Aging behavior of Cu-rich precipitates in Fe-3% Si-Cu alloy

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Abstract
Fe-3%Si-Cu alloys with different Cu content were aging treated at 500 ~ 800 °C. In order to study the dynamic behavior of the aging precipitations, the microstructure and the aging precipitation behavior of copper-rich phase in these alloys under different aging heat treatment were tested by OM, TEM technology and Vickers hardness. The results show that the amount of the copper-rich precipitates in the two alloys are gradually increase with the aging time going after aging treated at 600 °C. Within the 10\textsuperscript{s} aging time, the size of the copper-rich precipitates of the two samples is below 20 nm. When it reaches 10\textsuperscript{5.5} s, the copper-rich precipitates have obvious cluster phenomenon and the size are not more than 100 nm. After being treated with different aging temperature, the hardness of Fe-3% Si-Cu alloys with different copper component increases first and then decreases with time going, with obvious aging hardening peaks. When the aging temperature is 500 °C and the aging time is 10\textsuperscript{4.5} s, the hardness of the two alloys reaches the maximum and they are 264 HV and 238 HV, respectively. The precipitation kinetics curve of the copper-bearing Fe-3% Si-Cu alloy is in the shape of C, which has been widely applied in many fields.

1. Introduction
In recent years, in order to meet the performance requirements of materials in the fields of high-speed rail, aerospace, ocean, and new energy, alloying treatment is still one of the important preparation methods for high-quality materials [1–4]. As an important non-ferrous metal element, copper can form a copper-rich phase enriched along the grain boundary under certain conditions, reducing the strength of the grain boundary and causing copper brittleness during the hot working of steel [5]. However, copper precipitating out Cu-rich precipitate in steel can fine grains and produce age-hardening effect [6, 7], which can improve the steel strength, impact toughness, fatigue resistance, corrosion resistance and welding property of low carbon steel [8–10]. Therefore, it has been paid more and more attention and increasingly studied. At present, the research and development of copper-containing steel in China and foreign countries concentrate on weathering steel, low-alloy high-strength steel, antibacterial stainless steel, and electrical steel [11–16], which has been widely applied in many fields.

Copper is an alloying element that does not form a compound with C and N, it can produce a strong precipitation strengthening effect in steel [17, 18]. There are four strengthening mechanisms that explain copper precipitation strengthening: misfit effect, chemical effect, modulus difference effect and dislocation core precipitate interaction effect [19]. Meanwhile, nano-Cu precipitated phase has good plasticity, which enables the steel to have high plasticity and strength [20]. The excellent performance in ductility and fracture toughness can
be explained by the existence of nanosized coherent Cu-alloyed precipitates and the interaction of these precipitates with screw dislocations in the ferritic matrix. Plasticity of body-centered cubic (bcc) Fe is facilitated by thermally activated motion of screw dislocations [21]. The fine Cu precipitates also have an excellent effect on grain refinement. Therefore, copper has been widely used in low carbon ferrite steel. The solubility of Cu in ferrite is extremely low, thus, many Cu atoms precipitate during the aging process, which increases the strength of the matrix. On subsequent further aging, the Cu-alloyed precipitates enrich progressively with Cu and elongate, indicating a transformation to the 9R or face centered cubic structure [21]. Some references proposed that, a solid solution of 1 wt.% Cu increases the strength by 40 ~ 50 MPa. After aging at 450 ~ 600 °C, the yield strength can be further increased by 100 ~ 200 MPa due to the precipitation of Cu [22]. The increase in tensile yield stress observed on aging a binary Fe–1.67 at.% Cu alloy quenched from 1000 °C and aged to maximum yield stress at 475 °C was 365 MPa [19].

Although precipitation strengthening of Cu-rich nanoparticles has been widely used to strengthen steels in low carbon ferrite steel [22], and the effect of solution and aging process on mechanical properties and magnetic properties et al has been reported, there are very few reports about the basic metallography research on the precipitation kinetic behavior of the copper-rich phase in the single-phase ferrite matrix. In low-carbon ferritic steel, when the second phase is nucleated and precipitated in the matrix, the PTT (Precipitation-temperature-time) curve of the precipitation of the second phase will change in the form of a C curve, since the chemical driving force for the precipitation of the second phase increases with the decrease of the precipitation temperature, and the diffusion coefficient of the solute element decreases with the decrease of the temperature [23, 24]. The fastest precipitation of the second phase can be achieved by holding temperature at the nose point temperature of the curve. Therefore, it is of great significance to study the precipitation law of copper in ferrite matrix for composition design and process matching of copper bearing low carbon ferrite steel, and it is very important to control the precipitation of copper-rich phase for the performance optimization of ferritic steel final products such as electrical steel and other. Because the microstructure of electrical steel containing 3% Si is ferrite, and the copper element has an important effect on the electromagnetic and mechanical properties of electrical steel. Thus, this paper takes Fe–3% Si-Cu alloy with single-phase ferrite as the research object, the aging precipitation process of the copper-rich precipitates at different temperatures is studied to explore the precipitation kinetic behavior of the copper-rich precipitates in Fe–3% Si-Cu alloy steel with single-phase ferrite matrix. The research provides a thorough knowledge of ferritic metallography related to engineering steels such as electrical steel et al, and it is of great significance to further enrich the mechanism of copper in ferritic steels.

2. Experimental

The DDVIF-25–60–5 vacuum induction furnace was used to smelt Fe-3% Si-Cu alloys with different components. The raw materials used were about 99.96% pure iron rods, 99.999% pure silicon, 99.99% pure copper, and 99% pure carbon. The components are shown in table 1. Under Experimentation, the preparation process of hot rolling and cold rolling of electrical steel is simulated. The smelted steel ingots were forged and hot-rolled to a thickness of 2.3 mm, and they were annealed at 840 °C for 15 min, they were then cold rolled to a thickness of 0.3 mm in multiple passes by a straight-drawn four-roll reversible cold rolling mill [25–27]. The cold-rolled samples were treated with solution treatment at 900 °C for 30 min to obtain uniform recrystallization microstructure. Finally, they were aging treated at 500 °C–800 °C for 3 s, 5 s, 10 s, 10^{1.5} s, 10^{2} s, 10^{2.5} s… 10^{5.5} s. The heat treatment cycle with temperature versus time in aging process are shown in table 2.

The AXIO VRET.A1 Zeiss optical microscope (OM) was used to observe the microstructure of the samples. The HV-30 Vickers hardness tester was used to test the hardness of the samples with different aging treatment. The JEOL2100F transmission electron microscope (TEM) and EDS technology were adopted to observe the distribution of the second phase particles.

| No. | C   | Si  | Cu  | Mn | Al | N  | S  | P  | The rest |
|-----|-----|-----|-----|----|----|----|----|----|----------|
| 1   | 0.0040 | 3.21 | 1.15 | 0.013 | <0.005 | 0.0050 | 0.0018 | 0.0078 | <0.01    |
| 2   | 0.0046 | 3.21 | 1.64 | 0.011 | <0.005 | 0.0042 | 0.0018 | 0.0078 | <0.01    |

Table 1. Fe-Si-Cu alloy component (wt.%).
3. Results and discussion

3.1. Microstructure of sample after solution treatment

In this experiment, in order to study the aging precipitation behavior of Fe-3% Si-Cu alloy, the cold-rolled samples were treated at 900 °C to finish complete recrystallization. The microstructure of 1# and 2# samples after solution treatment is shown in figure 1, both of which were single-phase ferrite structures. The microstructure corresponds to that of the phase diagram. The phase diagram of Fe-3% Si-Cu alloy was simulated and calculated with THERMO-CALC software (figure 2). After the heat treatment, the interference of the phase transformation, and the recovery and recrystallization of the cold-rolled samples can be eliminated to the hardness change of the samples. The aging treatment process of 500 ~ 800 °C was formulated according to the phase diagram.

![Figure 1. Microstructure of 1# and 2# samples after solution treatment.](image1)

![Figure 2. Fe-3%Si-Cu alloy phase diagram.](image2)

| Temperature/°C | time/s |
|----------------|--------|
| 500            | 3 5 10 | 10^1.5 10^2 10^2.5 10^3 10^3.5 10^4 10^4.5 10^5 10^5.5 |
| 600            | 3 5 10 | 10^1.5 10^2 10^2.5 10^3 10^3.5 10^4 10^4.5 10^5 10^5.5 |
| 700            | 3 5 10 | 10^1.5 10^2 10^2.5 10^3 10^3.5 10^4 10^4.5 10^5 10^5.5 |
| 800            | 3 5 10 | 10^1.5 10^2 10^2.5 10^3 10^3.5 10^4 10^4.5 10^5 10^5.5 |
3.2. The precipitation behaviors of the samples after aging experiment

The morphology of the precipitated phases of the two samples were tested by TEM technology in figure 3 after aging treatment at 600 °C by different times, the morphology, EDS energy spectrum analysis and the surface distribution of precipitates of 1# and 2# samples treated at 600 °C for 10’s in STEM imaging mode in figure 4, table 3, and figure 5. These show that the particles are copper-rich phases which are distributed diffusely in the matrix. The precipitation of copper-rich phase is complicated, and the evolution of its shape from spherical to ellipsoidal and then to rod-like shape is greatly related to its size, as well as the evolution of its structure and component [28]. Han Gang et al [29] combined 3D atom probe technology and high resolution transmission electron microscopy to obtain the crystalline structure evolution sequence of Cu precipitates at 680 °C at different critical tempering times as follows: Cu-rich nano-ordered clusters (B2 FeCu and BCC Cu)—9R Cu—detwinning 9R Cu—complex transition phase (9R + FCC)—FCC Cu. The precipitation of copper-rich phase

Figure 3. Precipitates of samples after aging treatment at 600 °C for different time.
particles maintains a certain crystallographic orientation relationship with the matrix. The orientation relationship between 9R Cu and a-Fe matrix is \((11\overline{4})_{9R} || (011)_{a}, [-110]_{9R} || [1\overline{1}1]_{a}\). The orientation relationship between Fcc Cu and a-Fe matrix is \((1\overline{1}1)_{\text{Fcc}} || (011)_{a}, [1\overline{1}0]_{\text{Fcc}} || [1\overline{1}1]_{a}\). Because of the solid solubility of copper in the \(\alpha\)-Fe matrix is very small, even if a small amount of Cu element is added to the steel, a small amount copper-rich precipitation phase can be obtained in the matrix after aging treatment. Therefore, the initial state microstructure of the two samples is ferrite and copper-rich phases, as shown in figures 3(a) and (b). Within 10^3 s of aging, the size of the copper precipitates of the two samples is very small, and the size of the copper-rich phase is below 20 nm. When the aging time reaches 10^5.5 s, the copper-rich phase has obvious cluster phenomenon and its size is not greater than 100 nm, as shown in figure 3(c)–(h). The precipitation of the

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Table 3. The corresponding data of EDS analysis of 1# sample (wt.%).

| NO. | Si  | Fe  | Cu  |
|-----|-----|-----|-----|
| point 1 | 2.63 | 70.25 | 27.12 |
| point 2 | 3.84 | 91.75 | 4.41 |

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Figure 4. Precipitates detected of 1# sample by TEM after aging treatment at 600 °C for 10^3 s.

Figure 5. Surface distribution of Cu of 2# sample detected by TEM after aging treatment at 600 °C for 10^3 s.
Cu-rich phase is caused by the continuous enrichment of Cu atoms [30]. During the aging process, the precipitations of the copper-rich phase of the two samples gradually increase with the aging time going, and the precipitated phases of the 2\# sample are more than that of the 1\# sample, and the surface distribution density is shown in Table 4. When the aging time reaches 10^{5.5} s, its surface distribution density does not decrease, indicating that there is still nano-scale copper-rich phase precipitation. R Prakash Kolli et al [31] explored the evolution of Cu precipitates after aging treated for 0.25 h ∼ 1024 h at 500 °C by using 3D atom probes. It was found that the average radius of the Cu precipitates gradually grows from the 1.2 ± 0.1 nm nano-clusters with a Cu content of 46.7 ± 4.3 at.% at the initial stage of nucleation for 0.25 h to a face-centered cubic Cu with the radius of 6.5 ± 0.7 nm, and the Cu content is 97.1 ± 0.8 at.% at later aging stage for 1024 h.

### 3.3. The hardness of the sample after aging test

Figure 6 shows the hardness curves of Fe-Si-Cu alloy after aging treatment at 500 °C ∼ 800 °C with different time. It shows that within the 10^{5} s of the aging treatment, the hardness of the 1\# and 2\# samples increases first and then decreases with aging time. There are three stages, including underaging, aging, and overaging, and

| No. | 0 s     | 10 s    | 10^{3} s | 10^{5} s |
|-----|---------|---------|----------|----------|
| 1\# | 2.55 × 10^{11} | 2.58 × 10^{11} | 2.71 × 10^{11} | 1.55 × 10^{12} |
| 2\# | 9.53 × 10^{11} | 1.07 × 10^{12} | 1.35 × 10^{12} | 1.69 × 10^{12} |

Figure 6. Aging curves of Fe-3%Si-Cu alloy annealed at different temperature.

Figure 7. Precipitation kinetic curve of Fe-3%Si-Cu alloy.

Table 4. Distribution density of the second phase after treated at 600 °C for different time (Pcs cm\(^{-2}\)).
there are obvious aging hardening peaks. Combining figure 3 and table 4, it can be seen that when it is aging treated at 600 °C for 10^3 s, the Cu-rich phase size is small, the surface distribution density is relatively large and it is uniformly dispersed, the hardness of the sample is the largest. After aging for 10^5 s, although the surface distribution density of the copper-rich phase increases, the obvious clustering of the copper-rich phase, its precipitation strengthening effect is weakened, the hardness of the sample decreases. As the aging temperature decreases, the hardness of the age hardening peaks of the two samples are both increased and the time of the age hardening peaks are both gradually procrastinated. This is because the phase transition driving force of the copper-rich precipitation is increased which fortify the precipitation tendency of copper-rich phase, meanwhile, the saturated solid solubility of copper in the matrix decreases and more copper is precipitated with the decrease of aging temperature. On the other hand, the precipitation process of copper in steel is a diffusion-type phase transition, when the temperature decreases, the diffusion coefficient of copper in steel is decreased, so copper can only be precipitated through small-scale diffusion. The interaction of the two reasons makes the size of the precipitation smaller and the number of particles larger at lower aging temperature, so that the hardness is increased. When the aging temperature is 500 °C and the aging time is 10^5 s, the hardness of the two alloys reaches the maximum. The hardness of the 1.64% Cu alloy is 264 HV, and the hardness of the 1.15% Cu alloy is 238 HV.

Figure 7 shows the precipitation kinetic curve of Fe-3% Si-Cu alloy with the change of hardness after aging treatment at 500 ~ 800 °C for different time. It is in a shape of ‘C’. This is because precipitation is a diffusion-type phase transition process, including nucleation and growth, and there is a certain incubation period. The precipitation kinetics is influenced by the dual control of the phase change driving force and the diffusion coefficient. At higher temperature, the diffusion coefficient of copper in α-Fe is larger, but the phase transition driving force is smaller, so the aging incubation period is longer. At lower temperature, the phase transition driving force is larger, but the diffusion coefficient of copper is smaller, so the aging incubation period is longer too. Only at the intermediate aging temperature of 600 ~ 650 °C, the combined effects of the phase transition driving force and the diffusion coefficient can result in the shortest precipitation incubation period. In this experiment, compared with the 1# and 2# aging kinetic curves, it can be seen that increase of the copper content to 1.64% in the alloy will significantly increase the supersaturation of copper in the steel, stimulation the precipitation tendency of copper, improvement the hardness of the sample after aging treatment, shorten the precipitation incubation period, and the curve shifted to the left obviously. That is, as the copper content increases in the steel, the precipitation of the copper-rich phase will be significantly promoted. The results are of great significance to better the strength and toughness of steel by the aging behavior of copper-rich phase and to research the recrystallization behavior of copper-bearing cold-rolled steels.

4. Conclusion

1. The precipitations of the copper-rich phase in Fe-3%Si-Cu alloys with different copper component are both gradually increase with the the aging time going at 600 °C. Within 10^3 s of aging time, the size of the copper-rich phase of the two samples is below 20 nm. When it reaches 10^5 s, the copper-rich phase has obvious clustering phenomenon and its size is not greater than 100 nm.

2. In this experiment, the hardness of Fe-3% Si-Cu alloys with different components increases first and then decreases with aging time going, and there is an obvious aging hardening peak. When the aging temperature is 500 °C and the aging time is 10^5 s, the hardness of the two alloys reaches the maximum. The hardness of the 1.64% Cu alloy is 264 HV, and the hardness of the 1.15% Cu alloy is 238 HV.

3. The precipitation kinetics curve of the copper-bearing Fe-3% Si-Cu alloy is in the shape of ‘C’. When the aging temperature is 600 ~ 650 °C, the precipitation incubation period is the shortest. The increase of the copper content in the alloy will shorten the incubation period of the precipitation kinetic curve and the curve shifted to the left obviously.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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