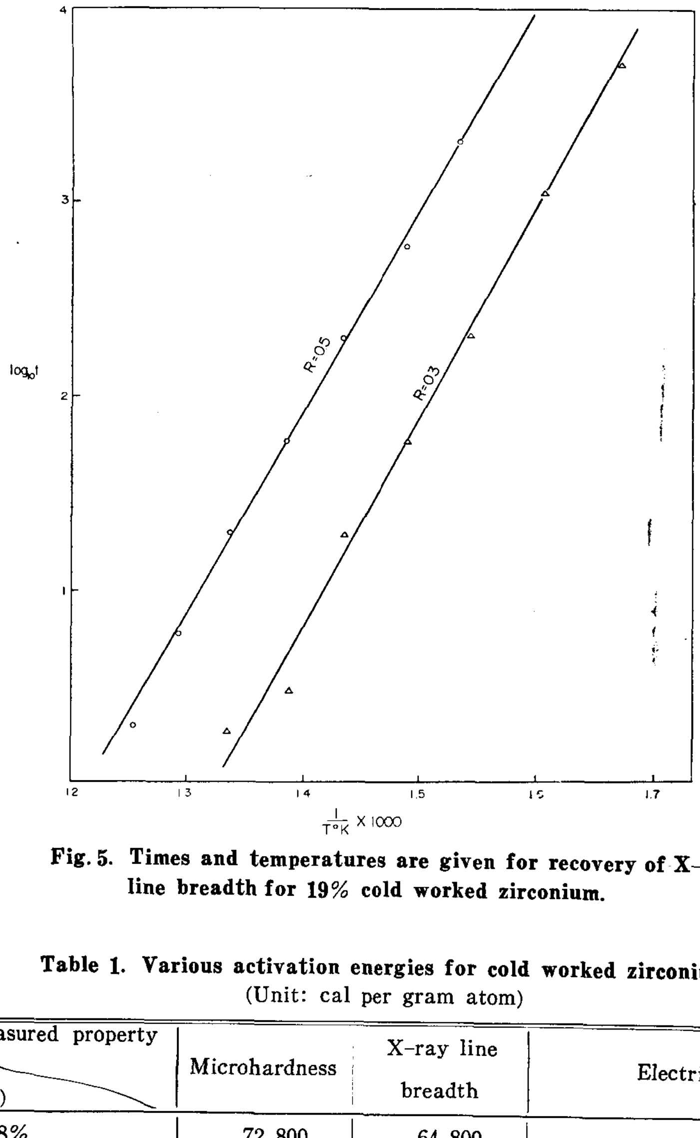

Fig. 5. **Times and temperatures are given for recovery of X-ray line breadth for 19% cold worked zirconium.**

Table 1. Various activation energies for cold worked zirconium
(Unit: cal per gram atom)

Measured property / Degree of cold work (%)	Microhardness	X-ray line breadth	Electrical resistivity
8%	72,800	64,800	
19%	64,800	56,400	
28%	58,600	48,500	
80%* (99.5% Zr)			20°C-315°C: 23,000-42,700 cal/gram atom 315°C-525°C: 53,000 cal/gram atom

* Work by DeSavo and Zignani[11]

The slopes of straight lines indicate the independency of the amount of recovery at the same degree of cold work.

Table 1 shows different activation energies for recovery of X-ray line broadening and hardness in 8%, 19% and 28% cold worked zirconium.

DeSalvo and Zignani,[11] who investigated the effect of impurity content on the recovery in electrical resistivity of 80% cold rolled zirconium, described that two temperature regions were detected in recovery process; the first extending from 20°C to 315°C has a variable activation energy between 23,000 cal per gram atom and 42,700 cal per gram atom and 42,700 cal per gramatom, and the second region extended to 525°C exhibited a single activation energy of 53,000 cal per gram atom. Even though the result that the region from 325°C to 525°C adopted in the present experiment has a single activation energy is well compared with those of Zignani *et al*, there is a difference between the values of activation energy. As shown in Table 1, activation energy obtained from the measurement of X-ray diffraction line broadening is somewhat less than that from hardness measurements regardless the degree of cold work. Thess differences among activation energies for three properties suggest that those are not the properties which could truely reflect the state of cold work. Early investigators[17,18] have studied the X-ray reflection from cold worked metal and concluded that X-ray line breadth is determined by long range strains and hence by the distribution of dislocation, whereas the increase in background and decrease in line intensity is determined by the volume of metal containing intense local strains and hence by the density of dislocation. Therefore the decrease of X-ray line breadth is attributed to the redistribution of dislocations before annihilation. On the other hand, hardness which would be dependent on the distribution and density of dislocation and subgrain size. Therefore it takes a longer time to recover than X-ray line breadth. The decrease in electrical reisti-vity which is brough about by cold working could be described in terms of behaviour of vacancies. It is suggested that the part of the electrical resistivity which begins to be recovered at low temperatures is mainly attributed to the recombination of vacancies or vacancy pairs during annealing.

Table 1 also shows that the activation energy for recovery depends on the degree of cold work. As the degree of cold work increases, the activation energy for recovery is decreased. Similar results were obtained by Perryman,[1] who studied the recovery in super-purity aluminum; 32,100 cal and 22,500 cal per gram atom for 20% and 80% cold working, respectively.

These decrease in activation energy could be explained in terms of stored energy. The stored ener [illegible] due to cold work provides the driving force [illegible] recovery and recrystallization and reduces the effective height of the barrier of activation energy to be overcome on annealing process.

It is thought to be that the decrease in activation energy for recovery in highly cold worked zirconium is attributed to the increase of stored energy.

4. Conclusion

From the results of the present investigation, the followings can be concluded:

1. Readings of Knoop microhardness and X-ray diffraction line breadth showed that both hardness and X-ray line broadening do not show remarkable decrease below 300°C.
2. In the temperature range of 325°-525°C, activation energy for recovery exhibits a single stage indepednent of temperature.
3. Activation energy for recovery was decreased as the degree of cold work increased.

The calculated activation energies for recovery of X-ray line breadth in 8%, 19% and 28% cold worked zirconium were 64,800 cal/gram atom, 56,400 cal/gram atom and 48,500 cal/gram atom, respectively in the temperature range of 325°C-525°C, and those of harndess were 72,800 cal/gram atom, 64,300 cal/gram atom and 58,600 cal/gram atom. respectively.

4. Activation energy for recovery of X-ray line breadth is less than that of hardness regardless of the degree of cold work. This phenomenon could be explained in terms of the redistribution and annihilation of dislocation.

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