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A Study on the Defect Annealing of Hafnium Metal By Positron Annihilation Techniques

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양전자소멸기법을 이용한 하프늄금속의 격자결함 회복에 관한 연구

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Abstract

Positron annihilation characteristics and microhardness of 25% cold worked and isochronally annealed hafnium specimens were measured to study recovery and recrystallization stages of hafnium specimens. The annihilation lifetime of positrons in hafnium has been measured for the distinct cases of annihilation in the annealed lattice and annihilation after trapping at lattice defects generated by cold deformation at room temperature. The annihilation lifetime in the annealed lattice was 187 ± 3.7 psec, whereas it was 217 ± 4.2 psec for positrons trapped at deformation-induced defects (mostly dislocations). The changes in Doppler broadening and hardness showed similar trend in the recrystallization range, however, the measured value of Doppler broadening variation were quite sensitive to changes in the recovery region in which the variation in hardness value was completely insensitive. Recovery of cold worked hafnium initiated at about 623 K and recrystallization occurred at around 1023 K.

요 약

소둔시편 및 소둔 후 냉간가공한 하프늄시편에 대하여 양전자수명을 조사하였다. 소둔시편에서의 양전자수명은 187±3.7 psec인 반면, 소둔 후 냉간가공한 시편에서 격자결함에 포획된 양전자의 수명은 217±4.2 psec로 측정되었다. 양전자소멸측정 및 미세경도측정 방법을 이용하여 등시소둔에 의한 냉간가공시편의 회복 및 재결정 거동을 조사하였다. 재결정단계에서는 양전자소멸측정과 미세경도측정값이 유사한 경향을 나타냈으나, 회복단계에서는 양전자소멸측정값이 매우 현저하게 변화하는 반면, 미세경도값은 거의 변화하지 않았다. 하프늄의 회복단계는 623 K부터 시작되며 재결정온도는 1023 K정도로 측정되었다.

1. Introduction

The use of positron annihilation techniques to examine the behavior of defects in metals have been well–established. When an energetic positron from a suitable radioactive source enters condensed matter, it rapidly loses almost all of its kinetic energy through electromagnetic interactions and quickly reaches the thermal energy of approximately kT which is 0.02 eV at room temperature (thermalizes), and eventually annihilates with an electron producing two γ–rays in the dominant decay mode [1]. The thermalized positron is assumed to be at rest when annihilation occurs. Hence, the momentum of the electron–positron center of mass and the resultant γ–ray energy depends mainly on the momentum of the electron with which the positron annihilates. From these γ–rays one can obtain information on the electrn density and momentum. Three measurements have been developed to analyze these annihilation γ–rays: positron lifetime, the angular distribution of the γ–rays and the Doppler broadening of the annihilation γ–energies [2].

In the investigation of defects in metals by means of positron annihilation, the positive charge of the positron interacts with the potential near a defect in a crystal. This leads to a reduced probability of the positron staying near defects with an effective positive charge and an increased localization of the positron at defects with an effective negative charge. The latter type of defect constitutes a potential well for the trapping of the positron which is very susceptive to such trapping [3]. Once a positron is trapped at such a defect the probability is high that it will annihilate with a lower–energy conduction electron, since ion cores with their higher–energy electrons are lacking in the defect region.

Positron annihilation is sensitive to the type of defects as well as to the defect concentration. In metals, positrons can be trapped by vacancies and their agglomerates as well as by dislocations, but not by interstitials. Because of this specific sensitivity, positron annihilation method has been applied to the studies of annealing and clustering behavior of vacancies in irradiated, plastically deformed and quenched metals[4] and the annealing behavior of dislocations in plastically deformed metals[5].

The recovery of lattice defects(mostly dislocations) in metals produced during plastic deformation is extensively studied because of the wide scientific and technological interest[4]. There are three distinct processes occuring during annealing a cold worked metals: recovery, recrystallization and grain growth. It was customary to follow these three processes with observation of hardness and microstructure.

Hafnium is used as a control material in the stainless–clad form for some of the present–day pressurized water reactors and its failures in the reactor in the U.S. and Taiwan as well as Korea were recently reported[6], but its metallugical characteristics are not well known.

In this work, attempts have been made with use of the positron annihilation techniques to obtain informations on positron annihilation characteristics and annealing behavior of lattice defects in the deformed hafnium metal.

2. Experiment

2.1. Specimen Preparation

Hafnium specimens(99.9% purity) were prepared from rods of 6.4mm in diameter obtained from the Nilaco Co. in Japan. The rods were cut into disk-shaped specimens of 1.0 mm thickness by an EDM wire cutting machine. All specimens were mechanically polished to make even, parallel, and mirror-like surfaces to get better surface condition for positron annihilation measurement and then annealed at 1123 K for 3 hours under vacuum of 10^{-6} torr. Polishing was started with a 600 grid SiC turning wheel and then with 1000 and 1200 grid turning wheel, and ended with use of 0.5 m alumina slurry. Fig. 1 shows round type grains which is the typical microstructure of annealed hafnium specimens.

Annealed specimens were used as a reference for positron annihilation studies to calibrate lifetime and Doppler broadening parameters. Cold-worked specimens were prepared by pressing polished specimens to an extent of 25% reduction in thickness at room temperature using a hydraulic press to examine effects of defects produced by cold working. The microstructure of cold worked hafnium specimen is shown in Fig. 2. It shows slightly elongated grains compared to Fig. 1, also the matrix is mixed with twinned grains caused by cold working.

Fig. 1. Microstructure of the Annealed Hafnium Specimen : Annealed at 1123 K for 3 Hours ; Etched in the Solution Containing 5%HF, 45%HNO_3 and 50% H_2O ; 500X, Polarized Light

Fig. 2. Microstructure of the Cold Worked Hafnium Specimen : Cold Reduced 25% in Thickness ; Etched in the Solution Containing 5%HF, 45%HNO_3 and 50% H_2O ; 500X, Polarized Light.

Isochronal annealing treatments of the specimens were done at a temperature between 473 K and 1173 K under vacuum. Successive annealing temperatures were increased in steps of 50 K and the annealing time was 1 hour at each temperature. One hour isochronal anneal between 473 and 1173 K was given based on the results of various experiments in Reference [7]. The temperatures were measured with thermocouples(K-type) in contact with the specimens.

2.2. Positron Annihilation Measurements

The experimental techniques available for positron studies include the lifetime, angular correlation, and Doppler broadening measurements. In this study the lifetime and Doppler broadening measurements were used. The positron source used was 6μCi ^{22}Na. Concentrated ^{22}NaCl aqueous solution was diluted with distilled water and the solution was dropped by a very fine syringe on the thin Kapton plastic film of 3.28 mg/cm^2. After evaporating the water the film was folded in order to keep ^{22}Na in between the two films. The source was then sandwiched by two identical specimens.

The positron lifetime was measured by a fast--fast coincidence system. In this system γ-rays are detected by two plastic scintillators mounted on the photomultiplier tube(PMT). The energy of γ-rays is converted to voltage pulse whose height is proportional to the energy of detected γ-rays. This pulse is sent to the constant fraction differential discriminators(CFDD) which can determine the energy range and generate the timing information if the input pulse is within the preset energy windows. The energy windows of the start-side and stop-side CFDD's were set around 1.28 MeV and 0.511 MeV γ-rays, respectively. The start signal and the delayed stop signal are fed to a time analyzer. The time-to-amplitude converter(TAC) determines the time interval between the detection of start side and stop side timing information. The measured information is sent to the multi-channel analyzer(MCA) through an analog-to-digital converter(ADC) to form a time spectrum. The details of the system used for positron annihilation measurements are described elsewhere [2,8]. The time spectrum was analyzed by a computer program that make use of trapping model.

In the trapping model [9] it is assumed that positrons in vacancy-type defects and those in the perfect metal decay at rates λ_1 and λ_2 respectively and that positrons are trapped in these defects at a rate μc, where c is the concentration of defects. Let n_1 and n_2 be the number of trapped and free positrons respectively. Then from general considerations,

$$\frac{dn_1}{dt}=-\lambda_1 n_1+\mu c n_2$$

$$\frac{dn_2}{dt}=-\lambda_2 n_2-\mu c n_2$$

With the boundary conditions that initially no positrons are trapped we have for the rate of annihilation at time t

$$p(t)=-N^{-1}\frac{d}{t}(n_1+n_2)$$

$$=\frac{\lambda_1\mu c\ \exp(\lambda_1 t)+(\lambda_2-\lambda_1)(\lambda_2+\mu c)\exp[(-\lambda_2-\mu c t]}{\lambda_2+\mu c-\lambda_1}$$

In the model the mean lifetime is given by

$$\tau=N^{-1}\int_0^\infty (n_1+n_2)dt=\lambda_1{}^{-1}(\lambda_1+\mu c)/(\lambda_2+\mu c)$$

The computer program incorporates both resolution function and source components in the fit [8,10].

The Doppler broadening lineshape of positron annihilation was measured by a high purity Ge detector. The energy resolution was 1.64 keV(FWHM) for the γ-ray of 1.28 MeV. The energy of γ-rays which are absorbed in the Ge detector is converted to the pulse whose amplitude is proportional to the absorbed energy. This pulse is amplified and only the signal which is equivalent to the energy around 0.511 MeV is selected and converted to the digital signal by ADC. This digitized signal is collected with use of MCA through a spectroscopy amplifier and an ADC. The lineshape of the Doppler broadening energy spectrum can be analyzed using the lineshape parameters. With lineshape techniques one examines the number of counts within certain regions of the momentum spectrum. A number of ways are available to define the lineshape. With reference to Fig. 3, one may compare areas within various energy(channel number)ranges such as the ratio of the central region to the total area [P/(P+B+W)=P–parameter], the wing regions to the total area [W/(P+B+W)=W–parameter] or the central to the wing regions [P/W–parameter]. The first indicates the fraction of conduction– and low momentum core–electron annihilation, which is linearly related to the percentage of trapped positron, the second the fraction of high momentum core–electron annihilation and the last the ratio of conduction and low momentum core– to high momentum core–electron annihilations[11]. There is no general rule about how many channels, i.e. the width of the energy, to be selected as a peak or wing areas since line–shape is different from that for one metal to another[12], and it also depends on the detector and the source and other equipment factors used. In this work the P/W lineshape parameter was used. There is another lineshape parameter R introduced by *Mantle and Triftshauser*[5] which may yield information about the type of defects. The R parameter is defined using P and W parameters as follows :

$$R=\left|\frac{P-P^{f}}{W-W_{f}}\right|=\left|\frac{P_{t}-P_{f}}{W_{t}-W_{f}}\right|$$

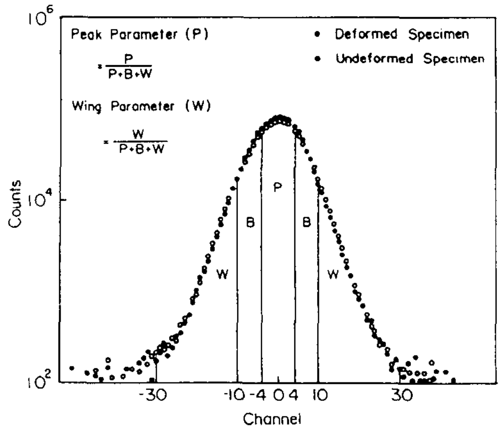

Fig. 3. The Lineshape of Doppler Broadening Spectrum and Related Parameters.

Where P_f, W_f and P_t, W_t are the characteristic values of the lineshape parameter for the free and trapped states, respectively. R parameter is characteristic of the type of defects involved and is independent of the trap concentration. Several types of trapping sites may be present but it is assumed here that one type dominates. The lineshape parameters were measured with the same counting rate of 250~260 counts/sec.

Positron lifetime and Doppler broadening lineshape parameters P/W were measured for annealed and 25% cold worked specimens. Using the reference value for annealed specimens, the average lifetime and Doppler broadening lineshape parameters were measured for 25% cold worked specimens, and then the lifetime at dislocations were calculated. The lifetime analysis was performed by the one or two trap component method after source lifetime was determined by analysis of single lifetime component and set to these results. Each Doppler broadening measurement was lasted for about 2 hours in order to obtain a total number of counts of 2×10^{6} and lifetime measurement was lasted for 5~6 hours in order to obtain a total number of counts of 1.4×10^{6}.

2.3. Micorhardness Measurements

The annealing studies on cold worked specimens were carried out using positron lifetime and Doppler broadening lineshape measurements. Since the positron annihilation measurement is an indirect index for the extent of defect annealing, microhardness was measured for isochronally annealed specimens using the Kentron microhardness tester to supplement the Doppler broadening results. The microhardness was expressed by Knoop hardness number which has the following relation ;

$$KN=L/A_{p}=L/(\ell\, C_{p})$$

where,

KN=Knoop hardness number

L=load in kilogram

A_p=unrecovered projected area in square milimeters

ℓ=measured length of the long diagonal of the indentation in milimeters

C_p=constant relating ℓ to the unrecovered projected area of the indentation

The length, ℓ, was measured with the microscope of 250 times magnification after the specimens were loaded for 15 seconds at 500g load.

The results of microhardness measurement were compared with the positron annihilation measurements.

3. Results and Discussion

The lifetime spectra for annealed and cold worked hafnium specimens could be fitted to a single-variable exponential curve. The fitted value of the lifetime for the annealed hafnium specimen was found to be 187±3.7 psec and the lifetime of the source itself was 418±8.3 psec. The results of the positron annihilation measurements for annealed and cold worked hafnium specimens were summarized in the Table 1.

Mostly dislocations are generated in metals by plastic deformation at room temperature [13]. The longer values of the lifetime for cold worked hafnium specimens compared to that for annealed hafnium specimens reflect positron trapping at dislocations and subsequent annihilation at these low-electron-density sites. Furthermore, the observation of a single lifetime component for these specimens indicates that the defect density is high enough for trapping all positrons. The trapping of positrons at dislocations where the density of high-momentum core electrons is diminished also results in preferential annihilation with low-momentum valence electrons. This accounts for the larger value of Doppler broadening lineshape parameter P/W, i.e., narrower Doppler broadening lineshapes, for cold worked hafnium specimens compared to that for the annealed hafnium specimens. Doppler broadening lineshape parameter P/W showed a relatively large increase(23%) following cold working.

The dislocations in an actual metal sample are never perfect straight lines, rather they always contain jog. All the changes in the positron annihilation parameters observed when dislocations are present comes from point-defect-like positron traps associated with the dislocations, and that dislocation lines themselves might be too narrow to accommodate positrons, while jogs on the other hand could provide enough space for trapping positrons [14].

Fig.4 shows the variation of the Doppler broadening lineshape parameter P/W with isochronal annealing temperature for cold worked hafnium specimens. The Doppler broadening lineshape parameter P/W, which is a measure of the ratio of annihilation at conduction, low-momentum core electrons to that at high-momentum core-electrons, decreased pro

Table 1. Results of Positron Annihilation Measurements for Cold Worked/Annealed Hafnium Specimens Given Various Treatments

Treatment	Lifetime		Relative intensity	DB lineshape
	τ_1(ps)	τ_2(ps)	I_2(%)	parameter P/W
Annealed	187±3.7	–	–	6.87±0.01
Cold-worked	217±4.2	–	–	8.43±0.01
Source	418±8.3	–	–	

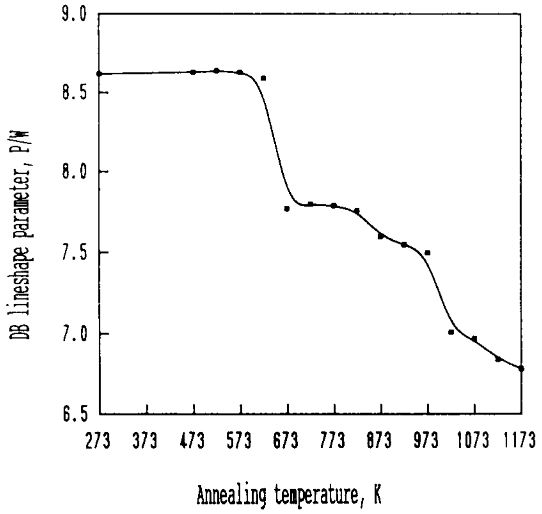

Fig. 4. Variation of the Doppler Broadening Lineshape Parameter P/W with Isochronal Annealing Temperature for Cold Worked Hafnium Specimen

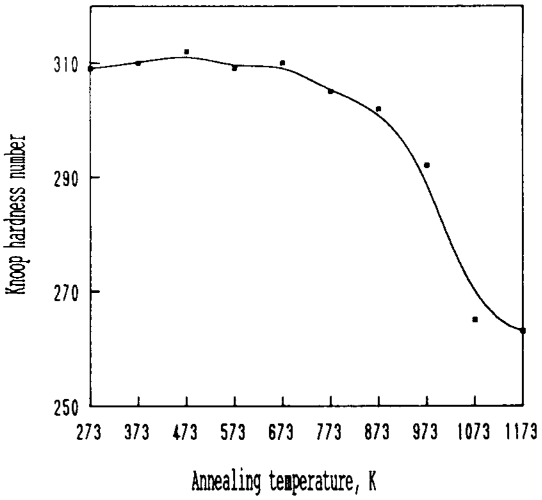

Fig. 5. Microhardness as a Function of Isochronal Annealing Temperature for Cold Worked Hafnium Specimen

nouncedly in two stages for specimens isochronally annealed at around 623 K and 1023 K. The isochronal annealing was terminated at about 1173 K. It was inferred that recovery of the specimen occurred in the first annealing stage at about 623 K, whereas recrystallization of the specimen occurred in the second stage at about 1023 K as shown in Fig.4. This result was in good agreement with the results of D.E.Thomas and E.T.Hayes [7]

Fig.5 shows the results of microhardness measurements for isochronally annealed hafnium specimens. It can be seen from these results that recrystallization occurred at around 973 K. This result shows good agreement with the results of positron annihilation measurements. Although the Doppler broadening lineshape was rather sensitive to the recovery process, it was not possible, however, to detect recovery stage by the hardness measurements. It is well known that isothermal anneals at successively higher temperatures will not normally produce changes in the hardness or optical microstructure during recovery range[15]. As the isochronal annealing temperatures increase, the recrystallization range is passed through and the hardness(as well as other macroscopic strength parameters) decreases drastically, and the optical microstructure reveals that new strain-free grains have nucleated and grown. Finally, at still higher temperatures the grain growth regime mostly produces progressively larger grain size in the optical microstructure [15].

Fig.6 shows the single lifetime for the 25% cold worked specimen as a function of isochronal annealing temperature. The single lifetime changed monotonously from its cold worked value toward the annealed reference lifetime. The single lifetime appeared to be rather insensitive to annealing stages.

The R-parameter remained constant during isochronal annealing within statistical accuracy (Fig.7). Its value was too small to indicate the existence or formation of vacancy agglomerates. The R value of 1.55 was typical for dislocations and dislocation loops in hafnium. This indicates that positron trapping occurs dominantly at dislocations and interstitial clusters in plastically de-

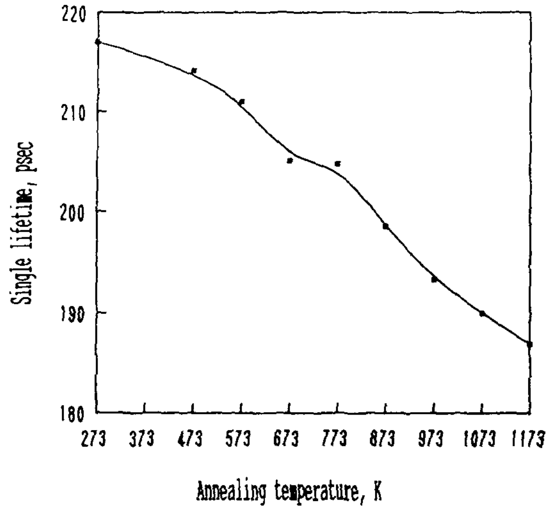

Fig. 6. Positron Single Lifetime as a Function of Isochronal Annealing Temperature for Cold Worked Hafnium Specimen

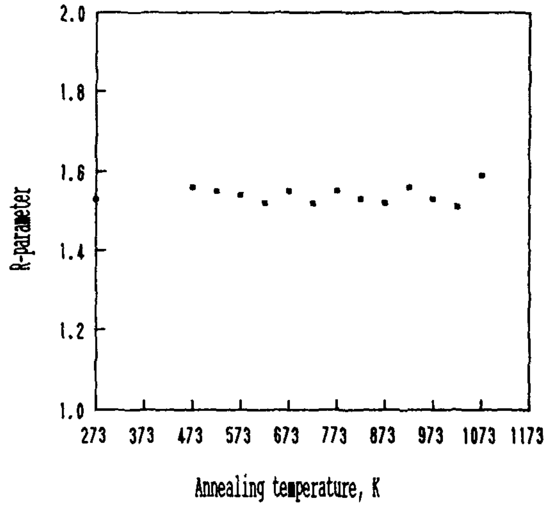

Fig. 7. R-Parameter as a Function of Isochronal Annealing Temperature for Cold Worked Hafnium Specimen

formed hafnium specimens during annealing, whereas vacancy agglomerates are either not formed or its density is too small to cause an observable effect in the presence of the high density dislocation [5].

4. Conclusions

Positron annihilation measurements for annealed and cold worked hafnium specimens were made to investigate positron annihilation characteristics and behavior of defects on isochronal annealing. The results obtained from the positron annihilation study were summarized as follows:

Positron lifetimes were measured for annealed and cold worked specimens. The lifetime was 187 psec for annealed hafnium specimens, 217 psec for cold worked hafnium.

It is inferred that mostly dislocations are generated in hafnium metals by plastic deformations at room temperature and the positron annihilation method could be applied to identification of the type of defect.

The changes in Doppler broadening and hardness of 25% cold worked and isochronally annealed specimens showed similar trend in the recrystallization range, however, the measured value of Doppler broadening variation were quite sensitive to changes in the recovery region in which the variation in hardness value was completely insensitive. Recovery of cold worked hafnium initiated at about 623 K and recrystallization occurred at around 1023 K.

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