



## Mechanical alloying process of vanadium powder with 1.7 wt.%Y addition

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### ABSTRACT

Alloying process of vanadium–yttrium powders using mechanical alloying (MA) method was studied. Vanadium powder was compressed after 10 h MA, while yttrium powder was comminuted into small particles. Although yttrium powder was broken into small particles, yttrium scarcely dissolves into vanadium powder. Alloying of yttrium started after 20 h MA and finished after 40 h MA. Molybdenum particle, which came from milling vessels and balls, mixed into vanadium powder after 40 h MA and molybdenum started to dissolve into vanadium powder after 60 h MA. After 80 h MA, Y<sub>2</sub>O<sub>3</sub> particles formed in vanadium powder. Oxygen required for the formation of Y<sub>2</sub>O<sub>3</sub> particles was probably discharged from the vessel wall and balls after flaking of those surface layers. Since prolonged MA caused powder contamination, optimum MA time for making V–1.7Y alloy was 40 h.

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### 1. Introduction

Mechanical alloying (MA) is one of promising method to produce materials far from equilibrium with supersaturated solid solution. For example, although solubility of copper in iron is extremely small at room temperature [1], MA method can produce Fe<sub>1-x</sub>Cu<sub>x</sub> ( $x = 0.2, 0.5, 0.8$ ) alloy [2]. Solubility of yttrium in vanadium is also quite small at room temperature [3]. Alloys of V–(1.6–2.6) wt.%Y fabricated by MA method have excellent properties for application of fusion reactor structural material [4–7]. Although MA method has been widely used for making alloys with supersaturated solid solution, the effects of MA conditions on MA products still have not been well understood. One of crucial MA conditions for determining property of MA products is the MA time. Shorter MA time leads unsatisfied dissolution of solute element. On the other hand, too-long MA wastes time and would induce unfavorable changes of MA powder, such as contamination from vessels and balls. It is thus important to know appropriate time of MA. In the present study, dissolution process of yttrium into vanadium powder during MA has been examined to find the appropriate condition for MA time in a V–Y alloy.

### 2. Experimental procedures

Pure vanadium and yttrium powders, whose chemical compositions are listed in Table 1, were used as starting materials. The powders were mixed to produce the nominal composition of

V–1.7Y (mass%). The powders were subjected to MA in a purified Ar atmosphere. MA treatments were conducted by a three mutually perpendicular directions agitation ball mill with vessels and balls made of TZM (Mo–0.5%Ti–0.1%Zr) [8,9]. The weight ratio of balls to powder was approximately 5. The agitation speed was 400 rpm and MA time was between 10 and 80 h. Morphology of the powders during MA was examined by scanning electron microscopy (SEM). Structure of the powders was investigated by X-ray diffractometry (XRD). Microstructures were analyzed by transmission electron microscopy (TEM). Colloidal powders for TEM observation were prepared as follows; powders were ultrasonically dispersed in ethanol and then a micro-grid was dipped into the surface of the ethanol to pick up colloidal powders. Specimens were examined with analytical JEM2000FX and JEM2000EX microscopes operating at 200 kV. High resolution TEM observation was also carried out by using JEM3010 microscope operating at 300 kV. Composition of powders after MA was examined by energy dispersive X-ray spectroscopy (EDS) equipped with TEM.

### 3. Results

Fig. 1(a) shows SEM image for vanadium and yttrium powders before MA treatment. The vanadium powders were plate of about 50 μm in thickness. Surface of the vanadium powder was relatively flat. Yttrium powders were block in shape having steps on the surface. Fig. 1(b)–(f) show SEM images of powders after MA for 10, 20, 40, 60 and 80 h. After 10 h MA, vanadium powders were severely compressed and elongated. Surface of the powders became uneven. The powders were comminuted finer after 20 h MA. Size of powder varied from 10 to 250 μm in diameter. Aggregation of

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**Table 1**  
Chemical composition of the powders used in the present study (mass%).

	O	N	C	H	Fe	Al	Si	Ca	Mg
V powder	0.1145	0.061	0.0091	0.0004	0.005	0.048	0.027	–	–
Y powder	1.39	0.052	–	–	<0.02	–	–	<0.01	<0.01

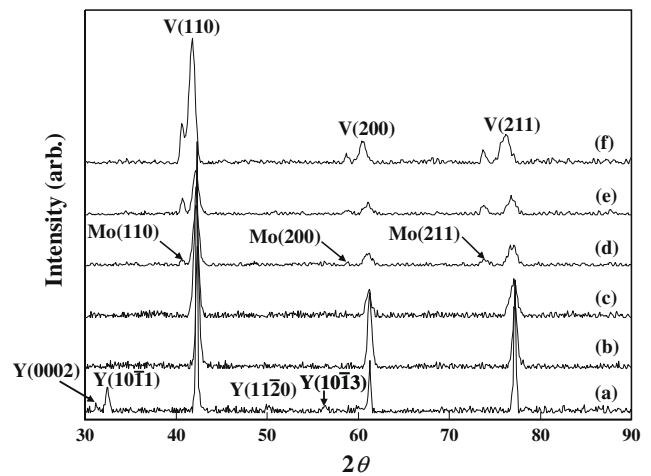
powders occurred after 40 and 60 h MA. The size of the aggregated powders was about 200  $\mu\text{m}$  in diameter. The aggregated powders were comminuted after 80 h MA. Morphological changes of powders during MA are summarized as follows; compression, comminution, aggregation and comminution.

XRD profile for mixture of vanadium and yttrium powders before MA is shown in Fig. 2(a). Diffraction peaks from vanadium and yttrium were clearly detected. Fig. 2(b)–(f) illustrate XRD profiles for the powders after MA for 10, 20, 40, 60, and 80 h, respectively. Diffraction peaks of yttrium disappeared after 10 h MA as shown in (b), whereas those of molybdenum were detected after 40 h MA. Diffraction peaks of vanadium gradually shifted toward lower diffraction angle after 20 h MA, indicating that lattice parameter of vanadium increased during MA.

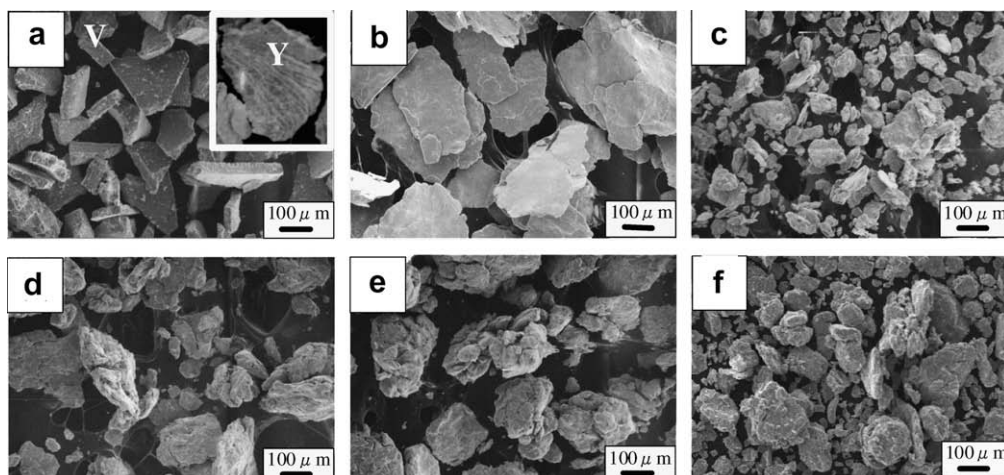
Change in lattice parameter of vanadium powder after MA for 0 to 80 h is shown in Fig. 3. Nelson–Riley plot [10] made from XRD profile in Fig. 2 was applied to determine the lattice parameter of vanadium. The lattice parameter was almost constant until 20 h MA, and it increased after 20 h MA. After 40 h MA, the lattice parameter clearly increased to 3.046 Å. Dotted line in Fig. 3 denotes the theoretical lattice parameter of vanadium assuming that all yttrium powder dissolved in the vanadium matrix, i.e. lattice parameter of V–1.7Y alloy, 3.041 Å. We applied simple hard-sphere model to calculate the theoretical lattice parameter of V–1.7Y alloy, supposing radius of yttrium atom in hcp lattice stays even in bcc lattice. The lattice parameter after 40 h MA was very close to that of the theoretical lattice parameter of V–1.7Y alloy. Thus, yttrium completely dissolved in vanadium powder after 40 h MA. Additional MA for 20 h keeps lattice parameter constant. However, the lattice parameter increased again after 60 h MA.

Fig. 4(a) shows TEM bright field image of a vanadium powder after 10 h MA. Very fine grains of about 20 nm in diameter can be observed as indicated by arrows. Selected area diffraction (SAD) pattern taken from the area indicated by a circle in (a) is shown in Fig. 4(b). Debye rings from both vanadium and yttrium were observed. Yttrium particles co-exist with vanadium powder. This implies that yttrium powder does not dissolve in vanadium

after 10 h MA. TEM observation of vanadium powders after 40 h MA revealed that Debye rings of yttrium disappeared. EDS analysis revealed that yttrium concentration in vanadium powder after 40 h MA reached nominal composition of V–1.7Y. Although pure molybdenum started to be observed after 40 h MA in XRD, molybdenum was hardly detected within vanadium particle. Weak diffraction spots of  $\text{Y}_2\text{O}_3$  appeared in SAD pattern after 80 h MA. High resolution TEM image for the vanadium powder after 80 h MA is shown in Fig. 5(a). Fig. 5(b) shows Fourier transformed pattern, showing vanadium and  $\text{Y}_2\text{O}_3$  diffraction spots. Inverse Fourier transformed image constructed by using (2 1 1)  $\text{Y}_2\text{O}_3$  diffraction is shown in Fig. 5(c). Fig. 5(c) showed that small  $\text{Y}_2\text{O}_3$  particle, about 3 nm in diameter, precipitated in the vanadium powder after 80 h MA.



**Fig. 2.** XRD profiles for the powders after MA treatments for (a) 0, (b) 10, (c) 20, (d) 40, (e) 60 and (f) 80 h, respectively.



**Fig. 1.** SEM images of powder after MA treatments for (a) 0, (b) 10, (c) 20, (d) 40, (e) 60 and (f) 80 h, respectively. Yttrium powder before MA is shown in an inserted figure on the right-upper corner of Fig. 1(a).

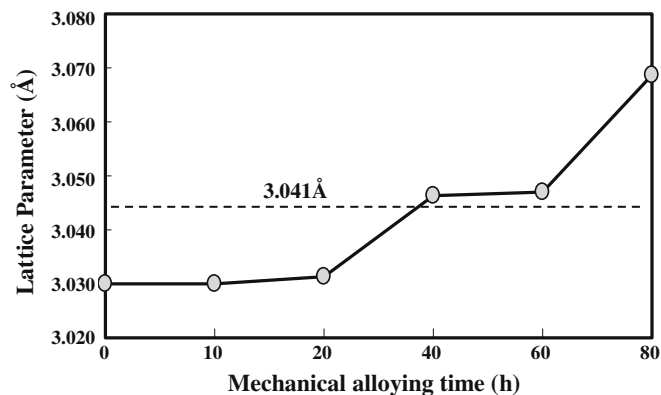


Fig. 3. Change in lattice parameter of vanadium powder after MA treatments from 0 to 80 h. Dotted line indicates the lattice parameter of V-1.7Y, 3.041 Å.

#### 4. Discussion

After 10 h MA, diffraction peaks of yttrium disappeared in the XRD profile. However, TEM observation revealed that yttrium powders still existed separately in the vanadium powders. Furthermore, lattice parameter of vanadium powder after 10 h MA was the same as that of the powder before MA. It is apparent that yttrium does not dissolve into vanadium powder after 10 h MA. These results suggest that only limited characterization is possible for the MA process with XRD. After 20 h MA, lattice parameter of vanadium powder increased, indicating that alloying of yttrium into vanadium started. After 40 h MA, lattice parameter of vanadium attained the value where all yttrium powders dissolved in vanadium powder. EDS analysis showed that after 40 h MA yttrium

content in vanadium powder reached nominal composition of V-1.7Y. Therefore, alloying of yttrium has finished after 40 h MA. Although diffraction peaks by molybdenum appeared in the XRD profile after 40 h MA, EDS analysis showed that molybdenum was scarcely contained within vanadium powder after 40 h MA. Although intensity of diffraction peaks of molybdenum in XRD increased with increasing MA time, lattice parameter of vanadium powder after 60 h MA was almost the same as that after 40 h MA. This implies that molybdenum particles, which come from milling vessels and balls made by TZM, exist independently of vanadium powders until 60 h MA. After 80 h MA, on the other hand, lattice parameter of vanadium powder increased again. This is probably because molybdenum dissolved into vanadium powder and expanded vanadium lattice since the atomic radius of molybdenum is larger than that of vanadium. It can be concluded that since prolonged MA causes molybdenum contamination, 40 h MA is appropriate to make mechanically alloyed powder of V-1.7Y.

$Y_2O_3$  particles were observed in the vanadium powder after 80 h MA. Since yttrium powder had already dissolved into the vanadium powder with 40 h MA, such  $Y_2O_3$  particles are thought to precipitate from vanadium matrix. After 80 h MA, large amount of molybdenum which came from milling vessels and balls were observed, indicating destruction of surface of milling vessels and balls. Oxygen could come out from inside milling vessels and balls after peeling off those surface layers. Emitted oxygen from milling vessels and balls might induce yttrium oxidation, forming  $Y_2O_3$ .

#### 5. Conclusion

Alloying of yttrium in vanadium powder occurred after 20 h MA and finished with 40 h MA. Prolonged MA, such as 80 h MA, induced serious molybdenum contamination from milling vessels

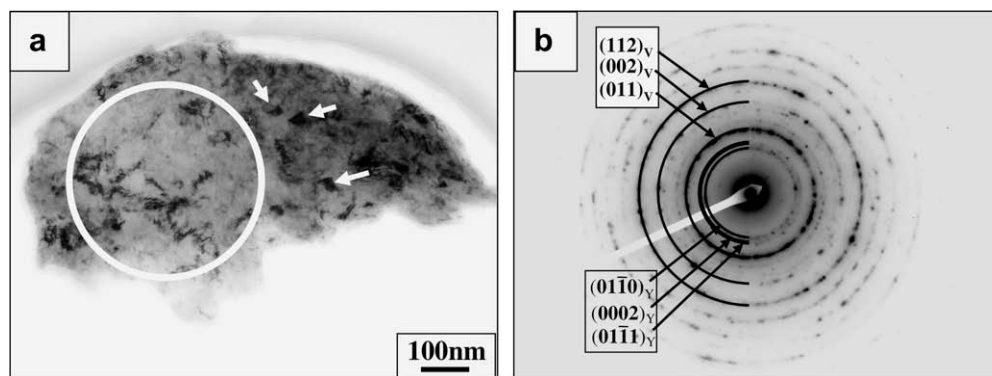


Fig. 4. (a) Bright field image of powder after MA treatment for 10 h, (b) selected area diffraction pattern taken from the area indicated by a circle in (a).

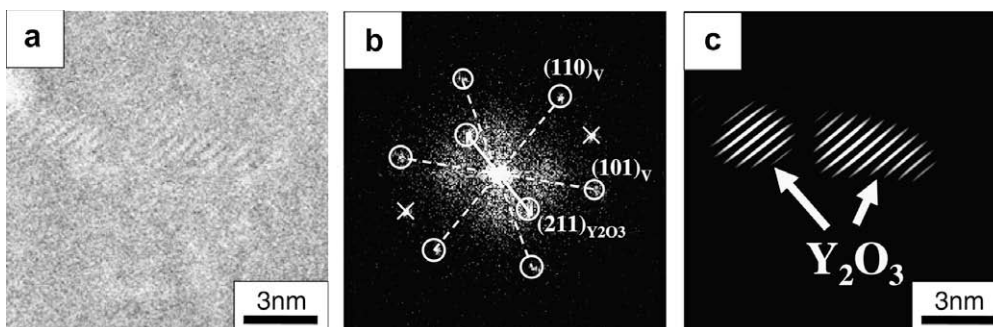


Fig. 5. (a) High resolution TEM image for powder after 80 h MA, (b) Fourier transformation (FT) pattern, (c) inverse FT image made by using  $(211)_{Y_2O_3}$  reflection shown in (b).

and balls. Furthermore, after 80 h MA,  $Y_2O_3$  particles precipitated due to oxidation of solute yttrium. The introduction of oxygen into powder probably occurred from inside milling vessels and balls after peeling off those surface layers by prolonged MA. Optimum MA time should be selected so that dissolution of powder completed without contamination. Therefore, 40 h MA is optimum condition for making a V–1.7Y alloy.

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