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# Effect of alloying elements addition on coarsening behavior of pearlitic cementite particles after severe cold rolling and annealing

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**Abstract**

The coarsening kinetics of cementite (θ) particles in severely cold-rolled and annealed pearlite in Fe–0.8 mass% C alloys with various contents of Cr, Mn and Si were investigated, and the effect of alloying elements was discussed. The results showed that severely cold-rolled pearlitic cementite spheroidized rapidly during annealing at 923 K in the Fe–0.8C alloys, and the coarsening of θ particles is strongly suppressed by the addition of Cr, Mn and Si. The coarsening kinetics of θ particles obeys the relationship, $d = kt^n$, and the staged change appears on the coarsening kinetics curves. In Fe–0.8C alloy, the solute atoms diffused mainly along dislocations at the first stage, but they diffused mostly along the grain boundaries during the subsequent annealing. The addition of Cr or Mn restrained coarsening of θ particles due to decrease of diffusivity of carbon atoms, but this suppression effect weakened after a long-time annealing (more than 3 h). The addition of Si accelerated exclusion of carbon atoms from the rolled α-Fe, thus it changed the diffusion pattern of solute atoms and increased the *n* value at the initial annealing stage (∼0.6 ks). During the subsequent annealing (0.6–10.8 ks), the addition of Si suppressed the coarsening of θ particles pronouncedly.


*Keywords:* High carbon steel; Cementite; Coarsening kinetics; Alloying elements; Cold rolling

## 1. Introduction

Recently, the cementite (θ) has been used to ultra-refine the microstructures in steels [1–4]. For the pearlitic steels, both reduction of the interlamellar spacing of pearlite (ISP) and thinning of the thickness of lamellar θ ($t_\theta$) occur during heavy cold rolling [3–5], and θ lamellae spheroidize rapidly during subsequent annealing, which leads to the formation of (α + θ) micro-duplex structures [3,6–8]. The refinement of θ particles can result in the refinement of α grain size by pinning effects, so the coarsening behavior and size control of θ particles are very important for obtaining the (α + θ) micro-duplex structures in steels.

Many research reports have focused on the kinetics of precipitation and coarsening of θ particles during the tempering of martensite. Lifshitz–Slyozov–Wagner (LSW) [9,10] theory predicts that the coarsening kinetics of carbide particles can be described by a power law relationship:

$$d^q - d_0^q = k_0(t - t_0) \quad (1)$$

and in order to investigate the coarsening mechanism of the carbide particles, Eq. (1) can be simplified as follows:

$$d = kt^n \quad (2)$$

where $n = 1/q$, $d_0$ and $d$ are the initial and final particle sizes, respectively. Coarsening rate constant $k$ and exponent $n$ are the functions related to the solubility, boundary energy and diffusion of atoms, wherein $n$ is a parameter dependent on the coarsening mechanism of the carbide particles. Based on the difference of coarsening mechanism of carbide particles, $n$ can be 0.20, 0.25, 0.33 or 0.50 contingent on whether the rate controlling mechanism is assumed to be determined by diffusion via dislocation pipes ($n = 0.20$) [11], along grain boundaries ($n = 0.25$) [12], through the crystal lattice ($n = 0.33$) [13], or across a particle matrix interface ($n = 0.50$) [14]. Experimentally, $n$ usually takes in a range of values from as low as 0.10 to as high as 0.50 [15].

It is known that coarsening of θ particles can be suppressed by the addition of a third alloying element during the tempering

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Table 1
Chemical compositions of the tested alloys (mass%)

| Alloy | C | Si | Mn | Cr | Fe |
|---|---|---|---|---|---|
| Fe–0.8C | 0.78 | <0.03 | <0.03 | – | Bal. |
| Fe–0.8C–1Cr | 0.78 | <0.03 | <0.03 | 1.00 | Bal. |
| Fe–0.8C–1Mn | 0.82 | <0.03 | 0.97 | <0.03 | Bal. |
| Fe–0.8C–1Si | 0.80 | 0.99 | <0.03 | <0.03 | Bal. |
| Fe–0.8C–2Mn–1Si | 0.79 | 1.00 | 2.00 | – | Bal. |

Table 2
Interlamellar spacing of pearlite and thickness of lamellar θ before cold rolling (as transformed)

| Alloy | ISP (nm) | $t_\theta$ (nm) |
|---|---|---|
| Fe–0.8C | 260 | 43 |
| Fe–0.8C–1Cr | 64 | 11 |
| Fe–0.8C–1Mn | 121 | 17 |
| Fe–0.8C–1Si | 97 | 19 |
| Fe–0.8C–2Mn–1Si | 116 | 15 |

of martensite in Fe–C alloys [13,15–17]. However, for cold-rolled pearlite, the coarsening behaviors of carbide during the subsequent annealing become more complicated than that during the tempering of martensite, because heavy cold deformation and alloying elements were induced into the steels. For lamellar pearlite, the addition of alloying elements can reduce the ISP [8], but its effect on the coarsening behavior of θ particles during the annealing in cold-rolled eutectoid steels has not been clarified yet.

The present study aims to examine the coarsening behavior and mechanism of θ particles during annealing of heavily cold-rolled eutectoid pearlitic steels with the addition of alloying elements such as Cr, Mn and Si, which will provide support for the development of ultra-fine-grained plates of high carbon steels.

## 2. Experimental procedure

An Fe–0.8 mass% C binary alloy and three Fe–X–0.8 mass% C (X: 1 mass% Cr, 1 mass% Mn or 1 mass% Si) ternary alloys and an Fe–2 mass% Mn–1 mass% Si–0.8 mass% C quaternary alloy were used. Their chemical compositions are listed in Table 1. The other impurities, such as P and S, are less than 50 ppm in these alloys. Ingots were produced by vacuum induction melting and hot-rolled to 15 mm thick plates. They were homogenized at 1473 K for 86.4 ks. Each specimen was austenitized at 1123 K for 1.8 ks, quenched in a salt bath and isothermally held at 873 K for 0.6 ks for pearlite transformation, and followed by air-cooling. The as-transformed specimens were cold-rolled by 90% thickness reduction and isothermally annealed at 923 K for various periods (30 s, 120 s, 0.6 ks, 1.8 ks, 10.8 ks and 36 ks), then quenched into water. Microstructure observations for TD plane (containing the rolling direction and the normal direction) were made using scanning electron microscope (SEM) and transmission electron microscope (TEM). The specimens for SEM observation were etched with 1% natal after mechanical polishing and observed with a Hitachi S3100H microscope. Thin foils for TEM observations were cut by an electrode discharge machine to 0.5 mm × 0.5 mm × 3.0 mm, mechanically thinned to 50 μm thickness, and electropolished by a twin-jet polisher with 5% perchloric acid and acetic acid solution at 36 V and 284 K. TEM observations were performed with a Philips CM200 electron microscope.

ISP and thickness of θ lamella ($t_\theta$) in each as-transformed specimen was determined by using the TEM micrographs on which θ lamellae interface was parallel to the incident beam. The θ particle sizes in the specimens annealed at 923 K were determined using SEM. Using the image analysis software (Analysis), which digitizes an image from the photograph, the stained carbides were identified based on gray level and separated for analysis. The area ($A$) of a two-dimensional section at the polished plane was measured for each particle, and converted to an equivalent circle diameter (ECD $= \sqrt{4A/\pi}$) of the particle. At least, several micrographs were taken with magnifications from 3000 to 20,000 for each specimen. The total number of measured particles ranged from approximately 500 to 1300, depending on material and annealing periods at 923 K.

## 3. Results and discussion

### 3.1. Effects of alloying elements on the spacing and thickness of pearlite lamellae

Table 2 shows the measured results of ISP and $t_\theta$ for the as-transformed alloys. It is obviously found that as the addition of alloying elements the ISP and $t_\theta$ decreased to more than 50% as compared with 0.8C steel. As for the effect of the alloying elements on refining ISP, Cr is the most effective, the second one is Si, and the combined addition of Si and Mn is more effective than that of single Mn. As for the effect on refining $t_\theta$, Cr is also the most effective alloying element, Mn is the second one and the combined addition of Mn and Si is more effective than the single addition of them. Therefore, it indicates that the addition of Cr, a strong carbide forming element, can refine ISP and $t_\theta$ effectively in the eutectoid alloys. Although the effect of Mn and Si is not more significant than that of Cr, they also refine the ISP and $t_\theta$ greatly compared with the Fe–0.8C alloy. This provides a structure base for obtaining the (α + θ) micro-duplex structures in the eutectoid alloys after cold rolling and annealing.

### 3.2. The suppression effect of alloy elements on coarsening of θ particles

The isothermally transformed pearlite has typical lamellar morphology. After cold rolling by 90% thickness reduction, some pearlitic θ lamellae are strongly bent, the others are thinned, refined even partially dissolved [3–5]. The cold deformation induces a high density of dislocations into α-Fe (matrix), which pile up against the θ lamellae boundaries, even nipped off the θ lamellae [5,18]. As a result, the spheroidization of the deformed θ became easier and more rapid during the subsequent annealing, even within several seconds in this work. However, the spheroidization of lamella θ without deformation needs very