Open Research Online

The Open University's repository of research publications and other research outputs

Inclusion agglomeration in electrified molten metal: thermodynamic consideration

Journal Item

How to cite:

Zhao, Z. C. and Qin, R. S. (2017). Inclusion agglomeration in electrified molten metal: thermodynamic consideration. *Materials Science and Technology*, 33(12) pp. 1404–1410.

For guidance on citations see [FAQs](#).

© [not recorded]

<https://creativecommons.org/licenses/by-nc-nd/4.0/>

Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1080/02670836.2016.1270729>

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

oro.open.ac.uk

Inclusion agglomeration in electrified molten metal: thermodynamic consideration

Z.C. Zhao^{1,2} and R.S. Qin^{1,2*}

1. School of Engineering & Innovation, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

2. Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK

Abstract: The effect of electric current on inclusion agglomeration in molten metal has been investigated. It is found that the agglomeration is dependent on the electric current density, distance between inclusions and orientation of electric field. Electric current retards the agglomeration unless two inclusions are aligned along or closely to the current flow streamlines and the distance between inclusions is less than a critical value. The mechanism is also validated in the computation of cluster agglomeration. The numerical results provide a comprehensive indication for the current-induced inclusion removal and current-induced inclusion elongation. When the inclusions are in long thin shape, the calculation predicts the current-induced microstructure alignment and current-induced microstructure refinement phenomena.

Keywords: Molten metal, Inclusion, Agglomeration, Electric current

*Corresponding author, email rongshan.qin@open.ac.uk

Introduction

Many non-metallic inclusions are detrimental to materials mechanical properties such as fatigue life,¹ fracture toughness,² impact resistance and creep resistance.^{3,4} However, they are favourable in fabrication of fine microstructure by providing extra heterogeneous nucleation sites in solidification, solid-state phase transition and recrystallization, e.g. acicular nucleation in steels.⁵ Recently, electric current has been implemented to expel inclusions from molten steel in order to fabricate super clean steel. It is reported that the electric current pulses can push up the cleanliness of steels from $< 20 \mu\text{m}$ ^{6,7} to that of $< 0.7 \mu\text{m}$ ⁸ maximum inclusion's size in molten steel. The experiments were inspired from a numerical calculation which considered only a single inclusion submerged in molten metal and moved perpendicularly to the current flow direction.⁹ The calculation reveals a free energy reduction when an inclusion moves from the inner part of steel to the surface due to the different electrical conductivities between inclusion and the molten steel matrix. Electric current acts as a driving source to expel the lower conductive non-metallic inclusions from the higher conductive metal matrix. Agglomeration was not able to be considered in the single inclusion model. The relative motion, the way of interaction and the configurational evolution among multiple inclusions under electric current processing have not been investigated.

In fact, the electric current processing models based on single inclusion assumption are dominant in literature. For examples, the effect of electric current on alloys nucleation was based on the consideration of a single crystal nucleus to form in an infinite large liquid metal matrix.¹⁰ The effect of electric current on the crack healing was also based on the consideration of a single ellipsoidal crack to shrink in the solid metal matrix.¹¹ The effect of electric current and magnetic field on materials separation considered a single biological cell to move in a plasma blood matrix too.^{12,13} Agglomeration and coalesce¹⁴ under electric

current are important phenomena in materials processing. A model containing multiple inclusions is required to simulate these processes. The aim of the present work was to develop a multi-inclusion model to study the effect of electric current on agglomeration.

Modelling of electric current-assisted materials processing has several different levels of consideration. They are based on the electron-phonon interaction,^{15,16} electron-dislocation interaction,^{17,18} collective motion approximation,^{19,20} thermodynamic consideration,^{21,22} respectively and so on. Experimental investigation has provided very rich evidences on using electric current to affect microstructure,^{23,24} crystallographic texture,^{25,26} workability,^{27,28} and processing environments.^{29,30} In the present work, thermodynamic consideration is implemented to investigate the inclusion agglomeration behaviour under electric current.

Thermodynamic consideration

Inclusions have different electrical resistivity from that of the liquid metal matrix. Motion of inclusions inside the liquid metals causes the change of electric current density distribution. The current density $\vec{j}(r)$ is determined by the local electrical conductivity $\sigma(r)$ and electrical potential gradient $\nabla\phi(r)$ via Ohm's law

$$\vec{j}(r) = -\sigma(r)\nabla\phi(r) \quad (1)$$

where r is a point in three-dimensional space. The electrical potential inside the bulk inclusion (ϕ_i) and matrix (ϕ_m) obeys the followings Laplace equations

$$\Delta\phi_i(r) = 0 \quad (2.1)$$

$$\Delta\phi_m(r) = 0 \quad (2.2)$$

At the inclusion-liquid metal interface, ϕ_i and ϕ_m satisfy the following boundary conditions

$$\phi_i = \phi_m \quad (3.1)$$

$$\sigma_i \nabla_n \phi_i = \sigma_m \nabla_n \phi_m \quad (3.2)$$

where ∇_n represents the normal gradient to the interface. The distribution of electrical potential in the considering space can be obtained by numerical solution of Eqs. (2) and (3). The distribution of electric current density can be obtained by substituting the numerical results for the distribution electrical potential into Eq. (1). The motion of inclusions changes the materials spatial configuration. The electric current distribution for each configuration can be obtained numerically. The electric current free energy corresponding to each configuration can be obtained by following equation²²

$$G_e = -\frac{1}{8\pi} \int_V \int_V \frac{\mu(r') \vec{j}(r') \cdot \vec{j}(r)}{|r - r'|} dr dr' \quad (4)$$

Where μ is the magnetic permeability of the phase. r and r' represent different points in materials. The integration of each point goes throughout the whole system. In agglomeration, the chemical free energy is not changed because the volume fraction of each phase remains a constant value. The change of strain-stress energy can be ignored because stress can be released quickly in liquid matrix. The system free energy contains only the interface free energy and electric current free energy. If one considers only the motion of inclusions toward or away from each other without actual touching or detaching, the total interface area remains and hence the interfacial energy. The electric current free energy is the dominant thermodynamic quantity in this case. An infinite small displacement between two inclusions (δr) can cause current density distribution to change from $\vec{j}$ to $\vec{j}_{\delta r}$. This will cause following free energy change:

$$\delta G_e = \frac{1}{8\pi} \int_V \int_V \frac{\mu(r') \vec{j}(r') \cdot \vec{j}(r) - \mu(r') \vec{j}_{\delta r}(r') \cdot \vec{j}_{\delta r}(r)}{|r - r'|} dr dr' \quad (5)$$

The force to drive the motion of inclusion can be calculated via

$$\vec{F}(r) = -\frac{\delta G_e}{\delta r} \quad (6)$$

It can be seen from Eq.(4)-(6) that the driving force for inclusions' motion and agglomeration is proportional to the square of average electric current density.

Numerical calculations

When the space is discretized into cubic lattice, a lattice is occupied by either α phase (e.g. inclusion) or β phase (e.g. liquid metal). The interface between α and β is supposed to have zero thickness (i.e. classical Stephan approximation) and located at the middle between the neighbouring α and β lattices. This gives the electrical conductivity of an element between lattices α and β as

$$\sigma_{\alpha\beta} = \frac{2\sigma_\alpha\sigma_\beta}{\sigma_\alpha + \sigma_\beta} \quad (7)$$

It can be easily demonstrated that Eq. (7) is also valid when $\alpha=\beta$, which describes the element in bulk phase. The electrical potential is calculated using the relaxation method by iteration of the following expression

$$\phi_\alpha = \sum_{\beta=1}^N \phi_\beta \sigma_{\alpha\beta} / \sum_{\beta=1}^N \sigma_{\alpha\beta} \quad (8)$$

where N is the total numbers of neighbouring lattices. N=6 when the nearest neighbours are considered in three-dimensional space. The electric current density along element $\alpha\beta$ can be obtained from the electrical potential at lattices α and β respectively. The free energy change during the motion of inclusions for a displacement of δr can be obtained by²²

$$\Delta G_e = \frac{1}{8\pi} \sum_\alpha \sum_\gamma \frac{\mu(r_\alpha) \vec{j}(r_\alpha) \cdot \vec{j}(r_\gamma) V_\alpha V_\gamma - \mu(r_\alpha) \vec{j}_{\delta r}(r_\alpha) \cdot \vec{j}_{\delta r}(r_\gamma) V_\alpha V_\gamma}{|r_\alpha - r_\gamma|} \quad (9)$$

where V_α and V_γ are the volume of lattice- α and lattice- γ , respectively.

Results and discussions

Agglomeration behaviour of two inclusions

Figure1. A schematic diagram for the configuration of inclusions and electric potential

A cubic lattice with logistic domain $300 \times 120 \times 11$ is defined to represent the liquid metal matrix and inclusions. The length of each element is 10^{-3} m. The electrical conductivity of liquid metal is $10^5 \Omega^{-1} m^{-1}$ and that of inclusion is $10^2 \Omega^{-1} m^{-1}$. Those values are similar to the electrical conductivities of liquid steel and MnS inclusion, respectively. An electric potential difference of 20 volts is applied horizontally to the left and right sides of the logistic domain. This value is selected to mimic the experimental parameters reported in literatures.^{8-9,28} The average current density across the liquid metal is calculated to be around 6.67×10^6 A/m². Two identical spherical inclusions with radius of 2 mm are introduced into the matrix. A two-dimensional section in the three-dimensional computational logistic domain is illustrated in Fig.1 schematically. The free energy is only meaningful when a reference state is defined. In consideration of two inclusions to move toward each other along a direction perpendicular to the current, the state with $\Delta y = 6$ was set as the reference. In the case when two inclusions move in a direction parallel to the electric current streamline, the state with $\Delta x = 8$ was set as

the reference. The numerical results for the change of electrical current free energy during the inclusions moving toward each other along vertical and horizontal directions are presented in Fig.2(a) and Fig.2(b), respectively.

Figure 2. The change of electric current free energy during the motion of two inclusions: (a) The change of distance Δy along a direction perpendicular to current. (b) The change of distance Δx along the direction parallel to current. The applied voltage is 20 volt. The average current density is calculated to be around 6.67×10^6 A/m².

It can be seen from Fig. 2(a) that the free energy decreases sharply and monotonically when the inclusions move away from each other. In another word, the free energy increases sharply if two inclusions move toward each other for agglomeration. The negative tangent of the free energy change curve gives a positive force according to Eq. (6), which is repulsive. Fig. 2(a) shows that electric current drives inclusions to move away from each other and toward the surface along the direction perpendicular to current. This result agrees with the theoretical prediction and experimental observation of current-induced inclusion removal.⁸⁻⁹ The extra information revealed in the present work is that the inclusion agglomeration along this direction will be retarded by the electric current. Fig. 2(b) shows that the electric current free energy drops very sharply when two inclusions move toward each other when the distance

between them is smaller than a critical value. When the distance between two inclusions is larger than the critical value, inclusions try to move away from each other in order to reduce electric current free energy. This means that electric current promotes the agglomeration when the inclusion population density is higher than a critical value, but retard the agglomeration in other case. In the present case, the critical distance is 36 grids length. It is worth to point out that magnitude of free energy change in Fig. 2(a) is 10 times larger than that of in Fig. 2(b). In general, inclusions might be configured in a direction between the perpendicular and parallel directions to the current, the overall driving force from electric current to agglomeration can be calculated by its components in those two principle orthogonal directions.

Figure 3. A schematic diagram showing the possible microstructure transformations driven by electric current: From (a) to (b) electric current drives inclusions to agglomerate; From (c) to (d) electric current drives long thin inclusions to align along electric field direction; From (e) to (f) electric current drives long thin inclusion to breakup.

In combination of the mechanisms revealed in Fig. 2(a) and 2(b), it can be suggested that for a system containing high population density of inclusions the agglomerate tends to form along the electric field direction but to separate in the perpendicular direction, as illustrated from Fig. 3(a) to 3(b). This is in agreement with the experimental observation of the current-induced orientation of sulphides in medium carbon steel.³¹ For inclusions with long thin shape, electric current may cause alignment along the electric field direction, as illustrated from Fig. 3(c) to 3(d). Such phenomena has been reported in literature.³² There is another possibility if the thin long inclusions are aligned perpendicular to the electric field as illustrated in Fig. 3(e), the inclusion might, if possible, break up and form finer inclusion particles as illustrated in Fig. 3(f). The kinetics for the electric-current-driven structure breakup has been discussed using the interface instability theory.³³ The similar experimental observations were reported in electropulsed low carbon steel, as is shown in Fig. 4, where carbides along the electric field direction are prolonged but that microstructures cross the electric current flow streamlines were broken.³⁴ The local microstructure appears very similar to that of the pearlite. However, the carbide has not been confirmed to be cementite and the crystallographic orientations between carbide and ferrite are not checked if following that of Pitsch-Petch relationship.

Agglomeration behaviour of inclusion clusters

The computation of cluster agglomeration utilizes a cubic lattice with logistic domain $320 \times 128 \times 8$. The total inclusion clusters occupy $32 \times 32 \times 2$ nodes in all the simulations. The rest of the parameters such as the length of each element, electrical conductivity of inclusion and matrix, and the electric potential difference are the same as that in the two inclusions simulation. Fig. 5 illustrates some configurations of inclusion clusters. The change of electric

current free energy during the agglomeration of 16 pieces of thin long clusters into 8, 4, 2 and 1 are calculated for different cases, namely the inter-spaces are 2 mm and 4 mm and the orientations are parallel and perpendicular to the current, respectively.

Figure 4. Electric current drives carbides microstructure to change at ambient temperature.³⁴ (a) the SEM image. (b) and (c) show that carbides are elongated along current. (d) carbides are broken up when electric current cuts the microstructure.

Figure 5. A schematic diagram shows the evolution of inclusion cluster configurations.

Figure 6. The change of electrical free energy when the clusters are agglomerated from 16 pieces to 8, 4, 2 and 1 piece. (a) Agglomeration along a direction perpendicular to current. (b) Agglomeration along a direction parallel to current.

Fig.6 presents the numerical results for the clusters agglomeration. The reference state is chosen as the agglomeration completed. It can be seen from Fig. 6(a) that the cluster agglomeration causes the electric current free energy to increase. From the case of $\Delta y = 4$ to $\Delta y = 2$ the electric free energy increases. This implies that the electric current prevents the clusters from moving toward each other along the direction perpendicular to current. Electric current also retards the clusters agglomeration. Fig. 6(b) shows an opposite behaviour. Electric current enhances the clusters agglomeration and also promotes the clusters to move toward each other. The results are in agreement with that of the two inclusions agglomeration discussed earlier in this work.

Other factors in inclusion agglomeration

This work has focused on the effect of electric current on inclusion agglomeration. There are a few other factors not mentioned in this work. a). The mass density of inclusions is usually different from that of the molten metal. Buoyant force will affect the motion of inclusions and

their clusters. The agglomeration will hence be affected by the mass density difference. b). Stokes flow caused by the motion of inclusions and their clusters will, in turn, affect the motion of suspended inclusions. The agglomeration will be affected by the motion-flow interaction. c). The convection due to temperature difference in the molten alloys will affect the motion of inclusions and their agglomeration. d). New inclusions may form due to oxidation in the high temperature molten metal. e). The melt and inclusions suffer different Lorentz force due to their electric conductivity difference. This may cause additional convection. f). A forced flow may be caused by electric current and its induced magnetic field in melt. These factors will affect inclusion agglomeration on top of to the effect of electric current. We are working toward the integration of those effects by putting the electric current effect to the smoothed particle hydrodynamics model,³⁵ and will publish the results in future.

Conclusions

The electric current free energy has been calculated when two inclusions move toward each other along two orthogonal orbits. One is parallel to and another is perpendicular to the electric current flow direction. In the direction perpendicular to the current, free energy increases when the distance between two inclusions reduces. In the direction parallel to the current, however, there is a critical distance to distinguish the behaviour. Free energy increases when the distance between two inclusions reduces until reach the critical value, then decreases sharply until agglomeration. This implies that the electric current retards the inclusion agglomeration unless the inclusion population density is very high. In that case, thin long inclusion clusters may form and will be aligned with the current flow direction. Numerical calculation on the agglomeration of inclusion clusters confirms the same behaviour. The effect of electric current on inclusion agglomeration is proportional to the

square of electric current density, and is related to the distance between inclusions nonlinearly. The mechanisms revealed in the present work have provided some suggestions for understanding of the inclusion removal, microstructure refinement and alignment that have been reported in literature, and have suggested some new perceptions for liquid metal processing.

Acknowledgements

The work was financially supported by EPSRC (EP/L00030X/1) and the Royal Society Newton Advanced Fellowship (NA150320). The authors are grateful to Prof. Andy Howe for comments and suggestions.

References

1. S. K. Dhua, A. Ray, S. K. Sen, M. S. Prasad, K. B. Mishra and S. Jha: 'Influence of nonmetallic inclusion characteristics on the mechanical properties of rail steel', *J. Mater. Eng. Perform.*, 2000, **9**, 700-709.
2. O.V. Abramov, V. L. Girshov, R. A. Oganyan and A. P. Zuev: 'Effect of residual oxygen and nonmetallic oxide inclusions on the mechanical properties of high-speed steel 10R6M5', *Met. Sci. Heat. Treat.*, 1981, **23**, 563-565.
3. A. Ray, S.K. Paul and S. Jha: 'Effect of inclusions and microstructural characteristics on the mechanical properties and fracture behaviour of a high- strength low- alloy steel', *J. Mater. Eng. Perform.*, 1995, **4**, 679-688.
4. L. F. Zhang and B.G. Thomas: 'Inclusions in continuous casting of steel', XXIV National Steelmaking Symposium, Morelia, Mich, Mexico, 2003, 138-183.
5. J. M. Gregg and H. K. D. H. Bhadeshia: 'Solid-state nucleation of acicular ferrite on minerals added to molten steel', *Acta Mater.*, 1997, **45**, 739-748.

6. D. Apelian, R. Mutharasan and S. Ali: 'Removal of inclusions from steel melts by filtration', *J. Mater. Sci.*, 1985, **20**(10), 3501-3514.
7. X.F. Zheng, P.C. Hayes and H.G. Lee: 'Particle removal from liquid phase using fine gas bubbles', *ISIJ Int.*, 1997, **37**(11), 1091-1097.
8. X.F. Zhang and R.S. Qin: 'Controlled motion of electrically neutral microparticles by pulsed direct current', *Sci Rep.*, 2015, **5**, 10162.
9. X.F. Zhang and R.S. Qin: 'Electric current-driven migration of electrically neutral particles in liquids', *Appl. Phys. Lett.*, 2014, **104**, 114106.
10. R. S. Qin and B. L. Zhou: 'Effect of electric current pulses on grain size in castings' *Int. J. Non-Equilib. Proc.*, 1998, **11**, 77-86.
11. R.S. Qin and S.X. Su: 'Thermodynamics of crack healing under electropulsing' *J. Mater. Res.*, 2002, **17**, 2048-2052.
12. A. Kolin: 'An electromagnetokinetic phenomenon involving migration of neutral particles', *Science*, 1953, **117**, 134-137.
13. H. Watarai, M. Suwa and Y. Iiguni: 'Magnetophoresis and electromagnetophoresis of microparticles in liquids', *Anal. Bioanal. Chem.*, 2004, **378**, 1693-1699.
14. H.X. Jiang, J. He, J.Z. Zhao: 'Influence of electric current pulses on the solidification of Cu-Bi-Sn immiscible alloys', *Sci. Rep.* 2015, **5**, 12680.
15. T. N. Todorov, D. Dundas, E. J. McEniry: 'Nonconservative generalized current-induced forces', *Phys. Rev. B*, 2010, **81**, 075416.
16. T. N. Todorov, J. Hoekstra, A. P. Sutton: 'Current-induced embrittlement of atomic wires', *Phys. Rev. Lett.* 2001, **86**, 3606.
17. P. S. Ho, T. Kwok: 'Electromigration in metals', *Rep. Prog. Phys.*, 1989, **52**, 301-348.
18. O. A. Troitskii: 'Electromechanical effect in metals', *JETP Lett.* (English version), 1969, **10**, 11-14.

19. H. Mizubayashi and S Okuda: ‘Structural relaxation induced by passing electric-current in amorphous $\text{Cu}_{50}\text{Ti}_{50}$ at low-temperatures’, *Phys. Rev. B*, 1989, **40**, 8057-8060.
20. R. Takemoto, M. Nagata and H. Mizubayashi: ‘Effects of passing electric current on the elastic property of amorphous $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{50}\text{Ti}_{50}$ ’, *Acta Mater.*, 1996, **44**, 2787-2795.
21. Y. Dolinsky, T. Elperin: ‘Thermodynamics of nucleation in current-carrying conductors’, *Phys. Rev. B*, 1994, **50**, 52–58.
22. R.S. Qin, A. Bhowmik: ‘Computational thermodynamics in electric current metallurgy’, *Mater. Sci. Technol.*, 2015, **31**, 1560-1563.
23. X. L. Liao, Q. J. Zhai, J. Luo, W. J. Chen, Y. Y. Gong: ‘Refining mechanism of the electric current pulse on the solidification structure of pure aluminum’, *Acta Mater.*, 2007, **55**, 3103-3109.
24. R. S. Qin, E. I. Samuel and A. Bhowmik: ‘Electropulse-induced cementite nanoparticle formation in deformed pearlitic steels’, *J. Mater. Sci.*, 2011, **46**, 2838–2842.
25. G. L. Hu, G. Y. Tang, Y. H. Zhu and C. H. Shek: ‘Electropulsing induced texture evolution in the recrystallization of Fe-3% Si alloy strip’, *Metall. Mater. Trans. A*, 2011, **42**, 3484-3490.
26. X. L. Wang, W. B. Dai, R. Wang, X. Z. Tian and X. Zhao: ‘Enhanced phase transformation and variant selection by electric current pulses in a Cu–Zn alloy’, *J. Mater. Res.*, 2014, **29**, 975-980.
27. M. J. Kim, K. Lee, K. H. Oh, I. S. Choi, H. H. Yu, S. T. Hong, H. H. Han, ‘Electric current-induced annealing during uniaxial tension of aluminum alloy’, *Scripta Mater.*, 2014, **75**, 58-61.
28. W.J. Lu, R.S. Qin: ‘Influence of κ -carbide interface structure on the formability of lightweight steels’, *Mater. Des.*, 2016, **104**, 211–216

29. W.B. Dai, J.K. Yu, C.M. Du, L. Zhang, X. L. Wang: 'Refinement of inclusions in molten steel by electric current pulse', *Mater. Sci. Technol.*, 2015, **31**, 1555-1559.
30. W.B. Dai, X.L. Zhou, X. Yang, G.P. Tang, D.B. Jia, N.L. Cheng, J.K. Yu, 'Formation of dense inclusion buildup on submerged entry nozzle by electric current pulse', *Acta Metall. Sinica-English Lett.*, 2016, **29**, 500-504.
31. X.F. Zhang, W.J. Lu, R.S. Qin, 'Oriented sulphides induced by electric current in medium carbon steel', *Phil. Mag. Lett.*, 2015, **95**, 101-109.
32. A. Rahnama, R.S. Qin: 'Electropulse-induced microstructural evolution in a ferritic–pearlitic 0.14% C steel', *Scr. Mater.* 2015, **96**, 17–20.
33. L. Klinger, L. Levin: 'Interface instability in an electric field', *J. App. Phys.*, 1995, **78**, 1669-1672.
34. A. Rahnama, 'TMPC-property relationship of strong steels', PhD Thesis, Imperial College London, 2015.
35. J. Monaghan, 'Smoothed particle hydrodynamics', *Ann. Rev. Astrono. Astrophys.*, 1992, **30**, 543–574.