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Recycling process of WC-Co cermets by hydrothermal treatment

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Hydrothermal extraction process of Co binder phase from WC-Co cermet was investigated in order to establish a novel recycling system of WC-Co cermet scraps. When the cermet chips were hydrothermal-treated in hydrochloric acid above 110°C, Co binding phase was efficiently extracted and the cermet chips were disintegrated into relatively large fragments. After hydrothermal treatment, WC sintered body become very brittle and pulverized easily by ball milling and the mean particle size of thus obtained WC particle became similar to that of virginal WC particle. The recycled WC powder was a little easier to undergo oxidation than the virginal WC powder, so that the mechanical properties of recycled WC-Co cermets were degraded. However, the degradation of mechanical properties was prevented only by drying the WC powder more carefully. This hydrothermal process will be one of the recycling systems for WC-Co cermets.

1. Introduction

WC-Co cermets are known to have excellent mechanical properties such as high hardness and high transverse rupture strength, which are stable in a relatively wide temperature range. Therefore, they are widely used as cutting tools, metallic molds, high wear-resistant tools, etc. and the amount of consumption is increasing year after year. However, both tungsten and cobalt are important rare metals especially in Japan, since virginal tungsten and cobalt resources are imported from China or Africa. Thus, from the viewpoint of the resource recovery and the suppression of energy consumption, the development of an efficient recycling procedure for WC-Co cermets is required.

Various recycle processes of WC-Co cermets, such as chemical modification method, thermal modification method, zinc melt method, cold stream method and electrochemical method have been investigated and some of them are actually employed in industry [1–6]. However, these conventional methods have many problems to be solved and they are not always established technologies. For example, chemical modification method requires comparatively large-scale equipment and it takes relatively long reaction time. The recycling by thermal modification process usually undergoes the decomposition of WC and it leads to the formation of η phase, which degrades the mechanical properties. Zinc melt and cold stream processes have problems with contamination by undesirable elements. Although there are no tungsten resources without WC scraps in Japan, the recycle rate of WC-Co cermet retains only about 20% and the rate is still decreasing. Therefore, we need to develop more economical and high-quality recycling procedure.

Hydrothermal treatment is a well-known process to prepare crystalline powders or single crystals in the field of material science. One of the merits of this method is relatively low energy consumption because of the high chemical reactivity and excellent solubility of materials in hot water. These properties of hot water can be applied to the pulverizing process of WC-Co cermet. Some reports and patents [7–10] exist about the recycle technique of WC-Co cermets utilizing the excellent solubility in acidic solution under hydrothermal conditions. In those patents, cobalt-binding phase in the cermets was efficiently removed by hydrothermal treatment in acidic solutions. Yamasaki *et al.* reported the extraction of cobalt-binding phase by hydrothermal treatment and found that $FeCl_3$-HCl-NH_4Cl solution is the most effective solution for the selective extraction of Co-biding phase from cermets. However, the properties of recycled powder and the re-sintered compacts of WC-Co cermets are not reported.

Authors already reported about the recycle procedure using hydrothermal treatment in order to recover ceramic powder resources from the stable sintered body [11, 12]. Sasai *et al.* reported [11] the recycling systems of WC-Co cermet scraps by both dry and wet recycling processes. It proved that hydrothermal treatment is an available technique for recovering WC powder from the cermets. In this paper, more details on extraction and disintegration process of WC-Co cermets by

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hydrothermal treatment are reported. WC powder are recovered from the treated cermets and re-sintered with Co powder to prepare recycled cermet chips in order to investigate the mechanical properties.

2. Experimental procedure

2.1. Sample preparation

WC-Co cermet disk chips (15 mm in diameter × 5 mm in height) were used as specimen. The particle size of WC in the cermet was 1–5 μm and the content of Co binder phase was 20 wt%. The specimens and treatment solution were charged into PTFE-lined autoclave containers and hydrothermal-treated. The treated specimens were filtered and washed with distilled water. Ball milling of the hydrothermal-treated specimens was performed with ethanol for 24 h using stainless steel balls in a PE pot. Re-sintering of the recovered WC powder was also performed according to the following procedure. At first, the recycled WC powder and virginal Co powder were mixed by ball milling for 24 h using ethanol as a dispersion solution. After drying in an oven at 50°C for 24 h or in a vacuum drying oven at 100°C for 24 h, powders were uniaxially pressed and sintered at 1380°C for 1 h.

2.2. Characterization

The crystalline phases were identified by X-ray diffractometry (XRD; Rigaku RINT-2500) using Cu K_α radiation with a monochromator. The microstructures were examined by scanning electron microscopy (SEM; Jeol, JSM-6330F). Elemental distribution analysis in the recovered powder was conducted by the energy dispersive X-ray spectroscopy (EDS; Jeol, JFC-2140). Before elemental distribution analysis, the surface of the sample was etched by Murakami reagent (10 g NaOH + 10 g $K_3Fe(CN)_6$ + 100 ml H_2O). The amount of eluted metal was estimated by measuring the concentration in the treatment solution after hydrothermal treatment using ICP-AES (Perkin-elmer Japan, 3300DV). The composition and binding energy of the surface of the samples were examined by X-ray photoluminescence spectroscopy (XPS; Shimazu, ESCA3300). The percentage content of carbon in the samples was analyzed by CHN coder (Yanaco, MT-6). The density of the sintered body was measured in water by the Archimedes method. The Rockwell A hardness was measured according to CIS-027 by Japanese. The transverse rupture strength of the WC-Co cermets was measured according to Japan Cemented Carbide Tool Manufacturer's Standards.

3. Results and discussion

3.1. Hydrothermal treatment of WC-Co cermets

Fig. 1 shows the amount of Co binder phase extracted from WC-Co chip by hydrothermal treatment at 110°C for various times. 1N aqueous solution of HCl, H_2SO_4 or HNO_3 was used as treatment solution. When using HCl aq. solution, the amount of extracted Co ion increased linearly with increasing treatment time up to 24 h, and then it was saturated above 24 h. In the case of H_2SO_4 aq. solution, relatively large amount of Co ion was extracted below 24 h. However, the extracted amount was saturated above 24 h and the amount was in a lower level than that of HCl aq. solution. In contrast, in the case of HNO_3 aq. solution, the extracted amount of Co ion increased lineally with the hydrothermal treatment time up to 50 h, however, the amount was much less than those of other treatment solutions. Fig. 2 shows the XRD profiles of the specimens hydrothermal-treated in various acidic solutions at 110°C for 24 h. From the XRD diffraction patterns, no Co binder phase was detected on the surface of hydrothermal-treated specimen. However, only when HNO_3 was used as the treatment solution, WO_3 was detected. Therefore, relatively low Co extraction ability of HNO_3 was attributed to the formation of WO_3 layer on the surface of specimen, which disturbed the elution of Co ions. From the result of Figs 1 and 2, HCl aq. solution was employed as the treatment solution in the following experiments.

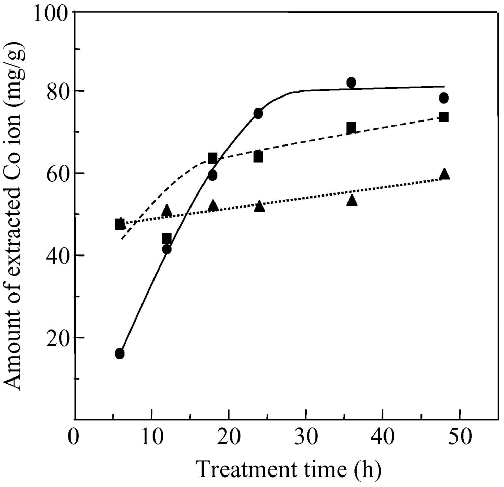

Figure 1 Relation between hydrothermal treatment time and amount of extracted Co ion. Treated in 1 N aqueous solutions of ●: HCl, ■: H_2SO_4, ▲: HNO_3 at 110°C for 24 h.

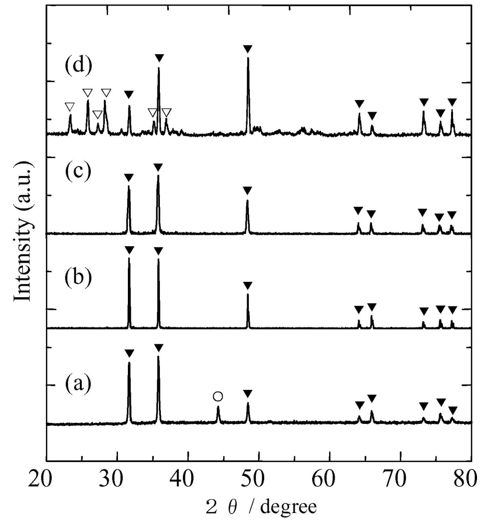

Figure 2 XRD profiles of WC-Co cermet chips hydrothermal-treated in various acidic solutions. (a) Original WC-Co cermet chip and specimens treated at 110°C for 24 h in 1 N aqueous solution of (b) HCl, (c) H_2SO_4 and (d) HNO_3 (treated at 110°C for 24 h). ▼: WC, ○: Co, □: WO_3.

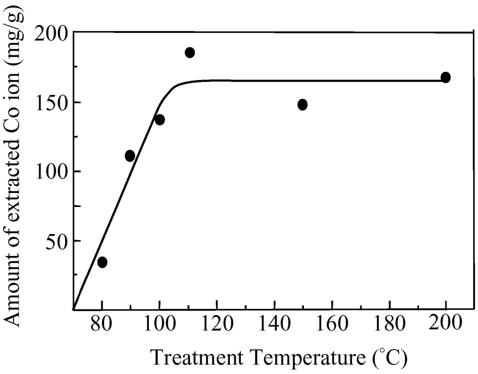

Figure 3 Relation between hydrothermal treatment temperature and amount of extracted Co ion. Specimens are treated in 6 N HCl aqueous solution for 24 h.

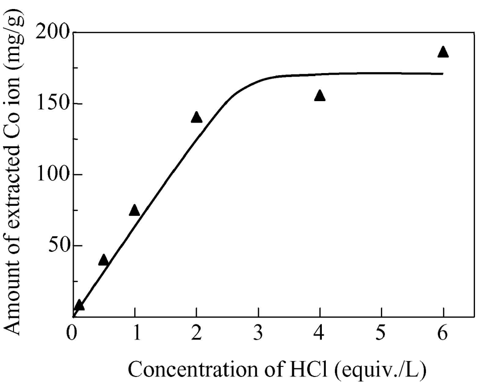

Figure 4 Relation between concentration of HCl and amount of extracted Co ion. Specimens are treated at 110°C for 24 h.

Fig. 3 shows the relation between the amount of extracted Co ion and hydrothermal treatment temperature. 6N HCl aq. solution was used as the treatment solution and the treatment time was 24 h. When the treatment temperature was below 100°C, the amount of extracted Co ion increased lineally with increasing concentration of HCl. In contrast, when the processing temperature is more than 110°C and more, the Co binder phase was removed form the cermet chips almost completely. Fig. 4 shows the amount of extracted Co ion by hydrothermal treatment using HCl aq. solutions with various concentrations. The treatment conditions were at 110°C for 24 h. When the concentration of HCl was relatively low (<2N), the amount of extracted Co ion increased lineally with increasing concentration of HCl, then saturated at ~170 mg/g at the concentration of HCl above 2N.

Fig. 5 shows the change in appearances of the specimens hydrothermal-treated in various concentrations of HCl. When relatively dilute HCl solution was used as the treatment solution, only the corner part of a pellet collapsed into thin fragments of WC sintered body. With increasing the concentration of HCl, percentage of the fragmented parts increased, and almost all portions of the cermet chip except the central part was disintegrated at HCl concentration of 6N. In this experiment, the core part of all the specimens remained uncollapsed. Considering the above results, the optimum hydrothermal treatment condition was determined as at 110°C for 24 h in 6N HCl aq. solution. Fig. 6 shows the

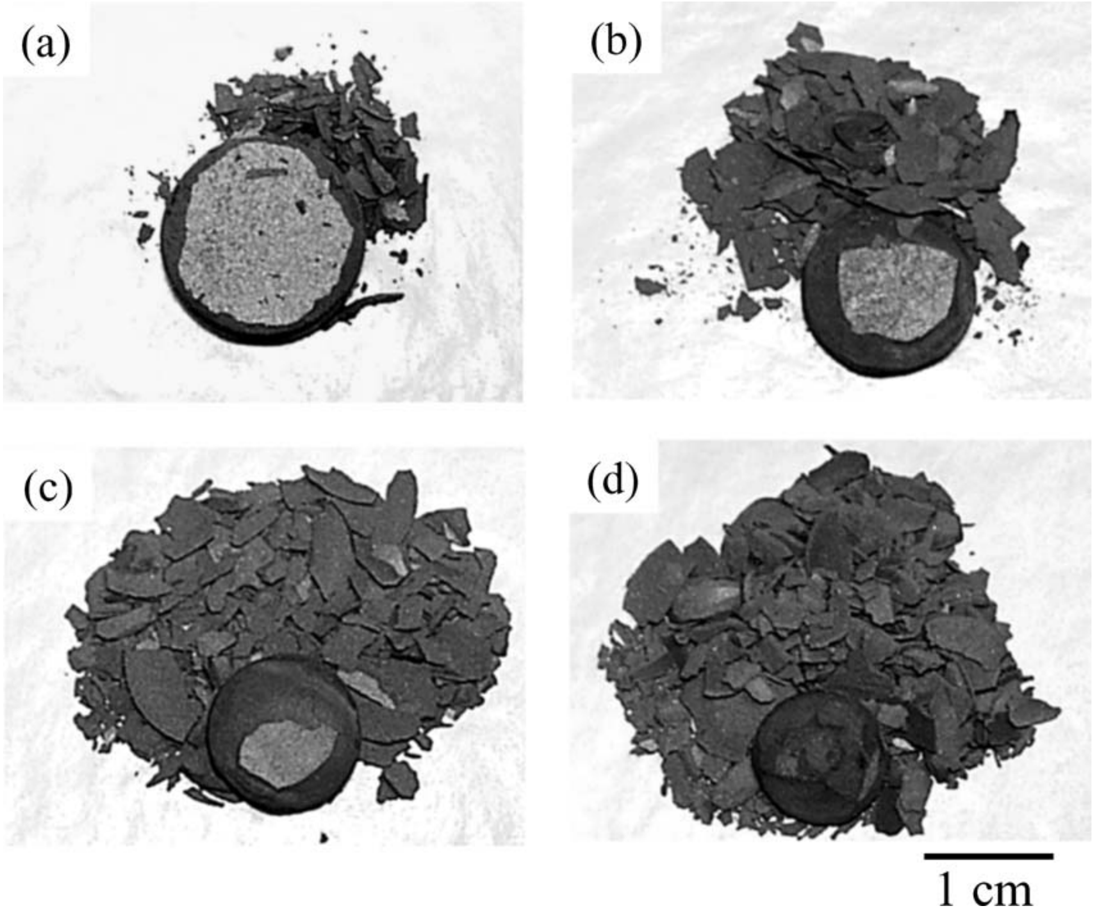

Figure 5 Appearances of hydrothermal-treated WC-Co cermet chips hydrothermal-treated in various concentrations of HCl aqueous solutions: (a) 0.5 N, (b) 2 N, (c) 4 N, and (d) 6 N.

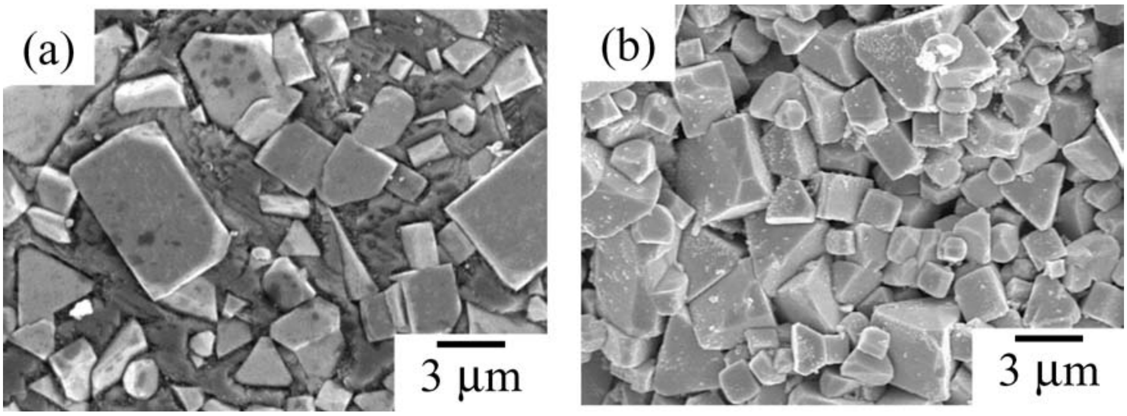

Figure 6 Microstructures of the surfaces of original and hydrothermal-treated WC-Co cermet chips. (a) Original WC-Co cermet chip and (b) hydrothermal-treated WC-Co cermet chip.

surface microstructures of as-received WC-Co cermet chip and hydrothermal-treated specimen at 110°C for 24 h in 6N HCl. On the microstructure of as-received WC-Co sintered body, Co binder phase was observed at the grain boundary of WC sintered body (Fig. 6a). After the hydrothermal treatment, the Co binder phase was completely removed from the grain boundary of WC sintered body (Fig. 6b). No damage was observed on the WC grains after hydrothermal treatment but only Co binder phase was extracted. Therefore, the reason of disintegration of the specimen must be the release of the residual stress of the sintered body according to the extraction of Co binding phase. The WC-Co sintered body was uniaxially-pressed before sintering and it should have the uniaxially residual stress. This may be also the reason for the morphology of the disintegrated fragments having thin plate-like shapes.

3.2. Re-sintering of recovered WC powder

Re-sintering of the recovered WC powder was attempted using the fine WC powder reclaimed from the hydrothermal-treated fragments. Fig. 7a shows the SEM of the powder ball-milled for 24 h with ethanol. The virginal WC powder for sintering was also shown for comparison. The WC sintered body pulverized into fine particles easily. The grain size of pulverized power was less than 3 μm, which is a little smaller than that of virginal WC powder. The morphology of the ball-milled particle was rather squarish. Fig. 8 shows XRD profiles of the ball-milled and virginal WC powder. The XRD patterns of ball-milled powder showed only WC phase without contamination by any other crystalline impurities and degradation of crystallinity. It was proved that Co binder phase was completely removed not only on the surface of the specimen but also inside of the fragments.

The ball-milled powder was dried in a drying oven at 50°C for 24 h, and then mixed with virginal Co powder to form the green body for re-sintering. Table I summarizes the density and mechanical properties of the sintered bodies prepared from virginal WC powder and recovered powder. The density of the re-sintered specimen was lower than that prepared from the virginal WC powder. This may be caused by the morphology of the recovered WC particle being more squarish than that

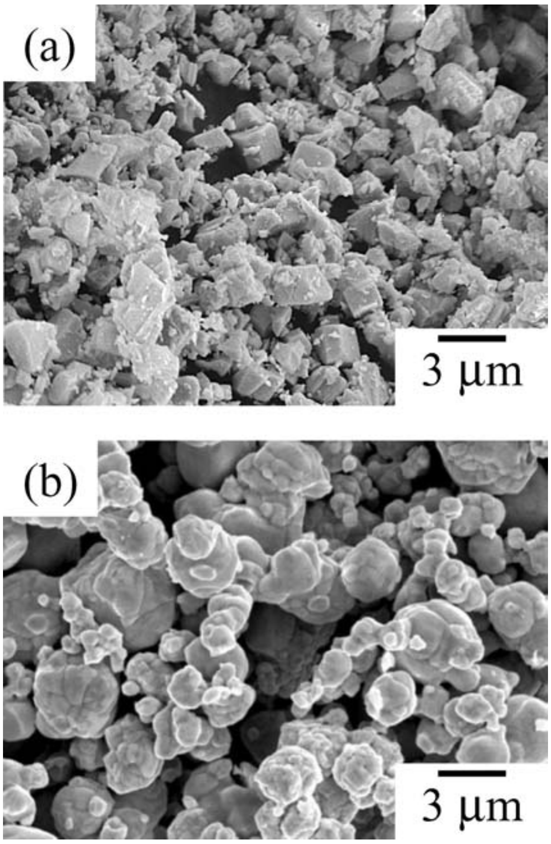

Figure 7 Appearances of the recovered and virginal WC powders. (a) Recovered WC powder and (b) virginal WC powder.

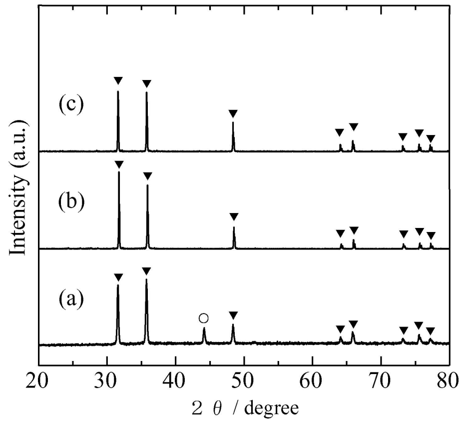

Figure 8 XRD profiles of the recovered and virginal WC powders. (a) Original WC-Co cermet chip, (b) recovered WC powder, and (c) virginal WC powder. ▼: WC, ○: Co.

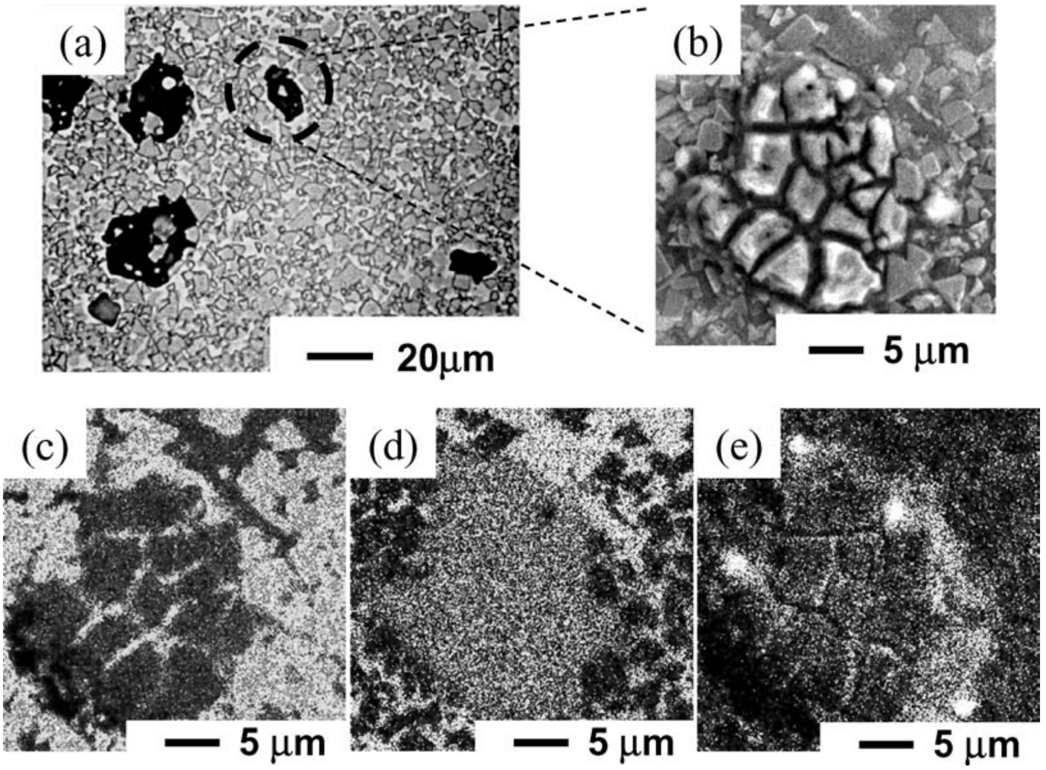

Figure 9 Optical microscopy and SEM-EDS images of the etched surfaces of the recovered WC-Co cermet chip. (a), (b) optical microscopy of the etched surface, (c) mapping image of tungsten, (d) mapping image of cobalt, (e) mapping image of carbon.

of virginal WC powder. This squarish morphology will decrease the tapping density of green body and the sintered density also. The Rockwell hardnesses of the re-sintered specimens showed the values are almost equivalent to that of the sintered body from virginal WC powder. However, the bending strength of the re-sintered specimen possesses a relatively small value. Insufficient densification of the sintered body must be one of the reasons for the low bending strength of re-sintered body. However, the decrease in bending strength seems to be too large compared with the difference in sintered density. Fig. 9 shows the optical microscopy and SEM-EDX images of the surface of the recycled WC-Co cermet. Prior to the microscopic observation, surface of the cermets was etched by Murakami reagent in order to remove tungsten from the surface of the specimen. In Fig. 9a and b, relatively large grains (dark parts) were observed only on the surface of the recycled chip. By EDX analysis, these large grains were found mainly to consist of carbon and cobalt. Therefore, this relatively large grain must be composed of tungsten, cobalt and carbon before etching. From the CHN coder analysis, the percentage content of carbon in the virginal WC powder was 6.15%, though it was 5.92%, in the recovered powder. This decrease in carbon content must be caused by the oxidation of WC phase. In fact, distinct peak of W-O binding was confirmed by XPS analysis on the surface of recovered powder as shown in Fig. 10. WC fine powder is known to be oxidized easily in air and the surface will be covered by thin oxide layer. Thus, WC fine powder should be stored usually under an inactive atmosphere. The existence of this oxidized phase on the surface of WC particle may cause the generation of CO_2 gas by means of the reaction with surrounding active carbon and induce the lack of carbon source. It is well known that the W-Co-C compounds named "η phases (Co_3W_3C, $Co_6W_6C_2$)" appear as by-products in sintering of WC-Co cermets and they form when the concentration of carbon is lower than the stoichiometry

TABLE I Density and mechanical properties of sintered bodies

WC powder source	Density (g/cm^3)	Rockwell A hardness (HRA)	Transverse rapture strength (kgf/mm^2)
Virginal WC powder	13.72	84.3	267
Recovered WC powder	13.40	83.1	216
Recovered WC powder (dried by vacuumed oven)	13.35	82.6	267

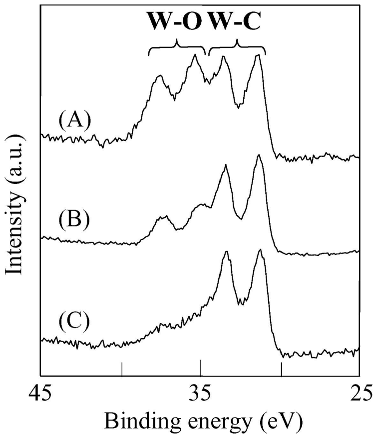

Figure 10 XPS spectra of W 4f orbital for (a) WC powder dried in an oven at 50°C for 24 h, (b) WC powder dried in a vacuum drying oven at 100°C for 24 h, (c) virginal WC powder.

of WC. Therefore, relatively large grains observed on the surface of recycled chips must be η phase formed by oxidation of the surface of WC particle. As observed in Fig. 7, the morphology of the recovered powder was more squarish than that of virginal powder. This difference in the particle shape makes the oxidation easer and causes the formation of η phase. Since η phase known to be more brittle than normal WC phase, grain boundary of the η phase must act as the defect, which decrease the transverse rupture strength of the recycled chips.

In order to depress the oxidation of WC powder in the recycle process, a vacuum drying oven was used for the drying of ball-milled powders instead of using a drying oven. By SEM observation of the surface of cermet chip obtained from the vacuum dried WC powder, it was proved that oxidation of the surface was efficiently depressed and no large grain of η phase was observed. Table I shows the mechanical properties of the recycled cermets prepared from the recovered WC powder by vacuum drying. The transverse rupture strength was not degraded compared with the cermets prepared from virginal WC powder.

The recycled powder obtained in this study had a problem on their stability in oxidizing atmosphere. However, the properties of recycled cermet chip was retained as well as the original one with careful treatment of drying process. This hydrothermal treatment procedure may be used as one of the excellent recycling systems for WC-Co cermets, if the milling or drying process of the recycled powder will be improved.

4. Conclusions

WC-Co cermets are hydrothermal-treated in acidic solutions with the aim of effective dissolution of Co binder phase, which was efficiently removed when the cermets were treated in hydrochloric acid. The optimum treatment condition was at 110°C for 24 h in 6N HCl aqueous solution. The treated WC sintered body was very brittle and disintegrated easily by ball milling. The mechanical property of the re-sintered cermets using the recycled WC powder was a little degraded by the formation of η phase because of the oxidation of WC particles. However, the degradation of mechanical properties of the recycled cermet chip was overcome by improving the dying process of recovered powder. This hydrothermal dissolution process of Co binder phase from WC-Co cermets must be one of the effective and economical recycling systems of WC-Co cermet scraps.

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