Separation method of W from X-ray targets using the difference of volatilization behavior of W, Mo and Re

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Minor metals such as tungsten (W), molybdenum (Mo) and rhenium (Re) are necessary for high performance products, and a steady supply of them is very important. These metals are used for the X-ray target of the X-ray computed tomography equipment. In this study, we studied a dry separation method of W from discarded targets using the difference of volatilization behavior of the metal oxides. We obtained a 96% separation rate of W from the target by grinding, oxidation (1073 K, 5 h) and volatilization (1223 K, 5 h).

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Minor metals such as tungsten (W), molybdenum (Mo) and rhenium (Re) are used for the X-ray targets of medical X-ray detection equipments such as X-ray computed tomography equipment.¹⁾ These metals are necessary for high performance products, and 30 kinds of minor metals, including W and Mo were appointed as strategic mineral resources.²⁾

Some recycling methods of W from discarded cemented tungsten carbide tools such as, oxidation-alkali leaching method,^{3,4)} alkali scorification method⁵⁾ and electrolytic process^{6–10)} have been reported. However, there were no reports about W recycle from discarded X-ray targets. In this report, we studied dry separation method of W from discarded X-ray targets. **Figure 1** shows the separation process. The process is divided into three parts: grinding, oxidation and volatilization. First, the discarded X-ray target was grinded and obtain grinded powder. Next, the powder was oxidized in air atmosphere. Finally, the oxidized powder was heated in vacuum atmosphere to volatile Re and Mo.

W powder (purity: 99.9%, grain size: 53 μm or less), Re powder (purity: 99.9%, grain size: 45 μm or less), Mo powder (purity: 99.8%, grain size: 63 μm or less), WO_3 powder (WO_3 -4 grade), Re_2O_7 powder (model number: REO02XB), and MoO_3 powder (model number: MOO02PB, purity: 99.9%) were used to examine the volatile behaviors. The WO_3 powder is made by Japan New Metals Co., and other powders are made by Kojundo Chemical Lab. Co.

Weight changes of the powders by heat treatment were measured by thermogravimetric analysis (HP-TG-DTA-2000S, Netzsch). The metal powders were heated to 1273 K in an air atmosphere and the metal oxide powders were heated to 1273 K in vacuum atmosphere (1 Pa).

The oxidation behaviors of the metal powder mixture were examined. The metal powders were mixed at the same weight (total: 3 g), and heat treated at 473–1273 K for 5 h in air atmosphere. Alumina crucibles were used for these heat treatments. After the heat treatments, the crystal phases of the samples were measured by the X-ray powder diffraction method (RINT2500HL, Rigaku). The measurement conditions were, X-ray source: Cu,

Fig. 1. Separation process.

X-ray output: 50 kV, and scanning speed: 1.0 deg/min. International Centre for Diffraction Data was used to identify the crystal phases.

The X-ray target has a W–Re alloy surface layer on the Mo alloy backing plate.¹⁾ The surface of the target was grinded. The grinding powder was heated at 873–1273 K for 5 h in air atmosphere. After the oxidation treatment, the powder was heated at 1223 K for 5 h in vacuum atmosphere (1 Pa). Aluminum crucibles were used for these heat treatments. After these heat treatments, the composition of powders were measured by X-ray fluorescence analysis (ZRX Primus II, Rigaku). The measurement conditions were as follows; X-ray tube: Rh target, X-ray output: 3 kV, analysis area: 10 mm in diameter, scanning step: 0.02 deg, and measurement time: 0.2 s.

Figure 2 shows the weight change of Re, Mo and W during the heat treatment in air atmosphere. The weight of Re decreased

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Fig. 2. Weight change behavior of Re, Mo, and W in air atmosphere.

Fig. 3. Weight change behavior of Re_2O_7 , MoO_3 , and WO_3 in vacuum atmosphere.

from 673 K and became almost 0 at 1073 K. The weight of Mo increased from 673 K and maximized at 1023 K. After that, the weight decreased and became almost 0 at 1273 K. The weight of W increased from 873 K and showed almost constant values above 1073 K.

Figure 3 shows the weight change of Re_2O_7 , MoO_3 and WO_3 during the heat treatment in vacuum atmosphere. The weight of Re_2O_7 and MoO_3 decreased from 473 and 873 K, and became almost 0 at 623 and 1023 K, respectively. On the other hand, WO_3 did not show noticeable weight change till 1273 K.

As shown in Figs. 2 and 3, the weight of Mo increased from 673 K, and the weight of MoO_3 was almost 0 at 1023 K. This indicates that the oxidation reaction of Mo started from 673 K, and MoO_3 volatilized more than 1023 K. In comparison, the weight of W increased from 873 K, and the weight of WO_3 did not show noticeable change till 1273 K. This indicates that the oxidation reaction of W started from 873 K, and WO_3 is almost stable till 1273 K.

The difference of weight change behaviors of these metals and metal oxides were supposed to be beneficial for the separation of Re, Mo, and W.

Figure 4 shows the results of the powder X-ray diffraction of the heat treatment of W, Mo, and Re mixed powders in air atmosphere. The oxidation reaction of W, Mo, and Re did not progress at 473 K. In comparison, the oxidation reaction of Mo and Re progressed at 673 K. MoO_3 and WO_3 were identified, and ReO_3 was not identified at 873 K. This indicates that the oxidation reaction of W and the volatilization reaction of ReO_3 progressed between 673 and 873 K. $\text{W}_{0.4}\text{Mo}_{0.6}\text{O}_3$ and $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$, which were multiple oxides of W and Mo, were identified at 1073 K, and

Fig. 4. Results of powder X-ray diffraction of heat treatment of Re, Mo, and W mixed powder.

Table 1. Results of X-ray fluorescence analysis of powders

Element	Constitution rate (wt %)	
	Surface area	Internal area
Re	4.1	2.1
Mo	19.1	69.2
W	76.8	28.7

Table 2. Results of X-ray fluorescence analysis of the powders after heat treatments in air. The powders were corrected from the surface area in Table 1

Element	Constitution rate (wt %)		
	873 K, 5 h, air	1073 K, 5 h, air	1273 K, 5 h, air
Re	1.8	—	—
Mo	24.8	17.2	5.2
W	73.4	82.8	92.9
Al	—	—	1.9

this indicated that MoO_3 and WO_3 reacted.¹¹⁾ WO_3 , $\text{W}_{0.4}\text{Mo}_{0.6}\text{O}_3$, $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$, $\text{Al}_2(\text{MoO}_4)_3$, and $\text{Al}_2(\text{WO}_4)_3$ were identified at 1273 K. Aluminum was not included in the mixed powder, so $\text{Al}_2(\text{MoO}_4)_3$ and $\text{Al}_2(\text{WO}_4)_3$ indicated that the alumina crucible reacted with the reaction products. WO_3 , which was not identified at 1073 K, was identified at 1273 K. It is thought that Mo volatilized from $\text{W}_{0.4}\text{Mo}_{0.6}\text{O}_3$ and $\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$.

Table 1 shows results of XRF of grinding powders of the discarded X-ray target. The powder from the surface area (about 5 mm in depth from the surface) contained W more than 76%, and the powder from the inside area contained Mo more than 69%. It indicated that W and Mo were roughly distributed by grinding the target. The grinding powder from the surface area was oxidized at 873–1273 K for 5 h in air atmosphere. **Table 2** shows results of XRF of the oxidized powders. In comparison with the surface grinding powder in Table 1, Re did not identified at 1073 and 1273 K. The quantity of Mo decreased more than 1073 K. In

Table 3. Results of X-ray fluorescence analysis of the powders after heat treatment at 950°C in vacuum atmosphere. The powders were corrected from the powders in Table 2

Element	Constitution rate (wt %)		
	873 K, 5 h, air → 1223 K, 5 h, vacuum	1073 K, 5 h, air → 1223 K, 5 h, vacuum	1273 K, 5 h, air → 1223 K, 5 h, vacuum
Re	0.8	—	—
Mo	6.5	3.7	5.6
W	92.7	96.3	92.7
Al	—	—	1.7

addition, Al was detected at 1273 K. It is thought that an alumina (Al_2O_3) crucible formed reaction products with the sample as shown in Fig. 4. The oxidized powders were heated at 1223 K for 5 h in vacuum atmosphere. **Table 3** shows the XRF results of the heat treated powders. We obtained a 96% separation rate of W, which oxidized at 1073 K, 5 h and volatilized at 1223 K, 5 h. In comparison, the quantity of Mo and W, which oxidized at 1273 K hardly changed. It is thought that Al–Mo–W multiple oxides that formed during the oxide treatment were stable during the volatilization treatment, preventing the volatilization of Mo.

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