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Ceramic layers formed on metals by reactive plasma processing

Masanobu Nunogaki[a,*], Masahiro Inoue[a], Takayoshi Yamamoto[b]

[a] *The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[b] *The Institute of Radio Isotope Center, Osaka University, 2-4 Yamadaoka, Suita, Osaka 565-0871, Japan*

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Abstract

Thick layers of ceramics mainly composed of TaC, ZrO_2 and Ti_2AlN were successfully synthesized on the surfaces of Ta, Zr and TiAl by means of novel plasma dry processing with or without 20 MeV-electron beam irradiation as the pretreatment. The thickness of these ceramic layers reached 10–100 μm under appropriate process conditions. Vickers hardness of the layers including TaC, ZrO_2 and Ti_2AlN were estimated to be approximately 3000, 1300 and 3500 Hv[kg/mm^2], respectively. The cross-sectional profiles of constituent elements graded gradually in the modified surface regions, suggesting that these ceramics must have some properties of functionally graded materials. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbides; Films; Hardness; Nitrides; Surfaces

1. Introduction

The authors have engaged in developing a new type of surface modification of metals with use of the reactive plasma process as the main processing and an ion or relativistic-electron beam as the preparative treatment.[1] Ceramics such as TaC, TiN, ZrC, ZrO_2 are excellent in hardness and melting (decomposition) points as 4000, 2900, 3500 and 2700 °C, respectively.[2] However, these ceramics manufactured by means of powder metallurgical processes have poor machinability and reliability compared to metals. Therefore, the form of thick layers that are reactively synthesized on the surfaces of metallic components promises to be a means of efficiently using these ceramics. The reactive plasma process apparatus which has been developed by the present authors[3] is advantageous to synthesize the thick ceramic layers rather than conventional plasma processes, because the processing plasma is quite reactive and the temperature of the specimens can be elevated to the range that the diffusion coefficients of C, N and O in the lattice of metals[4] become sufficiently large. Moreover, pretreatments with ion and electron beams are effective in facilitating the formation of modified layers. The preirradiation of low energy ions as the pretreatment was experimentally observed to be effective on surface nitridation of pure Al.[1] A relativistic electron beam irradiation is reasonably expected to aid an increase of thickness of modified layer because the defects induced by the irradiation enhance the diffusivity of C, N and O. In the present work, the reaction behaviors to form thick ceramic layers on Ta, Zr and TiAl are discussed.

2. Experimental procedure

2.1. Apparatus

The apparatus consisted of a vacuum vessel, specimen holder[?0x81?]@with tantalum heater, plasma source, gas unit and three power supplies, as shown in Fig. 1. The processing gases were CH_4, O_2 and a mixture of N_2 and H_2 mixed at a ratio of 5:2 for carburizing, oxidizing, and nitriding, respectively. The processing plasma was generated with PIG (Penning ion gauge)—type hf (high frequency) discharge below 0.1 Pa. A dc bias about 1 kV was applied between the specimen holder (as the cathode) and the anti-cathode. The temperature of specimens was controlled by Ta-heater installed on the specimen holder.

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* Corresponding author. Tel.: +81-66-879-8492; fax: +81-66-879-8494.
E-mail address: nunogaki@sanken-u.ac.jp (M. Nunogaki).

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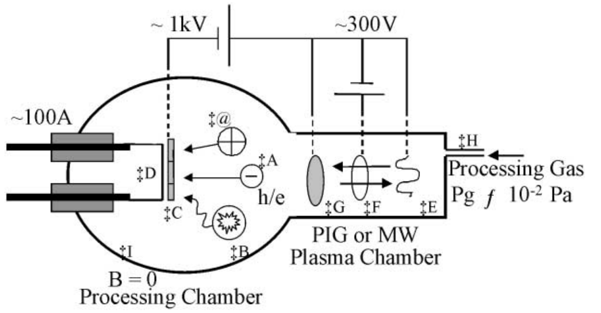

Fig. 1. A schematic drawing of apparatus: ions, hot electrons, exited atoms, specimens, Ta heater, filament, PIG anode, anti-cathode, gas feeder, vacuum vessel.

2.2. Procedure

Ta, Zr and Ti-48at.%Al plates of 8×5 mm^2 in area and 1–2 mm in thickness were polished to optical quality, and annealed at 350 °C for 3 h in a vacuum furnace ($\sim10^{-3}$ Pa). The irradiation with 20 MeV-electron beam was made on some plates for within 180 s at ambient temperature in air with a LINAC installed in our institute. The plasma process was performed at 1300 °C for 5 h for the carburizing of Ta, at 850 °C for 1 h for the oxidizing of Zr, and at 1100 °C for 2 h for nitriding of Ti-48at.%Al alloy, respectively.

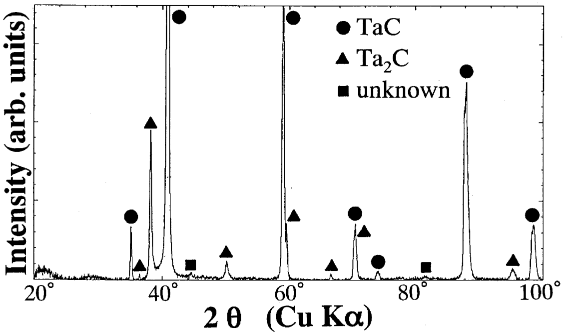

Fig. 3. XRD pattern of carburized Ta surface after the electron beam pre-irradiation with a fluence of 3×10^{15} cm^{-2}.

After the processing, the cross-sectional microstructure of the modified specimens was observed by scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA). The constituent phases of the modified layers were identified by X-ray diffraction (XRD). The hardness was measured using a Vickers indenter with a load of 25–50 g.

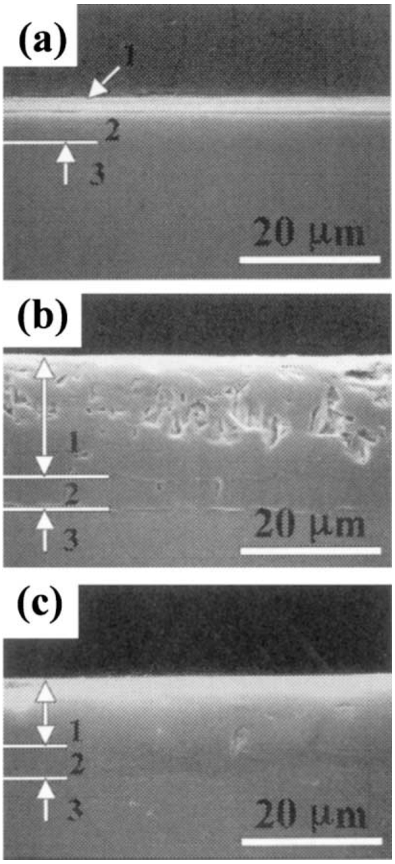

Fig. 2. Ta carbide layers formed at the sub-surfaces of Ta without the pre-irradiation (a) and after the pre-irradiation with a fluence to 3×10^{15}, (b) and 8.6×10^{15} cm^{-2} (c), respectively.

3. Results and discussion

3.1. Carburization of Ta

Because TaC has a very high melting point, the carburization of Ta plates was performed to form the surface layer composed of Ta carbides. Fig. 2 (a)–(c) show the cross-sectional micrographs of the specimens carburized at 1300 °C for 5 h without the pre-irradiation (a) and after the pre-irradiation with fluence of 3×10^{15} cm^{-2} (b) and 8.6×10^{15} cm^{-2} (c), respectively. Fig. 3 shows a typical XRD pattern measured using X-rays incident perpendicular to the sample surface. The main constituent phases are identified to be TaC and Ta_2C by

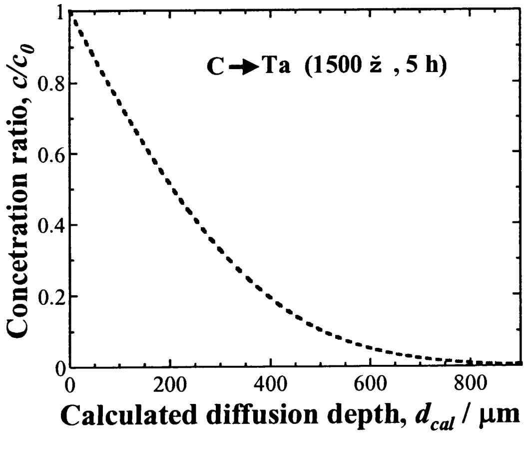

Fig. 4. Calculated diffusion depth profile of C in Ta substrate at 1500 °C for 5 h.

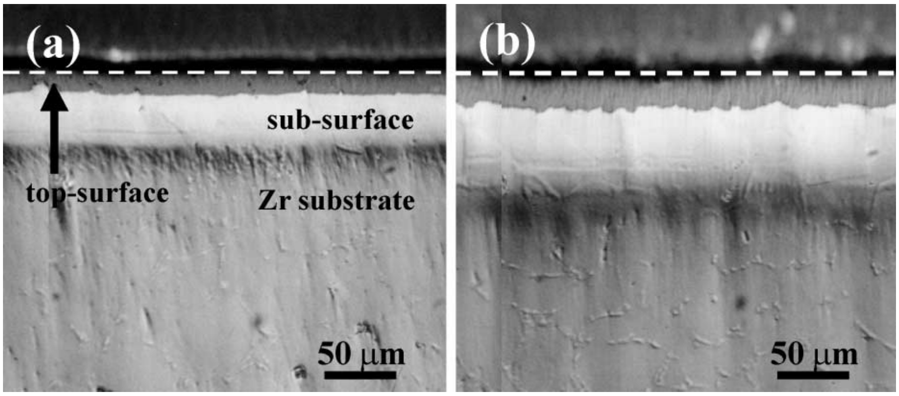

Fig. 5. Cross-sectional micrographs of Zr substrates oxidized at 850 °C for 1 h, (a) without the electron beam pre-irradiation and (b) after the pre-irradiation with a fluence of 1.8×10^{14} cm^{-2}.

this XRD pattern. The modified surface of the specimens is composed of two layers. Because the concentration of C decreases in the direction from the top surface to the inside of specimen, the top layer and the sub-surface layer are considered to consist of TaC and Ta_2C, respectively.

The thickness of the top- and sub-surface layers in the specimen without the pre-irradiation is approximately 2 and 5 μm as shown in Fig. 2(a). The modified layer is considered to be formed through the steps, which are the adsorption and subsequent diffusion of C, and then the ordering to form reaction products. The ideal diffusion depth of C in the lattice of Ta under the processing condition is estimated by the equations:

$$c = c_0\{1 - \mathrm{erf}(z)\} \tag{1}$$

$$z = x/2(Dt)^{1/2} \tag{2}$$

where erf represents the Gaussian error function, and c_0, c, D, t are concentration at top surface and at depth of x, diffusion coefficient and time respectively. Fig. 4 shows the calculated diffusion depth of C in Ta at 1300 °C for 5 h. According to this calculation result, the diffusion depth of C is estimated to be a few hundred μm. The discrepancy in diffusion depth between the experiment and calculation is likely to originate from ignorance of diffusion in the carbide layers in the calculation. Because the diffusion coefficients of C in TaC (9.90×10^{-13} cm^2/s at 1300 °C) and in Ta_2C (2.28×10^{-12} cm^2/s at 1300 °C) are much lower than that of C in Ta (2.59×10^{-8} cm^2/s at 1300 °C),[5] the layer growth is strongly restricted due to the low diffusivity of C through the lattice of carbides after the formation of these carbide layers. In order to synthesize thick carbide layers on the surface of Ta, the diffusion of C in Ta substrate is necessary to be enhanced prior to the formation of carbide layers.

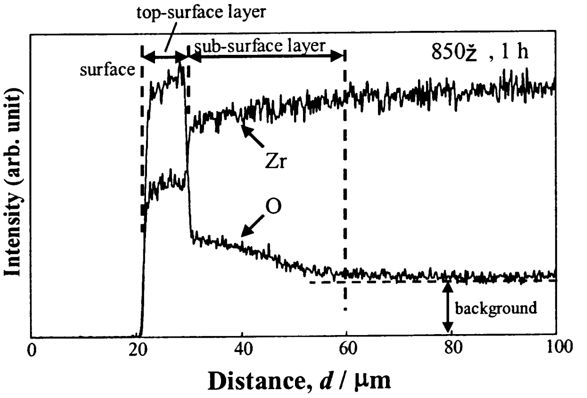

Fig. 6. Results of cross-sectional EPMA analysis of Zr specimen oxidized at 850 °C for 1 h without the pre-irradiation.

When a relativistic electron beam irradiates to metals, some primitive defects such as Frenkel pairs are generated. Because these defects are expected to play a role in enhancing the diffusivity of C in Ta, the electron beam irradiation was conducted as the pretreatment for the reactive plasma processing. As shown in Fig. 2(b) and (c), the thickness of the modified layers significantly increases with the pre-irradiation, but not always proportional to the fluence. The defects induced by the electron beam irradiation are believed to form small clusters (complex of defects), such as di-vacancies and di-interstitials.[6] Furthermore, macroscopic defects, such as dislocation loops, are generated with increasing fluence due to the accumulation of the clustering.[6] Hence, excess defect generation provides the trap sites to suppress the diffusivity. In the experimental conditions of the present work, the pre-irradiation with a fluence of 3×10^{15} cm^{-2} is suitable for obtaining the thick carburized layers. The hardness of the modified layer was measured to be 3000 Hv[kg/mm^2].

3.2. Oxidation of Zr

Zr is one of important candidate materials for first wall of blanket in an experimental fusion device, since it multiply neutrons through the reaction (n, $2n$). The first

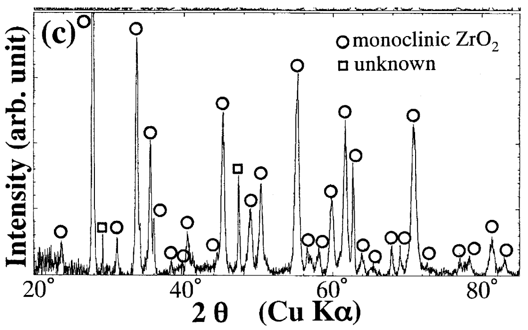

Fig. 7. XRD pattern of Zr specimen oxidized at 850 °C for 1 h without the pre-irradiation.

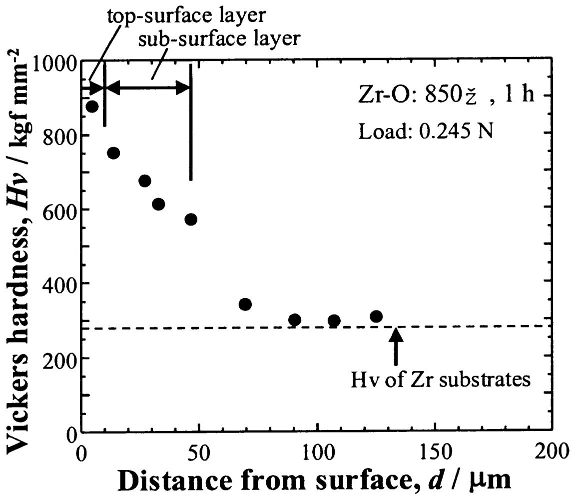

Fig. 8. Cross-sectional Vickers hardness of the oxidazed Zr substrate without the pre-irradiation.

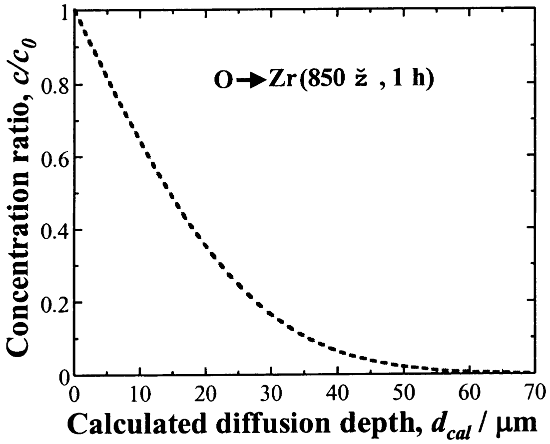

Fig. 9. Calculated diffusion depth profile of C in Zr at 850 °C for 1 h.

wall is required to be durable in an environment where there is an intense and high temperature plasma present. Therefore, in order to raise the melting temperature and to reduce the sputtering yield of the candidate material, a new surface modification technique needs to be developed. In this section, the reaction behavior of Zr substrate with an oxygen plasma is discussed as an example of surface treatment of Zr.

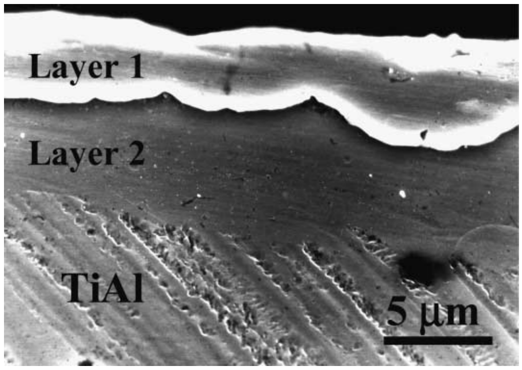

Fig. 10. Cross-sectional SEM micrograph of nitrided layers synthesized on Ti-48at%Al alloy at 1100 °C for 2 h. This sample were chemically etched with the Kroll's reagent for SEM observation.

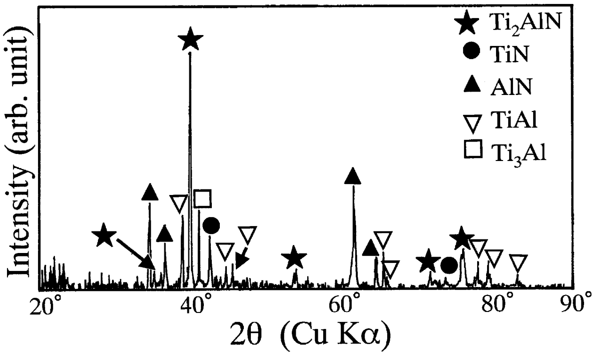

Fig. 11. XRD pattern of nitrided surface synthesized on Ti-48at.%Al alloy at 1100 °C for 2 h.

Figs. 5 (a) and 6 show the cross-sectional micrograph and EPMA line profiles of the oxidized Zr plates at 850 °C for 1 h without the electron beam pre-irradiation. Fig. 7 shows the XRD pattern measured using X-rays incident perpendicular to the sample surface. According to this XRD pattern (Fig. 8), the main constituent phase of the top-surface layer is monoclinic ZrO_2. The total thickness of the top- and sub-surface layers is estimated to be 40–50 µm. The EPMA line profiles clearly indicate that the top-surface layer has a high oxygen content, and that the oxygen content gradually decreases in the sub-surface layer. The distribution of O corresponds to the depth profile of the hardness as shown in Fig. 8. In the sub-surface layer which is a Zr disordered alloy with O, the hardness gradually decreases as decreasing the oxygen content.

Fig. 9 shows the calculated diffusion depth of O in Zr estimated using Eqs. (1) and (2) under the process condition for the specimen shown in Fig. 5(a). In contrast to the case of the carburization of Ta, the calculated diffusion depth of O approximately agrees with the total thickness of the top- and sub-surface layers. Therefore, the diffusion of O is deduced to predominate to the kinetics of ordering to form the monoclinic ZrO_2 layer during the plasma oxidation of Zr substrates.

Fig. 5(b) shows the cross-sectional micrograph of the oxidized specimen after the pre-irradiation with a fluence of 1.8×10^{14} cm^{-2}. The thickness of the modified layers (both top- and sub-surface layers) significantly increases compared to that of the layers formed without the pre-irradiation. The hardness of this top-surface layer was estimated to be 3000 Hv[kg/mm^2] by a hardness test.

3.3. Nitridation of Ti aluminide

Ti aluminides, such as TiAl and Ti_3Al, are expected as a candidate material for high temperature structural applications. Because surface modification techniques need to be developed to improve the durability of Ti alumindes, nitridation of Ti-48at%Al alloy was performed by the reactive plasma process.

Fig. 10 shows the cross-sectional SEM micrograph of a Ti-48at%Al alloy nitrided at 1100 °C for 2 h. The top-surface layer exhibit much higher hardness (3500 Hv[kg/mm^2]) rather than the sub-surface layer and Ti-48at%Al substrate. Fig. 11 shows the XRD pattern of the nitrided specimen. The main constituent phase of the modified layer is identified to be a ternary nitride, Ti_2AlN from this XRD pattern. The direct nitridation is expected to be effective in improving durability of Ti aluminides since the ternary nitride has higher melting temperature and hardness than the substrates.

4. Conclusion

Thick and hard layers of ceramics, including TaC, ZrO_2 and Ti_2AlN, were successfully synthesized on the surfaces of Ta, Zr and TiAl by means of novel plasma processing with or without 20 MeV-electron beam irradiation as the pretreatment. The concentration of the constituent elements of the modified layers graded from the top surface to the inside of specimens. Further investigation will be continued in order to improve the durability of structural materials based on metals and intermetallics for high temperature applications.

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