Rapid communication

Mechanochemical reactions between Ag_2O and V_2O_5 to form crystalline silver vanadates

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Abstract

Solid-state reactions between Ag_2O and V_2O_5 were studied under ball-milling conditions. Single-phase crystalline $Ag_4V_2O_7$ was formed from the mixture of Ag_2O and V_2O_5 of corresponding (2:1) composition. The main component in the product when the Ag_2O mole fraction is less than V_2O_5 is amorphous $AgVO_3$, which is crystallized into needle-like α-$AgVO_3$ in the presence of water. Excess V_2O_5 was hydrated into $V_2O_5 \cdot nH_2O$ intercalated with Ag^+ ions. The mixtures with more than two parts of Ag_2O relative to V_2O_5 are composite materials of $Ag_4V_2O_7$ and Ag_3VO_4, together with Ag_2O. The crystalline phases in these systems resist attack by water.

1. Introduction

Mechanochemical formation of composite materials using ball milling is a classical but promising method for improving reaction at low temperatures without producing wastes. Binary oxides of Ag and V have been extensively studied for both scientific and practical interests [1–6]. The authors have recently found high reactivity between Ag_2O and V_2O_5 under ball-milling conditions. Amorphous $AgVO_3$ was easily formed by ball milling a mixture of equivalent amount [7]. A striking feature is that the amorphous phase can be crystallized into α-$AgVO_3$ through dissolution in water. The present study aims to obtain a deeper understanding of the reactions between Ag_2O and V_2O_5 by ball milling and related phenomena.

2. Experimental

The formation of the raw materials, V_2O_5 and Ag_2O, was described in the previous paper [7]. Both samples were dried in air at 110°C. Programmed ratios of these oxides were mixed to a total mass of 0.50 g. The sample

name was given by the mole ratio of Ag_2O to V_2O_5 as M-1/1. Ball milling was conducted in air using a planetary-type ball mill, Frisch P7, which was composed of two vessels ($25\,cm^3$) and balls made of agate. The vessels with 0.25 g samples were milled at 2840 rpm.

The reaction process was followed by X-ray diffraction (XRD) measurements using a Rigaku RAD-2R diffractometer with $CuK\alpha$ radiation. The texture changes of the samples were studied by an electron microscope (HITACHI, H8100) and by surface area measurements using N_2 adsorption at −196°C. In all of the systems, the surface area was increased by ball milling in approximately the first 10 min, and reached a constant value within the experimental periods. The thermal properties of the samples were analyzed by thermogravimetry-differential thermal analysis (TG-DTA) (ULVAC, TGD-7000) in air, for which the heating rate was set at 5°C min^{-1}.

3. Results and discussion

3.1. Crystal growth of composite oxides of Ag_2O and V_2O_5 by solid-state reaction using ball milling

In spite of the mechanical stability of the raw samples, Ag_2O and V_2O_5, the mixtures of both are strongly

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affected by ball milling, giving an amorphous phase. In all of the systems with Ag_2O mole fraction less than that of V_2O_5, the structure of the raw materials was almost destroyed after only 5 min ball milling, and a small amount of V_2O_5 remained. Any other crystalline forms were not produced after further treatment. When the Ag_2O mole fraction was larger than that of V_2O_5, crystalline phases were formed by prolonged ball milling. One example is shown for M-2/1 in Fig. 1. Sharp XRD peaks for Ag_2O and V_2O_5 disappeared on ball milling for 5 min. Then definite XRD peaks for the $Ag_4V_2O_7$ [8] appeared as ball milling proceeded, with reaction almost complete after 1 h treatment (omitted). The reaction occurs according to

$$2Ag_2O + V_2O_5 = Ag_4V_2O_7. \qquad (1)$$
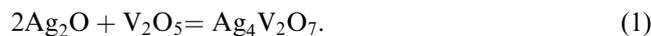
The thermal properties of the ball-milled and just mixed M-2/1 samples were studied by TG-DTA measurements (Fig. 2). The DTA curve, trace a1, shows marked waving endothermic peaks up to 150°C, which correspond to the weight loss due to dehydration of the sample (trace a2). In the case of a sample that has simply been mixed (trac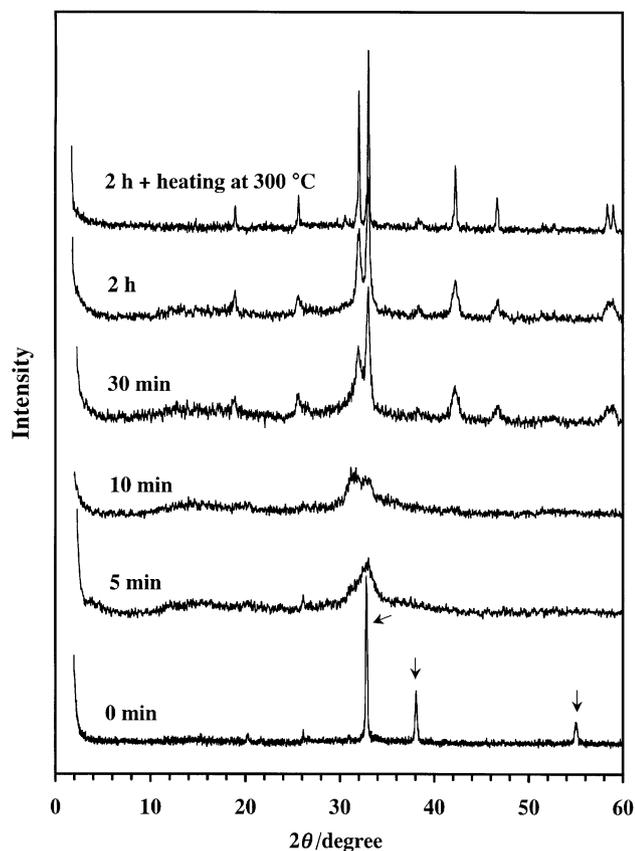es b1 and b2 in Fig. 2), such peaks are not marked, suggesting that the ball-milled sample has a high affinity for water vapor in air, forming a hydrated phase in the surface. The sample treated at 300°C shows a somewhat improved crystal structure of a just-formed sample. These facts suggest that ball milling markedly facilitates reaction (1) and that, once formed, the $Ag_4V_2O_7$ is resistant to mechanical treatment. A similar phenomenon was found previously in δ-$AgVO_3$, which are well-crystallized needle-like particles and which retained its crystallinity after ball milling: needles were just broken [9]. Although, as can be anticipated by the roughness of the procedures, the materials produced are not composed of homogeneous particles under the electron microscope. However, there are large crystalline parts of $Ag_4V_2O_7$ (Fig. 3), which are composed of fairly large moiré patterns inside, indicating the presence of twisted structures. The crystal domain is at most 100 nm, which can substantiate the well-defined XRD pattern of ball-milled sample in Fig. 1.

When Ag_2O and V_2O_5 were just mixed at corresponding compositions and heated to form $Ag_4V_2O_7$, they reacted at 376°C to form $Ag_4V_2O_7$ and α-$AgVO_3$, followed by melting of the former at 387°C (traces b1 and b2 in Fig. 2, XRD analyses not shown). The α-$AgVO_3$ phase was molten at 458°C (trace b2) that is somewhat lower than that of the pure one [10]. The molten phase did not give single-phase $Ag_4V_2O_7$ when cooled.

Fig. 1. XRD pattern changes of the $2Ag_2O$ plus V_2O_5 mixture (M-2/1) produced by ball milling. Times for milling are given on each XRD pattern. Peaks arrowed for the 0 min sample are due to Ag_2O and the others due to V_2O_5.
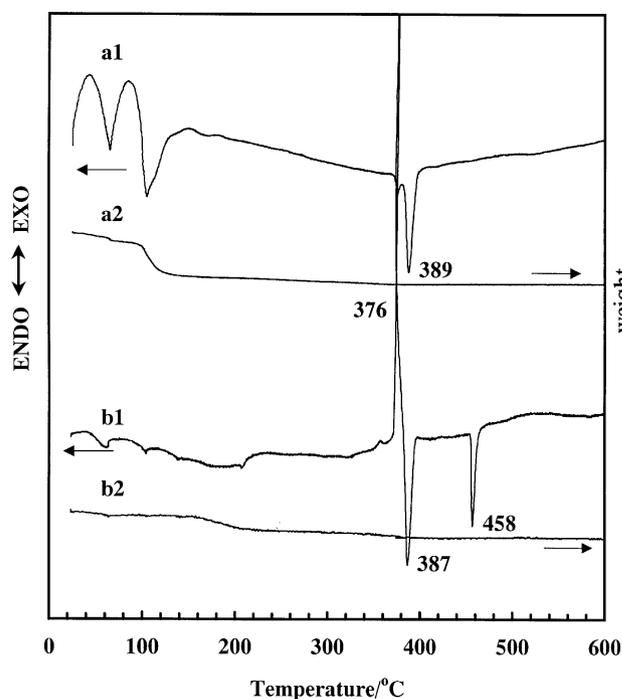

Fig. 2. TG-DTA curves for the $2Ag_2O$ plus V_2O_5 mixtures just mixed and ball milled. Ball-milled one for 2 h: a1, DTA; a2, TG. The sample just mixed: b1, DTA; b2, TG.
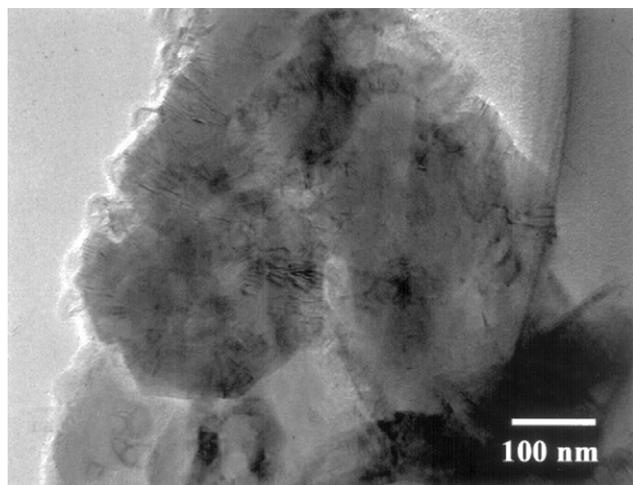
Fig. 3. Electron micrograph of M-2/1. Some Moiré patterns in the sample suggest the presence of the twisted structures of $Ag_4V_2O_7$. Fine particles are seen as fragments of the product and raw materials, traces of which have remained even after long ball milling.

Ball milling of mixtures that have an Ag_2O content more than double the V_2O_5 content is complicated and is not appropriate for producing single phase of silver vanadate (Fig. 4). In the case of M-3/1, $Ag_4V_2O_7$ has grown more markedly than the formation of Ag_3VO_4 corresponding to the mixing ratio, and both phase remain at stationary composition even after long ball milling. Heat treatment of the ball-milled sample (M-3/1) up to 300°C led the crystallization of the β-Ag_3VO_4 phase and $Ag_4V_2O_7$ components. Further heat treatment above 400°C gave α-Ag_3VO_4 and $Ag_4V_2O_7$ mixtures. The transition from β-Ag_3VO_4 to α-Ag_3VO_4 is opposite direction to the result reported by Horino et al. [9]. It is not possible to explain this fact but coexistence of other phase should be concerned with this. Anyhow, these facts suggest us to say that in the ball milling process there is a tendency to form the product that is different from the programmed one, if it is stable against mechanical treatment. According to Fleury and Kohlmuller [1], any phases have not been identified when the Ag_2O content is increased further than 3 times that of V_2O_5. Rationally, some of the Ag_2O phase should remain in the system.

In the case of M-4/1, the main product is α-Ag_3VO_4, along with excess Ag_2O that is not detected by XRD. The fact that $Ag_4V_2O_7$ has not been found here indicates that surplus amount of Ag_2O reacts with V_2O_5 directly to form α-Ag_3VO_4. It is interesting to find low-temperature phase of α-Ag_3VO_4 has increased its crystallinity by heating up to 300°C and does not transform into high-temperature phase β-Ag_3VO_4 whose transition point has been reported to be 100°C [9]. The reason for this is not clear now. Excessively present Ag_2O was confirmed by the appearance of Ag phase when heated above 200°C, which was observed by

the weight loss by using TGA measurement. With M-5/1, the product is more complicated and is not apparently assignable to any structures reported so far. Even at this high Ag_2O content, Ag_2O phase disappeared by ball milling, probably by forming some amorphous compound with V_2O_5. But the presence can be detected by the appearance of Ag phase at temperatures higher than 300°C, Fig. 4.

3.2. Interaction of the ball-milled Ag_2O-V_2O_5 mixtures with water

Fig. 5 shows the XRD patterns of the samples hydrated with 5 ml of water from the ball-milled samples. It is known that the amorphous V_2O_5 phase can be hydrated to form $V_2O_5 \cdot nH_2O$ sol [11,12]. The layered structure of $V_2O_5 \cdot nH_2O$ can be ion-exchangeably intercalated with cations [13]. At low concentrations, Ag^+ ions are introduced between the layers [14]. This is the case in the M-0.166/1 system, as seen in the curve in Fig. 5, where several kinds of layered compounds coexist.

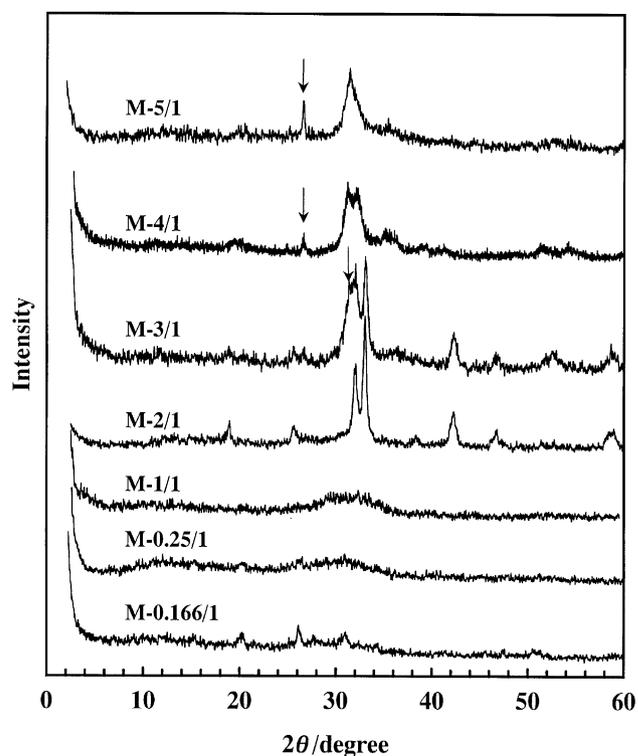In the case of M-1/1, as reported previously, the hydration effect is remarkable: well-defined α-$AgVO_3$ is

Fig. 4. XRD patterns for Ag_2O–V_2O_5 mixtures ball milled up to stationary state. Ball milling times are: M-0.166/1, 2 h, in which small peaks are due to V_2O_5; M-0.25/1, 2 h; M-1/1, 2 h; M-2/1, 5 h, in which a pattern is singly assigned to $Ag_4V_2O_7$; M-3/1, 4 h, in which $Ag_4V_2O_7$ and α-Ag_3VO_4 (arrowed) coexist; M-4/1, 2 h, α-Ag_3VO_4 and unknown material (arrowed); M-5/1, 10 h, deformed α-Ag_3VO_4 and unknown material (arrowed).

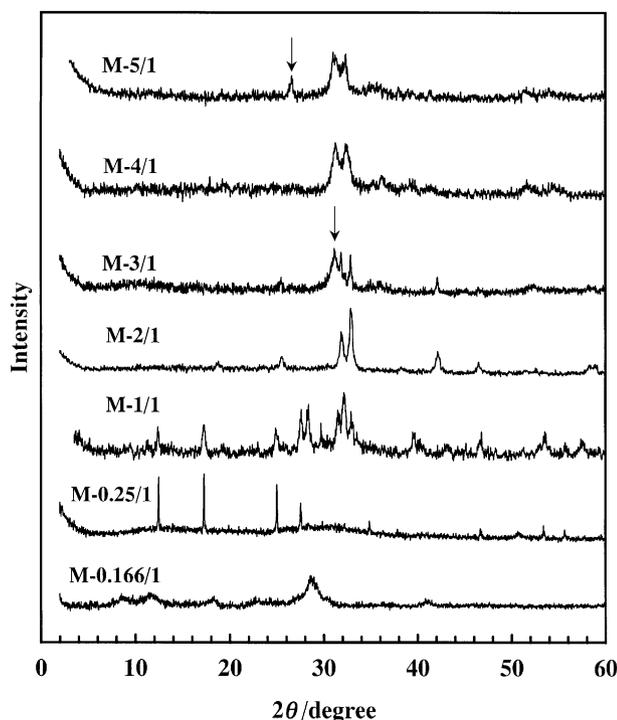Fig. 5. Effect of hydration on the structure of ball-milled Ag_2O–V_2O_5 mixtures. Samples: M-0.166/1, $V_2O_5 \cdot H_2O$ intercalated with Ag^+; M-0.25/1, sharp peaks are due to α-$AgVO_3$; M-1/1, α-$AgVO_3$; M-2/1, $Ag_4V_2O_7$; M-3/1, $Ag_4V_2O_7$ and α-Ag_3VO_4 (arrow); M-4/1, α-Ag_3VO_4; M-5/1, α-Ag_3VO_4 and unknown material (arrowed). Ball-milled samples (ca. 0.3 g) were kept in contact with liquid water (5 ml) at room temperature for 1 week.

formed [14]. Between M-0.166/1 and M-1/1, there are sharp peaks due to α-$AgVO_3$ [15] and less well-defined broad peaks due to $V_2O_5 \cdot nH_2O$ intercalated with Ag^+.

$Ag_4V_2O_7$ (M-2/1) is very stable against water, as can be seen in Fig. 5. Contact with water sharpened the XRD patterns of Ag_3VO_4 for samples M-3/1, M-4/1, and M-5/1. This suggests that the deformed form of the crystalline phases in the ball-milled sample were dissolved into water. However, once crystalline forms of α-$AgVO_3$, $Ag_4V_2O_7$, and Ag_3VO_4 are produced, they are stable against water.

4. Conclusions

The mechanochemical reactivity of Ag_2O–V_2O_5 mixtures was studied by varying the mixing ratios. A single-phase $Ag_4V_2O_7$ was formed by ball milling of the mixture $2Ag_2O$:V_2O_5. The ball-milled samples of other compositions are mixtures of V_2O_5, amorphous $AgVO_3$, $Ag_4V_2O_7$, Ag_3VO_4, and Ag_2O, the compositions of which vary as a function of mixing ratio.

The amorphous $AgVO_3$ phase was crystallized into α-$AgVO_3$ through hydration. V_2O_5 is hydrated into $V_2O_5 \cdot nH_2O$, which is intercalated with Ag^+. Crystalline phases formed by ball milling are stable against water.

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