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Electrocapillary Phenomena in Material Processing

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Abstract

Formation mechanism of emulsification is being studied by using “electrocapillarity” which had been once developed to study the structure of “electrical-double layer”. First the characteristics of electrocapillary curve of KCl aqueous solution/Hg system used for the cold model have been investigated to understand the ionic structure near the interface in comparison with the case of real (liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ /liquid steel) system. Then the emulsification phenomena at the meniscus(the interface) with and without imposing the electric potential have been observed by using a high speed camera. Finally the mechanisms of newly found phenomena have been discussed by taking account of the theory of electrocapillarity.

Key words : Interfacial tension, Electrocapillarity, Emulsification, Refining, Continuous casting

Introduction

Interfacial phenomena between the ionic liquid(e.g. molten slag and molten flux) and the liquid metal(e.g. molten steel) are closely related both to the refining efficiency and to the cast qualities through the emulsification between two phases at the meniscus. Because the direct observation of the interfacial phenomena of slag/steel system is difficult, various simulation experiments using (1)the water, oil or the other transparent liquid for slag and (2)the mercury or other liquid metal for steel[1,2] have been conventionally performed to propose hypothesis of the emulsification mechanism. However the different properties of the materials for the cold model experiment often gives rise to the erroneous understanding for these phenomena. Applying different materials for cold model also does not allow the quantitative explanation for the effect of the specific property, such as interfacial tension or viscosity, on the meniscus phenomena. This study is first undertaken for more profound comprehension on the meniscus disturbance inducing emulsification by using the electrocapillary method mainly from the view point of interfacial tension. As the first part, the fundamental data, a relationship between the interfacial tension and the imposing electric potential, has been investigated. Then the change of interfacial phenomena by imposing the electric potential has been examined by using a high speed camera to discuss the mechanism of emulsification.

Electrocapillarity of Electrolyte Solution/Liquid Metal System

Review of Conventional Studies

Fig.1 shows the effect of electric potential(ϕ) on the interfacial tension(δ) between slag and liquid iron reported by Esin et al[3]. It shows that δ decreases monotonically with increasing ϕ . This tendency is explained by the simple models, such as Helmholtz model and Gouy-Chapman model[4] shown in Fig.2. According to these models the cation layer on the interface electrically attracted by imposing negative potential to metal decreases the interfacial tension due to the repulsion of the same polarity of ions(cations) in the layer.

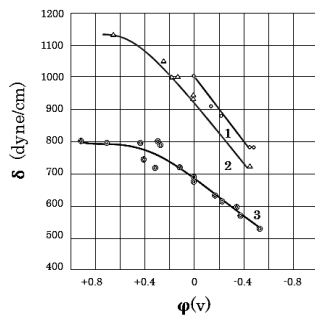


Fig. 1: Electrocapillary curve of Fe-C alloy in molten slag
(1; 2.5% C, 2; 3% C, 3; 4% C-Fe)

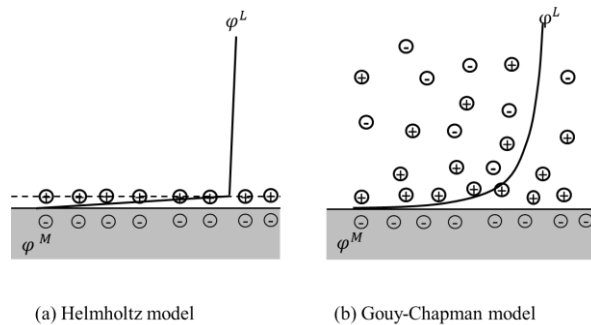


Fig. 2: Two models for the electrical double layer structure

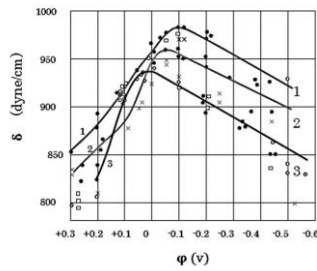


Fig. 3: Electrocapillary curves for iron/CaO-SiO₂-Al₂O₃ system (1;42mol%, 2;44mol%, 3;50mol% CaO)

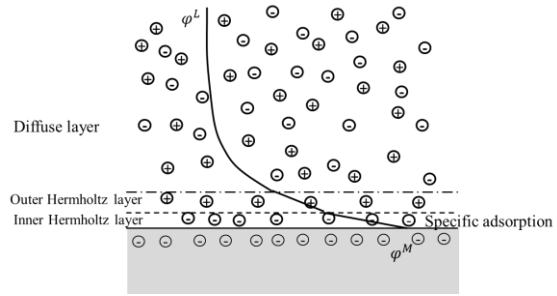


Fig. 4: Grahame's electric double layer model

On the other hand Patrov reported the different results[5] as shown in Fig.3, in which the interfacial tension has a peak near 0v and decreases with increasing the electric potential both by negative and positive imposition. Also it is reported that the chemical composition of slag affects the interfacial tension.

Electrocapillarity of KCl Aqueous Solution/Hg system

Direct observation of the interfacial phenomena at KCl aqueous solution/Hg by using electrocapillarity has been conducted as described in the next chapter. In order to obtain the quantitative data for the electrocapillary characteristics of this system, dependence of interfacial tension on the electric potential has been investigated by using the apparatus as in Fig.5. A droplet of Hg(≈1g) was placed on the horizontal glass plate in the pool of KCl aqueous solution filling the transparent container. Both phases were electrically connected to the potentiostat by fine Pt wires insulated by alumina coating. The imposed electric potentials were in the range of -3V to +3V, and the concentrations of KCl aqueous solution(C_{KCl}) were 0, 0.5, 1.0, 1.5mol/ℓ.

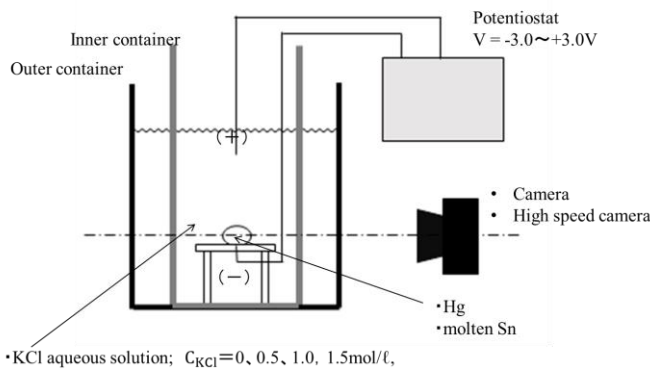


Fig. 5: Experimental apparatus for measurement of Hg droplet shape(interfacial tension) in KCl aqueous solution.

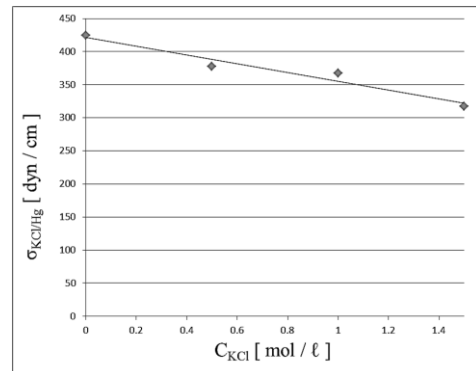


Fig. 6: Effect of KCl concentration on the interfacial tension between KCl aqueous solution and Hg.

Fig.6 represents that the interfacial tension decreases linearly with increasing KCl concentration.

Fig.7 shows the shape of Hg droplet; (a) $\phi=0.8v$, (b) $\phi=1.8v$. The droplet shape becomes flatter by increasing the imposing electric potential.

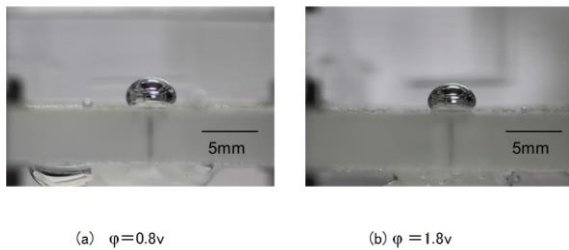


Fig. 7: Effect of imposed electric potential on the shape of Hg droplet.

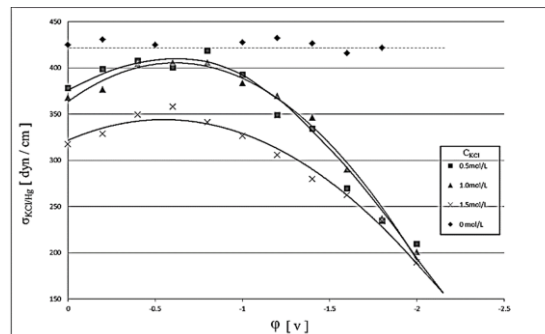


Fig. 8: Effect of imposed electric potential and KCl concentration on the interfacial tension between KCl aqueous solution and Hg droplet.

The effect of imposed electric potential in different concentrations of KCl aqueous solution on the interfacial tension is summarized in Fig.8. In the case of pure water(without KCl) the electric potential has no effect on the interfacial tension, while the electric capillary curves appear in case of KCl electrolyte aqueous solution. The curve has a peak named “ECM; Electrocapillary Maximum” and the electric potential which gives ECM is named “Electric potential for ECM; E_{ecm} ”. The value of ECM seems to be the same when C_{KCl} is below 1mol/l, while it decreases if C_{KCl} is more than 1mol/l. These results also could be explained by the Grahame’s model[6] shown in Fig.4; (i)even in case of no imposition of the electric potential, the specific adsorption layer of anion(Cl^-) decreases the interfacial tension, (ii) increasing the electric potential to E_{ecm} increases the interfacial tension by attracting cation(K^+) outside the specific adsorption layer which neutralizes the effect of cation to increase the interfacial tension up to ECM. Then, (iii)when the electric potential exceeds the E_{ECM} , the accumulated population of cation(K^+) near the interface increases the repulsion force to decrease the interfacial tension again. These tendencies are similar to those of the iron/slag system reported by Patrov.

Effect of Interfacial Tension on The Interfacial Phenomena at KCl Aqueous Solution/Hg System

Experimentals

As one of examples of emulsification phenomena, the generation and the extinction of Hg particles under the imposition of electric potential have been investigated by using the apparatus in Fig.9. 2D-pool of KCl aqueous solution(1 mol/l) and Hg was held in acrylic transparent container. At the center of pool a PVC tube(i.d.=3mm) introduced Ar gas in the Hg pool to generate the emulsion(fine Hg particles). Hg pool was connected to the negative electrode, while the KCl aqueous solution was connected to the positive one of the potentiostat. The meniscus phenomena have been observed by the high speed camera.

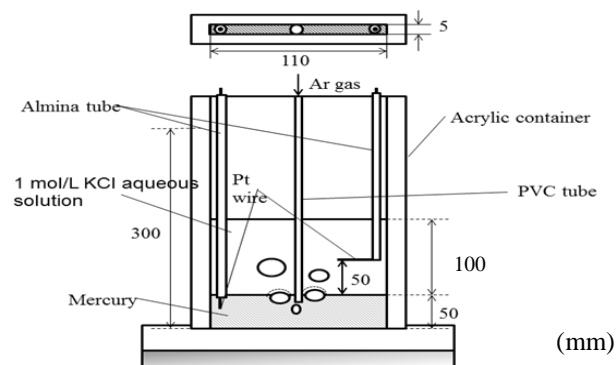


Fig. 9: Experimental apparatus for the observation of interface between KCl aqueous solution and Hg.

Results and Discussions

Fig.10 shows the Hg particles formed on the meniscus of Hg pool by injecting Ar gas at the flow rate of 0.6l /min. They are generated by Ar bubbles coming out to the meniscus. The size of particles distributes from 0.5mm to several mm in diameter. The particles are scarcely combined with the Hg pool in case of no imposition of the electric potential. On the other hand they disappear(combined with Hg pool) at instance just after imposing the electric potential of 2.0v as shown in Fig.11.

It is also noted that the small local convections have been observed at the imposition of electric potential.

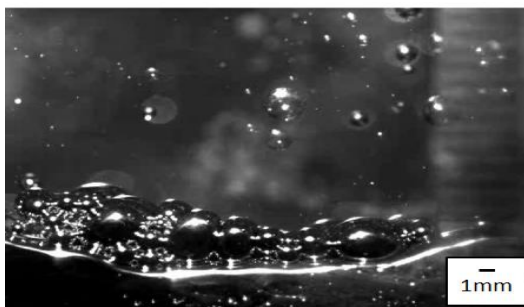


Fig.10: Accumulation of Hg particles generated by gas injection(no imposition of electric potential) .

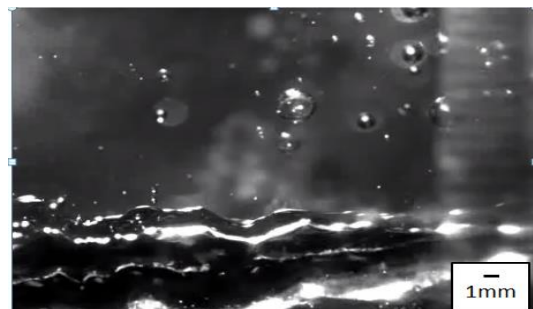


Fig.11: Extinction of Hg particles just after the imposition of electric potential.

Fig.12 proposes the mechanism of behaviour of Hg particles on the meniscus without and with imposing the electric potential. Hg particles formed by injecting Ar gas stay on the meniscus and hardly unite with Hg pool. In KCl aqueous solution Hg particles are covered with the layer of anion(Cl^-) as a specific adsorption layer. Also the meniscus of Hg pool(the interface of Hg and KCl aqueous solution) is covered with a specific adsorption layer of Cl^- ion. A repulsion force between two anion layers prevents combining Hg particles with Hg pool as shown in the upper figure of Fig.12. On the other hand as shown in the lower figure, the imposition of negative electric potential in Hg pool(2v) decreases the interfacial tension at meniscus to help the combine of the particles with the pool. If the difference of interfacial tension between $\langle \blacksquare \rangle$ KCl aqueous solution/Hg meniscus and $\langle \blacktriangle \rangle$ Hg particle/Hg meniscus is dominant, which means the distribution of interfacial tension along meniscus is non-uniform, the local convection flow(Marangoni convection) will be generated. These vigorous local convections observed at the experiment will promote the combination of Hg particles with the Hg pool.

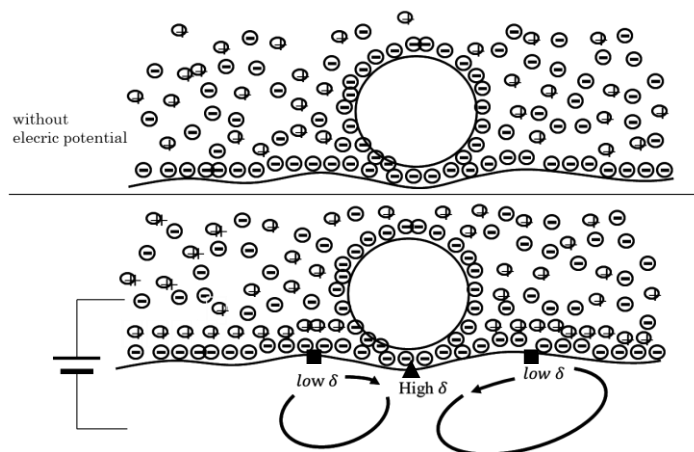


Fig. 12: Proposed mechanism of behaviour of Hg particles on the meniscus without and with imposing the electric potential.

Conclusions

The characteristics of electrocapillary curve of KCl solution/Hg system has been investigated to understand the ionic structure near interface in comparison with the case of liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ /liquid steel system. The mechanism of behavior of Hg particles at the meniscus has been then investigated with “electrocapillary method” by using a potentiostat and a high speed camera. It is proposed that the specific adsorption layer prevents the involvement of particle formed by Ar injection into the meniscus, while the electric potential decreases the interfacial tension in a non-uniform manner to cause a micro-local marangoni convection to take these particles into the lower phase(Hg) through the meniscus.

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