

Ultra-fine particles of amorphous TiO₂ studied by means of positron annihilation spectroscopy

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Microscopic structures and mechanical properties of amorphous TiO₂ ultra-fine particles have been studied by positron annihilation spectroscopy. A positron lifetime of about 1.5 ns was found as the longest lifetime component τ_3 which is attributed to the ortho-positronium annihilation in open space. The lifetime τ_3 and the corresponding intensity I_3 was independent of atmosphere: vacuum and various gasses. Accordingly, a micro-void is contained inside the particle as the open space. An intermediate lifetime τ_2 was approximately 0.4 ns. The intensity I_2 was strongly affected by the atmosphere. No effect was found for the particles, the surface of which was coated by silicon dioxide film. This component is arisen from the positron annihilation on the particle surface and the particles contain the surface cracks. When the volume of particles packed in an ampoule was decreased by 1/4 times by compression, the longest component as well as the intermediate one disappeared and only the shortest-lifetime component τ_1 of about 0.24 ns remained. To conclude, the particles are so soft that the micro-voids and the surface cracks are collapsed by compression. © 1998 Kluwer Academic Publishers

1. Introduction

The physical and chemical properties of ultra-fine particles may differ from those of equivalent bulk material because of a nanometer size and a high surface-to-volume ratio. One factor with great influence on their properties is their microscopic structure. Positron annihilation spectroscopy is powerful for structure study. The physical quantities of positron annihilation such as the positron lifetimes, the intensities of lifetime components and the momentum distribution of annihilation radiation quanta are highly sensitive for the surface structures and the defects. Furthermore, the spectroscopy can be practically attained in any atmospheric gasses. Jean et al. carried out the *in-situ* study of gas adsorption on ultra-fine particles [1]. The identification of the positron annihilation sites, the surface of the ultra-fine particle and its inside, is possible by the examination of gas-atmosphere effects on the annihilation. Then it is possible to characterize the surface and inside structures of the ultra-fine particle based on careful consideration of the positron annihilation.

A micro-void was found by positron annihilation spectroscopy in sintered nanocrystalline particles [2–4]. Würschum et al. studied the compression effect on free-volume in nano-crystalline materials and deduced a soft behavior of the interfaces from the decrease of the mean lifetime of positrons with the increase in pressure [5]. Mechanical compression may affect the particle structures if the particles themselves are relatively soft. Ultra-fine particles in amorphous phase are considered to be porous and soft. Their micro-

scopic structures are probably changed by the particle compression. We consider that the study of compression effects on the microscopic structures of amorphous particles is important for progressing in widespread use of the particles.

In the present work, the structure of amorphous TiO₂ ultra-fine particles has been studied by positron annihilation spectroscopy, changing gaseous atmosphere and compacting the particles. We discuss the surface configuration as well as the inner defects.

2. Experimental

The sample used was an ultra-fine particle of amorphous TiO₂ (commercially available as IT-S from Idemitsu Kosan Co. Ltd.) which is hereafter abbreviated to *a*-TiO₂. The *a*-TiO₂ particles were 20 nm in average diameter, and 135 m²/g in specific surface-area. The density of the particle itself was 3.10 g/cm³. The volume density was 0.06 g/cm³ when the particles were not compacted but free in air. The chemical components of *a*-TiO₂ were amorphous TiO₂ (~90 wt %), H₂O (9.0 ~ 8.1 wt %), C (1.0 ~ 1.9 wt %), As (<1 wtppm), Pb (<1 wtppm) and Cl (<1 wtppm). *a*-TiO₂ coated with a silicon-dioxide film (IT-OD10 manufactured by Idemitsu Kosan Co. Ltd.) was also used (abbreviated to *a*-TiO₂(Si)).

The sample particles were put in a glass ampoule and held free from any mechanical compression. A positron source of 0.56 MBq ²²NaCl, inserted between two Kapton films, was buried in the sample particles.

One end of the ampoule was connected to a vacuum system and the other to an atmosphere-gas container, separated by a breakable seal. First, the positron annihilation lifetime and the Doppler-broadened annihilation-radiation for the sample in air were measured by a conventional fast-fast coincidence system and by a pure Ge detector system, respectively. Then, the ampoule was degassed to about 5×10^{-6} Torr, and the measurements for the sample in vacuum were carried out. Finally, the atmosphere gas was introduced from the gas container by breakage of the seal. The sample was kept for 25 hr in the gas atmosphere and then the effects of gas atmosphere on the positron annihilation were examined.

The time resolution of the lifetime-measurement system was 250 ps and the energy resolution of Doppler-broadening measurement system was 1.1 keV. The lifetime spectrum was analyzed, after subtracting the component of positron annihilation in the source, with the aid of computer program PATFIT88 [6]. A line-shape parameter S was calculated as the ratio of counts in a central area of Doppler spectrum to the total number of counts after subtraction of background noise.

The a -TiO₂ with the positron source was put in a glass ampoule. The piston rod of the ampoule was pressed and the compression effect on positron annihilation was studied with the same systems mentioned above. The volume density of a -TiO₂ was changed in a range from 0.06 g/cm³ to 0.32 g/cm³.

The crystalline phase of the sample was examined with a transmission electron microscope, JEM 100C operating at 100 kV.

3. Results

3.1. Electron diffraction

The electron diffraction pattern indicated that the structures of the a -TiO₂ and the a -TiO₂(Si) were amorphous. The configuration of both particles was somewhat irregular. Electron microscope images of defects such as surface cracks and inner voids were not obtained, probably due to their small size and their presence in the amorphous phase.

3.2. Lifetime for a -TiO₂ and a -TiO₂(Si) in various atmospheres

The lifetime spectra obtained for compression-free a -TiO₂ in various atmospheres were successfully decomposed into three exponential-decays with χ^2 of about 1.0. The lifetimes and the corresponding intensities for a -TiO₂ are listed in Table I, together with those for a -TiO₂(Si). The lifetimes ranged from $\tau_1 = (210 \sim 246) \pm 6$ ps, $\tau_2 = (450 \sim 455) \pm 20$ ps and $\tau_3 = (1400 \sim 1500) \pm 90$ ps, respectively.

The intensities I_1 and I_2 greatly depended on gas atmosphere. I_1 decreased from 57% to 35% while I_2 increased from 37% to 55% when the atmosphere was changed from air to vacuum. I_1 and I_2 recovered to the initial values after re-exposure of the a -TiO₂ to air. I_3 was almost independent of atmosphere. When the a -TiO₂ in vacuum was exposed to oxygen of 150 Torr in pressure, I_1 and I_2 changed from 35% to 49% and

TABLE I Lifetimes and intensities of positrons in amorphous TiO₂ particles (a -TiO₂) and those in the particles coated by SiO₂ films (a -TiO₂(Si)). The values in parentheses are those obtained for the a -TiO₂ re-exposed to air after evacuation.

		Air	Vacuum 3×10^{-6} Torr	Oxygen 150 Torr
a -TiO ₂	τ_1 (ps)	235 ± 6 (230 ± 5)	210 ± 5	246 ± 6
	I_1 (%)	57 ± 1 (56 ± 1)	35 ± 1	49 ± 1
	τ_2 (ps)	450 ± 20 (440 ± 20)	450 ± 20	455 ± 20
	I_2 (%)	37 ± 1 (36 ± 1)	55 ± 1	43 ± 1
	τ_3 (ps)	1500 ± 100 (1500 ± 100)	1400 ± 80	1500 ± 90
	I_3 (%)	6 ± 2 (8 ± 2)	10 ± 1	8 ± 1
a -TiO ₂ (Si)	τ_1 (ps)	242 ± 4	241 ± 4	
	I_1 (%)	33 ± 1	31 ± 1	
	τ_2 (ps)	380 ± 20	400 ± 20	
	I_2 (%)	65 ± 1	66 ± 1	
	τ_3 (ps)	1700 ± 100	1600 ± 130	
	I_3 (%)	2 ± 1	3 ± 2	

from 55% to 43%, respectively. I_1 and I_2 changed with the same tendency when argon of 150 Torr in pressure was lead as atmosphere gas. To conclude, I_1 in vacuum is low compared with that in atmosphere gasses of air, oxygen and argon, I_2 is complementary to I_1 , and I_3 is almost independent of the atmosphere.

The lifetime τ_1 in a -TiO₂ was decreased from 235 ~ 246 ps to 210 ps when the sample atmosphere was changed from air to vacuum. No significant changes in τ_2 and τ_3 were observed through changing the atmosphere gasses : air, oxygen and argon and vacuum. In the a -TiO₂(Si), the three lifetimes and the intensities were almost independent of the atmosphere.

3.3. Lifetime for a -TiO₂ under compression

As the a -TiO₂ was compressed, only the shortest lifetime component remained and the two longer components disappeared. Fig. 1 shows the lifetime spectrum for compression-free a -TiO₂ with the volume density of 0.06 g/cm³ and the spectrum for the compressed a -TiO₂ of 0.32 g/cm³ in volume density. The lifetime was clearly shortened by the compression. Fig. 2 demonstrates the decreases of I_3 and I_2 and the increase of I_1 as the a -TiO₂ was compressed. The S -parameter was decreased with an increase of the volume density by the compression as shown in Fig. 3.

4. Discussion

4.1. Lifetime components and particle configuration

The lifetime of free positrons in a -TiO₂ particles corresponds to the observed τ_1 because τ_1 was the shortest component. The para-positronium annihilation contributes to τ_1 . Tanigawa et al. reported the lifetime of free positrons in crystal TiO₂ to be 0.178 ns [7]. The longer τ_1 in the present study is understood in terms of the lifetime extension in an amorphous material.

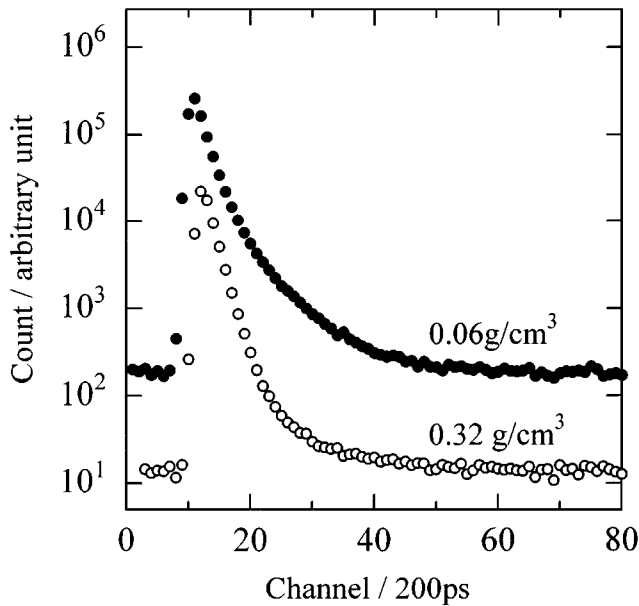


Figure 1 Lifetime spectra for *a*-TiO₂, the volume density of which is 0.06 g/cm³ (a) and 0.32 g/cm³ (b).

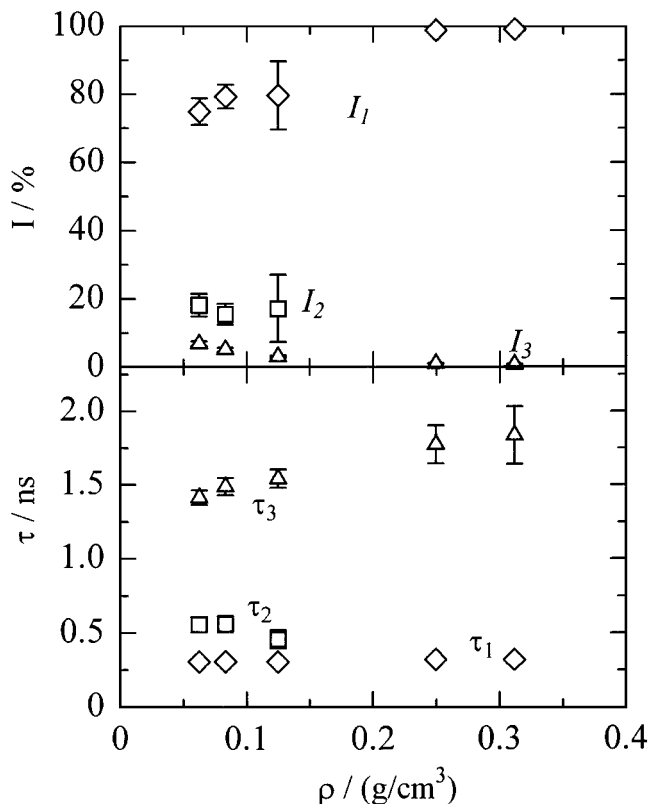


Figure 2 Variations of lifetimes τ and intensities I for *a*-TiO₂ with volume density ρ .

The complementary intensities I_1 and I_2 for *a*-TiO₂ changed with the change of atmosphere. The positron annihilation *in* the particles, denoted by τ_1 and I_1 , is insensitive to the atmosphere but the annihilation *outside* of them should be seriously affected by the atmosphere. Therefore, the change in I_2 is primary and that in I_1 is a result of the I_2 change. We conclude that the intermediate lifetime τ_2 of 0.450 ~ 0.455 ns is arisen from positron annihilation on the particle surface.

The length of τ_2 for *a*-TiO₂(Si) was almost equal to that for *a*-TiO₂. If the particle surface is smooth and

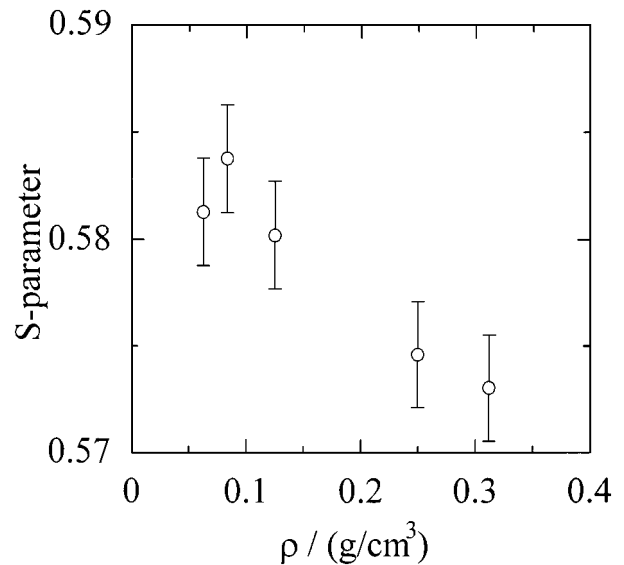


Figure 3 Change in S-parameter for *a*-TiO₂ as a function of volume density ρ .

the smooth surface of *a*-TiO₂(Si) is covered tightly by silicon dioxide film, the length of τ_2 for *a*-TiO₂(Si) should be different from that for *a*-TiO₂. The similar lifetimes show that the surface state seen by the positrons is nearly the same for both particles. No significant effects of atmosphere on I_2 for *a*-TiO₂(Si) indicate that the surface as the positron annihilation site is separated from atmosphere gas. We conclude that the cracks were formed on the surface of both particles and that the crack-openings of *a*-TiO₂(Si) were sealed by silicon dioxide films.

The I_2 for *a*-TiO₂ in the gas-atmosphere was lower than that in vacuum. This fact reveals that the gas-molecules are adsorbed on the crack surfaces and they reduce the fraction of positron annihilation on the surface. The longer τ_1 in gas atmosphere compared with that in vacuum is explained in terms of the lower I_2 in atmospheric gas. The lifetime of free annihilation τ_1 is increased by the decrease of annihilation fraction in the other channels such as surfaces or defects.

Taking into consideration that $\tau_3 = 1400 \sim 1500$ ps, this lifetime is attributed to the ortho-positronium annihilation in a free space. No oxygen quenching was observed for τ_3 , and I_3 was almost independent of atmosphere gas. The free space must be included inside the particles. We conclude that the *a*-TiO₂ particles contain a large number of voids in which the positron are annihilating.

4.2. Void size

A void size is generally obtained when a positron annihilates in the void. Tao [8] and Eldrup *et al.* [9] showed a simple relation between a radius R of spherical void and an ortho-positronium lifetime τ ,

$$\tau = (1/2)[1 - (R/R_0) + (1/2\pi) \sin(2\pi R/R_0)]^{-1}, \quad (\text{ns}) \quad (1)$$

and

$$R_0 = R + \Delta R, \quad (2)$$

where the potential energy for positronium is infinitely high at R_0 and the electrons spread out from R_0 into the void with a thickness ΔR . We obtained the void radius $R = 0.22 \sim 0.23$ nm, substituting the observed $\tau_3 = 1.4 \sim 1.5$ ns into τ with the use of $\Delta R = 0.166$ nm which gives reasonable values for various materials. The obtained void-radius corresponds to $2.2 \sim 2.3\%$ of the average particle radius of 10 nm.

4.3. Mechanical property of α -TiO₂

When the α -TiO₂ was compressed, both the longest lifetime component and the intermediate one disappeared, and only the shortest component remained. This indicates that, after compression, almost all of positrons annihilate in the particles. The vanishing of annihilation in the voids and on the surface cracks arises from their collapse by the compression. We deduce that the α -TiO₂ particles are sponge-like particles containing micro-voids inside and narrow cracks on the surface. The vestiges of voids and cracks may remain after the compression. The positron lifetime at these vestiges is probably almost equal to the lifetime of free annihilation in the amorphous particle.

The decrease in S-parameter with compression is explained in terms of the decrease of para-positronium fraction and the complementary increase in bulk annihilation, followed by the decrease of annihilation on

the surface cracks and the inner voids. Conclusively, the disappearance of lifetime component in the inner voids and surface cracks by the compression indicates that the amorphous TiO₂ particles are very soft and that they connect each other through compression.

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