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Structural stability and mechanochemical activity of titanium nitride prepared by mechanical alloying

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Pure titanium nitride (TiN) was synthesized by mechanical alloying (MA). In order to prevent the contamination from the MA vial and atmospheric gas, the MA steel vial was replaced with a titanium vial and atmospheric gas was deoxidized using sponge titanium heated to 623 K. The mechanochemical activity during MA was estimated from the gas purification temperature. The investigation of thermal and pressure stability by thermal treatment and hot isostatic pressing (HIP) revealed that titanium nitride, TiN, was stable on heating to 1173 K under a vacuum, but became unstable under a high pressure, 100 MPa.

1. Introduction

Mechanical alloying (MA) has been used to prepare solid-solution alloys, intermetallic compounds, amorphous alloys and ceramic materials [1, 2]. It has been reported by several authors that some impurities arise from contamination by experimental devices, carrier gases and atmospheric gases [3, 4]. In order to clarify the structural stability and mechanochemical activity of MA products based on titanium, the chemical modification of their properties brought about by contamination by impurities from the MA system must be prevented, since titanium has a strong chemical affinity for various elements. In this study, contamination from the MA steel vial and atmospheric gases was prevented by replacing the material of the vial with titanium and deoxidizing the carrier gas with heated sponge titanium.

Results are presented of the structural changes and chemical reaction accompanied by mechanical alloying, thermal treatment and HIP processing for a titanium-TiN system. The mechanochemical activity of titanium at the atomic level during MA was also estimated by varying the temperature of the deoxidizing sponge titanium.

2. Experimental procedure

Powdered titanium nitride was prepared from pure titanium powder by employing a high-energy ball mill (Mitsui Miike attritor MA-01D, Japan) under a nitrogen atmosphere. In order to prevent contamination by impurities from experimental devices, the stainless vial, balls and arms were replaced with pure titanium ones. Nitrogen and argon gases of 99.99 and 99.999% purity, respectively, were purified using a deoxidizing silica tube filled with sponge titanium heated at 573, 623 and 673 K. Nitriding was carried out for 36, 72, 108 and 144 ks under a purified nitrogen-gas flow.

To investigate the thermal and pressure stability of titanium nitride, part of the powder obtained was annealed in a vacuum at 873, 973, 1073 and 1173 K and then consolidated by hot isostatic pressing (HIP) under *P–T* conditions of 100 MPa at 1273 K. All powders and HIP samples were characterized by X-ray diffractometry (XRD) using MoK_α radiation. The thermal properties of powders and HIP bulk samples were analysed by differential thermal calorimetry (DSC, Perkin-Elmer DSC7) heating from 473 to 973 K at 0.33 K s^{-1} in an Ar gas atmosphere. Additionally, the filed powder from the HIP bulk sample was also examined by XRD and DSC. The microstructures of the samples were observed by transmission electron microscopy (TEM, Akashi-002B) under an acceleration voltage of 200 kV. This report mainly describes (in detail) the results for samples mechanically alloyed for 108 ks.

3. Results and discussion

The titanium powder easily adhered to a vial during MA in a deoxidized Ar-gas atmosphere. Such easy adhesion was not obtained with either non-deoxidized Ar gas or N_2 gas. The XRD profile changed with increasing MA time under a non-deoxidized nitrogen-gas atmosphere, as shown in Fig. 1. According to the profile of the powder prepared by MA for 108 ks, the main peaks of TiN ((1 1 1) and (2 0 0) for $2\theta = 16.8$ and 19.3° respectively) and α-titanium ($(1 0 \bar{1} 0)$, (0 0 0 2) and $(1 0 \bar{1} 1)$ at 15.9, 17.2, and 18.0°, respectively) are slightly detected, and broad peaks of complex oxides around 10° are clearly observed. Oxidation of titanium powder during MA is also detected until the

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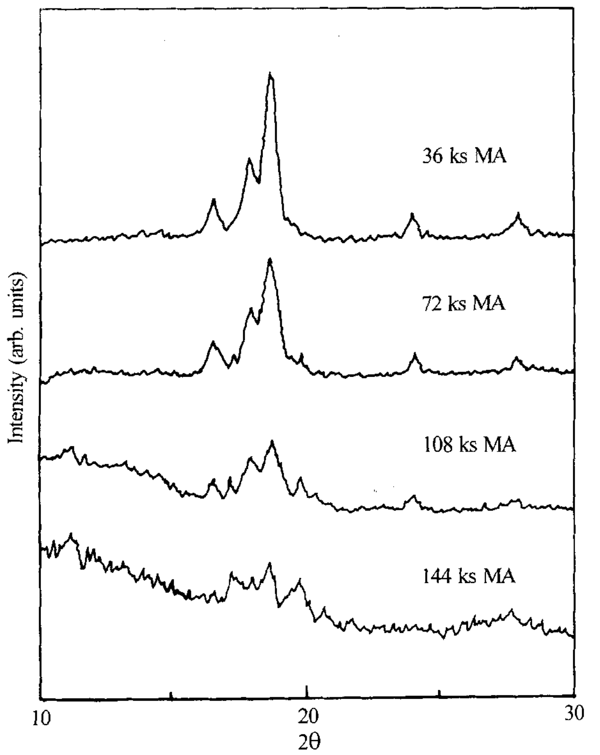

Figure 1 Change in the XRD profiles with MA time under a non-deoxidized nitrogen atmosphere.

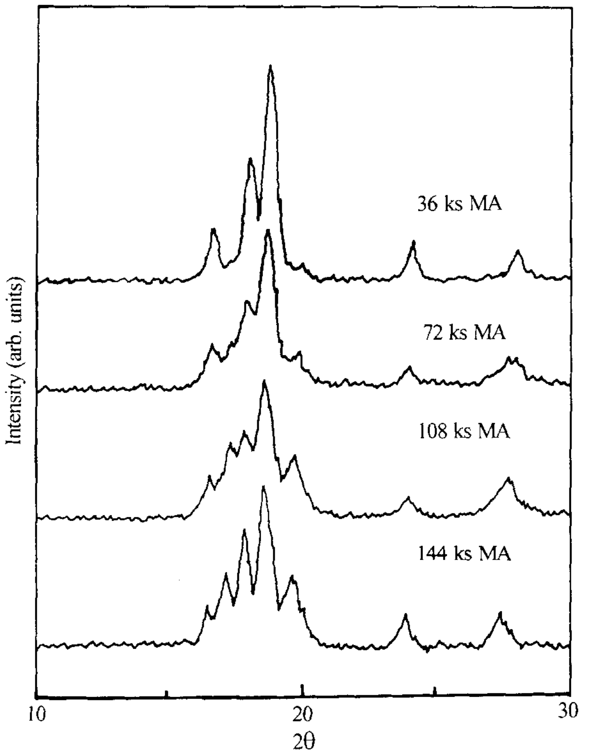

Figure 2 Change in the XRD profiles with MA time under a deoxidizing nitrogen atmosphere.

sponge titanium reaches 573 K. Fig. 2 shows the XRD results of nitrified powder prepared by MA under deoxidizing nitrogen gas at 623 and 673 K; no titanium-oxide peak is found around 10°. The nitrogen content of the powder mechanically alloyed for 108 ks was determined as 6.55 wt % by chemical analysis.

The peak shift to small angles in the XRD pattern of α-titanium was carried out by solving nitrogen (see Fig. 2, 144 ks MA) [5]. It is expected from the Ti-N phase diagram (see [6]) that Ti_2N and/or a δ-phase should be produced at low temperature. In fact the TiN phase, the high-temperature phase, increases with MA time, while neither a Ti_2N nor a δ-phase is detected. Such a result, that a metastable phase is produced by MA, was also found in a Ti–Mo system [7]. Synthesis of pure titanium nitride (TiN) is almost achieved by MA for 216 ks without any contamination from the MA device and atmospheric gas, as achieved by our MA processing method.

From the critical temperature of deoxidizing N_2 gas, it is speculated that the temperature of the mechanochemical reactions at the atomic level during MA are lower than those of sponge titanium heated in deoxidizing nitrogen gas to 623 K. Furthermore, if the activation energy required to oxidize a MA powder with a fresh surface is considered to be lower than that of sponge titanium, the equivalent temperature of the titanium powder rubbed during MA must be rather low at the atomic level.

The microstructure of the titanium-nitride-mixture powder prepared by MA for 108 ks was observed by TEM. The result is shown in Fig. 3. The surface of a particle was divided into nano-crystallines showing lattice images of titanium nitride, and the interior of the particle was composed of lattice images of α-titanium and titanium nitride. This observation shows that nitriding of the powder advances from the surface to the interior.

A sample of mixed powder containing α-titanium and TiN which was produced by MA for 144 ks was

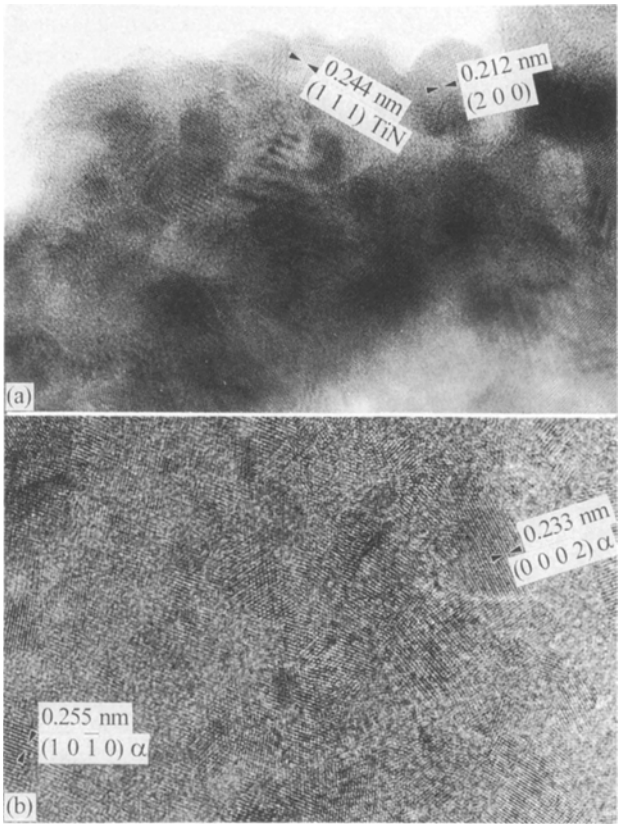

Figure 3 Transmission electron micrographs of a mixed powder of titanium and titanium nitride prepared by MA for 108 ks: (a) the surface of a particle and (b) the interior of a particle.

annealed at various temperatures to investigate the thermal stability of its structure. As shown in Fig. 4, the peaks of TiN do not change when the sample is annealed to 1173 K in vacuum. However, part of the α-titanium annealed above 923 K became so active as to be oxidized when it was exposed to air at room temperature. Fig. 5 shows the heat flow of the reference powder-material (TiN, Johnson-Matthey), the powder samples obtained by MA for 108 and 144 ks, the HIP sample obtained from the powder by MA for 108 ks, and its filed powder sample. The thermal characteristics of the 144 ks MA powder are similar to that of the reference powder, but the sample of 108 ks MA powder shows a remarkable endothermic reaction above 773 K. The TiN compound becomes unstable on heating and nitrogen atoms must be solved into the titanium matrix. The HIP bulk sample consolidated from the powder of 108 ks MA showed the same simple DSC curve as a pure titanium nitride, but the heat flow of the powder obtained by filing the HIP sample was similar to that of the sample composed of titanium and TiN.

Fig. 6 shows the XRD patterns of the HIP bulk sample and the filed powder of 108 ks MA. The TiN peaks disappear and all peaks are identified as a titanium–nitrogen solid solution. In HIP processing, the complete bulk sample could not be made from powder of high nitrogen content (over 1.2 wt %), corresponding to MA for more than 72 ks. HIP samples prepared from the powder were broken into many small fragments on cooling at 0.1 MPa. From the

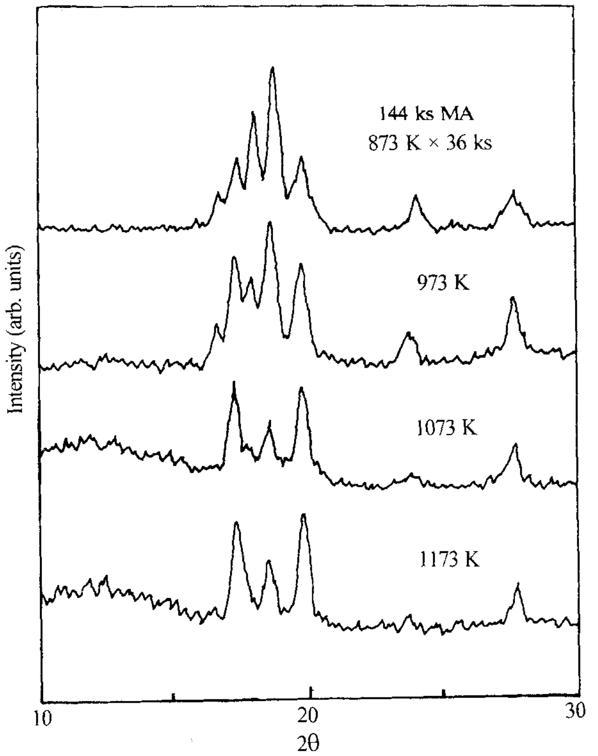

Figure 4 Change of the XRD profiles with annealing temperature to examine the thermal stability of the mixed powder containing α-titanium and titanium nitride.

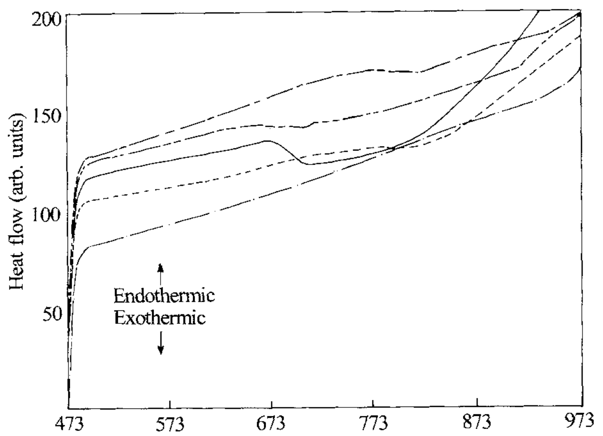

Figure 5 DSC traces of: (– - -) the pure TiN powder, (- - - -) the powder of 108 ks MA and (——) 144 ks MA, (– – –) the HIP sample consolidated from the powder of 108 ks MA, and (–·–) its filed powder.

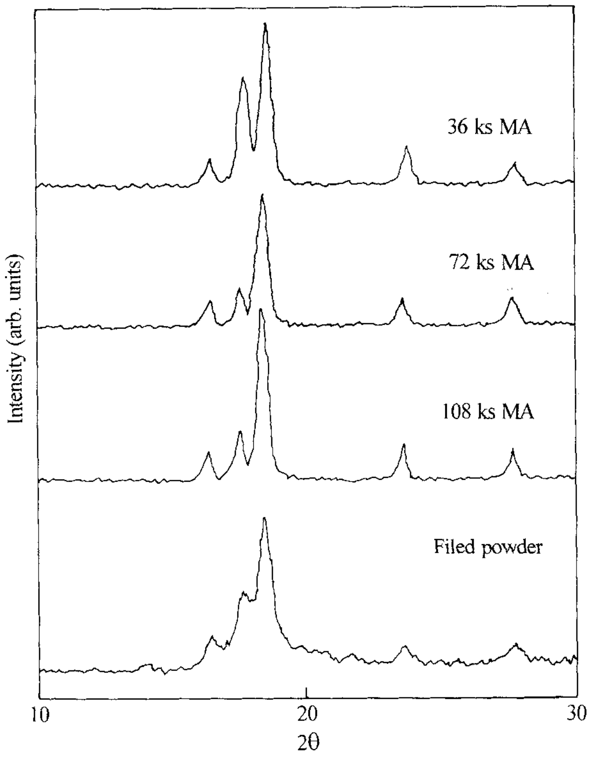

Figure 6 XRD profiles of HIP bulk samples for various MA times and the filed powder from the HIP bulk sample of 108 ks MA.

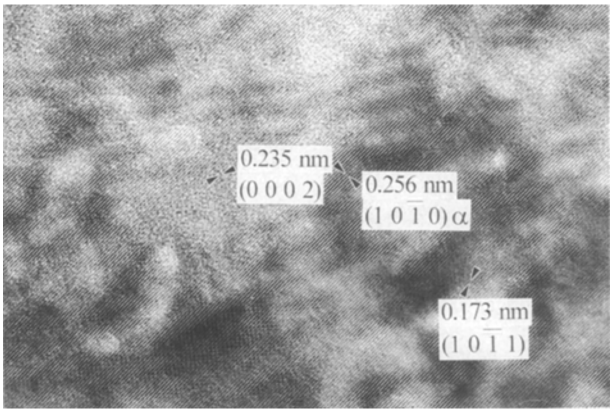

Figure 7 A transmission electron micrograph of the HIP sample obtained from the powder of 36 ks MA.

TEM results, lattice images of α-titanium can be seen which do not contain any titanium nitride (see Fig. 7). The Vickers hardness, H_V, of the HIP sample prepared from the powder mechanically alloyed for 108 ks was 1100 kg mm^{-2}.

4. Conclusion

Titanium nitride, TiN, is stable for heating to high temperatures under vacuum, but it is unstable for heating under high pressures.

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