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Separation and Determination of Zirconium Carbide in Zr$_{50}$Al$_{10}$Ni$_5$Cu$_{30}$ Bulk Metallic Glass Matrix Composites Containing ZrC Particles

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The method of separation and determination of zirconium carbide in Zr$_{50}$Al$_{10}$Ni$_5$Cu$_{30}$ bulk metallic glass matrix composites containing zirconium carbide particles has been developed.

The zirconium carbide was not dissolved though the metallic glass specimen was dissolved with 6 kmol m$^{-3}$ hydrochloric acid of the room temperature.

After complete dissolution of the metallic glass matrix specimen with 6 kmol m$^{-3}$ hydrochloric acid of the room temperature, the undissolved zirconium carbide was separated by filtration with the membrane filter having the pore size of 0.2 μm. The separated zirconium carbide was fused with the potassium hydrogen sulfate in the platinum crucible. The concentrations of zirconium, copper, aluminum and nickel in the filtrate and the insoluble residue were determined respectively by inductively coupled plasma-optical emission spectrometry.

The zirconium concentration in the filtrate and the insoluble residue were constant irrespective of the dissolution time. Copper, aluminum and nickel were not detected in the insoluble zirconium carbide.

It was confirmed that the zirconium carbide in the Zr$_{50}$Al$_{10}$Ni$_5$Cu$_{30}$ bulk metallic glass matrix had been quantitatively separated and determined. [doi:10.2320/matertrans.M2009334]

Key words: zirconium carbide, Zr$_{50}$Al$_{10}$Ni$_5$Cu$_{30}$ bulk metallic glass, separation and determination, 6 kmol m$^{-3}$ hydrochloric acid, filtration, inductively coupled plasma-optical emission spectrometry

1. Introduction

Metallic glass, a glassy solid with the metallic bonding is prepared by quenching supercooled liquid-alloy under the glass transition temperature before the crystallization takes place. Due to the non-crystalline structure, metallic glass exhibits characteristic mechanical, physical and chemical properties which are different from those of the conventional crystalline alloys. A Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ is well known to be one of the best bulk glass formers with excellent mechanical properties such as high fracture strength ~2 GPa, high elastic limit ~2%, and low Young’s modulus ~80 GPa at room temperature. In general, metallic glass as well as Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ bulk metallic glass (BMG) deforms almost elastically and the fracture takes place along a localized maximum shear plane without distinct plastic elongation under the uni-axial compressive or tensile modes. In order to improve this lack of plasticity, bulk metallic glass matrix composites (BMGMCs) have been developed up to date with dispersing various reinforcements such as ceramics, hard metals, and even porosities. The first BMGMC of Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ alloy has been developed with ZrC dispersoids which were doped directly into the metallic molten alloy. The Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ BMGMC with ZrC dispersoids exhibits, in this paper, higher fracture strength and larger plastic strain under a uniaxial compressive mode as compared with the monolithic counterpart. Later, it is reported by the same authors that much higher composite effects on the mechanical properties were achieved in this BMGMC with ZrC particles formed by an in-situ reaction, Zr+C (graphic particle) → ZrC during the ingot preparation by the arc-melting. More recently, the strengthening mechanism in the Zr$_{55}$Al$_{10}$Ni$_5$Cu$_{30}$ BMGMC with the in-situ ZrC dispersoids has been discussed by mean of the neutron diffraction method.

In the analysis, accurate and quantitative evaluation of ZrC in this Zr$_{50}$Al$_{10}$Ni$_5$Cu$_{30}$ BMGMC was required for estimating the characteristic, i.e. actual composition of the matrix glass and dispersoids, and elastic modulus, of the materials. We have reported in previous work that TiC in in-situ TiC particle reinforced Fe$_3$Si base alloys could be isolated and determined by dissolution with 6 kmol m$^{-3}$ hydrochloric acid. The aim of this work was to develop a method for quantitative separation and determination of ZrC in metallic glass matrix composites containing ZrC particles.

2. Experiment

2.1 Specimen and reagents for analysis

The metallic glass matrix specimen of 100 mm in length and 3 mm in diameter was shaved off by lathe and the shaved chips were used for chemical analysis.

Reagent ZrC powder (95%, Kojundo Chemical Laboratory Co. Ltd.) was used for the standard sample.

Standard solutions (1.00 mg/mL) for determination of ICP-OES were prepared by dissolution of high purity metal or reagent as follows. Zirconium standard solution: One hundred milligrams of zirconium metal (>99.999%, Mitsuwa Chemicals Co. Ltd.) was dissolved with a mixture of hydrofluoric acid and nitric acid. Twenty mL of 9 kmol m$^{-3}$ sulfuric acid was added to the solution, and the solution was evaporated until the hydrofluoric acid and the nitric acid were completely removed. Then the solution was adjusted to 100 mL with pure water accurately.

Nickel and copper standard solutions: One hundred milligrams of nickel metal (99.998%, The Nilaco Corp.) and copper metal (99.999%, Mitsuwa Chemicals Co. Ltd.) were dissolved with 10 mL of 7 kmol m$^{-3}$ nitric acid respectively.
Then the solutions were adjusted to 100 mL with pure water accurately respectively.

Aluminum standard solution: One hundred milligrams of aluminum metal (99.998%, Wako Pure Chemical Industries, Ltd.) was dissolved with 10 mL of 6 kmol⋅m\(^{-3}\) hydrochloric acid. Then the solution was adjusted to 100 mL with pure water accurately.

Silicon standard solution: Silicon dioxide (99.999%, Furuuchi Chemical Corp.) of 0.4280 mg which was ignited over 1000°C beforehand and dried in a desiccator, was fused with 2.0 g of sodium carbonate. Then the solution was adjusted to 200 mL with pure water accurately. This standard solution was stored in a polyethylene bottle.

All reagents used were analytical-reagent grade and pure water by distilled and ion-exchanged was used for all preparation procedure.

Membrane filter used was polycarbonate type membrane filter with diameter of 25 mm and pore-size of 0.2 μm (Toyo Roshi Kaisha, Ltd.).

2.2 Apparatus

The Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) used was IRIS Advantage DUO made by Thermo Fisher Scientific Co. Ltd.

3. Results and Discussion

3.1 Separation of ZrC from metallic glass

For study the separation method of ZrC from Zr\(_{50}\)Al\(_{10}\)Ni\(_{15}\)Cu\(_{35}\) bulk metallic glass matrix composites containing ZrC particles, dissolution methods of reagent ZrC powder and metallic glass specimen with several acids were investigated.

Lay reported the corrosion resistance of ZrC to acids as shown in Table 1.\(^{10}\) A hydrochloric acid of the room temperature alone did not dissolve ZrC though almost all the acids shown in Table 1 more or less dissolved ZrC.

The reagent ZrC powder and shaved chips of metallic glass matrix specimen were dissolved respectively with nitric acid, hydrochloric acid and aqua regia of the room temperature or on hot plate. The results of dissolution were shown in Table 2. It was found from the results of Table 2 that the acid which did not dissolve ZrC was only a hydrochloric acid of the room temperature though it dissolved the metallic glass matrix specimen.

Table 1 Corrosion resistance of zirconium carbide to acids.\(^{10}\)

<table>
<thead>
<tr>
<th></th>
<th>HCl</th>
<th>HNO(_3)</th>
<th>H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (b)</td>
<td>A (20)</td>
<td>C (20)</td>
<td>C (b)</td>
</tr>
<tr>
<td></td>
<td>B (20)</td>
<td>B (20)</td>
<td>C (b)</td>
</tr>
<tr>
<td>H(_3)PO(_4)</td>
<td>HClO(_4)</td>
<td>HF</td>
<td>HCl +</td>
</tr>
<tr>
<td>B (20)</td>
<td>A (20)</td>
<td>A (20)</td>
<td>A (20)</td>
</tr>
<tr>
<td></td>
<td>C (b)</td>
<td>C (b)</td>
<td>C (20)</td>
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<tr>
<td></td>
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<td>C (20)</td>
</tr>
</tbody>
</table>

A: ZrC not dissolved at indicated temperature (°C).
B: ZrC reacts slightly at indicated temperature (°C).
C: ZrC reacts considerably at indicated temperature (°C).
b: Boiled solution

A Zr\(_{50}\)Al\(_{10}\)Ni\(_{15}\)Cu\(_{35}\) bulk metallic glass matrix composites containing ZrC particles was dissolved with 6 kmol⋅m\(^{-3}\) hydrochloric acid of the room temperature for 3 days. After complete dissolution of metallic glass matrix specimen, the insoluble residue was separated from the solution by filtration through membrane filter with having the pore-size of 0.2 μm, washed with dilute hydrochloric acid, pure water, ethyl alcohol, and dried in desiccators. The collected insoluble residue was analyzed by X-ray diffraction (XRD) and its XRD pattern was shown in Fig. 1. The XRD pattern of reagent ZrC powder was also shown in Fig. 1. The XRD pattern of insoluble residue was identical to that of reagent ZrC powder. From the result of XRD shown in Fig. 1, the insoluble residue by dissolution with 6 kmol⋅m\(^{-3}\) hydrochloric acid of the room temperature was identified ZrC. The scanning electron micrograph of the insoluble residue was shown in Fig. 2. The insoluble residue was less than about 10 μm in diameter.

From the above experiment results, it was found that ZrC particle contained in Zr\(_{50}\)Al\(_{10}\)Ni\(_{15}\)Cu\(_{35}\) bulk metallic glass matrix composites were separated from metallic glass matrix by dissolution with 6 kmol⋅m\(^{-3}\) hydrochloric acid of the room temperature.

3.2 Dissolution of ZrC

Zirconium carbide was not able to be dissolved completely with the acids shown in Table 2. A part of ZrC remained though ZrC was considerably dissolved by dissolution with the acids shown in Table 2. Zirconium carbide was not able to dissolve even with a mixture of hydrofluoric acid and nitric acid. However it was found from some experiment results
that ZrC could be dissolved easily by fusion with potassium hydrogen sulfate in platinum crucible.

3.3 Determination of all composite elements in metallic glass matrix specimen

The quantitative separation and determination method of ZrC in Zr$_{50}$Al$_{10}$Ni$_{5}$Cu$_{30}$ bulk metallic glass matrix composites containing ZrC particles was investigated. All composite elements of metallic glass matrix specimen including ZrC were determined. After 50 mg of metallic glass matrix specimen was dissolved with 10 mL of aqua regia on hot plate, the solution was filtered with membrane filter having the pore size of 0.2 μm. The insoluble residue on filter paper was washed with dilute hydrochloric acid and pure water. The filtrate and washed solution were collected in a beaker that contained 10 mL of 9 kmol/L sulfuric acid to prevent hydrolysis of zirconium. The insoluble residue on filter paper was transferred into platinum crucible. The insoluble residue and filter paper in the crucible were done ashing and fused with 1.5 g of potassium hydrogen sulfate. Amounts of zirconium, copper, nickel and aluminum in filtrate and insoluble residue were determined by ICP-OES respectively. Amounts of silicon, hafnium and manganese that might be contaminated during the making process of metallic glass were also determined by ICP-OES. Moreover oxygen and carbon were determined by inert gas fusion/infra-red absorption method and combustion/infra-red absorption method respectively. Analytical results were shown in Table 3. The analytical results of silicon, hafnium, manganese, oxygen and carbon not listed in Table 3 were 0.12, 0.011, 0.010, 0.021 and 1.14% respectively. The total sum of the obtained analytical results was almost 100%.

3.4 Quantitative determination of separated ZrC

After the dissolution of the metallic glass matrix specimen with 6 kmol·m$^{-3}$ hydrochloric acid of the room temperature, the insoluble residue was separated by the filtration, and then the amounts of zirconium, copper, nickel and aluminum in filtrate and insoluble residue were determined by ICP-OES respectively.

Fifty milligrams of metallic glass matrix specimen was dissolved with 10 mL of 6 kmol·m$^{-3}$ hydrochloric acid of the room temperature in a glass beaker for 3 days. After the reaction was finished, the solution was filtered with membrane filter having the pore-size of 0.2 μm. The insoluble residue on filter paper was washed with dilute hydrochloric acid and pure water. The filtrate and washed solution were collected in a beaker that contained 10 mL of 9 kmol·m$^{-3}$ sulfuric acid to prevent hydrolysis of zirconium. Subsequently the solution was evaporated to a little volume by heating on hot plate. After the solution had cooled to room temperature, it was transferred into a 50 mL volumetric flask with pure water. A constant amount of yttrium as internal-standard element was added to the solution and the solution was adjusted to 50 mL with pure water accurately. The concentration of zirconium, copper, nickel and aluminum in the solution were determined by ICP-OES.

The insoluble residues on filter paper were washed with diluted hydrochloric acid and pure water and transferred into a crucible of platinum. The insoluble residue and filter paper in the crucible were done ashing and fused with 1.5 g of potassium hydrogen sulfate. The fused salt was dissolved with 2 mL of 9 kmol·m$^{-3}$ sulfuric acid and transferred into a 50 mL volumetric flask with pure water. A constant amount of yttrium as internal-standard element was added to the solution, and the solution was adjusted to 50 mL.
with pure water accurately. The concentration of zirconium, copper, nickel and aluminum in the solution were determined by ICP-OES.

Analytical results were shown in Table 3. The determined value of zirconium in the filtrate and washed solution (soluble zirconium) was 62.3%, though the determined value of zirconium in the metallic glass specimen including ZrC was 68.9%. The concentration of zirconium in the insoluble residue (insoluble zirconium) was 6.70%. The total sum of concentration of soluble zirconium and insoluble zirconium was same as a concentration of zirconium in the metallic glass specimen including ZrC. The determined values of copper, nickel and aluminum in the filtrate and washed solution (soluble elements) were same as the determined values in the metallic glass matrix specimen including ZrC. On the other hand, all of them were not detected in insoluble residue.

### 3.5 Dissolution time

Influence of the time of the dissolution with 6 kmol m\(^{-3}\) hydrochloric acid of the room temperature on analytical result was examined. Fifty milligrams of the metallic glass matrix specimen including ZrC and 10 mg of reagent ZrC powder were dissolved respectively with 10 mL of 6 kmol m\(^{-3}\) hydrochloric acid of the room temperature and the dissolution time was changed. After the dissolved solution was filtered with membrane filter, concentration of zirconium, copper, nickel and aluminum in the filtrate and the insoluble residue were determined by ICP-OES respectively. Analytical results of soluble and insoluble zirconium were shown in Fig. 3. The concentrations of soluble and insoluble zirconium in reagent ZrC powder and metallic glass specimen including ZrC were constant irrespective of dissolution time. The concentrations of copper, nickel and aluminum in the filtrate were same as the determined values in metallic glass specimen including ZrC and constant irrespective of dissolution time. On the other hand, all of them were not detected in the insoluble residue irrespective of dissolution time.

From mentioned experimental results, it was confirmed that ZrC in metallic glass matrix specimen including ZrC was separated quantitatively by dissolution with 6 kmol m\(^{-3}\) hydrochloric acid of the room temperature.

### 4. Conclusions

The method of separation and determination of ZrC in Zr\(_{50}\)Al\(_{10}\)Ni\(_{30}\)Cu\(_{30}\) bulk metallic glass matrix composites containing ZrC particles was developed.

Zirconium carbide was not dissolved though metallic glass specimen was dissolved with 6 kmol m\(^{-3}\) hydrochloric acid of the room temperature. Copper, aluminum and nickel were not detected in the separated zirconium carbide. The concentration of zirconium in separated ZrC was constant irrespective of the dissolution time.

It was confirmed that zirconium carbide in the Zr\(_{50}\)Al\(_{10}\)Ni\(_{30}\)Cu\(_{30}\) bulk metallic glass matrix was quantitatively separated.

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REFERENCES