X-ray Elastic Constants of Sintered High Chromium Steel Containing Titanium Nitride : Comparison of Models

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Abstract

Sintered high chromium steel containing titanium nitride has high wear-resistance and heat-resistance. This material is used in practice for valve seats, which are one of the parts in diesel engines for automobiles. The purpose of this study is to carry out a fundamental investigation on an application of the method of x-ray stress measurement to this material in order to make clear the state of residual stress and to evaluate the material strength. As this material consists of two constituents (phases), the stresses in each phases (so-called phase stresses) are expected to be different from each other. The material has also some pores due to the manufacturing process of powder metallurgy. Therefore, its x-ray elastic constants differ from those in single phase state due to the disturbance of the state of stress caused by the existence of the second phase and the pores. As the x-ray elastic constants are important for the x-ray stress measurement, it is necessary to make clear such influence. From the point of view mentioned above, a theoretical analysis was carried out in this study as the first step in the investigation of the influence of the volume fraction of the second phase (titanium nitride) on the composite x-ray elastic constants (CXEC) of this material. The micromechanics approach developed by Lin and Mura, which is called the Eshelby/Mori-Tanaka model in this study, was used for analyzing phase stresses in each phase. The relation between the x-ray elastic constants and the volume fraction of titanium nitride was calculated in this manner for both 211 diffraction of the matrix and 420 diffraction of the second phase. The result was compared to those calculated according to the Voigt model, the Reuss model and the self-consistent model respectively, as well as those obtained experimentally.

Introduction

Composite materials consist of different constituents which have different physical and chemical properties from each other. When residual stress occurs in the material as a result of the fabrication or external stress is applied to the material, different state of stress will be built up in each phase due to misfit of elastic moduli between them. X-ray stress measurements are a promising experimental technique for determining such inhomogeneous states of stress. Since each constituent generally has a different crystal system and lattice constants, diffraction beams
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will emerge so that their directions differ from each other. One can easily measure diffraction beams which originate from each constituent separately. This leads to the conclusion that it is possible to obtain stress in each constituent, the so-called phase stress, separately through the conventional x-ray method such as the sin²ψ method.

There is also a theoretical way for analyzing the state of stress in composite materials, which is called the Eshelby method. It is effective for problems in which the material has a lot of inhomogeneous inclusions, using the Mori-Tanaka theory. Moreover, it also becomes applicable to materials which contain many kinds of inhomogeneous inclusions such as cavities and a third phase, using the method developed by Taya et al. These theoretical methods are also useful for the calculation of the x-ray elastic constants of composite materials.

In this paper, a sintered Fe-Cr/TiN composite material was studied using the method of stress measurement and the Eshelby method. The dependency of the x-ray elastic constants and phase stresses on the volume fraction of the second phase (i.e. TiN) was discussed.

THEORY

**Determination of Phase Stress Using X-ray Diffraction Technique**

The fundamental equation for the method of x-ray stress measurement is expressed as

\[
\varepsilon_{\phi\psi} = \left( \frac{S_2}{2} \right)_{\text{phase}} (\sigma_{11} \cos^2 \phi + \sigma_{22} \sin^2 \phi - \sigma_{33}) \sin^2 \psi + \left( \frac{S_2}{2} \right)_{\text{phase}} \sigma_{33} + S_1 (\sigma_{11} + \sigma_{22} + \sigma_{33})
\]  

where \( \varepsilon_{\phi\psi} \) is a normal strain determined by the x-ray method, and \( \sigma_{ij} \) are stress components in the sample coordinate system. The 1, 2, 3 axes are assumed to be the principal stress directions. \( \phi \) and \( \psi \) are angles which express the orientation of the strain \( \varepsilon_{\phi\psi} \) as shown in Fig. 1. Symbol "i" indicates a phase, for example i=M means matrix and i=I the second phase. The symbol "phase" in the x-ray elastic constants means the phase x-ray elastic constants (PXEC) for the "I" phase. \( S_1 \) and \( S_2 \) are the x-ray elastic constants and have the following relations to Young's modulus (E) and Poisson's ratio (ν)

\[
S_1 = -\frac{\nu}{E}, \quad S_2 = \frac{1+\nu}{E}
\]

When \( \phi=0 \) eq(1) leads to

![Fig. 1 Coordinate systems for specimen and measurement.](image-url)
The above equation can be used to obtain phase stresses from x-ray data.

\[
\sigma_{11}^i - \sigma_{33}^i = \left( \frac{2}{S_2} \right)_{\text{phase}} \left( \frac{\partial \varepsilon_{\psi \theta} (\phi = 0)}{\partial \sin^2 \psi} \right)_{\text{phase}} \tag{3}
\]

Determination of Macro- and Microstresses

When an external stress (\(\sigma^0\)) is applied to composite materials, the second kind stress, so-called microstress will emerge due to mechanical interaction between matrix and the second phase as shown in Fig. 2. The macrostress, which is defined as the first kind stress, is emerged in the material due to the external stress, is as same as \(\sigma^0\). From the equilibrium condition for microstresses in each phases, we have:

\[
\begin{align*}
\sigma^0 &= (1 - f)\sigma^M + f\sigma^I \\
\sigma^M &= f(\sigma^M - \sigma^I) \\
\sigma^O &= (f - 1)(\sigma^M - \sigma^I) \\
(1 - f)\sigma^m + f\sigma^\Omega &= 0
\end{align*}
\tag{4}
\]

where \(\sigma^m\) is an average microstress in the matrix, \(\sigma^\Omega\) that in the second phase, \(\sigma^M\) is an average phase or total stress in the matrix, \(\sigma^I\) that in the second phase respectively. \(f\) indicates the volume fraction of the second phase. As all the phase stresses can be obtained from the x-ray experiment, the above equation provides both macro- and microstresses.

Calculation of Composite X-ray Elastic Constants (CXEC)

The composite X-ray Elastic Constant (CXEC) is given as the slope of the relation between the slope of \(\varepsilon_{\psi \theta} \) vs. \(\sin^2 \psi\) plots and the applied stress. It usually differs from the phase x-ray elastic constant owing to the occurrence of microstresses. In order to distinguish both the x-ray elastic constants, CXEC is expressed by the symbol "composite" as shown in eq (5). One of the

Fig. 2 Macro and Micro stress.
CXEC for the "T" phase, \( \left( \frac{s_2}{2} \right)_{\text{composite}} \), then can be expressed as

\[
\left( \frac{s_2}{2} \right)_{\text{composite}}^i = \frac{\partial}{\partial \sigma_{11}^0} \left( \frac{\partial \varepsilon_{11}^p}{\partial \sin^2 \psi} \right)^i = \frac{\partial (\sigma_{11} - \sigma_{33})}{\partial \sigma_{11}^0} \left( \frac{s_2}{2} \right)_{\text{phase}}^i = 3B^i \left( \frac{s_2}{2} \right)_{\text{phase}}^i \tag{5}
\]

Eq (5) shows that CXEC \( \left( \frac{s_2}{2} \right)_{\text{composite}}^i \) is 3B\(^i\) times PXEC \( \left( \frac{s_2}{2} \right)_{\text{phase}}^i \) which can be calculated using eq (8) with mechanical elastic constants and the volume fraction of the second phase.

**Eshelby/Mori-Tanaka Model**

Lin and Mura show, using the Eshelby's method and the Mori-Tanaka method, that the following equations hold when isotropic spherical inhomogeneous inclusions with volume fraction f are embedded in an isotropic matrix.

\[
\sigma_{11}^M - \sigma_{33}^M = 3B^M \left( \sigma_{11}^0 - \sigma_{33}^0 \right) - 3B_1 f \left( \Delta \varepsilon_{11}^p - \Delta \varepsilon_{33}^p \right) \tag{6a}
\]

\[
\sigma_{11}' - \sigma_{33}' = 3B^i \left( \sigma_{11}^0 - \sigma_{33}^0 \right) - 3B_1 (1 - f) \left( \Delta \varepsilon_{11}^p - \Delta \varepsilon_{33}^p \right) \tag{6b}
\]

where \( \Delta \varepsilon^p_1 \) is the difference in plastic strain between the second phase and matrix. \( B^M, B^i, B_1 \) are expressed as

\[
B^i = \frac{\mu^i}{3R}, \quad B_1 = \frac{2(\beta - 1)\mu^M \mu^i}{R}, \quad B = \frac{\mu^M - \beta(\mu^M - \mu^i)}{3R} \tag{7}
\]

\[
\beta = \frac{2(4 - 5\nu^M)}{15(1 - \nu^M)}, \quad \mu^M = \frac{E^M}{2(1 + \nu^M)}, \quad \mu^i = \frac{E^i}{2(1 + \nu^i)} \tag{8}
\]

\[
R = \mu^M - \beta f(\beta - 1)(\mu^M - \mu^i) \tag{9}
\]

where \( E^M \) and \( \nu^M \) are Young's modulus and Poisson's ratio of the matrix and \( E^i \) and \( \nu^i \) are those of the second phase.

**Experimental**

**Materials and Specimens**

Four kinds of Fe-Cr/TiN composite materials, having different volume fractions of, TiN were manufactured by sintering. Table 1 shows the chemical components for both the powders for the matrix (JIS-SKD11) and the second phase (TiN). Other material properties are listed in Table 2. The sintering conditions used for the materials are as follows; After holding at 923 K for 100 min., they were held at 1505 K for 120 min. and thereafter were cooled rapidly in N\(_2\) gas. Moreover, they were tempered under the condition of 983 K for 120 min. Fig. 3 shows microstructures obtained from cross sections of the material. Fig. 4 shows results of the analysis on Fe and TiN components in the materials by Energy Dispersive X-ray Analysis. From Fig. 3 and 4, we can see that TiN particles are dispersed uniformly. Fig. 5 shows diffraction rings obtained from each material using an imaging plate and Co-K\(_\alpha\) radiation. It is found in Fig .5 that there are two diffraction rings in each pattern. The diffraction rings which have smaller diameters and stronger diffraction intensity in each photograph are those for the 211 reflection.
from the matrix. The other rings that have larger diameters and weaker intensity are those for the 420 reflection from the second phase. From the fact that diffraction rings from the matrix are uniform in their intensity, it is found that in the matrix the crystal grains are fine and have random orientations. The intensity of TiN is stronger due to the increase of the content of TiN, and that of the matrix decreases correspondingly. This results from the change in the ratio of the volume of the matrix to that of the TiN.

Table 1 Chemical components.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>V</th>
<th>N</th>
<th>O</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Bal.</td>
<td>12</td>
<td>0.95</td>
<td>0.78</td>
<td>1.951</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hard particle (TiN)</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22.0</td>
<td>0.48</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2 Physical properties.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>TiN0</th>
<th>TiN10</th>
<th>TiN20</th>
<th>TiN30</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN fraction, wt.%</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>f, vol.%</td>
<td>0</td>
<td>13.8</td>
<td>27</td>
<td>38.8</td>
</tr>
<tr>
<td>Bulk density ρ, Mg/m³</td>
<td>7.63</td>
<td>7.14</td>
<td>6.84</td>
<td>6.30</td>
</tr>
<tr>
<td>Young’s modulus, GPa</td>
<td>212.7</td>
<td>222.2</td>
<td>235.7</td>
<td>273.0</td>
</tr>
<tr>
<td>Poisson’s ratio ν</td>
<td>0.302</td>
<td>0.275</td>
<td>0.272</td>
<td>0.265</td>
</tr>
</tbody>
</table>

Fig. 3 Microstructure of specimens.

Fig. 4 Component analysis results. (TiN10)
X-ray Diffraction Experiment

An x-ray machine with parallel beam optics (Rigaku MSF-2M) was used in the experiment. The x-ray diffraction conditions were as follows; For matrix, Matrix211(2θ=156°) was measured using Cr-Kα radiation and for the second phase (TiN), TiN420(2θ=142°) was measured with Co-Kα radiation. Other conditions are listed in Table 3. Raw powders of each constituent were used for determining stress free diffraction angles.

Results and discussion

The curves in Fig. 6 are the result of the calculation of the relation between the x-ray elastic constant $\frac{s_2^{\text{phase}}}{2}$ and the volume fraction of TiN. The results obtained by the method developed by Endo et al. are also shown in the figure for comparison with the Eshelby/Mori-Tanaka method explained above, where the method of Endo et al. is equivalent to the Eshelby method and
provides a solution to the case when spherical inhomogeneous inclusions are embedded in an infinite material. The elastic constants used in the Endo et al. model, are those which were calculated by the Voigt, Reuss and Eshelby/Mori-Tanaka models respectively in order to compare them with each other. In Fig. 6, the representations as Endo et al. (Voigt) mean that the curves were the result obtained using both the Endo et al. model and the elastic constants from the Voigt model. The PXEC for the matrix was obtained from a specimen containing only matrix material and was used in the calculation for the matrix. For the TiN phase, a theoretical value was calculated using the Kröner model and elastic constants for a single crystal of TiN and was used for the PXEC of TiN.

It is seen in Fig. 6 that the relation among the models is; Endo et al. (Reuss) < Endo et al. (Eshelby/Mori-Tanaka) < Endo et al. (Voigt). The difference between the models is relatively small near \( f=0 \), and increases as \( f \) increases. For the matrix, each model has the same value when \( f=0 \), but the values are different for the TiN phase. This is because TiN is the second phase. Each models for the second phase has the same value when \( f=1 \), where the composite consists of only TiN. It is also noted that \( \sigma_{11}(\sigma_{11} - \sigma_{33})/\partial \sigma_{11}^0 \) is equal to 1.0 when the composite consists of a single material.

Plots in Fig. 6 show results obtained in this experiment. For matrix 211 diffraction, the experimental results agree with theoretical ones when the volume fraction of TiN is less than \( f=0.138 \) (10 wt.%). And they have smaller values when the volume fraction exceeds this value. The difference between the experimental and theoretical results increases when the volume fraction of TiN becomes larger. This would be, due to the increase of TiN, TiN particles tend to contact each other so that the assumption in the theory that all the particles are dispersed with no contact is not
satisfied any more. The increase of TiN also affects the stress relaxation area at the surface of the material, where the stresses are smaller than those inside the material. Since the stresses obtained by the x-ray method are the average taken over only the surface layer depending on the penetration depth of x-rays, the stresses by the x-ray method tend to be smaller than those inside the material, which corresponds to theoretical expectation.

The sintered materials usually include a certain content of pores. This required the consideration of pores in the results obtained in this experiment. From our investigation using the theoretical model which Taya et al. developed for composites which consist of three or more kinds of materials, it is found that the effect of the pores is within the range of scatter of the experimental data under the conditions of this study and does not have a large influence.

Furthermore, in the measurements on the TiN phase it was difficult to obtain the slope of the experimental data due to weak diffraction intensity. Especially, this was so when the TiN was less than 10 wt.%, so that these data were omitted in Fig. 6.

**Conclusion**

The x-ray elastic constants for sintered Fe-Cr/TiN composites were studied using both theoretical and experimental methods. The results of both methods showed that the composite x-ray elastic constants (CXEC) are different from the phase x-ray elastic constants (PXEC) due to the interaction between the constituents. The results agree with each other when the volume fraction of TiN is less than \( f=0.138 \). When much more TiN is present in the material, the experimental results showed smaller values than those obtained by the theoretical models used in this study. The difference between them becomes larger when the TiN content increases.

**References**

3) Mori, T. and Tanaka, K., Acta. Metal., 21(1873), 571