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On the quantitative analysis of secondary carbide and carbon in $(Ti_{1-x}M_x)C$ solid solutions via XRD measurements

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Abstract

Based on the structure factor calculations, the change in the (1 1 1) and (2 0 0) diffraction peak intensities of NaCl type $(Ti_{1-x}M_x)C$, (M = W, Mo, Ta, and Nb), solid solutions was related to their composition and carbon non-stoichiometry. The validity of the derived function was confirmed by the results obtained from the whole pattern computer simulation. The experimental results were also compared with the theoretical ones for the $(Ti_{1-x}W_x)C$ solid solution phase.

Keywords: (Ti, M)C solid solutions; Composition; Diffraction peaks; Carbides; XRD

1. Introduction

Cermets used in cutting tool applications are composed of carbide and metallic binder phases. Various mixtures of transition metal carbides such as TiC, WC, NbC and Mo_2C are commonly used as the hard phases along with Ni and Co as a binder [1,2]. Therefore, the densification of cermet materials is based on liquid-phase sintering and the fundamental mechanism for the final microstructure is dissolution and precipitation. Dissolution and precipitation processes are complicated and the compositions of the hard phases vary significantly based on the stability of the carbides involved in the system of interest [3–5]. This makes it difficult to determine the exact compositions of the various hard phases, especially when several solid solution phases are formed in the system.

Recently, monolithic $(Ti_{1-x}W_x)C$ solid solution phases were reported and found to exhibit exceptional characteristics in terms of their microstructure and mechanical properties [6]. However, the exact composition of the solid solution phase after the sintering process is difficult to determine unless sophisticated analytical tools such as SEM/EDS and TEM/EDS are employed. In addition, the compositional changes, especially those involving carbon, in solid solution carbide during and after processing is a primary concern in the hard materials industry. Therefore, we attempted to find a simple approach to determine the composition of the solid solution phase by means of the XRD pattern intensity for industries mass-producing (Ti, M)C-type carbides. We first derived a simple relationship between the diffraction peak intensity and composition using structure factor calculations. Then, we validated the result by conducting computer simulations of the XRD patterns for various solid solution phases. Finally, the experimental results were compared with the predicted ones for the case of the $(Ti_{1-x}W_x)C$ system.

2. Experimental

The analytical functions relating the (1 1 1) and (2 0 0) diffraction peak intensities to the solid solution composition were derived based on the structure factor calculations. Among the parameters used to calculate the intensity of a diffraction peak, the structure factor varies most sensitively with the composition. Therefore, we assumed that the intensity of the peak can be determined

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solely from the structure factor, though in actual practice, there can be a slight variation depending on other factors.

In order to verify the derived equations, we calculated the powder diffraction patterns by computer simulation which includes other parameters, such as the polarization factor, strain factor and instrumental broadening. We used the software, Jade 7 (Materials Data, Inc.).

The raw materials used to produce the $(Ti_{1-x}W_x)C$ powders were anatase-TiO_2 (99+% purity), WO_3 (99+% purity) and graphite-carbon. These were mixed at the target composition using a high-energy milling machine (Fritsch Pulverisette 5). Tungsten carbide balls were mixed with the oxide powders at a ball-to-powder weight ratio of 40:1. A tungsten carbide vessel was used and milling was conducted at a speed of 250 RPM for a period of 20 h. The milled oxide powders were converted into carbide powders through carbothermal reduction at 1200–1300 °C in a vacuum.

The carbide powders were compacted and sintered at 1510 °C for 2–4 h in a vacuum. The sintered specimens were mechanically ground and polished. XRD analysis was done with a Rigaku D-Max2500 diffractometer equipped with Cu Kα ($\lambda = 1.54056$ Å) radiation source and a rotating anode. From the measured raw data, the Kα_2 peaks were removed by the peak deconvolution and the intensity was measured by integrating the area under the diffraction peak. The same software was used (Jade7) for the data processing.

3. Results and discussion

3.1. Analytical approach via structure factors

In the case where W replaces Ti in TiC, the intensity of the diffraction peaks would be expected to increase, because W has more electrons than Ti. That is, the X-ray scattering factor of W is bigger than that of Ti. The relative intensity also changes as a function of the composition, since the magnitude of the increment depends on the diffraction planes. When W replaces Ti, the absolute intensity of each peak increases. However, the intensity of a certain plane, after being normalized by the highest peak, may appear to be decreased in the diffraction pattern.

Assuming that the change in intensity is a function of the structure factor alone, the intensity of each peak can be described by a simple equation. For the two main peaks of TiC, the structure factors are described as follows;

$$F_{111} = 4(f_{\mathrm{Ti}} - f_{\mathrm{C}})$$
$$F_{200} = 4(f'_{\mathrm{Ti}} + f'_{\mathrm{C}})$$

When the mole fraction of W that replaces Ti is x, for example, the above structure factors can be written as follows:

$$\begin{aligned} F^{\mathrm{W}}_{111} &= 4[(1-x)f_{\mathrm{Ti}} + xf_{\mathrm{W}} - f_{\mathrm{C}}] = F_{111} + 4(f_{\mathrm{W}} - f_{\mathrm{Ti}})x \\ F^{\mathrm{W}}_{200} &= 4[(1-x)f'_{\mathrm{Ti}} + xf'_{\mathrm{W}} + f'_{\mathrm{C}}] = F_{200} + 4(f'_{\mathrm{W}} - f'_{\mathrm{Ti}})x \end{aligned} \tag{1}$$

Therefore, the differences in the intensity increment between the (1 1 1) and (2 0 0) peaks are attributed to the different atomic scattering factors of Ti and W in these planes. The absolute intensity of each peak can be described using the scattering factors of Ti, W and C along with appropriate constants, as follows:

$$\begin{aligned} I^{\mathrm{W}}_{111} &= \mathrm{C}_{111}|F^{\mathrm{W}}_{111}|^2 = \mathrm{C}_{111}[(f_{\mathrm{Ti}} - f_{\mathrm{C}}) + (f_{\mathrm{W}} - f_{\mathrm{Ti}})x]^2 \\ I^{\mathrm{W}}_{200} &= \mathrm{C}_{200}|F^{\mathrm{W}}_{200}|^2 = \mathrm{C}_{200}[(f'_{\mathrm{Ti}} + f'_{\mathrm{C}}) + (f'_{\mathrm{W}} - f'_{\mathrm{Ti}})x]^2 \end{aligned} \tag{2}$$

It should be noted that I^{W}_{111} and I^{W}_{200} in Eq. (2) are the absolute intensities and would be normalized by the highest intensity peak. In the case of pure TiC, the (2 0 0) peak is the highest peak. When the intensity is plotted with respect to the W content, the I^{W}_{200} curve rises quickly to cross the I^{W}_{200} curve, which decreases gradually with the W content. The junction concentration of W, X_{crit}, where I^{W}_{111} equals I^{W}_{200}, can be found by equating the two equations in Eq. (2). Therefore, we can calculate the intensity of the 2nd main peak using equations, Eqs. (3) and (4).

When $X < X_{\mathrm{crit}}$, the (2 0 0) peak is the strongest peak, (1 1 1) peak intensity with respect to the (2 0 0) peak will be:

$$I_{111} = 100\frac{I^{\mathrm{W}}_{111}}{I^{\mathrm{W}}_{200}} = 100\frac{\mathrm{C}_{111}}{\mathrm{C}_{200}}\left(\frac{(f_{\mathrm{W}} - f_{\mathrm{Ti}})x + (f_{\mathrm{Ti}} - f_{\mathrm{C}})}{(f'_{\mathrm{W}} - f'_{\mathrm{Ti}})x + (f'_{\mathrm{Ti}} + f'_{\mathrm{C}})}\right)^2 \tag{3}$$

When $X > X_{\mathrm{crit}}$, the (1 1 1) peak is the highest peak, (2 0 0) peak intensity with respect to the (1 1 1) peak will be:

$$I_{200} = 100\frac{I^{\mathrm{W}}_{200}}{I^{\mathrm{W}}_{111}} = 100\frac{\mathrm{C}_{111}}{\mathrm{C}_{200}}\left(\frac{(f'_{\mathrm{W}} - f'_{\mathrm{Ti}})x + (f'_{\mathrm{Ti}} - f'_{\mathrm{C}})}{(f_{\mathrm{W}} - f_{\mathrm{Ti}})x + (f_{\mathrm{Ti}} + f_{\mathrm{C}})}\right)^2 \tag{4}$$

We multiplied 100 to set the strongest intensity to 100.

The values of the two constants, C_{111} and C_{200}, can be obtained from the intensities of the (1 1 1) and (2 0 0) peaks of pure TiC. We determined them from the computer simulation with the known structure information of pure TiC [ICSD#5840]. The analytical functions proposed by Waasmaier and Kirfel [7] were used to calculate each atomic scattering factor. The scattering factors calculated for Ti, C, W, Mo, Nb and Ta are listed in Table 1 for the (1 1 1) and (2 0 0) peaks.

The absolute intensities of the (1 1 1) and (2 0 0) peaks for the different solid solution carbides, (Ti, M)C, were determined using the formula shown in Eq. (5) below:

$$I^{i}_{hkl} = \mathrm{C}_{hkl}|F^{i}_{hkl}|^2 = \mathrm{C}_{hkl}[(f_{\mathrm{Ti}} - f_{\mathrm{C}}) + (f_i - \mathrm{f}_{\mathrm{Ti}})x]^2 \tag{5}$$

where i can be W, Mo, Nb or Ta. The same proportional constants, C_{111} and C_{200}, are used for all compositions, which are obtained from the initial peak intensities of pure TiC.

Table 1
Calculated scattering factors for various elements

	f_{Ti}	f_{C}	f_{W}	f_{Mo}	f_{Nb}	f_{Ta}
(1 1 1) Peak	16.046	3.557	62.489	33.180	32.300	61.652
(2 0 0) peak	15.119	3.161	60.299	31.613	30.797	59.510