Heat treatment induced orientation change of nanometer-sized interphase precipitated TiC in a Ti-bearing Steel

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Abstract

The microstructure of titanium carbides of Ti-bearing steel has been investigated using transmission electron microscopy (TEM). The attempt of this study is to reveal morphologies and orientation relationships of titanium carbides obtain from the specimens isothermally treated at α/γ two-phase temperature for different times. The orientation relationships are identified by selection area diffraction patterns (SAD) in TEM. The coarse plate-like carbides with diameter above 15 nm exhibit Nishiyama-Wasserman orientation relationship. This results is different from previous studies which claimed that the fine plate-like carbides with diameter about 5-15 nm exhibited Baker-Nutting orientation relationship and are thinner in thickness. The change in orientation is discussed according to the invariant line theory proposed by Dahmen in 1982.

Keywords: titanium carbide, Baker-Nutting, Nishiyama-Wasserman, invariant line

摘要

利用穿隧式電子顯微鏡觀察碳化鈦析出物在含鈦鋼中之微結構。本研究分析碳化鈦在不同時間之兩相區恆溫時效所產生的微結構與方位關係。利用擇區繞射技術可以鑑定其方位關係因而得到較粗化的析出物(大於 15nm)與基地維持 Nishiyama-Wasserman 方位關係。該結果與過去所認爲較細緻的析出物與基地維持 Baker-Nutting 方位關係大不相同。而 Dahmen 於 1982 年提出的不變線概念可用來討論這個方位轉變。

關鍵詞：碳化鈦，Baker-Nutting 方位關係，Nishiyama-Wasserman 方位關係，不變線。

1. Introduction

Environmental problems and consumers' safety impose conflicting requirements on automotive bodies: they are expected to be lighter as well as stronger [(1)]. For these reasons, high strength low alloy (HSLA) steels, i.e. low carbon steels alloyed with Nb, Ti, and V, have become widely used in all industries [(2)]. Titanium and niobium additions play as the important role in delaying recrystallization and retarding grain growth in austenitizing process [(3)]. Titanium and vanadium alloyed elements play as carbides forming which offer the strength from precipitation hardening [(4)].

The precipitation hardening is normally considered to be associated with a few contributions to the strength of conventional HSLA steels. However, the nanometer-sized precipitation can dramatically increase the

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strength of HSLA steels according to Ashby-Orowan mechanism [5]. The precipitation process well known as "interphase precipitation [6]" is considered to be a powerful way to form nanometer-sized precipitates. The precipitates nucleate on the γ/α interface during austenite to ferrite transformation and finally the microstructure possess nanometer-sized precipitates and nanometere-spaced dispersion. The discrete interphase precipitation process [6] leads to fine carbides with a very fine banded distribution in the ferrite matrix.

The crystal structure of titanium carbides is NaCl-type structure; that is cubic F lattice (B1 structure). The orientation relationship (OR) of NaCl-type carbide associated with ferrite matrix can be classified into three categories according to precipitation reaction modes: (1) the carbides forming in supersaturated austenitic solid solutions adopt cube-to-cube orientation relationship with austenite matrix. After the austenite to ferrite transformation, the OR between carbides and ferrite inherits OR between austenite and ferrite. (2) the carbides forming in supersaturated ferritic solid solutions adopt Baker-Nutting (B-N) orientation relationship [7] with ferrite matrix. The Baker-Nutting orientation relationship is described as $(100)_{carbide}//(100)_{ferrite}$ and $[011]_{carbide}//[001]_{ferrite}$. (3) the carbides nucleate on the moving γ/α interface during transformation, known as interphase precipitation and also adopt the same variants of Baker-Nutting (B-N) orientation relationship with ferrite matrix[6].

It seems that a complete study on the interphase precipitation has founded. In fact, the interphase precipitation $M_{23}C_6$ carbide has been systematically and comprehensively studied by observations of transmission electron microscopy and the theory of austenite to ferrite transformation [8]. Yet, for NaCl-type carbides there are some topics on the orientation relationship mechanism should be studied in detail. A recent work about precipitation control done by Chenchenin *at al.*[9], shows finer titanium nitrides exist B-N OR with ferrite matrix and the coarser nitrides existNishiyama-Wasserman (N-W) orientation relationship[10]. In our work, we concerned in the orientation relationship of titanium carbides with ferrite matrix. In present paper, the morphology of the nanometer-sized TiC carbides is observed and the orientation relationship between the carbides and ferrite matrix is examined. Besides, an important phenomenon of orientation relationship transition from B-N OR to N-W OR will be proposed here.

2. Experimental Procedure

Table.1 shows the chemical composition of the steels used in the present study. The HSLA steels were produced by China Steel and obtained in normalized condition.

Table.1 Chemical composition of steels in present study(weight percent).

Fe	C	Si	Mn	Ti	P	S(ppm)
balance	0.100	0.100	1.430	0.185	0.010	41

The simulation of the heat treatment was conducted on a Dilatronic III RDP deformation dilatometer of Theta Industries, Inc. All specimens were machined to 3mm diameter cylindrical rods of 6mm length. The specimens were austenized at 1200℃ for 3 minutes to dissolved carbides and then cooling to the temperatures 100℃ above the Ar3 temperatures at the cooling rate 20 ℃/s. The Ar3 temperature about 655℃ was determined by the dilatometer cooling the specimen from 1200℃ to room temperature at the cooling rate 20 ℃/s. The specimens were isothermal at 755℃ for 5minutes, 10minutes, 30minutes, and 60minutes and then were quenched to room temperature at the cooling rate 100 ℃/s. Fig. 1 shows a schematic diagram of the dilatometric experiment. Hence, A tempering heat treatments for 3 days are performed in high temperature furnace after the heat treatment of dilatometer because it's risky for the dilatometer to work at high temperature for such a long time.

Transmission electron microscopy (TEM) specimens were prepared from 0.20mm thick discs. The discs were thinned to 0.06 mm by abrasion on SiC papers and then twin-jet electropolished using a mixture of 5% perchloric acid,25% glycerol, and 70% ethanol at -3 ℃ using a 20V polishing potential. They were examined on JEM-2000EX scanning transmission electron microscope with energy dispersive x-ray spectrometer (STEM) operated at 200kV and 160kV.

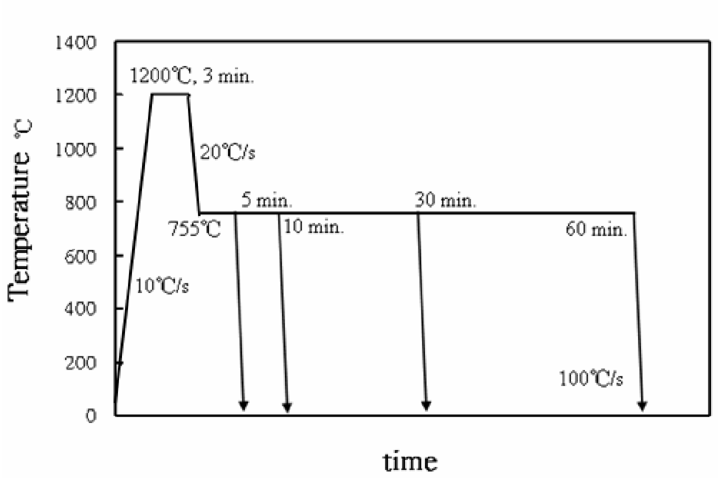

Fig. 1 Schematic diagram of Heat Treatment in Dilatometer. All specimens are austenized at 1200℃ and rapid cooled to 755℃. Specimens are isothermal at 755℃ for different time 5, 10, 30 and 60min, and finally quenched to the room temperature.

3. Results and Discussion

3.1 Distribution of titanium carbides

The size of titanium carbides changes with isothermal time as shown in Fig. 2(a) to 2(d). Although the size of carbides depends on the contrast of TEM image, it's obvious that carbides in Fig. 2(a) are much smaller than carbides in Fig. 2(d). Moreover, the carbides in Fig. 2(d) lose its banded distribution of interphase precipitation. This is because the coarsening process occurs in the time range, 60minutes. Coarse carbides grow at expense of finer ones during coarsening process.

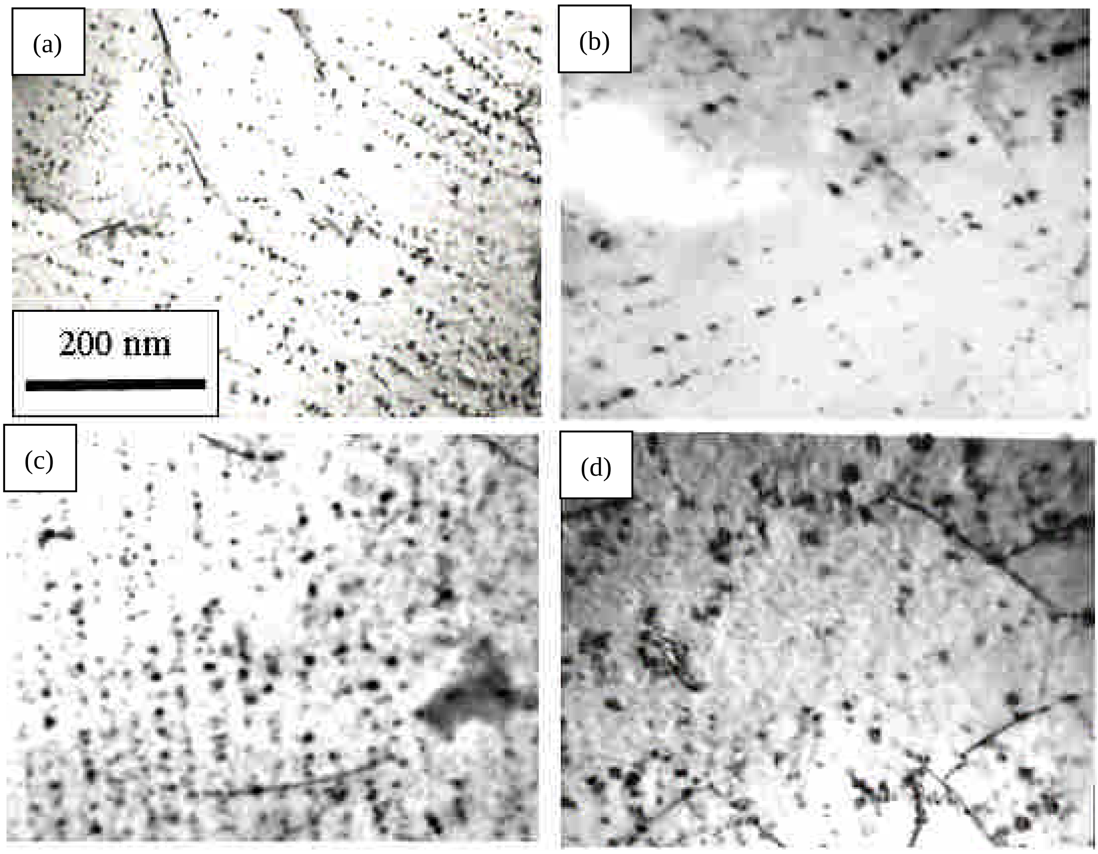

Fig. 2 Microstructure of titanium carbides of specimen isothermal at 755℃ for (a) 5, (b) 10, (c)30, and (d) 60mins.

3.2 Orientation of titanium carbides

Because of the special mechanism of interphase precipitation, the carbides of interphase precipitation distribute densely in each grain. Fig. 3(a) shows two adjacent grains with carbides, and the center dark field image shows in Fig. 3(b). The selection area diffraction pattern is shown in Fig. 3(b) where carbides adopt two different variants of Nishiyama-Wasserman (N-W) (10) OR as shown in Fig. 3(d) and 3(e). NW OR is often described as $(011)_{bcc}//(111)_{fcc}$ and $[100]_{bcc}//[1\bar{1}0]_{fcc}$. Notice that this orientation relationship is different from previous studies [6] in which carbides exist Baker-Nutting orientation relationship. These two variants of N-W ORs imply that the precipitates don't nucleate in the austenitic grain but in the ferritic grains or on transforming interfaces. If the carbides nucleate in the previous austenitic grain, the carbides should process only one variant of N-W OR.

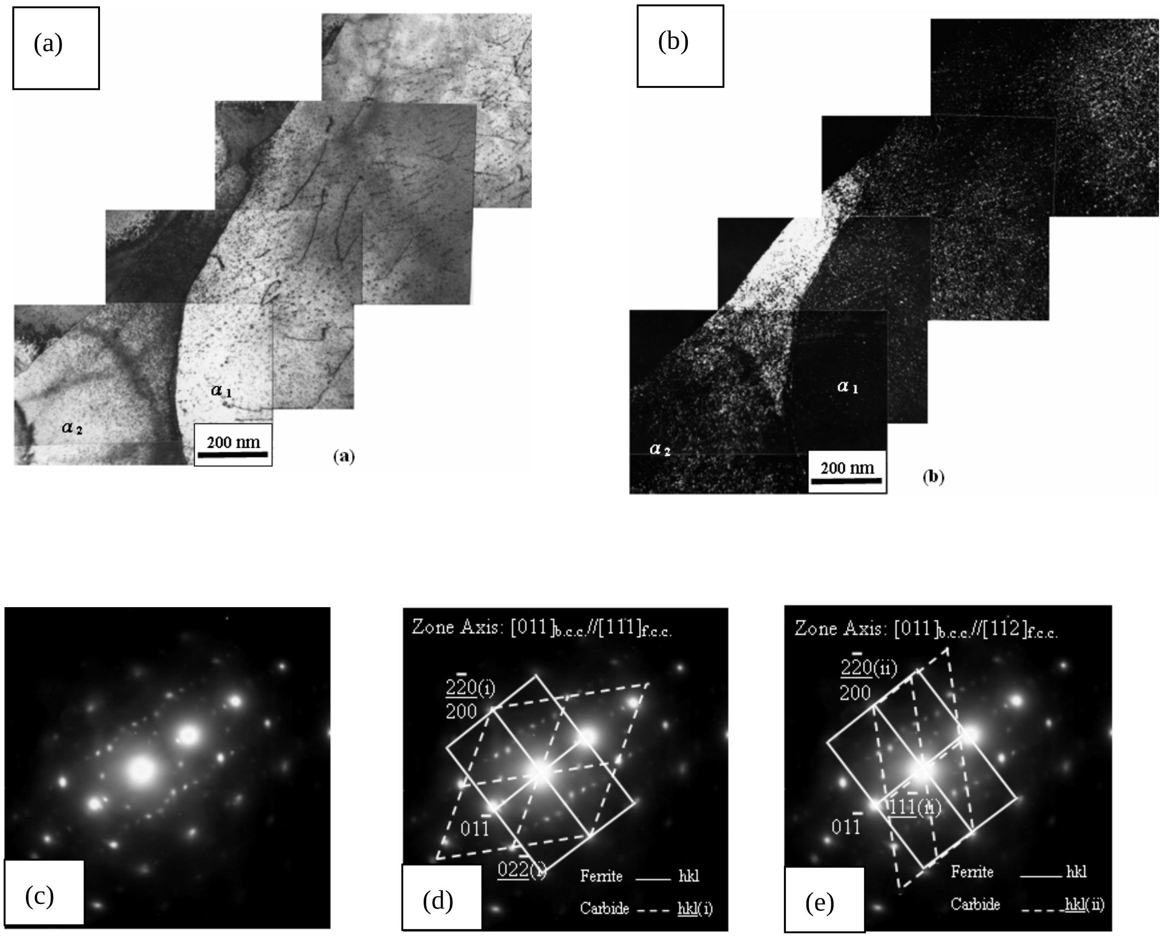

Fig. 3 Bright field (a) and dark field image (b) of titanium carbides in two ferrite grains. The specimen is isothermal at 755℃ for 60 min. The SAD pattern(c) is taken along zone axis $[011]_{ferrite}$. Two variants of N-W ORs are observed in (c) One orientation relationship is shown in (d), which subscript ”i” and the other one in (e), which subscript ”ii.”

3.3 Morphology and orientation of coarsening carbides

TEM image in Fig. 3(a) displays the carbides in the specimen isothermally treated at 755℃ for 3 days. It is obvious that the long-term holding leads to rather coarse particles of TiC. Owing to sectioning effect, these TiC particles appear to be disc-like with a diameter range from 15 nm to 25 nm. Consequently these particles have a much higher contribution on electron diffraction. SADP as shown in Fig. 3(b) clearly presents that the coarse TiC particles adopt N-W OR with ferrite matrix. The result provides strong evidence to suggest that B-N OR can transfer to N-W OR during the coarsening of TiC particles.

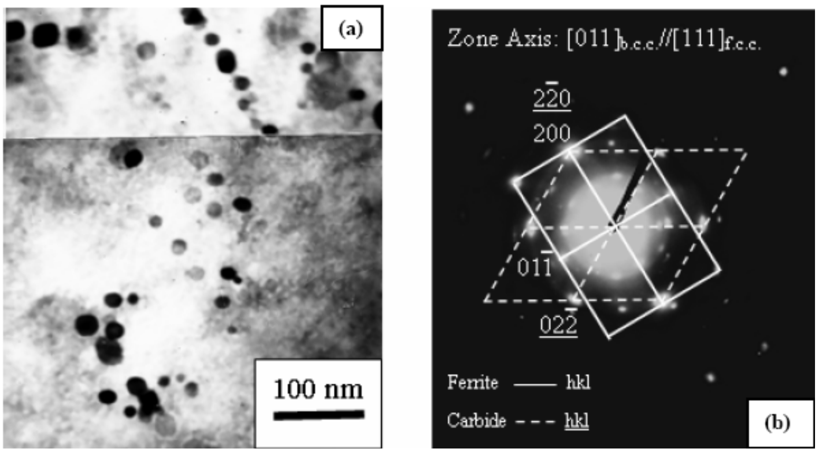

Fig. 3 TEM image (a) for TiC particles in the specimen isothermally treated at 755℃ for 3 days. The corresponding selected area diffraction patterns (b) showing the carbides hold an N-W OR with ferrite matrix.

3.4 Interconnection between N-W and B-N OR

The interconnection between B-N and N-W OR's is with profound interest. Dahmen [11] presented an excellent review concerning orientation relationships in BCC/FCC systems, and asserted that all the well-known OR's of one set of crystal systems are connected with each other by some small relative rotation. He hypothesized that a precipitate lattice tends to be related to matrix lattice by an invariant line strain. The invariant line lies in the precipitate/matrix. A habit plane which contains an invariant line and another direction of small strain can minimize the elastic strain energy of a coherent plated nucleus. In this section, the concepts of the invariant line strain and the algebra analysis proposed by Dahmen have been followed to investigate the interconnection between B-N and N-W OR's for TiC (FCC) in Ferrite (BCC).

A homogeneous transformation $\hat{A}$, which describes the invariant line strain, can be decomposed into a rigid body rotation $\hat{R}$ through some angle θ and a pure deformation $\hat{D}$. If two dimensional meshes are projected along rotation axis and the matrix $\hat{D}$ is referred to the principal axes of the deformation have only diagonal elements. The invariant line strain can be described as:

$$\hat{A} = \hat{R}\hat{D} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix} \qquad (1)$$

An invariant line, a vector $\hat{u}$, is unchanged under the operation of invariant line strain:

$$(\hat{A} - \hat{I})\hat{u} = 0 \qquad (2)$$

Since the vector $\hat{u}$ is not a zero vector, and then the determinant of $(\hat{A} - \hat{I})$ must be zero. That is:

$$\det\begin{vmatrix} a\cos\theta - 1 & b\sin\theta \\ -a\sin\theta & b\cos\theta - 1 \end{vmatrix} = 0, \qquad (3)$$

which when solved for θ gives :

$$\theta = \cos^{-1}\frac{1 + ab}{a + b}. \qquad (4)$$

The principal distortions a and b can be expressed as a constant multiplying the ratio of FCC lattice parameter to BCC lattice parameter. Several researches have confirmed that the Baker-Nutting OR is predominant between NaCl-type carbides/nitrides and ferrite matrix [11]. In this work, the rotation angle θ necessary to produce an invariant line by rotation around the normal to (110) FCC plane, which is parallel to (1 0 0) BCC plane, can be described as:

$$\theta = \frac{1 + \frac{1}{2\sqrt{2}} r^2}{(\frac{1}{\sqrt{2}} + \frac{1}{2}) r}, \qquad (5)$$

where r equals to the ratio of FCC lattice parameter to BCC lattice parameter (a_{FCC} / a_{BCC}). Fig.4 displays superposition of the set of parallel planes $(100)_{BCC} // (110)_{FCC}$, which is under B-N OR. When the rotating angle θ equals to 0, the precipitate exists B-N OR. As θ increases to 9.7°, the precipitate holds N-W OR. From the discussion above, there must be something different in our precipitation system. The rotation angle θ varying with ratio of lattice constants can be produced as shown in Fig. 5. It presents a remarkable result that an invariant line strain appears after the rotation with θ= 7.6° along $[110]_{FCC}$ as the ratio of lattice constants equals to 1.506 for TiC/ferrite. After this rotation, the OR between titanium carbides and ferrite matrix changes from B-N to approximate N-W. The rotation angle 7.6° is nearly the same with the angle between B-N and N-W OR's($[110]/9.7^{O}$). It is apparent that interconnection between B-N OR's and N-W OR's in TiC/ferrite system can be demonstrated using the model that two phases tend to be related by an invariant line strain.

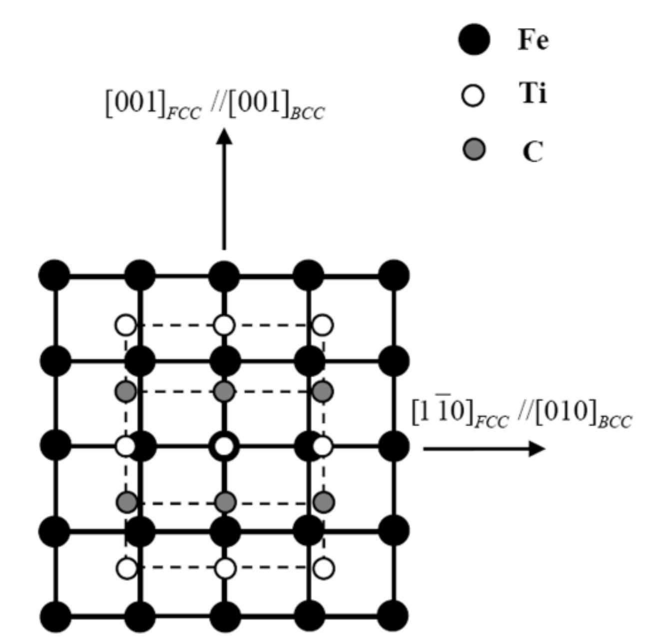

Fig.4 Superposition of {100} planes of BCC (full circles) and {110} planes of FCC (open circles). The shadowed circles represent the additional atoms in NaCl-type FCC lattice.

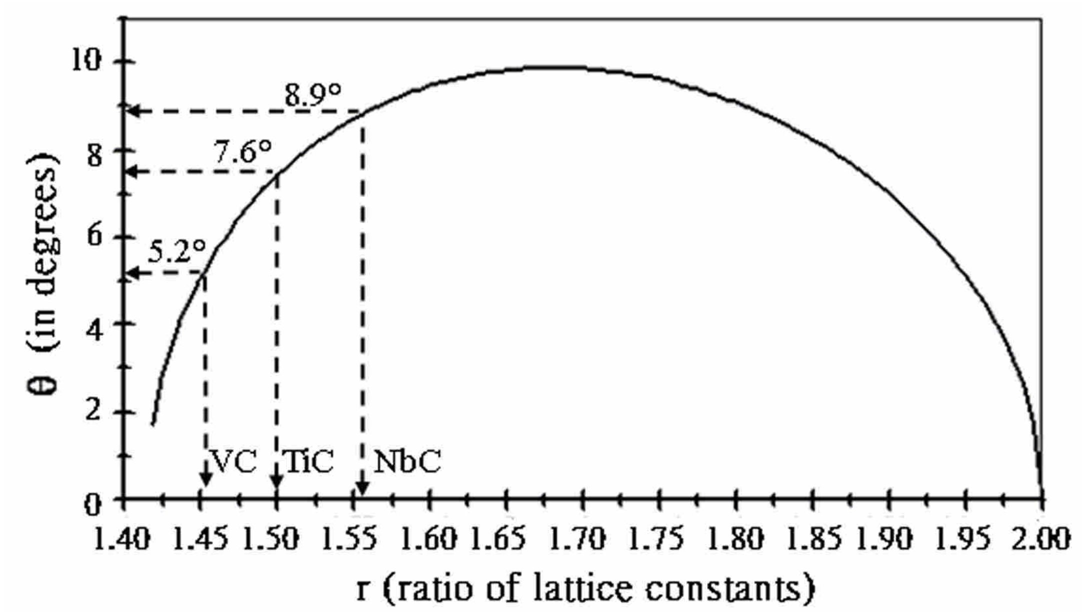

Fig. 5 Rotation angle θ producing an invariant line around the normal of $(110)_{FCC}//(100)_{BCC.}$ as a function of ratios of lattice constants.

4. Conclusion

In previous work, the orientation relationship of the interphase precipitation in this system is only one variant of the Baker-Nutting orientation relationship for tiny TiC carbides. In our present work, Nishiyama and Wasserman orientation relationship is found the interphase precipitation of titanium carbides in ferrite matrix. Moreover, two variants of NW OR in one ferrite grain prove that the titanium carbides precipitate in ferrite matrix or on the transforming interfaces rather than in previous austenite matrix. It is deduced from above that the coarsening process causes the orientation relationship transaction. This phenomenon can be realized by Fig. 6. The carbides exist only one variant of B-N OR with ferrite matrix during nucleation and growth. And carbides change to multi-variant N-W OR's during coarsening. Therefore, the heat treatment can introduce the precipitates to change the orientation with respect to matrix. The concept of invariant line can consist with this change in OR's.

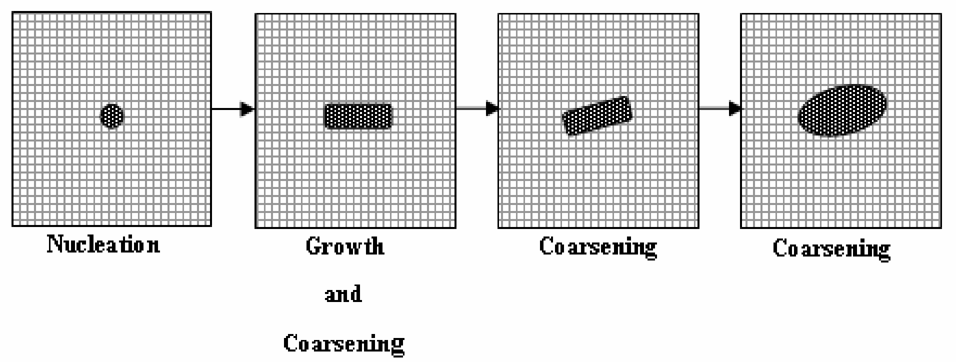

Fig. 6 Orientation relationship transaction occurs during coarsening of the carbides.

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