



# Quantitative carbide analysis using the Rietveld method for 2.25Cr–1Mo–0.25V steel

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## ABSTRACT

It is usually difficult to quantitatively determine the mass fraction of each type of precipitates in steels using transmission electron microscopy and traditional X-ray powder diffraction analysis methods. In this paper the Rietveld full-pattern fitting algorithm was employed to calculate the relative mass fractions of the precipitates in 2.25Cr–1Mo–0.25V steel. The results suggest that the fractions of MC,  $M_7C_3$  and  $M_{23}C_6$  carbides were evaluated precisely and relatively quickly. In addition, it was found that the fine MC phase dissolved into the matrix with prolonged tempering.

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## 1. Introduction

2.25Cr–1Mo–0.25V steel has been widely used for the hydro-cracking and hydro-desulfurization reactors in energy industry. The carbide precipitated during heat treatment generally plays a key role on the resistance to creep and to hydrogen damage [1–4]. Therefore, to quantify the precipitation evolution during heat treatment is critical to control the microstructure and to establish the theoretical relationship between microstructure and mechanical properties.

As an alternative technique, X-ray powder diffraction (XRD) is perhaps the most powerful method of obtaining quantitative phase information from multi-component mixtures. However, X-ray analysis is traditionally dependent on a number of parameters, including sample characteristics, purity and availability of standards. In addition, line overlap may reduce the number of measurable lines, particularly with complex diffraction patterns. Typically, few reflections from each phase are used which limit the precision of the results and make analyses more susceptible

to the effects of primary extinction and preferred orientation [5–10]. Since the Rietveld method [11,12] uses a full-pattern fitting algorithm, all lines for each phase are explicitly considered and overlapping lines are not problematic. The use of all lines in a pattern minimizes the uncertainty in the derived mass fractions and the effects of nonlinear detection systems. The effects of primary extinction are also reduced, as all reflections from each phase are used in the analysis rather than just the strongest one. However, it has been scarcely used in such scientific area as quantitative analysis of carbide precipitation in CrMoV steels, although XRD technique is frequently utilized.

## 2. Experimental Procedures

### 2.1. Experimental Techniques

The hot-rolled steel plate with a thickness of 20 mm used in the investigation came from a 150 kg vacuum-induction melt with

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**Table 1 – Chemical composition of the experimental steel as received (wt.%).**

C	Mn	Si	P	S	Cr	Mo	V	Fe
0.13	0.55	0.05	0.012	0.003	2.23	0.98	0.24	Balance

the chemical composition given in Table 1. The steel was heat-treated as follows: 1 h at 940 °C, slow water quenching, followed by 2, 5 and 10 h tempering respectively at 720 °C, slow water quenching.

The precipitates were electrolytically extracted using the 5%KCl-1%Citric acid distilled water solution. The residue was separated using a membrane filter with 0.05 μm pores. Therefore, the carbide's mass fraction of the sample can be expressed as:

$$f = \frac{m_c}{m_0 - m_t} = \frac{m_c}{\Delta m} \times 100\% \quad (1)$$

where  $m_c$  is the mass of carbide extracted from the specimen,  $m_0$  is the original mass of specimen before electrolyzing and  $m_t$  is the final mass of specimen after electrolyzing.

The extracted carbide powder was analyzed by Rigaku D/max-2550 X-Ray diffractometer with  $\text{CuK}\alpha$  radiation and graphite monochromators. The diffraction data was collected for each specimen from 30 to 90° 2θ with a step width of 0.02° and a count time of 2.0 s per step.

## 2.2. Rietveld Refinement

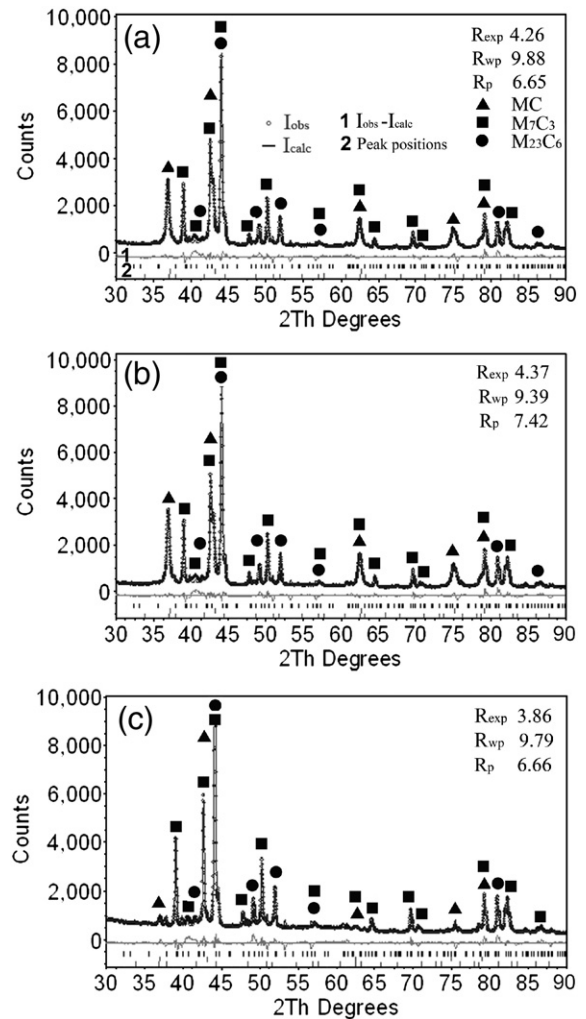
A Rietveld refinement involves the fitting of the full experimental diffraction pattern with calculated profiles and background. The model utilized to describe the intensity corresponding to the  $i$ th step ( $Y_i$ ) can be written as:

$$Y_i = Y_{bi} + \sum_{\beta} S_{\beta} \sum_K L_{\beta K} |F_{\beta K}|^2 e^{-2M_{\beta}} P_{\beta K} A_K \eta (2\theta_i - 2\theta_{\beta K}) \quad (2)$$

where  $\beta$  and  $K$  are the phase label and the Bragg reflection index respectively,  $S_{\beta}$  is the scale factor,  $L_{\beta K}$  contains the Lorentz, polarization and multiplicity factors,  $F_{\beta K}$  is the structure factor,  $M_{\beta} = B \cdot \sin^2(\theta_{\beta}) / \lambda^2$  is the global temperature factor and  $B$  is the Debye–Waller factor,  $P_{\beta K}$  is the preferred orientation function,  $A_K$  represents the absorption correction function and  $\eta$  is the modified Thompson–Cox–Hastings

**Table 2 – Refined unit-cell parameters and relative mass fractions of the carbides for the final Rietveld refinement.**

Sample	Phase	$a$ (Å)	$b$ (Å)	$c$ (Å)	Space group	Relative mass fraction (%)
QT2	MC	4.1870	4.1870	4.1870	Fm-3m	28.72
	$\text{M}_7\text{C}_3$	7.0058	12.1445	4.5011	Pmcn	64.46
	$\text{M}_{23}\text{C}_6$	10.5775	10.5775	10.5775	Fm-3m	6.82
QT5	MC	4.1884	4.1884	4.1884	Fm-3m	31.01
	$\text{M}_7\text{C}_3$	7.0128	12.1477	4.5038	Pmcn	66.10
	$\text{M}_{23}\text{C}_6$	10.5940	10.5940	10.5940	Fm-3m	2.89
QT10	MC	4.1932	4.1932	4.1932	Fm-3m	6.87
	$\text{M}_7\text{C}_3$	7.0159	12.1529	4.5054	Pmcn	90.45
	$\text{M}_{23}\text{C}_6$	10.6014	10.6014	10.6014	Fm-3m	2.68



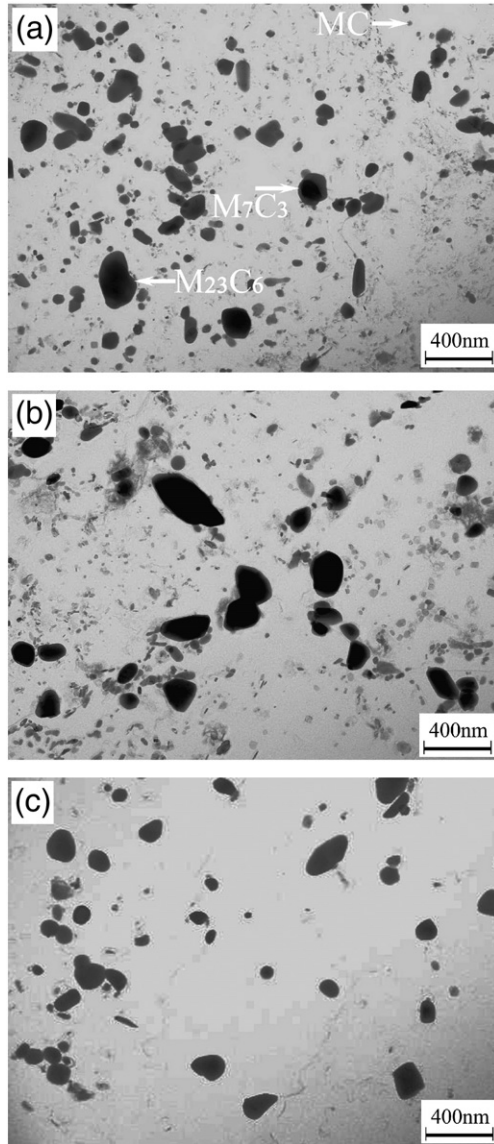
**Fig. 1 – Observed (curves), calculated (circles) and difference ( $I_{\text{obs}} - I_{\text{calc}}$ , 1) Rietveld fitting patterns for the carbide powder mixture, which was electrolytically extracted from the 2.25Cr-1Mo-0.25V steel as-tempered for (a) 2 h, (b) 5 h and (c) 10 h, respectively. The vertical short bars (2) are the peak positions respectively for the  $\text{M}_7\text{C}_3$ , MC and  $\text{M}_{23}\text{C}_6$  phases. In the following, ‘M’ stands for metallic elements, such as V, Mo, Cr, Fe, etc.**

Pseudo-Voigt reflection profile function [13] which approximates the effects of both the instrumental and specimen features. Finally,  $Y_{bi}$  represents the background intensity at the  $i$ th step. All these parameters are modified in a recurrent process in order to minimize the weighted squared difference

**Table 3 – Evolution of the carbide amount during tempering.**

Sample	Mass fraction of carbide (%)	Mass fraction of MC (%)
QT2	1.10	0.32
QT5	1.23	0.38
QT10	1.48	0.10

Note: The mass fraction of carbide in steel can be calculated by Eq. (1).



**Fig. 2 – Transmission electron micrographs of the extraction replica from the 2.25Cr-1Mo-0.25V steel as-tempered for (a) 2 h (50,000 $\times$ ), (b) 5 h (50,000 $\times$ ) and (c) 10 h (50,000 $\times$ ), respectively.**

between the experimental data  $Y_i$  and the theoretically predicted value  $Y_{\text{calc}}$  at each angular position:

$$\sum w_i (Y_i - Y_{\text{calc}})^2 = \text{Minimum} \quad (3)$$

where  $i$  varies from 1 to the number of observation, and  $w_i = 1/Y_i$  is the reciprocal of the variance associated to the  $i$ th observation.

The relative amount of each type of carbide in the residue is proportional to the product of the scale factor, as derived in the multi-component Rietveld analysis of the powder diffraction pattern, with the mass and volume of the unit cell. If all phases are identified and crystalline, the relative mass fraction  $\chi_\alpha$  of phase  $\alpha$  is given by [14]:

$$\chi_\alpha = \frac{S_\alpha Z_\alpha M_\alpha V_\alpha}{\sum_\beta S_\beta Z_\beta M_\beta V_\beta} \quad (4)$$

where  $S_\alpha$ ,  $Z_\alpha$ ,  $M_\alpha$  and  $V_\alpha$  are, respectively, the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit and the unit-cell volume of each phase  $\alpha$ .

### 3. Results and Discussion

Pattern fitting was done by means of the software, TOPAS, which is based on the Rietveld method. Rietveld refinement was applied over a relatively short angular range (30–90°  $2\theta$ ) to obtain the result more reliably. The initial unit-cell parameters for each phase are given in Table 2. These values were optimized in the refinement. The common overall parameters, background coefficients, zero shift, scale factor and phase profile parameters ( $U$ ,  $V$ ,  $W$  and  $X$ ,  $Y$ ,  $Z$ ) were the only parameters refined during the first stage, until an apparent convergence was reached. After this, the atomic occupancy ratio was optimized.

The Rietveld refinement pattern is illustrated in Fig. 1.  $R_{\text{exp}}$ ,  $R_{\text{wp}}$ ,  $R_p$  are the quality-of-fit parameters:  $R$ -expected,  $R$ -weighted,  $R$ -pattern. From these figures and  $R$  factors, it can be seen that the Rietveld method calculated pattern can successfully fit the severely overlapped peaks in the observed diffraction pattern.

The power of the Rietveld method in carrying out a quantitative phase analysis of multiphase samples with strong overlapping is evidenced in this study. The relative mass fractions of the carbides are shown in Table 2 and suggest the occurrence of dissolution of fine MC phase after 10 h tempering (Table 3 and Fig. 2). Tamura et al. also found the similar phenomenon in the 7Cr, 8Cr and 9Cr heat-resistant steels [15–18].

### 4. Conclusions

The relative mass fraction of each type of precipitates in 2.25Cr-1Mo-0.25V steel after heat treatment was accurately and reliably determined by the X-ray powder diffraction full-pattern fitting Rietveld method. Dissolution of MC particles was found to occur during tempering. The results suggest that this method could be a powerful technique to study the precipitation kinetics of carbides.

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### REFERENCES

- [1] Yokota T, Shiraga T. Evaluation of hydrogen content trapped by vanadium precipitates in a steel. *ISIJ Int* 2003;43:534–8.
- [2] Maruyama K, Sawada K, Koike J. Strengthening mechanisms of creep resistant tempered martensitic steel. *ISIJ Int* 2001;41:641–53.
- [3] Abe F. Bainitic and martensitic creep-resistant steels. *Curr Opin Solid State Mater Sci* 2004;8:305–11.
- [4] Schlögl SM, Svoboda J, Van der Giessen E. Evolution of the methane pressure in a standard 2.25 Cr-1Mo steel during hydrogen attack. *Acta Mater* 2001;49:2227–38.

- [5] Chung FH. Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponent analysis. *J Appl Crystallogr* 1974;7:519–25.
- [6] Smith ST, Snyder SL, Brownell WE. Quantitative phase analysis of Devonian shales by computer controlled X-ray diffraction of spray dried samples. *Adv X-Ray Anal* 1979;22:181–91.
- [7] Goehner RP, Reduction S. Display program for spectral data. *Adv X-Ray Anal* 1980;23:309–13.
- [8] Garbaskas MF, Goehner RP. Complete quantitative analysis using both X-ray fluorescence and X-ray diffraction. *Adv X-Ray Anal* 1982;25:283–8.
- [9] Hubbard CR. New standard reference materials for X-ray powder diffraction. *Adv X-Ray Anal* 1983;26:45–51.
- [10] Pawloski GA. Quantitative determination of mineral content of geological samples by X-ray diffraction. *Am Mineral* 1985;70:663–7.
- [11] Rietveld HM. Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Crystallogr* 1967;22:151–2.
- [12] Rietveld HM. A profile refinement method for nuclear and magnetic structures. *J Appl Crystallogr* 1969;2:65–71.
- [13] Young RA, editor. *The Rietveld method*. Oxford: Oxford University Press; 1996.
- [14] Bish DL, Howard SA. Quantitative phase analysis using the Rietveld method. *J Appl Crystallogr* 1988;21:86–91.
- [15] Tamura M, Ikeda K, Esaka H. Precipitation behavior of NbC in 9%Cr1%Mo0.2%VNb steel. *ISIJ Int* 2001;41:908–14.
- [16] Tamura M, Iida T, Kusuyama H. Re-dissolution of VN during tempering in high chromium heat resistant martensitic steel. *ISIJ Int* 2004;44:153–61.
- [17] Tamura M, Nakamura M, Shinozuka K. Tempering and precipitation behavior of 7 Pct Cr–0.1 Pct V–0.06 Pct Nb–0.08 Pct N steel. *Metall Mater Trans A* 2008;39A:1060–76.
- [18] Tamura M, Kusuyama H, Shinozuka K. Long-term stability of TaC particles during tempering of 8%Cr–2%W steel. *J Nucl Mater* 2007;367–370:137–41.