

# Study on the Precipitation of $M_2C$ in High Co-Ni Alloy Steel

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**High CoNi ultrastrength alloy steel is a typical tempered martensite steel in which the secondary hardening is accomplished by the precipitation of fine-scale alloy carbides with a black-white contrast in a bright-field image until peak hardening. The crystal structure of precipitates is well determined as hexagonal  $M_2C$  by microbeam diffraction. From their lattice image in a high-resolution transmission electron microscope,  $M_2C$  carbides are shown to be completely coherent with the ferrite matrix completely and to have their own structure.**

**Keywords** carbide, precipitation, ultrastrength alloy steel

## 1. Introduction

Secondary hardening alloys have been studied for decades. There has been extensive interest in the mechanism of secondary hardening and carbide precipitation during the second hardening reaction. It has been recognized for a long time that alloy carbides replace cementite during aging in secondary hardening alloy steel.<sup>[1]</sup> Many studies were conducted on the alloy carbide precipitation mechanism,<sup>[2,3]</sup> and it is clear that the secondary hardening is accomplished by the precipitation of fine-scale  $M_2C$  alloy carbide. During the secondary hardening reaction,  $M_2C$  forms as needles with hexagonal crystal structure, and the long direction of the needles is along the  $\langle 100 \rangle$  directions of ferrite.

The high Co-Ni ultrahigh strength steel is notable for its magnificent combination of high strength and toughness. Recent microstructural studies of secondary hardening behavior in AM100 steel<sup>[4,5]</sup> show that the alloy approaches optimum mechanical properties with high strength and hardness at the tempering temperature of 482 °C for 5 h. At this peak hardening condition, coarse cementites dissolve fully and the subsequent  $M_2C$  carbides remain very fine and fully coherent with ferrite. When the tempering time is prolonged or at a high tempering temperature,  $M_2C$  carbides lose their coherency, with the  $\alpha$ -Fe matrix accompanying the decrease of mechanical properties. It was suggested that the  $M_2C$  carbide may be in the form of a zone in the ferrite matrix. Atom probe and transmission electron microscopy (TEM) studies could not unambiguously determine the structure of carbides. In recent TEM studies on the microstructural evolution during precipitating hardening of AM100, Ayer and Mechmeier<sup>[5]</sup> observed that, when the alloy was under or at peak hardening, the  $M_2C$  carbides exhibited classical black-white strain contrast. This indicates the presence of coherency strain at the interface of carbides and ferrite matrix and

suggests that the  $M_2C$  at this stage might be in the form of a zone without its own structure.

In the present work, we studied the  $M_2C$  carbides precipitating in the alloy similar to AM100 and, especially at the peak-hardening condition, determined the carbide crystal structure by the microbeam diffraction technique, and observed the precipitates directly in a high-resolution transmission electron microscope.

## 2. Experimental

The steel was vacuum induction melting (VIM)/vacuum arc remelting (VAR) melted and rolled to 200 mm diameter rounds. Several pieces of blanks of steel were austenized at 885 °C for 1 hour, quenched in oil to room temperature, and immediately transferred to a cryogenic bath hold at  $-80$  to  $90$  °C for 15 min and, then tempered at 482 °C for 5 h.

The composition of the examined alloy steel is listed in Table 1. Thin samples for TEM of about 0.3 mm in thickness were cut from the above heat-treated pieces, and then normally ground to about 50  $\mu\text{m}$ , and electropolished in a perchloric acid-methanol solution. The specimen for the carbide crystal structure study was prepared by extracting replicas. All the samples were examined in a transmission electron microscope (JEOL JEM2000FX, Japan Electron Optics Ltd., Tokyo) at 160 kV. The fine precipitates were examined with microbeam diffraction. In this method, a diffraction pattern is formed by a finely converged electron beam illuminating only a very small area on the specimen. The precipitate lattice image and its interface with the matrix  $\alpha$ -Fe were observed in a high-resolution electron microscope (JEOL JEM-2010), with a resolution limit of 1.97 Å.

**Table 1** The composition of the examined steel in mass percent

C	Co	Ni	Cr	Mo	Mn	Si	Fe
0.23	13.70	11.58	3.12	1.25	0.06	0.05	balance

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### 3. Results and Discussion

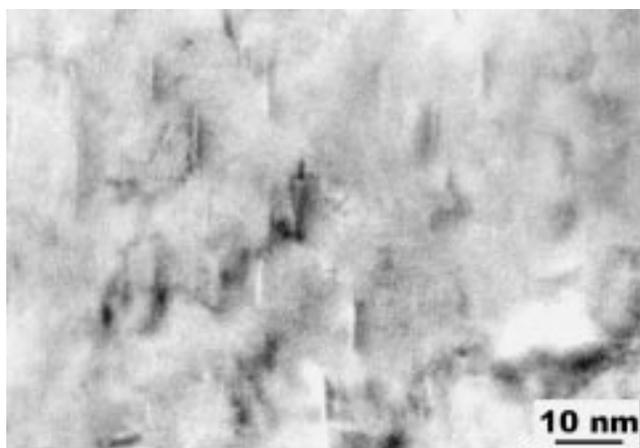
The sample tempered at 482 °C for 5 h was observed by TEM first. The needle-shaped precipitates in the matrix show that its long dimension is close-packed along the ferrite matrix  $\langle 100 \rangle_\alpha$  direction; as shown in Fig. 1 (the  $\alpha$  denotes ferrite), it is a typical bright-field image obtained close to the  $[100]_\alpha$  orientation, showing that a classical black-white contrast, which indicates the precipitates are coherent with the ferrite matrix. All of these results are consistent with the studies mentioned above.<sup>[4]</sup>

The needle-shaped precipitations are very fine, and in the thin samples it is almost impossible to get a clear diffraction spot pattern from the thin specimens, because of the interference of the matrix, to determine whether the precipitated carbides are  $M_2C$ . So we use the carbon replicas extracted from samples to determine the structure of the very fine carbides. In the extraction replicas, the carbides lose their original orientation with the matrix, and selected area diffraction gives a ring diffraction pattern for its very fine size, as seen in figure Fig. 2(a). It is indexed as hexagonal; the rings from the center to the

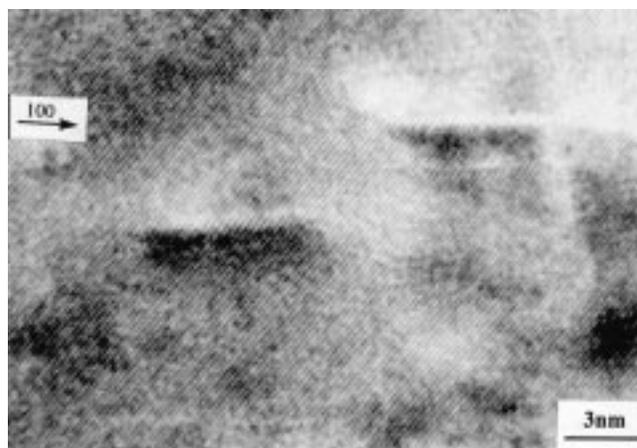
outside are (100), (011), (102), (111), (200), and (201), respectively. The crystal parameter is  $a = 2.87$  and  $c = 4.54$  Å, which is close to the result of former researchers.<sup>[4,5]</sup>

In order to determine the structure of the fine rod-shaped carbides, we employed a microbeam diffraction method; a diffraction spot pattern is taken with the very fine electron beam converged on the precipitates. Figure 2(b) and (c) are the micro-beam diffraction patterns of single needle-shaped precipitates; they are indexed as the axes  $[30\bar{3}1]$  and  $[\bar{1}102]$  of hexagonal structures, respectively.

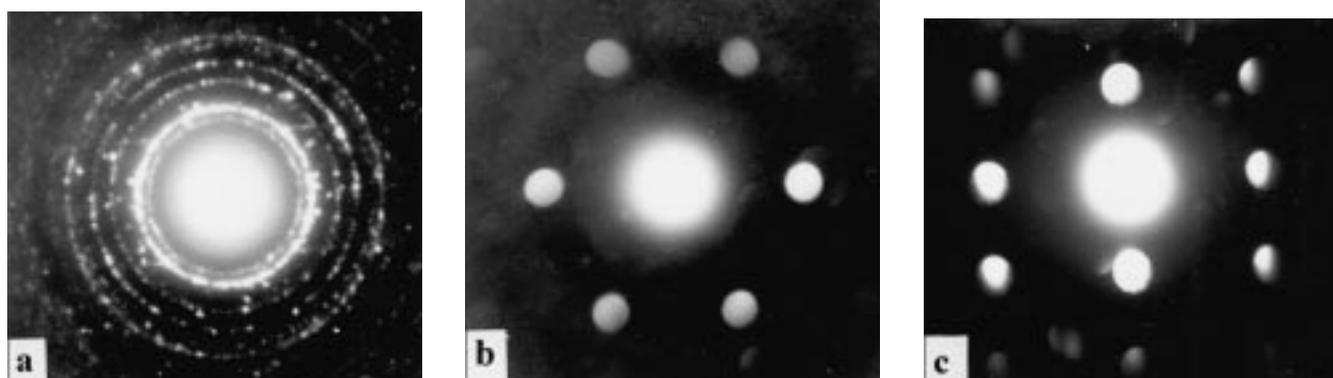
Figure 3 is a lattice image of the same sample in Fig. 1, which is taken in the  $[100]_\alpha$  orientation. In figure Fig. 3,  $M_2C$  precipitates, about 8 nm long and 1.3 nm in diameter, are obviously coherent with the matrix. The spacing of coherent planes of  $M_2C$  and the matrix are measured as 2.10 and 2.03 Å, respectively. With the lattices constants determined above, it is obvious that the matrix planes of  $(110)_\alpha$  are coherent with the (011) planes of  $M_2C$ . For the small difference in interplanar spacing of  $M_2C$  and  $\alpha$ -Fe, the lattice distortion is clearly shown in Fig. 3, and is the cause of the black-white contrast in the bright-field image in Fig. 1 due to coherency strain. It



**Fig. 1** Bright-field image taken in a near  $[001]_\alpha$  orientation for the specimen tempered at 482 °C for 5 h. The  $[100]_\alpha$  is along the vertical axis



**Fig. 3** The lattice image of  $M_2C$  precipitates in the same sample in Fig. 1, taken in the  $[100]_\alpha$  orientation



**Fig. 2** The diffraction pattern extraction replica of the specimen tempered at 510 °C for 5 h

is clear that  $M_2C$  precipitates have their own hexagonal structure other than in the form of a zone.

The above results prove that the secondary hardening phase in the high CoNi ultra-strength steel is very fine  $M_2C$  with hexagonal structure, and at its hardening peak, the  $M_2C$  is completely coherent with  $\alpha$ -Fe matrix.

#### 4. Conclusions

In the secondary hardening phase of needle-shaped precipitating carbides in high Co-Ni alloys, its long dimension is along the  $\langle 100 \rangle_a$  direction with a black-white strain contrast at the peak hardening condition. The crystal structure of carbides was well determined as hexagonal  $M_2C$ . An high-resolution

transmission electron microscope image showed that the carbides are completely coherent with the ferrite matrix and have their own structure.

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