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Surface modification of a metal into a thick ceramic layer and a model for analyzing the increased hardness

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Surfaces of metallic Ti have been modified successfully to thick layers of metalceramic, TiC, by reactive plasma processing. The carbonized surfaces consist of mixed layers of TiC and metallic Ti. TiC grains grow up on the Ti substrate with island forms. The metal Ti acts as a "paste" between the growing TiC grains. The hardness of the modified surface layers increases with processing temperature. The hardness reaches 5000 kg/mm² at a processing temperature of about 1300 °C, which is a value comparable to bulk TiC. Analysis of the XAFS spectrum and the diffraction profiles for the fabricated layers shows a reduction of the Ti-Ti distance from a distance of 3.07 Å for the bulk TiC to 3.025 Å. Using the results of the local structures around a Ti element by XAFS analysis, we will try to elucidate the abnormal hardness of the newly fabricated TiC by an analytical model.

Key words: TiC, Cermets, XAFS, Electron-nuclear interaction.

Introduction

Social circumstances in the near future demands complex- or multi-functional materials for a more complicated social infrastructure. As one of the technologies producing such materials, modification of the surfaces of metals into a ceramic state by reactive plasma processing is possibly a very good technique. In general, ceramics are fabricated by means of sintering or coating. These ceramics formed by sintering are rather too hard to finish mechanically with the correct dimensions. The surface layers of a metal modified into a ceramic state (cermets, or sometimes called new concept ceramics) produced by reactive plasma processing are remarkably easy to manufacture but have, nevertheless, the high hardness comparable to sintered materials [1, 2]. Our recent attempts using the reactive plasma processing [3] have shown that the surfaces of Ti, Ta, Zr, TiAl and Al have been modified successfully to produce thick layers in a metalceramic state; TaC, ZrO₂, Ti₂AlN and AlN, where the processing temperature was generally above 900 °C.

In this paper, we will describe the modification of surface layers of metallic titanium, and will discuss on the high hardness of the modified surface layers with an analytical model. Here, we suggest electron-nuclear interaction in the analytical model [4-6].

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Fabrication

The modified layers in this study were formed by the plasma-reaction of C atoms with the Ti metal substrate heated to ~1300 °C [7-9]. The implanted atoms react with the substrate metal, resulting in TiC compound. This compound grows into adequate grains in the Ti metal matrix, depending on the temperature of the substrate metal and the processing time. Thus, the carbonized layers on the Ti metal substrate consist of mixed layers of TiC and metallic Ti. The details of the process such as the apparatus, fabrication conditions, etc, are given in Ref. [3, 7]. Analyzing the evidence from electron probe microanalysis (EPMA) indicates a functionally gradient property (Fig. 1). The thickness of the modified layers fabricated at a processing temperature of 1300 °C and a processing time of 2 hours is evaluated to be about 10 µm on average. This situation



Fig. 1. EPMA profile of the modified Ti plate. The profile clearly shows the modification of the surface layer to TiC. Here, SE means total secondary electrons.

is confirmed indirectly from the X-ray diffraction pattern and by the X-ray absorption fine structure (XAFS) analysis described below.

Characterization of Layers Modified by Reactive Plasma Processing

We examined surface layers modified by the reactive plasma processing by means of measurement of Vickers hardness, X-ray diffraction analysis using Rietveld method and XAFS analysis. Figure 2 shows the Vickers hardness as a function of processing temperature. The hardness reaches 5000 kg/mm² at the highest processing temperature of about 1300 °C. This value is comparable to that of sintered material TiC despite the mixed and condensed layers of TiC compound and metallic Ti with small size grains. The increase in hardness with the processing temperature suggests that the grain size of TiC grows up with the processing temperature. The average hardness (h_{av}) of the TiC compound (h_{TiC}) and the metallic Ti (h_{Ti}) is expressed in the simplest case as $h_{av} = (\mathbf{a}h_{TiC} + \mathbf{b}h_{Ti})/\mathbf{A} = (\mathbf{a}/\mathbf{A})h_{TiC} + (\mathbf{b}/\mathbf{A})$ A) h_{Ti} , where A = **a** + **b**, and **a** and **b** are the volumes of the TiC compound and the metallic Ti in the modified surface layers, respectively. From the above description, the exponential increase in the hardness observed in this study (where the data points are fitted by the function, Aexp(α T) with A=2.1 and α =0.006, where T is the processing temperature) means that a higher chemical reaction rate occurs at higher temperatures, as observed in usual chemical processes, and this seems to be indirect evidence that the grains of the TiC compound are "pasted together" with metallic Ti.

The surface layers modified at $1300 \,^{\circ}$ C were inspected by X-ray diffraction as shown in Fig. 3. Rietveld method for X-ray powder diffraction data is employed for detailed and quantitative analysis using the program RIETAN –94 [10]. The diffraction profile indicates the



Fig. 2. Hardness as a function of the processing temperature. The hardness increases with the processing temperature, and saturates at 1300 °C.



Fig. 3. X-ray diffraction profile. The upper part presents the profile of the fabricated sample, and the middle part and lower part are simulated profiles for TiC with the space group F_{m3m} and Ti metal with the space group $P_{6/mmc}$, respectively.

space group of the modified surface layers to be F_{m3m} with the NaCl structure, the same as bulk TiC, but shows that the average lattice parameter is reduced by about 1.0% (4.285 Å) from the value (4.3274 Å) of bulk TiC [11]. The diffraction pattern also suggests a sufficiently large size of the crystalline grains of the TiC compound to give clear Laue peaks. Simulations of the diffraction profiles of TiC with space group F_{m3m} and of metallic Ti with space group $P_{6/mmc}$ are represented in the Fig. 3 also. The majority of the modified surface layer is TiC with NaCl structure, and a small amount of metallic Ti exists in the modified surface layer.

To discover more detail about the microstructural properties leading to the unexpectedly high hardness and the reduced lattice parameter, XAFS spectra around the K-edge of the Ti atoms of the modified surface layer and bulk TiC for comparison have been made by a method detecting the fluorescent X-rays [12]. Analysis of the XAFS spectrum for the modified surface layer also shows a reduction of the Ti-Ti distance to 3.025 Å from a distance of 3.07 Å for the bulk TiC. The distance from XAFS analysis is somewhat shorter than the value (3.033 Å) found from the diffraction analysis. The distance between Ti and C, which is the first nearest atom, could not be clearly analyzed owing to weak back scattering of photoelectrons. The XAFS spectrum for the Ti-Ti circumstance is well analyzed by a rather small Debye-Waller factor, which means the specimen has a high hardness. In analyzing the XAFS spectrum of the modified surface layer, we found that the spectrum contains rather strong signals from the metallic Ti. These signals hardly come from the Ti



Fig. 4. Analytical model of the modified surface layer. Metallic Ti acts as a "paste" in this model.

substrate. Note that the incident and emitted X-rays are around the K-edge of the Ti atom and are lower in energy than the X-rays used for the diffraction measurements. Therefore, this indirectly supports the hypothesis that the metallic Ti remains and functions as a "paste" between the TiC grains. The origin of the reduced distances from those in the bulk and the higher hardness of the grown TiC compound can be deduced from microscopic point-of-view through an electronnucleus interaction. Here, we will discuss this semiphenomenologically.

Model Analysis

As described below, we examine electron-nucleus interaction to explain the unexpectedly high hardness of the modified surface layer [13-15]. The adiabatic potential between the atoms by which the micro-cluster is composed, consists of three kinds of interaction: an attractive and/or repulsive nucleus-nucleus interaction, an electron-electron repulsion, and an electron-nucleus interaction. It is reasonable to expect for the physical quantities of electronic states such as the energy gaps in the cluster to be different from those in the bulk, resulting in the different strength of the electron-nucleus interaction. This allows the configuration of the nuclei to rearrange, and their rearrangements again change the strength of the electron-nucleus interaction. As the result, the configuration of the atoms becomes adequately balanced. Here, the problem of the reduced lattice parameter and the high hardness is treated by a perturbation method up to the second order for simplicity. The Hamiltonian of the electron-nucleus interaction to the second order is expressed as follows:

$$H_{en}(r,Q) = A_1(r,R_0)Q + A_2(r,R_0)Q^2$$
(1)

where *r* is the electron coordinate, R_0 the equilibrium position of the atoms in the bulk, $A_1 (=\partial H_{en}/\partial Q|_{Q=0})$ and $A_2 (\partial^2 H_{en}/\partial Q^2|_{Q=0})$ represent the coupling strength for the first and second order electron-nucleus inter-

actions, respectively, in the totally symmetric space Q in normal coordinate systems. The full notation of the adiabatic potential between the Ti and C atoms within the TiC₆ framework of the cluster is written as:

$$U(r,Q) = \omega Q^2 + \langle A_1(r,R_0) \rangle Q + \langle A_2(r,R_0) \rangle Q^2 \qquad (2)$$

where ω_0 and $(\omega^2 = \omega Q^2 + \langle |A_2| \rangle)$ are the force constants of the non-perturbed material and of the cluster, respectively, and $\langle \rangle$ presents the average value in terms of the electron wave function. The new equilibrium position is $Q = -\langle |A_1| \rangle/(2\omega^2)$, or $R' = R_0 - \{\langle |A_1| \rangle/(2\omega^2)\}^{1/3}$. Here, R' corresponds to the equilibrium position in the synthesized TiC.

Hydrostatic pressure p as an outer-perturbation acts similarly to the electron-nucleus interaction described above. The work of the pressure is represented to be pQ, + γpQ to the second order and the adiabatic potential under the hydrostatic pressure is:

$$U(r,Q) = \omega Q^2 + pQ + \gamma p Q \tag{3}$$

where γ is an appropriate constant. The pressure *p* acts as a compression force with a positive sign and as an expansive one with a negative sign. Equations (2) and (3) are expressed in the same form. Thus, the state of the TiC synthesized here is recognized to be analogous to that under pressure. Assuming the effect in the present case, $\langle |A_2| \rangle > 0$, thus, $\omega^2 > \omega$ The force constant, ω_0 or ω_i is related to the bulk modulus or the totally symmetric elasticity. Therefore, the hardness of the synthesized TiC becomes greater. The theoretical model obtained from the above discussion is schematically drawn in Fig. 4.

Conclusions

Based on the fact of the reduction of bond distances between Ti-Ti in TiC and the qualitative model analysis, we reach the following conclusions. Small size modified grains of TiC are created in a Ti substrate. These grains of TiC grow at high processing temperatures in the hard metallic "sea", receiving high compressive tensions, as the time progresses, and the growing grains weld each other together with the metallic Ti, resulting in a high compressive tension in the TiC grains. This results in an exponential increase in the hardness as shown in Fig. 2 and in a shortening of the bond length. The residual metal Ti acts as a "paste" between the growing TiC grains. A schematic drawing of this situation is shown in Fig. 4. Furthermore, we found from the analytical model and the XAFS analysis that this is in the same state as if it were under high quasi-hydrostatic pressure. Significant features are easier manufacturability but with a high hardness which is created through the quasi-hydrostatic pressure under which the TiC grains exist. At present, we cannot understand why TiC grains do not grow larger, leaving only a small amount of metallic Ti. To understand this, a detailed study of the processing mechanism needs to be done.

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