Structure of nitride layer formed on titanium alloy surface by N$_2$-gas exposure at high temperatures

Y Takeda[1,4], K Iida[2], S Sato[2,3], T Matsuo[3], Y Nagashima[2], N Okubo[4], K Kondo[4] and T Hirade[1,4]

[1] Graduate School of Science and Engineering, Ibaraki University, 2-2-1, Bunkyo, Mito, Ibaraki, 310-8512, Japan

[2] Department of Physics, Tokyo University of Science, 1-3, Kagurazaka, Shinjuku, Tokyo, 162-8601, Japan

[3] Fukushima College, National Institute of Technology, 30 Nagao, Kamiarakawa, Taira, Iwaki, Fukushima, 970-8034, Japan

[4] Nuclear Science and Engineering Center, Japan Atomic Energy Agency, 2-4, Shirakata, Tokai, Ibaraki, 319-1195, Japan

E-mail: 2210080@alumni.tus.ac.jp

Abstract. Nitride treatment is used for hardening of titanium alloy surfaces. In this study, we prepare samples under two different conditions, (1) 810°C, for 600 min, and (2) 850°C, for 720 min. A depth-profile analysis of the surfaces of the samples is conducted through Doppler broadening measurements of positron annihilation gamma rays using a slow positron beam. Lager S-parameters are obtained near the surface for all samples. These parameters can be explained by the positron annihilation at the grain boundaries between the nano-grains confirmed by transmission electron microscope images. Furthermore, the variation in the W-parameters near the surface is independent of the variation in S–parameters, thus indicating a depth dependence of the W-parameters on the chemical composition of the precipitate at the grain boundaries, also confirmed by energy dispersive X-ray spectroscopy measurements. Variations in the W-parameters was observed to occur in the deeper regions, indicating that the nitrated layer is thicker in the sample prepared under condition (2) and the increased hardness of the sample surface measured using Vickers Hardness method is likely caused by this thicker nitrated layer.

1. Introduction

Titanium alloy is widely used in manufacturing of different objects, such as golf club heads and structural materials for aircrafts, because of its high strength, low weight and high corrosion resistance. The alloy surface can be significantly hardened through a nitride treatment of the surface, but there are some difficulties in the use of titanium nitride such as exfoliation and cracking of the surface layer because of increased stress. A previous study reported that these properties depend on the treatment temperature and time [1]. Two different nitride layers were reported to have formed on the surface, a TiN layer near the surface and a Ti$_2$N layer behind the TiN layer, and higher interfacial fracture toughness was observed near the thicker nitride layer [1]. Therefore, it is necessary to further study the structure of the nitride layer more to understand this interfacial fracture mechanism. One of our authors (S Sato) has already proven that samples prepared at higher temperatures for a longer period of time, i.e.

samples C and D in the present study, exhibit higher surface hardness, as shown in Table 1. In this study, a depth-profile analysis was conducted for the surfaces of the samples prepared through Doppler broadening (DB) of positron annihilation gamma-ray measurements [2]. The surface layers showing higher S values in samples C and D, i.e. the samples prepared at higher temperatures and for longer durations, were thinner than those of samples A and B, as shown in Figure 1. Hence, it is necessary to study the surface structures to determine the higher S-parameters. Transmission electron microscopy (TEM) and Energy dispersive X-ray spectrometry (EDS) were used to understand the structure near the surface in detail.
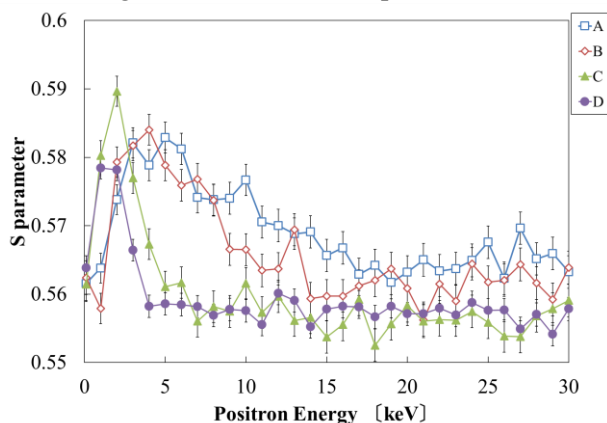
2. Experiment

DB measurements of positron annihilation gamma rays were conducted using a slow-positron beam line at the Tokyo University of Science [3]. The annihilation gamma rays were detected using a Ge semiconductor detector coupled with a NaI(Tl) scintillation detector. Measurements were performed at positron energies in the range of 0.1–30 keV and an energy interval of 1 keV. The measurement time and total count for the annihilation peak at each energy interval were 500 s and approximately 10000, respectively. The same procedures were performed several times for each sample.

The samples analysed were of titanium alloy (6 wt% aluminium, 4 wt% vanadium). A nitride layer was formed on the surface of each sample by heating under a nitrogen-gas atmospheric pressure of 1.3. Four samples were prepared under two different conditions: samples A and B were heated at 810°C for 600 min, and samples C and D were heated at 850°C for 720 min. Samples A and C were placed in the lower space and samples B and D in the upper space of the electrical furnace. The samples for TEM and EDS observation were prepared using focused ion beams (FIB) of gallium.

3. Results and Discussion

The TEM images for the four samples (A, B, C and D) are shown in Figure 2, indicating that the surfaces of these samples are covered with fine grains. The size of the grains were observed to be slightly different; however, they were found to be very small in general; i.e. less than 10 nm in size. The positron trap site in the nano-grained structures is formed mainly of grain boundaries as thermalized positrons can diffuse easily in grains and reach the grain boundaries [4]. The thicknesses of the nano-grain layers are approximately 200–300 nm for samples A and B and approximately 100–150 nm for samples C and D. Therefore, we conclude that the higher S parameters near the surface (Figure 1) are caused by the positron annihilation at the grain boundaries.

The depth dependences of S and W parameters are shown in Figure 2. Movements on the S–W plane are not on a diagonal line; hence, W-parameter variations provide qualitative information regarding
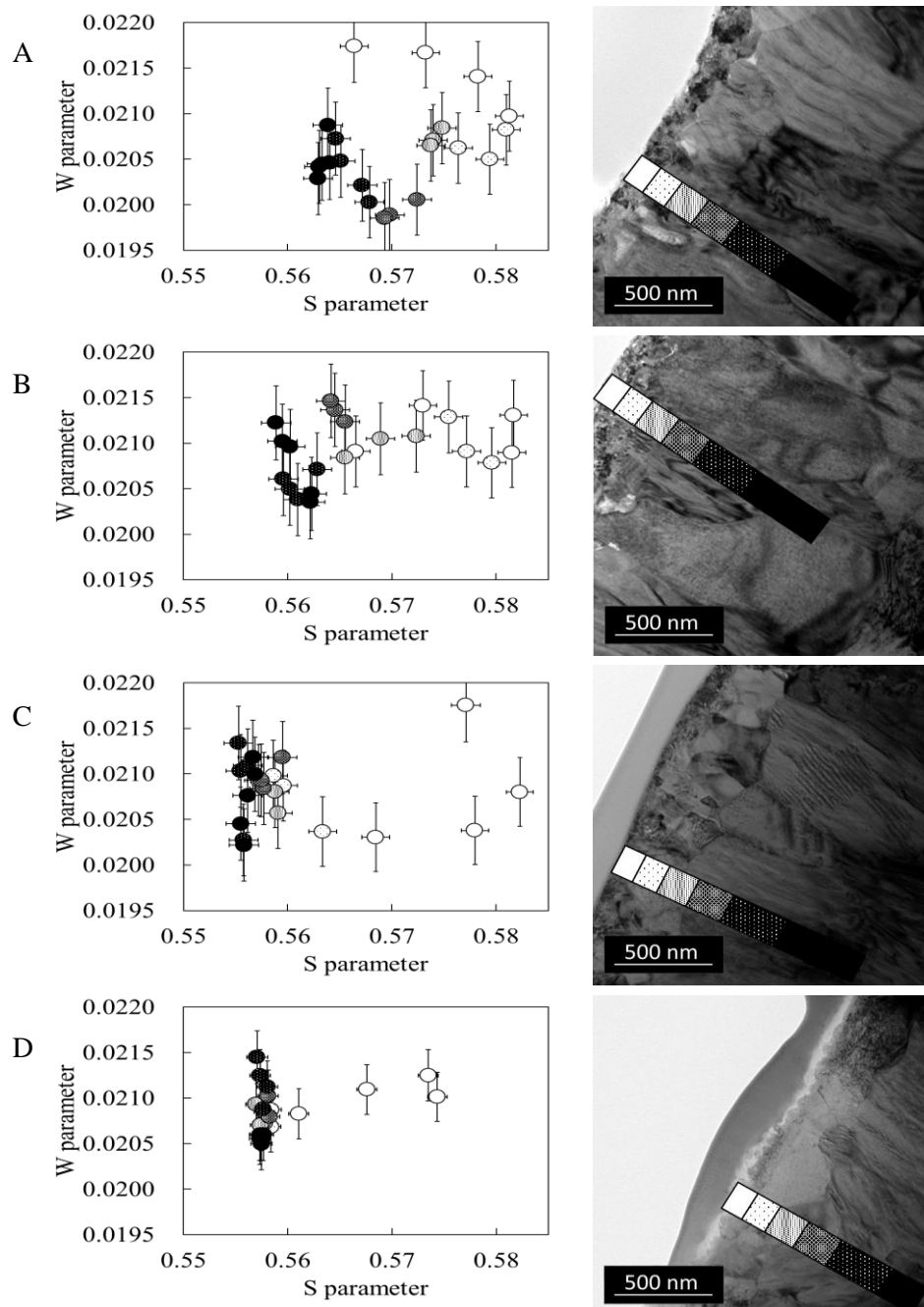

Figure 1.

Positron beam-energy dependence of the S-parameters of the samples prepared at 810°C for 600 min (A, B) and 850°C for 720 min (C, D).

Table 1. Vickers Hardness (VH) with 100 mN before and after nitriding treatment.
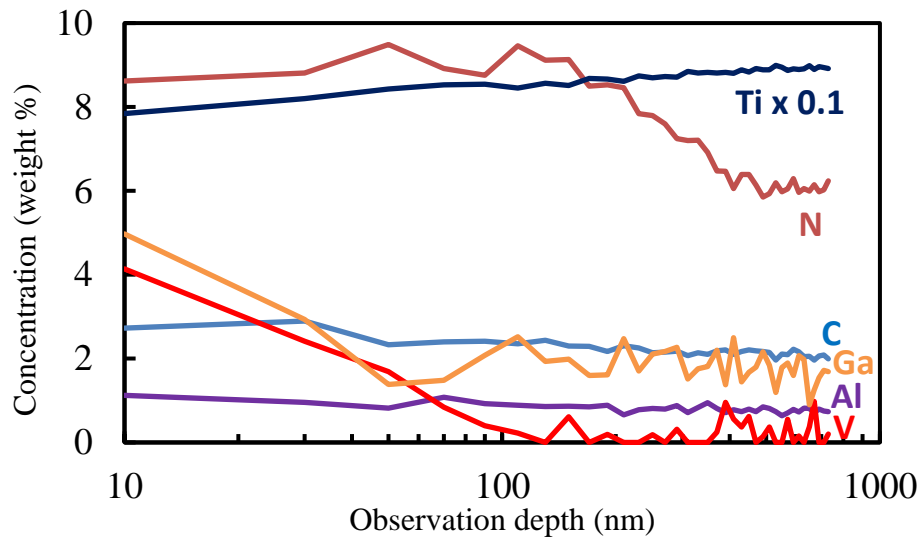
Virgin	(1) 810°C 600min		(2) 850°C 720min	
	A	B	C	D
354.1	724.1	729.0	1044.4	1036.2

the chemical elements present at the positron annihilation sites. The patterns in the plots, as shown in Figure 2, of the four samples correspond to the depth from the surface of the four TEM images. Larger S-values near the surface are explained by the positron annihilation at the grain boundaries [4], as mentioned above. At the depth where the S parameters change, the W parameters change independently, indicating that there is a depth dependence of the chemical composition of the precipitate at the grain boundaries.

The EDS results for sample C are shown in Figure 3. High nitrogen (N) concentration is observed up to a depth of 100 nm from the surface and it decreases gradually to almost half until the depth of 400 nm. This indicates that the layer showing higher N concentration (up to a depth of approximately 100 nm) contains TiN and the lower concentration layer contains Ti_2N. The thickness of the TiN layer

Figure 2. S–W plots and TEM images for samples A, B (810°C 600 min) and samples C, D (850°C 720 min). The grey shading in the plots corresponds to the shades on the bars in the TEM images indicating depth from the surface.

Figure 3.

Depth dependence of concentrations of elements measured by EDS. Carbon was coated on the sample surface when TEM and EDS samples were prepared using FIB. Implanted ions by FIB in the sample were observed to cause gallium contamination.

corresponds to the thickness of the nano-grain layer. In sample C, W parameter variations could be observed up to a depth of approximately 100 nm (Figure 2). According to the EDS measurement shown in Figure 3, density changes for Vanadium occur at the same depth region. Vanadium is likely to be the chemical element of the precipitate present at the grain boundaries.

The thicknesses of the nitrated layers with TiN and Ti_2N can be determined from the depths giving the lowest W values for the four samples. Hence, samples C and D have thicker nitrated layers than samples A and B. The thicker nitrated layers are probably the reason for the higher hardness in samples C and D.

The location of the occurrence of exfoliation near the surface is not known; however, a fracture along the grain boundaries can be a possible mechanism. W parameter variations appear near the surface and they are likely caused by the change in the chemical composition of the precipitate at the grain boundaries. DB measurements by slow-positron beams can be used a tool in the future to non-destructively estimate nitrated layers.

4. Conclusion

Higher S-parameters observed near the alloy surface can be explained by the positron annihilation at the grain boundaries in the nano-grained structures, as indicated by the TEM images. Variations of W-parameters that are independent of the changes in S-parameters indicate a depth dependence on the chemical composition of the precipitate at the grain boundaries. On the basis of the W-parameter variations, the nitride layers of samples C and D were found to be thicker than those of samples A and B. These thick nitride layers can be considered a reason for the increased hardness.

References

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