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**Effect of Oxygen Impurities
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Synopsis

To clarify the effect of oxygen impurities on positronium (Ps) formed in irradiation-induced voids, measurements of the angular correlation of two photon annihilation radiation (ACAR) have been done on vanadium samples doped with oxygen impurities and subsequently irradiated with fast neutrons of doses up to $5.5 \times 10^{20} \text{cm}^{-2}$ at about 400°C in the Japan Materials Testing Reactor (JMTR). It has been shown that slight contamination of voids with oxygen impurity atoms, presumably submonolayer adsorption on the void surface, causes Ps formation. On the other hand, the considerable contamination leads suppression of Ps formation. Energy loss process of Ps in voids is found to be also influenced by the surface contamination.

I. Introduction

In the investigation of voids in metals, the positron annihilation technique is known to be a very useful tool for the study of void formation process because of its ability to detect microvoids which cannot be observed with a conventional electron microscope [1-4]. Another important feature of this method is its possible application to the study of the internal states of voids, such as the surface segregation of interstitial impurities and gaseous molecules in voids.

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Since the first discovery of trapping of positrons in voids, positrons have been supposed to be trapped at the void internal surface and make free annihilation with one of the surface electrons. However, a marked narrow component of nearly zero momentum, which is an indication of positronium (Ps) bound state annihilation, has been observed in the angular correlation of annihilation radiation (ACAR) curve for niobium and vanadium [5-9]. Ps atom is the bound state between positron and electron and gives the narrow component when it annihilates from the singlet spin state (1S). But the other usual evidences of Ps formation, such as large 3-photon annihilation yields, a magnetic quenching effect and a long lifetime component (>1 nsec), have not been observed. It is therefore interesting to study the anomalous properties of Ps in voids in metals. In metals Ps cannot form in bulk matrix (including dislocations and single vacancies) because in the bulk states electron density is too high to permit the bound state of Ps which can exist only in three dimensional open space or voids. Then Ps annihilation radiations come absolutely from the voids, but not from the bulk matrix, and can give us useful information on states of the voids (such as void size, the internal surface contamination, gaseous molecules in voids). Actually preliminary results showed that the narrow component was sensitively affected by heating after irradiation and doping with gaseous impurities in vanadium and niobium [6-8].

Recent slow positron studies have shown that a part of the thermalized positrons, diffusing back from the bulk matrix, are re-emitted from the surface, as slow positron or as fast Ps, into open space and that the re-emission is sensitively affected by surface contamination, such as surface coverage of oxygen [10,11]. It is interest to investigate the effects of "internal-surface" contamination on Ps formed in voids and compare them with that from slow positron study.

Thus it is quite important to study the influence of impurities on Ps formed in neutron irradiated vanadium. In order to understand the physical and mechanical properties of materials containing irradiation-induced voids, it is very necessary to investigate the internal states of voids (such as surface segregation and gaseous molecules) for which very little is known.

II. Experimental

Samples of vanadium metals and vanadium-oxygen alloys were used

as listed in Tab.1. Controlled oxygen doping for samples I-a to -e was accomplished with a zirconium-wrapping method as described in our previous paper [8]. The contents of oxygen are presented in Tab.1. Samples II and III are undoped ones. Sample IV (V-1.0at.%O) alloy was prepared by heating vanadium sheet in a sealed quartz tube filled with oxygen gas at 1000°C. These samples were irradiated in the Japan Materials Testing Reactor (JMTR) to a dose of fast neutron of $1.0 \sim 5.5 \times 10^{20} \text{ n/cm}^2$ ($>1\text{MeV}$) at about 400°C as listed in Tab.1. Transmission electron microscope (TEM) observation revealed that the irradiated samples contained voids of about 30Å mean radius with density of the order of 10^{16}cm^{-3} as shown in Tab.1.

The angular correlation was measured at room temperature by a conventional long-slit apparatus of angular resolution of 0.63 mrad (FWHM) at the Oarai Branch with use of ^{64}Cu source of 1 Ci produced in the Hydraulic Rabbit Facility in the JMTR reactor.

Tab.1. Sample characteristics, irradiation condition, and void parameters (mean radius and density) obtained with a transmission electron microscope (TEM). For sample III no TEM observation has been made, however, we can assume this sample contains voids of nearly same radius and density as those of sample II, seeing that all these samples were irradiated under nearly the same condition.

Sample	Oxygen (at.ppm)	Neutron Irrad.		Void	
		Fluence (10^{20}n/cm^2)	Temp. (°C)	Radius (Å)	Density ($10^{16}/\text{cm}^3$)
I					
-a	< 10	1.0	430	30	2.3
-b	210			20	3.7
-c	690			17	8.1
-d	1000			28	1.7
-e	1600			28	1.4
II	190	5.0	380	28	4.1
III	560	5.5	380	-	-
IV	1.0×10^4	5.0	400	40	1.0

III. Results and Discussion

Fig.1 shows ACAR curves for the samples I-a to -e which were irradiated to a low dose of 1.0×10^{20} n/cm²[8]. Marked narrowing of the ACAR curve caused by irradiation shows positron trapping in the irradiation-induced voids. The ACAR curve narrows progressively with oxygen content. It should be noted that narrow components with FWHM of about 1mrad, being usual proof of Ps formation, are clearly seen at the top portion of the curves for I-b to -e but not for I-a with the least oxygen content. These ACAR curves can be decomposed into the sums of three Gaussians by least-squares fitting [7-9] as shown by the dashed and dotted curves in Fig.1, where the FWHM width of the narrow (N), intermediate (M) and broad (B) components are about 1mrad, 5mrad

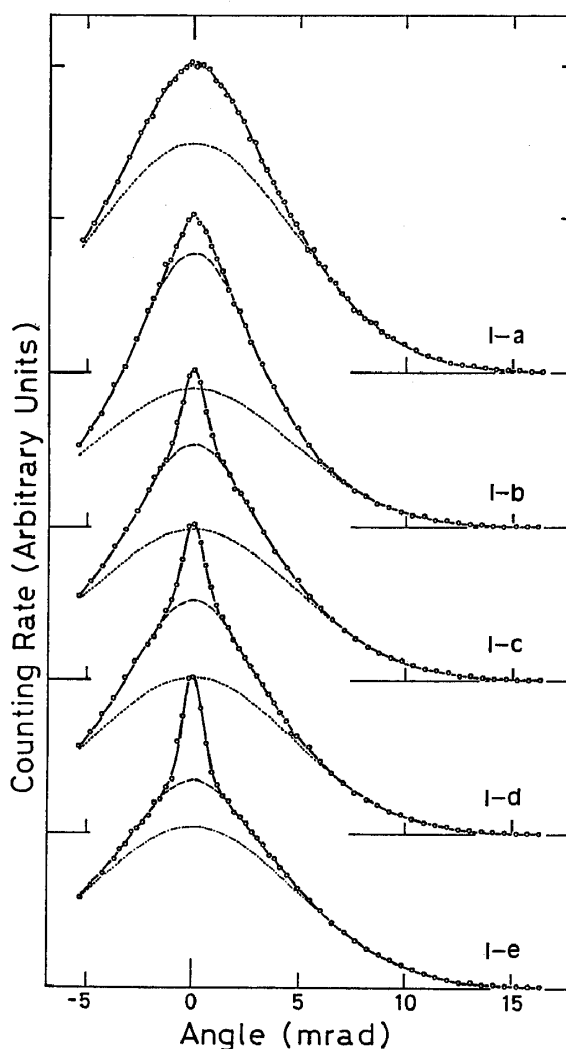


Fig.1. The ACAR curves for samples I-a to -e[8]. These curves are well decomposed into sums of three gaussians as stated in the text. The solid, dashed and dotted curves show the Gaussians decomposition.

and 11mrad respectively. The relative intensities of these components are designated as I_N , I_M and I_B respectively. This decomposition is physically justified as follows. The values of the FWHM widths of the $M(\Gamma_M)$ and $B(\Gamma_B)$ components are nearly independent of oxygen content as depicted in Fig.2(a), although the relative intensities of these components vary substantially with oxygen content in a complex way as shown later. Further these widths have been found to be nearly independent of sample temperature [7].

We can assume that M component is due to the annihilation of positrons trapped at the void surface and pick-off Ps. As stated below N component is due to self-annihilation of para-Ps formed in the voids. These two components come from the annihilation of positrons captured in the void as surface positron or Ps, but absolutely not from the bulk matrix. We call the sum of these components as the total void component: $I_V = I_N + I_M$. On the other hand B component comes from the annihilation of positrons in the bulk matrix other than the voids: $I_B = 1 - I_V$.

N component is detected only in the curves for the samples with an oxygen content higher than 210 at.ppm. This N component is attributed

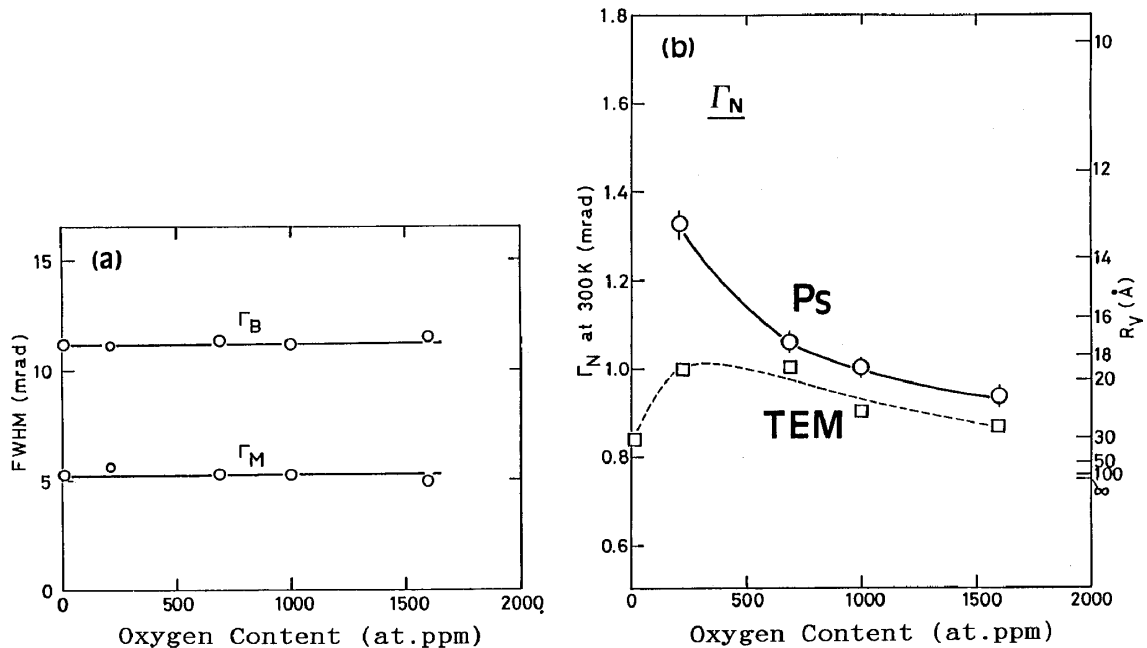


Fig.2. Dependence of the widths (FWHM), obtained from the unconstrained Gaussian decomposition. (a) $M(\Gamma_M)$ and $B(\Gamma_B)$ components. (b) $N(\Gamma_N)$ component; Open squares represent the prediction, as shown in the right vertical axis, from the simple model calculation with the void radius (R_V) from TEM observation.

to self-annihilation of free Ps confined in the voids [7-9]. Seeing the fact that Ps cannot exist in the bulk matrix, we have assumed a simple model in which free Ps is confined in an infinite spherical well potential with the void radius and its thermal excitation of the C.M.S. (center of mass) motion is given by Boltzmann distribution. With this model we have calculated the momentum distribution of the motion of Ps. The obtained momentum distribution is very close to a Gaussian with Γ_N of the experimentally observed N component. In Fig.2(b) the observed (circles) and the calculated (squares) values with use of the mean void radius in Tab.1 are shown: on the right vertical axis the theoretical prediction is scaled. At the higher content of oxygen than 690 at.ppm Γ_N agrees very well with the prediction of the simple theory: except the slight deviation which is probably due to more complex interactions between Ps and the void wall. This confirms that the Ps motion can be described by the simple model and suggests that Ps motion is well thermalized. On the contrary for sample I-b with the oxygen content of 210 at.ppm Γ_N is about 30% larger than the prediction from the simple model. It is well known that in metals Ps has a negative work function of a few electron volt [10]. Thus Ps will be thought to have a kinetic energy of a few electron volt when it leaves the void surface for the interior, then lose its energy very quickly, and eventually reach nearly thermal equilibrium state before the annihilation. The oxygen impurity atoms on the void surface could be presumably involved in this energy loss process. However, in the case of insufficient amounts of the oxygen impurities Ps would annihilate before reaching thermal equilibrium state, as in sample I-b of which effective temperature of the Ps motion is estimated to be about 300°C at the instant of annihilation. Similar effect was observed for samples II and IV as stated later. Thus oxygen impurity atoms, presumably on the void surface, are assumed to enhance the energy loss of Ps in the voids.

An important parameter for Ps in voids is the relative intensity of N component to the total void component, namely $i_N = I_N / I_V$, which gives a fraction of the singlet self-annihilation of Ps to the total positrons in the voids and depends only on characters of the void interior but essentially not on bulk properties such as void and dislocation densities [8,9]. In Fig.3 we plotted the dependence of I_V and i_N on oxygen content in samples I by open circles. I_V increases by doping of 210 at.ppm oxygen, but then decreases with further doping. This complex behavior cannot simply be related to dependence of the void density (Tab.1) which increases with doping up to 690 at.ppm

(sample I-c) but decreases by subsequent doping. The marked result in Fig.3(b) is that i_N increases linearly with increasing oxygen content, although I_V has the complex behavior with oxygen content as stated above. This indicates that the oxygen impurity atoms, which presumably are located on the void surface, give rise to Ps formation.

To confirm this we have measured ACAR curves for the undoped vanadium (samples II and III) and the V-1at.%O alloy (sample IV) which were irradiated to a dose of 5 times higher than that of sample I, because higher dose is expected to lead to much contamination on the

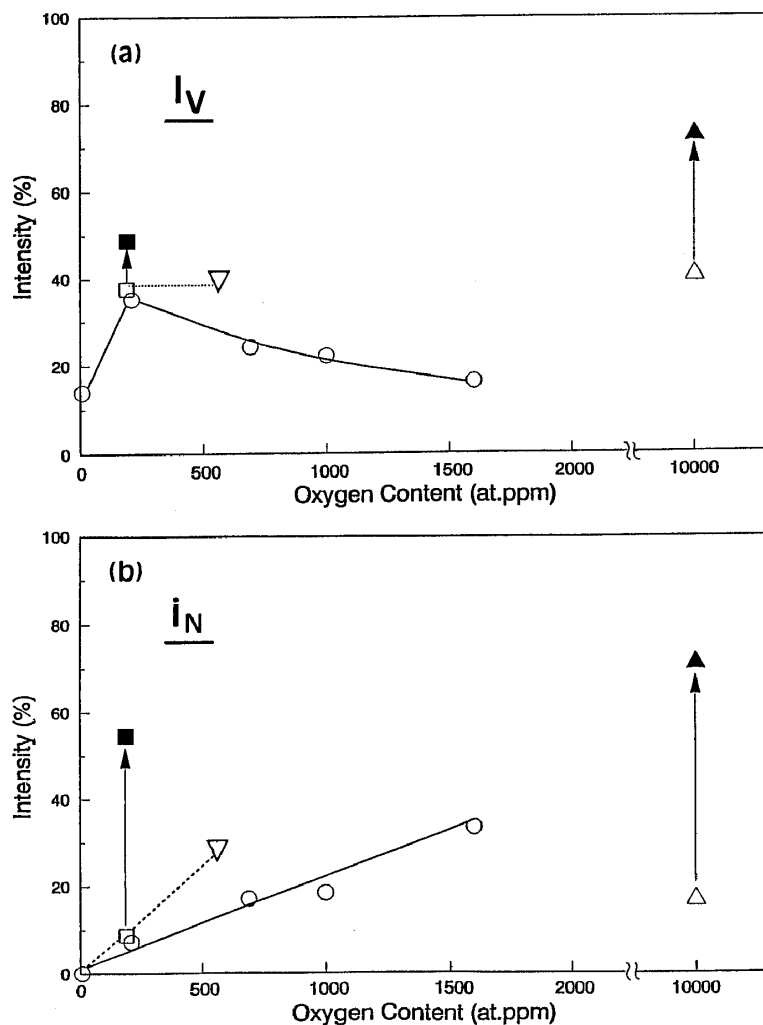


Fig.3. Effect of the oxygen doping on (a) the total void component intensity I_V and (b) the relative intensity (i_N) of the N component to the total void component for sample I (○), II (□,■), III (▽) and IV (△,▲). The solid line shows the results of the low dose irradiation on samples I, II and V. The dotted line represents that of the high dose irradiation on samples II and V. Vertical arrows attached to the data points of samples II and IV show change caused by the annealing at 600°C.

void surface and result in an increase in Ps formation. The obtained curves are shown in Fig.4 (sample II) and Fig.5 (sample IV). The curves after annealing at 600°C for 1 hour are also presented: our preliminary study revealed that i_N increased with annealing temperature up to 600°C and then decreased after heating at higher temperature [9]. This annealing behavior reflects some change in a state of the void interior, probably surface segregation of oxygen impurity, induced by annealing. These curves are decomposed into sums of 3 Gaussians as shown in the figures: here we have made an approximation that Γ_M can be fixed to be 5.3 mrad which is a mean value of the data shown in Fig.2(a) to decompose consistently the ACAR curve even with low intensity of I_M . Obtained Γ_N are 1.40 and 1.31 mrad for sample II and IV respectively. These widths are about 60% larger than the calculation by the simple model. However, in the annealed samples we have observed much reduction in Γ_N arising from the sufficient energy loss of Ps induced by annealing. Detailed study of the annealing behavior is now in progress and will be reported elsewhere shortly.

The intensities I_V and i_N for samples II, III and IV are also plotted in Fig.3. For these sample I_V is about 40% and nearly inde-

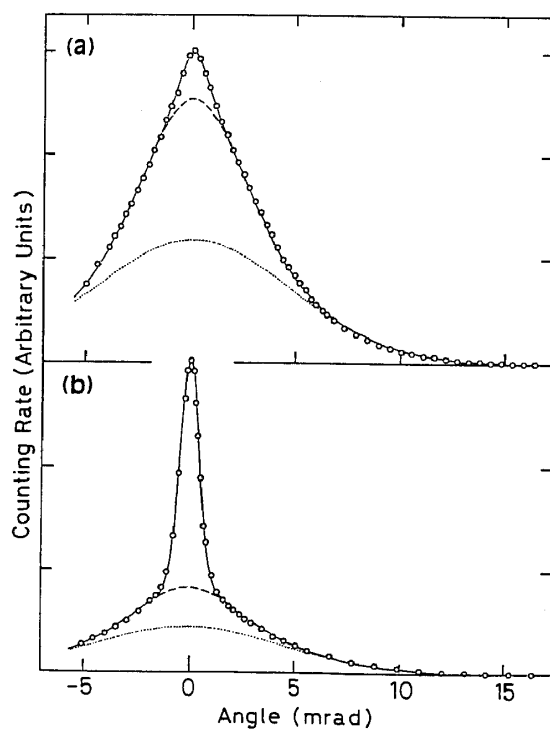


Fig.4. The ACAR curves for sample II of (a) as-irradiated state and (b) after the annealing at 600°C for 1 hour.

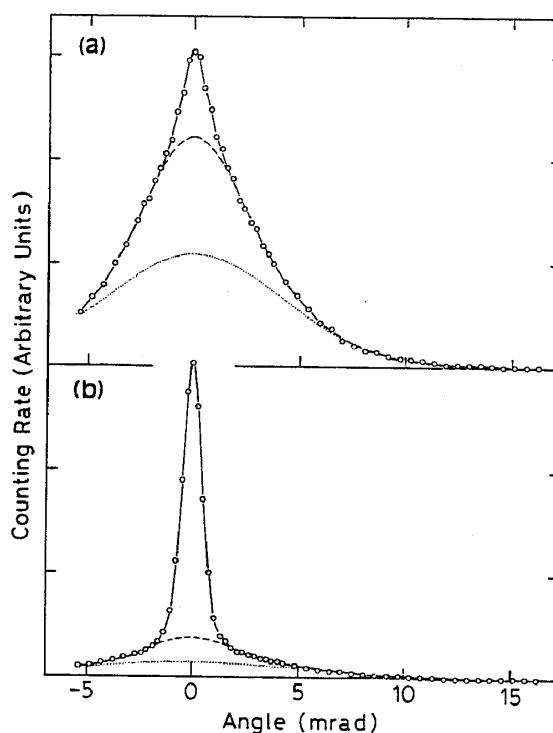


Fig.5. The ACAR curves for sample IV of (a) as-irradiated state and (b) after the annealing at 600°C for 1 hour.

pendent of oxygen content. A dashed line in Fig.3(b) shows increase in i_N due to the small doping of oxygen. In this case we observe that i_N increases with oxygen content at a higher rate than that of sample I. This shows that Ps formation increases with the irradiation dose and suggests that during irradiation oxygen impurity atoms migrate to the void and then accumulate on the void surface. This accumulation will lead to the surface segregation of oxygen and cause increase in Ps formation with the irradiation dose.

At this stage we cannot determine the coverage of oxygen impurity atoms on the void surface because of no experimental tools for it. However, the coverage is assumed to be much less than monolayer for all the samples, except sample IV, from simple estimation. The fraction of atoms on the void surface in a sample containing voids of 30\AA radius and of $1 \times 10^{16} \text{ cm}^{-3}$ density is evaluated to be 1×10^{-4} . It could be impossible for all the oxygen atoms to segregate on the void surface. Consequently it is natural to suppose that only a small fraction of the oxygen atoms can be located on the void surface.

For sample IV, I_N (Fig.5) and consequently i_N (Fig.3(b)) are not so high as expected from the case of the small doping, although this sample was doped with a large amount (1 at.%) of oxygen and then irradiated to a higher dose. Possible reason for this suppression of Ps formation will be found in the surface contamination state by oxygen. When the void surface is slightly contaminated, much less than submonolayer, oxygen coverage leads to a decrease in the trapping potential height for positrons at the surface or to a reduction in the work function of electrons with which the positrons form Ps atoms. These changes will reduce effective Ps energy relative to the energy of trapped positrons at the surface and then enhance Ps formation[8]. However in the case of the heavy doping as in sample IV, rather stable oxide layer would be formed during irradiation and probably cause increase in the electron work function. Such stable oxide layer can suppress Ps formation.

It should be noted that i_N of sample IV shows nearly the same increase as that of sample II by the annealing at 600°C . This implies that the surface oxygen contamination of the V-1.0at%O alloy after the annealing may be roughly the same as that of the undoped sample (II), regardless of much difference between those of the as-irradiated state.

IV. Concluding Remarks

Ps formation in the voids has been found to increase with doping of oxygen up to 1600 at.ppm and can be attributed to the slight contamination of the void surface with oxygen impurities. However Ps formation is observed to be suppressed in the V-1.0%O alloy, which is probably due to the considerable contamination of the void surface. The energy loss process of Ps is also markedly influenced by the surface contamination with oxygen impurities. We would like to point out that the observation of Ps in voids is not only of interest of positron physics but can provide us useful information about irradiation-induced voids, such as their surface and gaseous molecules contained.

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