Postprint: Theory and Detection Methods for Predicting Morphology of Second-Phase Particles in Steel

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Abstract

Controlling the morphology of second-phase particles (including non-metallic inclusions and carbonitrides) in steel is of great importance for mitigating the detrimental effects of non-metallic inclusions and enhancing the mechanical properties of steel. In this study, a predictive theoretical model for the morphology of second-phase particles in steel is established by introducing the Jackson index. The theory posits that the morphology of second-phase particles in steel is determined by their melting entropy, growth direction, and temperature (undercooling). Through non-aqueous solution electrolysis and RTO technology, combined with scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM), the three-dimensional morphologies and internal characteristics of various inclusions in four steel grades were analyzed. The measured morphologies of second-phase particles are consistent with theoretical predictions. Both theoretical and experimental observations confirm that when the Jackson index of second-phase particles is greater than 3, the morphology is faceted; when the Jackson index is less than 2, the morphology is non-faceted.

Full Text

Preamble

Morphology Prediction Theory and Experimental Measurement for Secondary Phase Particles in Steel

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Abstract

Controlling the morphology of secondary phase particles (including non-metallic inclusions and carbonitrides) in steel plays a crucial role in mitigating the harmful effects of non-metallic inclusions and improving steel mechanical properties. This work establishes a theoretical model for predicting secondary phase particle morphology in steel by introducing the Jackson factor. The theory demonstrates that particle morphology is determined by its entropy of fusion, growth direction, and temperature (undercooling). Using non-aqueous solution electrolysis combined with Room Temperature Organic (RTO) technique and SEM analysis, we examined the three-dimensional morphologies and internal characteristics of various inclusions in four steel grades. The experimentally observed particle morphologies align with theoretical predictions. Both theoretical and experimental results confirm that secondary phase particles exhibit faceted morphologies when their Jackson factor exceeds 3, and non-faceted morphologies when the factor is less than 2.

Keywords: secondary phase particle, morphology, Jackson factor, entropy of fusion, non-aqueous solution electrolysis, RTO technique

Non-metallic inclusions and secondary phase particles in steel cause property discontinuities in the steel matrix. Due to their generally different deformation resistance compared to the steel matrix during rolling, stress concentration readily occurs around inclusions, making them potential initiation sites for microcracks that can propagate into surface macro-defects, thereby affecting both surface quality and mechanical properties. Spherical secondary phase particles induce relatively mild stress concentration during rolling, whereas polygonal particles, particularly those with sharp corners, cause severe stress concentration and readily become microcrack sources [1,2]. Additionally, secondary phase particle morphology significantly influences steel machinability [3,4]. Kim et al. [5] demonstrated that controlling the morphology (spherical) and dispersion of Fe-Al intermetallic compound particles (B2) not only reduces their detrimental effects on steel toughness but also enables them to serve as effective secondary strengthening phases, yielding ultra-high-strength low-density Fe-Al-Ni alloys. Therefore, controlling secondary phase particle morphology is essential for reducing inclusion harm and improving steel quality. However, current research on morphology control remains insufficient, facing two major challenges: first, no comprehensive theoretical framework exists for morphology control, and the influencing factors have not been theoretically clarified; second, effective experimental methods are lacking, as conventional metallographic techniques only reveal a single cross-section of particles, preventing observation of their complete three-dimensional morphology.

Given the significance of crystal morphology control in materials science, geology, and jewelry studies, extensive research has been conducted on theoretical models for various melts including metallic [6–10], inorganic non-metallic [11–14], and organic solutions [15,16]. Liquid secondary phase particles behave as glassy phases and generally assume spherical shapes due to surface tension effects. Solid particle formation represents a crystallization and growth process of oxides or carbonitrides, analogous to nucleation and growth in other crystal systems, making existing crystal morphology research methods applicable to steel secondary phase particles. Several researchers [17,18] have attempted to study steel secondary phase morphology, but limitations in theory and experimental techniques have hindered comprehensive investigation. The authors previously applied the Jackson factor to control crystal morphology in multi-component mold fluxes to improve lubrication performance during high-Al advanced high-strength steel continuous casting [19], though the theory' s applicability to steel secondary phase particles requires further validation.

To address metallographic method limitations, researchers developed electrolytic and acid dissolution techniques. However, acidic solutions dissolve basic components within particles (e.g., calcium aluminates, sulfides), distorting their true morphologies and limiting analysis to acid-resistant particles such as Al O . Fang Keming [20] developed an organic solution electrolysis method that avoids particle damage during extraction, providing a powerful approach for observing complete particle morphologies.

This work establishes a theoretical model for predicting secondary phase particle morphology in steel using the Jackson factor. Non-aqueous solution electrolysis and RTO embedding/sectioning techniques were employed to characterize three-dimensional morphologies and internal features of secondary phase particles, with theoretical predictions validated against experimental observations.

1. Theory for Predicting Secondary Phase Particle Morphology in Steel

Jackson [6,7] first established a theoretical framework for predicting crystal/melt interface morphology in metallic melts using statistical thermodynamics, based on the principle of minimum interface free energy. The theory correlates interface structure with crystal morphology: rough crystal/melt interfaces correspond to non-faceted crystals, while planar interfaces correspond to faceted crystals. A dimensionless parameter, the Jackson factor, serves as the morphology criterion and has been successfully applied to metallic melts, organic solutions, and some simple inorganic oxide melts. Solid secondary phase particle formation in steel satisfies Jackson' s assumptions, allowing extension of this theory to predict steel secondary phase morphologies.

Jackson [6,7] derived the relative free energy expression for solid/liquid interfaces as:
) ln(1

where ΔF represents crystal interface free energy during solidification, N is the number of crystal lattice sites at the interface, k is the Boltzmann constant, and T is thermodynamic temperature.

Letting X denote the fraction of interface sites occupied by crystal atoms, is the Jackson factor, defined as [?]:

(hkl) (hkl) (hkl) represents the crystal growth orientation index, defined as the ratio of interface unit cell atoms to coordination number, which is a constant between 0.5-1.0 [21] that may vary with growth direction. ΔH and ΔS denote the enthalpy and entropy of fusion, respectively; T is the melting point; and R is the gas constant.

[Figure 1: see original paper] illustrates the relationship between relative interface free energy and X calculated from equation (1). When < 2, the minimum relative free energy occurs at X = 0.5, corresponding to the "roughest" crystal/melt interface and, according to Jackson' s theory, non-faceted crystal morphology. Conversely, when > 3, the minimum occurs at X = 0 or X = 1, representing the "flattest" interface and faceted crystals. Thus, crystal morphology can be predicted through the Jackson factor magnitude.

Equation (2) demonstrates that secondary phase particle morphology depends on intrinsic properties (entropy of fusion), growth direction, and temperature (undercooling). The Jackson factor, proportional to fusion enthalpy, physically represents the entropy difference between crystal and melt: larger values indicate greater order in the formed crystal, manifesting as faceted morphologies, while smaller values yield non-faceted shapes. As shown in [Figure 1: see original paper], the critical for faceted crystals is approximately 3, while non-faceted crystals have a critical value near 2. Extensive observations of metallic crystal morphologies have validated this criterion [6,7].

It should be noted that equation (2) applies only under equilibrium conditions. In non-equilibrium situations such as undercooled melts, the two equalities in equation (2) do not hold because the Gibbs free energy of fusion ΔG ΔH - TΔS. For undercooled melts at temperature T, the entropy of fusion can be approximated using the value at the melting point when the specific heat difference between liquid and solid phases is small or undercooling is moderate.

[Figure 2: see original paper] shows a schematic of the non-aqueous solution electrolysis apparatus, using the specimen as anode, stainless steel tube as cathode, and anhydrous methanol solution as electrolyte. The anodic reaction is shown in equation (4) and cathodic reaction in equation (5). For electrolysis, specimens were machined into cylindrical rods (8–12 mm diameter, ~80 mm length). Electrolysis was conducted at 0–5 °C with current density of 30–60 mA/cm² for 4 hours. After electrolysis, specimens were ultrasonically cleaned, and the electrolyte was collected and vacuum-filtered to separate particles by size, followed by elutriation to obtain size-fractionated secondary phase particles.

Four steel grades were examined, with compositions listed in Table 1 : Al-killed steel (A), Si-killed steel (B), low-carbon steel (C), and high-carbon steel (D).

Steels A and B primarily contained non-metallic inclusions, while steels C and D mainly contained carbonitrides. All specimens were sampled from casting bloom centers. To observe internal structures, the RTO embedding technique was employed: extracted particles were placed on a Cu cathode, with pure Cu as anode. Under applied current, Cu^2 dissolved from the anode and deposited onto the cathode, completely encapsulating particles (reactions shown in equations (6) and (7)). After encapsulation, particles were sectioned using fine abrasive paper for subsequent SEM or FSEM observation, as schematically illustrated in [Figure 3: see original paper].

3.1 Jackson Factor of Common Secondary Phase Particles

[Figure 4: see original paper] presents secondary phase particles extracted from steel B using non-aqueous electrolysis and their morphologies after RTO sectioning. Most inclusions in steel B appear spherical, with some showing internal precipitates after sectioning.

Table 2 lists Jackson factors for typical steel secondary phase particles, with thermodynamic parameters from references [22,23]. Based on values, particles can be classified into three categories: (1) < 2 (e.g., SiO , FeO, MnS) predicted to have smooth spherical or spheroidal non-polyhedral shapes; (2) particles with direction-dependent values that may be either >2 or <2 (e.g., CaF , CaO, TiC, CaSiO), potentially exhibiting faceted or non-faceted morphologies; and (3) particles with > 3 in all growth directions (e.g., Al O , TiN, various calcium aluminates), typically showing polyhedral or irregular shapes.

3.2 Morphologies of Typical Secondary Phase Particles

[Figure 5: see original paper] shows typical morphologies of Al O , MgAl O , and TiN inclusions in steel A, identified by EDS. These three particle types all exhibit faceted morphologies (Figures 5a, c, e). However, Al O and MgAl O sometimes appear spherical or spheroidal (Figures 5b, d), while TiN shows multi-angular gear-like shapes (Figure 5f). Table 2 indicates > 3 for all three phases, predicting faceted morphologies. The apparent discrepancy arises because metallographic methods only reveal a single plane, not the complete three-dimensional morphology.

Figures 6a and b show typical Al O inclusions extracted from steel A, while Figures 6c and d show typical inclusions from steel B. The Al O inclusions display faceted or irregular shapes with different facet orientations (Figures 6a, b). With values of 3.06–6.12 depending on growth direction (all >3), theoretical predictions of faceted morphology agree with observations. Figure 6c shows spherical CaO-SiO -MnO inclusions that were liquid at steelmaking temperatures and thus spherical due to surface tension. While Jackson factor cannot predict amorphous phase morphology, the physical meaning of ΔS suggests that liquid inclusions have completely disordered structures with ΔS 0, yielding minimal values that explain their spherical shapes. Figure 6d reveals numerous short rod-like or granular MnS precipitates on these liquid inclusion surfaces.

[Figure 7: see original paper] presents internal morphologies after RTO embedding and sectioning. Al O inclusions show dense interiors without precipitates (Figures 7a, b), explaining their hardness and deformation resistance. Sectioned spherical CaO-SiO -MnO inclusions contain near-spherical silica-rich phases (primarily SiO) with ellipsoidal or rod-like MnS at their edges (Figures 7c, d). While literature [24,25] reported similar MnS morphologies using metallographic methods, comparison with the three-dimensional morphology in Figure 6d reveals significant differences, demonstrating that two-dimensional observations can be misleading. Table 2 shows values of 0.29–0.58 for SiO and 0.44–0.87 for MnS, predicting non-faceted spherical or ellipsoidal shapes that match experimental observations. Figures 5-7 demonstrate that metallographic samples only reveal single planes, often providing incomplete or misleading information, whereas non-aqueous electrolysis combined with RTO technique clearly reveals three-dimensional morphologies and internal structures.

[Figure 8: see original paper] shows typical nitrides in steel C and carbides in steel D. EDS analysis identified TiN (cubic, Figure 8a) and AlN (Figures 8b, c) as the main secondary phases in steel C. TiN particles exhibit regular hexahedron-like shapes with = 3.15–6.29, consistent with theoretical predictions. AlN shows both faceted (Figure 8b) and smooth ellipsoidal (Figure 8c) morphologies. Limited thermodynamic data exist for AlN; Table 2 lists estimated values (2.62–5.24) based on vaporization enthalpy. AlN' s crystal structure resembles Al O but with significantly lower , suggesting it belongs to the second category described above.

Steel D contains various carbides; our group [26] identified MC, M C, M C, and M C as the main types through XRD. Typical extracted morphologies are shown in Figures 8d–f, revealing diverse shapes including faceted (Figure 8d), smooth short rod-like (Figure 8e), and curved rod-like (Figure 8f) carbides. Carbides have high melting points with scarce thermodynamic data. Table 2 lists TiC (MC) values of 1.38-2.76, placing it in the second category, consistent with observations. Reference [27] reported that H13 hot-work die steel (medium-carbon, ~0.40% C) contains MC, M C , and M C carbides with both faceted and spherical morphologies, confirming the broad applicability of our model.

The Jackson factor definition (equation (2)) indicates that secondary phase particle morphology depends on entropy of fusion, growth direction, and temperature (undercooling), enabling morphology control through regulation of growth direction and precipitation temperature. However, since some particles precipitate in the solid-liquid region or below the solidus line, steel composition and kinetic conditions may also significantly influence morphology, requiring further investigation for non-equilibrium undercooled systems.

Conclusions

(1) Conventional metallographic observation of steel secondary phase particles only reveals a single plane, making it difficult to obtain complete three-dimensional morphology information and sometimes leading to misinterpretation. Non-aqueous solution electrolysis combined with RTO technique enables clear observation of three-dimensional inclusion morphologies and internal structures, providing valuable information unattainable through metallographic methods.

(2) Secondary phase particle morphology in steel is determined by entropy of fusion, growth direction, and temperature (undercooling). The Jackson factor effectively evaluates morphology: particles with > 3 are generally faceted, while those with < 2 exhibit non-faceted spherical or spheroidal shapes. Al O , MgAl O , and TiN show faceted morphologies with direction-dependent variations; SiO and MnS are non-faceted; AlN and carbides may exhibit either faceted or non-faceted morphologies depending on growth direction.

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