Formation of metastable phases by high-energy ball milling in the Ti-O system

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Abstract. Investigation of the phase formation during mechanical alloying (MA) was systematically performed in the Ti-O system. Powder mixtures of Ti and TiO$_2$ with various compositions and single-phase Ti$_2$O, $\alpha$-TiO and $\alpha$-Ti$_2$O$_3$ powders were respectively subjected to planetary ball milling. According to X-ray diffractometry, high-temperature phases such as $\alpha$-Ti solid solution, $\gamma$-TiO and $\beta$-Ti$_2$O$_3$ were observed for Ti-33 at%O (after 4 h of MA), 40-55 at%O (8 h) and 60 at%O (4 h), respectively. The metastable phase formations are discussed from various viewpoints including local pressure, local temperature, point defects, impurity and repeated deformation. The phase formations by MA are explained by primitive unit cell volume of the crystal structure as an indicator.

1. Introduction
Mechanical alloying (MA) has been extensively studied as a non-equilibrium materials processing technique [1]. By MA, many metastable materials such as disordered phases, supersaturated solid solutions and amorphous phases have been produced [2].

While there are many reports on MA in metal-metal systems and oxide-oxide systems, there are very few reports on MA in metal-oxygen systems except oxide-dispersed alloys, such as the formations of FeO [3] or Fe$_3$O$_4$ [4] from Fe and Fe$_2$O$_3$ powders, and $\gamma$-TiO (high-temperature phase) from a near-equimolar mixture of Ti and TiO$_2$ powders [5, 6, 7]. Among metal-oxygen systems, the Ti-O system is particularly interesting since there are many phases including disordered phases and high-temperature ones in this system. Thus, the aim of this study is to investigate the phase formation by MA in various compositions of the Ti-O binary system. As for the nomenclature of each phase, we followed the equilibrium phase diagram assessed by Murray and Wriedt [8].

2. Experimental
Powders of Ti (98 %, < 45 $\mu$m) and anatase-type TiO$_2$ (99.8 %, 200 nm) were mixed in the compositions 33, 40, 45, 50, 55 and 60 at%O, and subjected to MA. Single-phase titanium oxides (Ti$_2$O, $\alpha$-TiO and $\alpha$-Ti$_2$O$_3$) were also employed as starting materials of MA. As for $\alpha$-TiO, a commercially available reagent (99.9 at%, < 150 $\mu$m) was used, while Ti$_2$O and $\alpha$-Ti$_2$O$_3$ were synthesized by the molten salt method from Ti and TiO$_2$ at 1000 $^\circ$C in a CaCl$_2$ flux. The phase of each starting material was confirmed by powder X-ray diffractometry (XRD).

The starting materials were placed in a sealed stainless-steel vessel with 160 g of stainless-steel balls with diameter of 9.5 mm under Ar atmosphere. MA was carried out using a planetary
ball mill (P-5, Fritsch) at 300 rpm of rotation speed up to 32 h. Ball to powder mass ratios were set to 20:1 for ball milling (BM) of Ti-TiO$_2$ mixtures, and 40:1 for BM of single-phase titanium oxides.

The starting materials and the products were analyzed by XRD using RINT2100CMJ (Rigaku) with Cu K$_\alpha$ radiation. Fe, Cr and Ni contamination from the milling media was quantified by energy dispersive X-ray spectrometry (EDX) using PHOENIX (EDAX) attached to a scanning electron microscope.

3. Results
Stable phases at ambient conditions and the phases obtained by BM for each composition are summarized in Table 1 together with density and primitive unit cell volume ($V_{pc}$) of each phase. The phases obtained by BM of single-phase titanium oxides were the same as those obtained by BM of Ti-TiO$_2$.

At 33 at%O, a hexagonal phase was identified by XRD, as shown in Fig. 1(a). Since stable Ti$_2$O phase is an ordered hexagonal phase with anti-CdI$_2$ structure [8], if existed, the superlattice reflections should be additionally observed. Such additional reflections are not identified in Fig. 1(a). Thus, the obtained phase is $\alpha$-Ti solid solution, which is stable at high temperatures above c.a. 600 °C [8].

In the range of 40-55 at%O, the peak pattern of $\gamma$-TiO was observed by XRD. Fig. 1(b) shows, for instance, the XRD pattern of Ti-TiO$_2$ after 8 h of BM at 50 at%O. It is known that $\gamma$-TiO phase possess NaCl-type crystal structure containing many vacancies at both Ti and O sites [9], and is a phase stable at high temperatures above c.a. 1250 °C across the wide range of 35-55 at%O [8]. Thus, the produced phases can be confirmed to be the phases stable at high temperatures. There is a report on the formation of $\gamma$-TiO$_{0.92-1.19}$ (47.9-54.3 at%O) by MA [6], which is consistent with our results.

At 60 at%O, $\beta$-Ti$_2$O$_3$, the high-temperature phase at this composition in the equilibrium phase diagram, was obtained, as shown in Fig. 1(c). Since both $\alpha$- and $\beta$-Ti$_2$O$_3$ have the corundum-type crystal structure [10], the formation of $\beta$-Ti$_2$O$_3$ was confirmed by the lattice parameter variation. While the estimated lattice parameters of initial $\alpha$-Ti$_2$O$_3$ were $a = 5.16$ Å, $c = 13.6$ Å, those of $\beta$-Ti$_2$O$_3$ after 2 h of BM were $a = 5.13$ Å, $c = 13.8$ Å.

4. Discussion
First of all, effects of impurities from the milling media on the metastable phase formations should be discussed. The total amount of Fe, Cr and Ni as impurities in the powders after 4, 8, 16 and 32 h of BM were within 3.2, 6.2, 13 and 22 at%, respectively. Because the Gibbs free energies of the reactions between the titanium oxides (33-60 at%O) and Fe, Cr or Ni are respectively more than +80 kJ per one mol of impurity atoms, which are much larger than the reported maximum excess energy stored in the material by MA (30 kJ/mol [2]), such reactions would not take place in this experimental condition. In addition, the produced phases within

![Figure 1. XRD patterns of (a) Ti-TiO$_2$ (33 at%O) after 4 h of BM, (b) Ti-TiO$_2$ (50 at%O) after 8 h of BM, (c) Ti-TiO$_2$ (60 at%O) after 4 h of BM, (▽: $\alpha$-Ti solid solution, • : $\gamma$-TiO, ⊖: $\beta$-Ti$_2$O$_3$, O : stainless steel.)](image-url)
Table 1. The stable phases and the phases obtained by BM together with primitive unit cell volume (Vpc) and density of each phase. The data of Vpc were taken from powder diffraction files (PDF). The file numbers are written in the parentheses.

| Atomic % of oxygen /% | Stable phases at ambient condition | Phases obtained by BM |
|------------------------|-----------------------------------|-----------------------|
| 33                     | Ti2O                              | α-Ti                  |
|                        | density 5.052                     | 5.052*                |
|                        | Vpc 36.75 (#11-218)               | 36.75*                |
| 40                     | Ti3O2                             | γ-TiO                 |
|                        | density 5.124                     | 5.141                 |
|                        | Vpc 62.13 (#12-754)               | 18.22 (#8-117)        |
| 45                     | Ti3O2 + α-TiO                     | γ-TiO                 |
|                        | density 4.972                     | 5.069                 |
|                        | Vpc 62.13 (#12-754), 107.85 (#23-1078) | 18.22 (#8-117)   |
| 50                     | α-TiO                             | γ-TiO                 |
|                        | density 4.919                     | 4.982                 |
|                        | Vpc 107.85 (#23-1078)             | 18.22 (#8-117)        |
| 55                     | α-TiO + α-Ti2O3                   | γ-TiO                 |
|                        | density 4.805                     | 4.877                 |
|                        | Vpc 107.85 (#23-1078), 104.5 (#43-1033) | 18.22 (#8-117)   |
| 60                     | α-Ti2O3                           | β-Ti2O3               |
|                        | density 4.568                     | 4.55***               |
|                        | Vpc 104.5 (#43-1033)**            | 105***                |

* Lattice parameters of α-Ti solid solution and those of Ti2O are almost equal [8].
** The value calculated from XRD data in this study was also 104.5 Å³.
*** Calculated from XRD pattern of Ti2O3 after 2 h of BM.

8 h of BM did not transform into other phases up to 32 h. Thus, in general, the impurities may not be a major factor of the observed metastable phase formations. But, in particular, the formation of β-Ti2O3 at 60 at%O is probably due to impurities, because the produced β-Ti2O3 by BM did not transform into α-Ti2O3 by heat treatment at 900 °C followed by subsequent furnace cooling.

Other factors are involved in the formation of the metastable phases. First, local pressure rise during BM can cause transformation into the denser phases [11, 12]. Density of each studied phase is also shown in Table 1, where the densities were calculated from the lattice parameters, number of atoms in the unit cell and the atomic masses, excluding γ-TiO. The densities of γ-TiO were estimated from the relationship between the oxygen content and the density of bulk polycrystal γ-TiO in the range of 44-56 at%O reported by Banus et al [9]. In the case of two-phase mixture, the average density was used. It is found from the table that in the range of 40-55 at%O, densities of the produced phases by BM are higher than the stable phases. Thus, it is possible to explain the metastable phase formations in these compositions by local pressure rise. However, the phase formations at 33 and 60 at%O cannot be then explained by the local pressure rise.

Since the produced phases in this study are all stable at higher temperatures, it is possible that local temperature rise caused the formation of high-temperature phases. However, there is no general consensus about how much effect local temperature rise has on reactions during BM. Effects of point defects are also possible for 33 and 50 at%O. Since anti-site defects occur in ordered phases by BM [13], it is possible that O atoms move to vacant sites and the phase
transforms into the disordered one.

Another factor related to the periodicity of structure is also conceivable, considering repeated deformation by BM, though less attention has been paid to it. If a dislocation is introduced into a long-period structure, the Burgers vector must be large enough to retain the structure. Otherwise, a planar defect appears or the crystal is fractured. Since a dislocation with such large Burgers vector is difficult to be introduced, the structure may be broken by accumulation of planar defects such as stacking faults during repeated deformation by BM. Therefore, the periodicity of the structure is a possible indicator related to phase stability under BM. The primitive unit cell volume \( V_{pc} \) would be appropriate as the indicator because it represents the size of the repeating unit and is inherent to the structure.

Table 1 also summarizes \( V_{pc} \) of each studied phase. In the range of 40-55 at\%O, the values of \( V_{pc} \) of the produced phases by BM are smaller than the stable phases. As for 33 and 60 at\%O, the \( V_{pc} \) values of the produced phases by BM are the same as or slightly larger than the stable phases. These phase formations at 33 and 60 at\%O are possibly explained respectively by introduction of point defects and existence of impurities as mentioned above. Thus, although some exceptions exist, it is suggested that the values of \( V_{pc} \) of the produced phases by BM are generally smaller than the stable phases. Then the \( V_{pc} \) can be an indicator of phase formations by MA. Also in other systems, for example, formations of disordered phase, \( V_{pc} \) of which is generally smaller than ordered one, are often observed by MA [2]. Besides, it is reported that longer-period structures are not formed by MA in the SrO-TiO\(_2\) system [14].

5. Summary

Ball milling (BM) has been performed on Ti-TiO\(_2\) powder mixtures and single-phase Ti\(_2\)O, \( \alpha\)-TiO and \( \alpha\)-Ti\(_2\)O\(_3\) powders. At 33 at\%O, \( \alpha\)-Ti solid solution containing O as solute was formed. In the range of 40-55 at\%O, \( \gamma\)-TiO was formed. At 60 at\%O, \( \beta\)-Ti\(_2\)O\(_3\) was obtained. All the produced phases are, according to the equilibrium phase diagram, not stable at room temperature, and stable at high temperatures. The metastable phase formations by BM were discussed from various viewpoints including local pressure, local temperature, point defect, impurity and repeated deformation. The phase formations by MA were explained by primitive unit cell volume of the crystal structure as an indicator.

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