Preparation of Ductile High Strength Cr and Co Base Filaments by Glass-Coated Melt Spinning

By Tomoko Goto* and Akihiro Yoshino**

Ductile high strength metallic filaments can be employed as reinforcement for brittle matrices such as fine ceramics. The glass-coated melt spinning of Cr and Co-base alloys was investigated as a means of producing a high strength and high toughness filament. The toughness was estimated from the area of stress-strain curves of the filament obtained. A continuous Cr–Ni–Fe–Si–B filament with a high toughness of 7000 MPa·% was obtained from the molten state at 1600 K for a winding speed up to 7.95 m/s.

Ductile high strength filaments of Co–Mn–Si–B alloys were also successfully produced. A Co$_{68}$Mn$_{10}$Cu$_2$Si$_5$B$_{15}$ filament had the highest toughness of 10050 MPa·% with tensile strength of 4740 MPa and elongation of 4.0%. The filament consisted of micrograins with a grain size of $40 \times 10^{-10}$ m.

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I. Introduction

Glass fiber and carbon fiber are widely used as a reinforcement in composite materials. Although these fibers have high strength and low density, they are generally brittle materials with low elongation and have only limited application. High toughness and high strength glass-coated metallic fibers however, show great promise for use in composite materials as reinforcement for brittle matrices such as fine ceramics.

We have studied the preparation of high strength and high toughness metallic filament using the method of glass-coated melt spinning$^{(1)}$. This method gives filaments for cooling rates more than $10^5$ K/s and micrograins with grain sizes smaller than $1000 \times 10^{-10}$ m for a suitable alloy composition. It is possible to obtain ductile high strength filaments by this method.

In a previous paper, ductile high strength Fe-base filaments were prepared by using this method, and it was found out that the addition of chromium resulted in the enhancement of toughness$^{(1)}$. The present paper describes the melt spinning of Cr and Co base alloys for preparation of a ductile high strength filament.

II. Experimental Procedure

The melt spinning of Cr and Co base alloys was carried out using the same method as that for Fe-base alloys$^{(1)}$. Parent alloys of the chromium or cobalt system with the melting point up to 1550 K were prepared by melting chromium or cobalt, boron and other elements in vacuum. About 1 g of the alloy was placed in a Pyrex glass tube and melted by r.f. induction heating in an argon atmosphere. When the glass tube containing the molten alloy was drawn, the alloy was stretched to form a glass-coated metallic filament and was coiled on a winding drum. The glass-coating was removed in a 45% HF aqueous solution. The tensile strength of the filaments produced by this method was measured with an Instron type machine, and the crystal structure was examined with an X-ray diffractometer.

III. Results and Discussion

1. Chromium base alloy filament

It is very important in the glass-coated melt...
spinning that the melting point of the metal is close to the flow point of the glass used and that the wettability between the molten metal and coating glass is good. In the case of Pyrex glass (the flow point of 1370 K), the melting point of the alloys have to be as high as 1580 K. The melting point of chromium (2100 K) is so high that it is difficult to obtain a chromium base alloy with the low melting point up to 1580 K, even if metalloids such as boron and silicon are added. The melting point of Cr–Ni binary alloys decreases to 1623 K at 45 at% Ni and then increases with increasing nickel element\(^\text{2}\). The melt spinning of Cr–Ni–B–Si system alloys was not successfully conducted because of their high melting point.

The melt spinning of Cr–Ni–Fe–B–Si system alloys was, therefore, carried out from the molten state at a temperature of about 1600 K with winding speeds ranging from 0.95 to 7.95 m/s. Continuous filaments of Cr–Ni–Fe–B–Si alloys were obtained within the range of winding speeds used. The filament obtained is shown in Fig. 1. The filaments have a lustrous smooth surface and are free from pinholes.

Variations in the average diameter with the winding speed were measured and the results are shown in Fig. 2. The diameter of the filament obtained decreases with increasing winding speed. A thicker filament is obtained, as the ratio of nickel to chromium in the alloys becomes smaller. The alloys with the small ratio such as 5/8 and 5/7 are considered to have a low melting point, and the diameter of the filaments obtained had some relations to the melting point of the alloys.

The average tensile strength of \((\text{Cr, Ni})_{75-x}\text{Fe}_x\text{B}_{20}\text{Si}_{5}\) filaments spun at various winding speeds at a melting temperature of 1600 K.

\[ egin{array}{c}
\text{Cr}_{40}\text{Ni}_{35}\text{Fe}_{10}\text{B}_{20}\text{Si}_{5} \quad \odot \quad \text{Cr}_{35}\text{Ni}_{35}\text{Fe}_{15}\text{B}_{20}\text{Si}_{5} \\
\text{Cr}_{35}\text{Ni}_{39}\text{Fe}_{10}\text{B}_{20}\text{Si}_{5} \quad \odot \quad \text{Cr}_{35}\text{Ni}_{35}\text{Fe}_{5}\text{B}_{20}\text{Si}_{5} \\
\end{array} \]

The average tensile strength of \((\text{Cr, Ni})_{75-x}\text{Fe}_x\text{B}_{20}\text{Si}_{5}\) filaments spun at various winding speeds was measured. The relations between strength and iron content are shown in Fig. 3. The tensile strength of the filament spun at a low winding speed is larger than that of the

![Fig. 1 Scanning electron micrograph of the surface of Cr$_{40}$Ni$_{35}$Fe$_{10}$B$_{20}$Si$_{5}$ filaments.](image)

![Fig. 2 Average diameter of Cr–Ni–Fe–B–Si system alloy filaments spun at various winding speeds at a melting temperature of 1600 K.](image)

![Fig. 3 Relation between average tensile strength and iron content of \((\text{Cr, Ni})_{75-x}\text{Fe}_x\text{B}_{20}\text{Si}_{5}\) filament spun at winding speeds of 7.95 m/s and 0.95 m/s.](image)
filament spun at a high speed. The effect of size on strength was not detected for the present filament, whereas the strength of IN 856 stainless-steel filament increased with decreasing diameter\(^{3}\). The maximum tensile strength and elongation are observed at 10 at\% Fe. A high average tensile strength such as 2670 MPa and an elongation of 3.6\% was attained for the Cr\(_{40}\)Ni\(_{25}\)Fe\(_{10}\)B\(_{20}\)Si\(_{5}\) (1) filament. The structure of this filament was amorphous, and a distinct range of plasticity was not shown on its stress-strain curve.

(Cr, Ni, Fe)\(_{75-x}\)M\(_x\)B\(_{20}\)Si\(_{5}\) (M\(_x\): Nb, Cu, Ti, Si, Mo) filaments were produced by the same method. The ductility appeared by addition of silicon, titanium, and copper. Stress-strain curves of the Cr\(_{35}\)Ni\(_{30}\)Fe\(_{20}\)B\(_{20}\)Si\(_{10}\) \((2)\) filament exhibited a range of plasticity with high tensile strength of 2300 MPa and elongation of 3.1\%.

The effect of the additional element was also examined for the Cr\(_{35}\)Ni\(_{30-x}\)Fe\(_{20}\)B\(_{20}\)Si\(_{10}\)M\(_x\) \((M_x): Cu, Mo, Nb, W, Mn, Al, C, Ti, Be)\) alloys. Values of the average tensile strength of the filaments spun at various winding speeds are listed in Fig. 4. The addition of a small amount of carbon and titanium results in the increases of strength and elongation. For example, Cr\(_{35}\)Ni\(_{29.5}\)Fe\(_{20}\)B\(_{20}\)Si\(_{10}\)C\(_{0.5}\) \((3)\) and Cr\(_{35}\)Ni\(_{29.5}\)Fe\(_{20}\)B\(_{20}\)Si\(_{10}\)Ti\(_{0.5}\) \((4)\) filaments have a high tensile strength more than 3000 MPa with elongation of 3.0\%.

The toughness of the (1), (3) and (4) filaments with high strength and elongation was estimated from the area of each stress-strain curve, and the maximum toughness observed is listed in Table 1. A high toughness of 7000 MPa·% is observed for these filaments.

### Table 1 Maximum toughness of ductile Cr-Fe-Ni-B-Si alloy filaments.

<table>
<thead>
<tr>
<th>Alloys filament</th>
<th>Winding speed (m/s)</th>
<th>Diameter (10(^{-3}) m)</th>
<th>Toughness (MPa·%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Cr(<em>{40})Ni(</em>{25})Fe(<em>{10})B(</em>{20})Si(_{5})</td>
<td>0.95</td>
<td>19</td>
<td>7300</td>
<td>2990</td>
<td>4.6</td>
<td>amorphous</td>
</tr>
<tr>
<td>(3) Cr(<em>{35})Ni(</em>{30})Fe(<em>{20})B(</em>{20})Si(<em>{10})C(</em>{0.5})</td>
<td>7.95</td>
<td>4</td>
<td>6900</td>
<td>2900</td>
<td>3.6</td>
<td>f.c.c. + b.c.c. + σ phase</td>
</tr>
<tr>
<td>(4) Cr(<em>{35})Ni(</em>{29.5})Fe(<em>{20})B(</em>{20})Si(<em>{10})Ti(</em>{0.5})</td>
<td>3.97</td>
<td>4</td>
<td>7200</td>
<td>4430</td>
<td>3.0</td>
<td>f.c.c. + b.c.c. + σ phase</td>
</tr>
</tbody>
</table>

σ phase: CrFe tetragonal

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2. Cobalt base alloy filament

It was difficult to obtain various chromium base alloy filaments because of the high melting point of chromium. Although the size effect on the strength was not found out, the amorphous Fe\(_{65}\)Co\(_{10}\)Si\(_{10}\)B\(_{15}\) filament with high tensile strength of 4400 MPa was produced in the previous work\(^{4}\). Then the melt spinning of Co-B system alloys was examined to prepare a ductile high strength metallic filament. Fine
filaments of cobalt base alloys with ferromagnetism can be also employed as an electronic or electrical equipment(5).

Continuous Co–B system alloy filaments were produced by the same method as for the chromium alloys. The diameter of the filaments obtained decreased with increasing winding speed and ranged from $4 \times 10^{-6}$ m to $18 \times 10^{-6}$ m. The average tensile strength and elongation of the $\text{Co}_{0.85-x}\text{M}_x\text{B}_{15}$ ($\text{M}_x$: Ni, Cr, Fe, Mn, Si) alloy filament spun at various winding speeds were measured and are shown in Fig. 5. The addition of silicon, manganese, iron and chromium results in the increase of tensile strength and elongation. Then the melt spinning of $\text{Co}_{0.80-x}\text{M}_x\text{Cr}_5\text{B}_{15}$ ($\text{M}_x$: Fe, Mn) alloys was examined, and the strength of the filaments obtained is shown in Fig. 6 and Fig. 7. The tensile strength and elongation increase, if manganese and chromium are added. Stress-strain curves of the $\text{Co}_{0.85-x}\text{M}_x\text{B}_{15}$ ($\text{M}_x$: Mn$_{10}$, Cr$_5$Mn$_5$, Cr$_{10}$Mn$_5$, Cr$_3$(Mn$_{10}$, Mn$_{10}$Si$_3$) filaments exhibited a slight range of plasticity. Especially, the $\text{Co}_{0.70}\text{Mn}_{10}\text{Si}_3\text{B}_{15}$ filament was a ductile material with a high average strength of 1890 MPa and a high elongation of 3.2%, as compared with the standard tensile strength of 254 MPa and elongation of 6% for pure cobalt.

Most crystal structures of these ductile filaments were amorphous mixed with $\alpha$ phase, showing the strong first maximum of the amorphous phase in the X-ray diffraction pattern. The melt spinning of $\text{Co}_{0.70-x}\text{Mn}_{10}\text{Si}_3\text{B}_{15}$M$_x$ ($\text{M}_x$: Nb, Cr, Cu, Ta, Be, Ti) alloys was carried out to prepare a filament having a higher toughness. Variations in the average tensile strength of the filament with the winding speed are shown in Fig. 8. The addition of titanium and copper results in the increase of strength and plasticity. For example the $\text{Co}_{0.68}\text{Mn}_{10}\text{Cu}_2\text{Si}_3\text{B}_{15}$ (5) filament is a ductile material with high tensile strength of 3560 MPa and high elongation of 3.1%, and

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**Fig. 5** Average tensile strength of $\text{Co}_{0.85-x}\text{M}_x\text{B}_{15}$ filaments spun at various winding speeds. $\text{M}_x$: ○ blank, ▲ Fe, □ Mn$_5$, ● Si$_{10}$, △ Cr$_5$, ▼ Ni$_{15}$.

**Fig. 6** Average tensile strength of $\text{Co}_{0.80-x}\text{M}_x\text{Cr}_5\text{B}_{15}$ filaments spun at various winding speeds. $\text{M}_x$: ○ blank, ● Fe, ○ Mn$_5$, ▲ Mn$_5$Cr$_5$. 
The effect of the addition of titanium was examined, and the results are also shown in Fig. 9. The high average tensile strength such as 3810 MPa was attained in the Co70Mn5Cr5Ti0.5Si5B14.5 (7) filament.

The toughness of the (5), (6) and (7) filaments with high tensile strength and high elongation was estimated from the area of each stress-strain curve. The maximum toughness and tensile strength observed are listed in Table 2. The highest toughness in these filaments is 10000 MPa $\%$.

Continuous amorphous wires with a high strength and a good ductility were produced in the Co-Si-B alloy system by a technique using melt spinning in rotating water$^6$. The wires have a circular cross-section 80–140 $\times 10^{-6}$ m in diameter. By cold drawing of about 50% reduction in area, tensile strength and elongation for the Co72.5Si12.5B15 amorphous wire definitely increased from 3450 MPa to 3580 MPa and from 3.0 to 4.3%, respectively$^8$. The highest toughness of 10000 MPa $\%$ was estimated from the stress-elongation curve of the Co72.5Si12.5B15 amorphous wire cold drawn to about 50% reduction. As the structure of the present Co75Si10B15 filament was a mixture of f.c.c. and orthorhombic (Co3B) phases, the cooling rate of the glass-coated melt spinning is considered to be lower than that of the rotating-water spinning method because of the coating glass. However, as filaments are rapidly quenched from the liquid state in the drawing process in the present method, the high toughness can be obtained without cold drawing.

Observation by transmission electron microscopy of the filaments with a cylindrical shape is very difficult because of poor transmission of electron. The crystal grain size of these filament was, therefore, measured from the
The apparent particle size, \( \varepsilon \), was determined by Scherrer's formula, 
\[
\varepsilon = \frac{1.05 \lambda}{\beta \cos \theta}
\]
where \( \lambda \) was the wave length of X-rays, \( \beta \) the integral breadth and \( \theta \) the Bragg angle. The particle size of the (5) and (7) filaments was determined at \( 40 \times 10^{-10} \text{m} \) and \( 35 \times 10^{-10} \text{m} \), respectively, by using the sharp first maximum of the amorphous phase mixed with \( \alpha \) phase. The particle size of the (6) filament was \( 110 \times 10^{-10} \text{m} \) from the profile of 110 in b.c.c. structure. A high toughness of the filament is due to its micropolycrystalline texture.

In conclusion, continuous ductile high strength filaments of Co-Mn-Si-B alloys more successfully produced from the molten state at a temperature of about 1600 K with winding speeds up to 3.97 m/s. The Co_{68}Mn_{10}Cu_{2}Si_{5}B_{15} filament had the highest toughness of 10050 MPa·% with a tensile strength of 4740 MPa with a high elongation of 4.0%. The filament was composed of fine crystal grains with a grain size of \( 40 \times 10^{-10} \text{m} \).

**REFERENCES**


<table>
<thead>
<tr>
<th>Alloy filament</th>
<th>Winding speed (m/s)</th>
<th>Diameter (10^{-10} m)</th>
<th>Toughness (MPa·%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Crystal structure</th>
<th>Particle size (10^{-10} m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5) Co_{68}Mn_{10}Cu_{2}Si_{5}B_{15}</td>
<td>3.97</td>
<td>5</td>
<td>10050</td>
<td>4740</td>
<td>4.0</td>
<td>amorphous + ( \alpha )</td>
<td>40</td>
</tr>
<tr>
<td>(6) Co_{68}Mn_{10}Ti_{0.5}Si_{5}B_{15}</td>
<td>0.95</td>
<td>10</td>
<td>9430</td>
<td>3210</td>
<td>4.7</td>
<td>b.c.c.</td>
<td>110</td>
</tr>
<tr>
<td>(7) Co_{70}Mn_{10}Cr_{5}Ti_{0.5}Si_{5}B_{14.5}</td>
<td>0.95</td>
<td>13</td>
<td>10020</td>
<td>4730</td>
<td>3.9</td>
<td>amorphous + ( \alpha )</td>
<td>35</td>
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