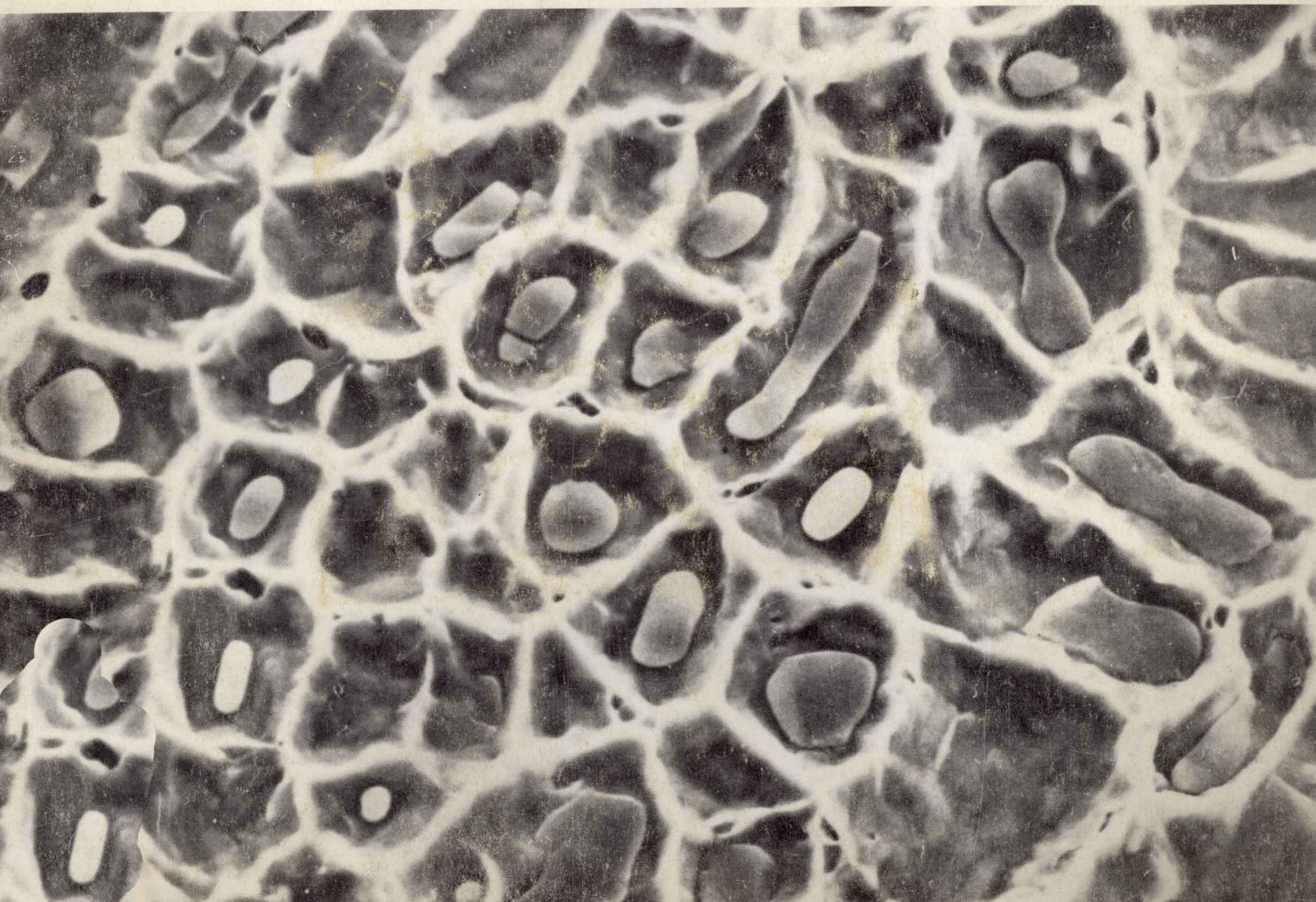
THE METALLURGICAL SOCIETY OF CIM
Iron and Steel and Materials Engineering Sections

SECOND INTERNATIONAL SYMPOSIUM ON THE EFFECTS AND CONTROL OF INCLUSIONS AND RESIDUALS IN STEELS

August 17 - 20, 1986

25th Annual Conference of Metallurgists

TORONTO '86



PROCEEDINGS

INTERNATIONAL SYMPOSIUM ON THE CONTROL AND EFFECTS OF INCLUSIONS AND RESIDUALS IN STEELS

A Symposium sponsored by the Iron and Steel, and the Engineering Sections of theMetallurgical Society of CIM

SYMPOSIUM COMMITTEE

J.D. Boyd, CANMET (Chairman)

D.A.R. Kay, McMaster University

D. McCutcheon, Stelco Inc.

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FOREWORD

These Proceedings contain the papers which will be presented at the symposium on "Effects and Control of Inclusions and Residuals in Steel", held in conjunction with the 25th Annual Conference of Metallurgists in Toronto, August, 1986. The symposium is sponsored by the Iron and Steel and Materials Engineering Sections of the Metallurgical Society of the CIM.

The proceedings comprise 20 papers which deal with the fundamentals of inclusion/ residual control in steel processing, techniques for characterizing inclusions and the effects of inclusions on various properties. It is evident that our understanding of the phenomena in all these areas is advancing rapidly.

As Symposium Chairman, I wish to acknowledge the significant efforts of the other members of the Organizing Committee, Alan Kay and Dennis McCutcheon, who represent the Iron and Steel and Materials Engineering Sections, respectively. We sincerely thank all the authors who contributed their good works, and thus made this symposium possible.

We extend a warm welcome to all symposium participants, especially those of you who have travelled from afar. It is our wish that you will have a technically stimulating meeting and a pleasant stay in Toronto.

J.D. Boyd
Symposium Chairman
August 5, 1986

International Symposium on Effects and Control of Inclusions and Residuals in Steels

PROGRAMME

MONDAY, AUGUST 18, A.M. PIER 4

8:55 – WELCOME
J.C. McKay, Chairman, Canadian Steel Industry Research Association

SESSION I – Control of Inclusions

Chairman - G.A. Irons, McMaster University, Hamilton, Ontario.

9:00 – Paper I-1 (3.1)
"The Effect of Water Vapour on the Rate of Oxygen Transfer Across a CaO-Al_2O_3-SiO_2 Slag"
K.G. Leewis, Technical University of Nova Scotia.

Oxygen transfer is limited by the rate of electron transport through ionic slags. Reducing this constraint allows the rate of oxygen transfer to increase by two to ten orders of magnitude. To date this has been achieved by providing either an external electrical path around or through the slag, or by the addition of metallic impurities such as iron. This work demonstrated that just the saturation of the reacting gases with water vapour doubles the rate of oxygen transfer across the model industrial slag into the liquid metal bath. An electrochemical mechanism is proposed and the industrial implications of this enhanced coupling of oxygen and hydrogen transfer are discussed.

9:30 – Paper I-2 (3.2)
"The Morphologies of Inclusions in LCAK Steels and Their Effects on the Active Oxygen Content"
G.R. Fitterer, Scientific Applications, Inc., Oakmont, Pa.

The scanning electron microscope and the oxygen probe have combined to cast new light on the theories regarding the deoxidation of steel with aluminum.

The SEM has revealed the true nature of the inclusions. Not only are alumina and hercynite formed, but also large highly oxidized liquid inclusions, containing as much as 77% of FeO, are present in steels, which contain more than 200 ppm of active oxygen-prior to deoxidation.

A meta-stable equilibrium is established between these inclusions and the residual aluminum, thus resulting in higher dissolved oxygen contents than generally believed.

10:00 – Paper I-3 (3.3)
"Inclusions in Calcium-Treated Steels"
S.V. Subramanian and D.A.R. Kay, McMaster University, Hamilton, Ontario.

The evolution of steel and inclusion chemistry in the calcium treatment of medium carbon, aluminum killed steels is related to a thermodynamic data base for the Ca-Al-S-O system.

10:30 - 10:45 – Break

10:45 – Paper I-4 (3.4)
"On-Line Inclusion Detection and Measurement in a Transformer Steel"
S. Kuyucak and R.I.L. Guthrie, McGill University, Montreal, Quebec.

A technique for the direct measurement of the number density, and size distribution of inclusions in molten metals, with particular reference to low melting point steel melts is described. Its principle of operation rests on establishing an electrical sensing zone through which inclusions pass for counting and sizing. The probe construction and testing, as well as data for inductively stirred melts of a low m.p. steel alloy are presented. Since measurements are made on a volume basis, as opposed to a surface examination, its implications with respect to statistical accuracy vis a vis surface analysis techniques are considered.

11:15 – Paper I-5 (3.5)
"New Configurations in Tundishes for Continuously Cast Steel Slabs"
K. Vo Thanh, Sidbec-Dosco Inc., and M. Rigaud, Ecole Polytechnique, Montreal, Quebec.

Present work was undertaken to optimize the tundish configurations for continuously cast steel slabs, through water modelling studies. The design criteria were selected to prevent vortex formation, to maximize the minimum residence time, and to minimize the dead volume in tundishes. Pertinent results will be presented stressing how a better separation of non-metallic inclusions during casting could be achieved through the appropriate modifications of tundishes, in use today.

11:45 – Paper I-6 (3.6)
"The Formation of Calcium-Containing Inclusions in Steels Melted by ESR"
A Mitchell, University of British Columbia, Vancouver, B.C., and F. Reyes-Carmona, National University of Mexico, Mexico City, Mexico.

The cast steel electrodes for ESR processing are not normally obtained from calcium-treatment processes, but instead ESR is expected to produce the desired level of sulphur removal and also of inclusion control. In this work, we examine the case of an aerospace low-alloy high-strength forging steel (SAE 434O) in respect to the formation of calcium aluminates and calcium sulphide during ESR using Al, or calcium silicide deoxidation; no deoxidation and an argon atmosphere, and using a series of slags with varying chemical activities of CaO, Al_2O_3 and SiO_2.

We conclude that the inclusion compositions are predictable, and hence controllable, on the basis of known slag thermochemistry; but also that the oxygen potential imposed by the deoxidation technique is a limiting factor in establishing the inclusion CaO/Al_2O_3 ratio. We also discuss the role of the calcium/aluminum ratio in establishing the inclusion removal mechanism and also in influencing the final ingot's inclusion size distribution. With the correct melting practice in this regard it is shown that this steel can be made by ESR to higher cleanness standards than by the VAR process and is, therefore, acceptable for aerospace uses with respect to inclusion-controlled properties.

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SESSION II – Control and Effect of Residuals

Chairman – D.A.R. Kay, McMaster University, Hamilton, Ontario

14:00 – Paper II-1 (11.1)
"Control of Residual Elements in EAF Steelmaking with Midrex Iron"
G.G. Carinci and J.A. Lepinski and B.G. True, Midrex Corporation, Charlotte, N.C.

There have been numerous innovations developed for electric arc furnace steelmaking during the last 30 years. By reducing costs, these innovations have stimulated the growth of EAF steelmaking throughout the world. To a great extent, the further growth of the EAF route will be tied to the market demand for higher quality products rather than to continued improvements in steelmaking economy.

As a result of slag-free tapping and ladle metallurgy, significant quality improvements have been realized in the areas of sulfur and phosphorus reduction, deoxidation and nitrogen, hydrogen and inclusion control.

However, EAF steelmakers worldwide are facing a new quality challenge - control of residual elements. This paper evaluates the various methods of controlling residual elements and explains why the use of MIDREX Iron is the most effective method available.

14:30 – Paper II-2 (11.2)
"Control of Residual Elements and Inclusions by Plasma Coupled Induction Furnace Refining"
F.L. Kemeny, I.D. Sommerville, A. McLean, University of Toronto, Toronto, Ontario.

The combination of plasma and induction heating provides many unique advantages in the refining of steel. The inductive stirring aids in the contact of slag with metal, thereby enhancing reactions and fluxing inclusions. The plasma provides both top heating to maintain a fluid and reactive slag, and atmosphere control through the choice of arc stabilizing gas.

In this work, 5 Kg steel melts were refined in a 25 KW induction furnace equipped with a 20 KW plasma electrode. The graphite plasma electrode could be operated as a D.C. cathode, a D.C. anode, or an A.C. electrode. The control of nitrogen, sulphur and oxygen contents was investigated and the results are compared to other refining processes.

15:00 – Paper II-3 (11.3)
"Tramp Element Control with Lanthanide (Rare Earth Metal) Additions to Alloy Steel"
C.I. Garcia, M.G. Burke, A.J. DeArdo, University of Pittsburgh, Pittsburgh, Pa., and G.A. Ratz, Molycorp. Inc.

It is generally accepted that temper embrittlement in alloy steels results from the combined effect of impurities (such as P, As, Sn and Sb) segregating to prior austenite grain boundaries. Temper embrittlement is manifested by a shift in the ductile to brittle transition temperature of alloy steels to higher temperatures.

Scavenger elements, such as the lanthanides (rare earth metals), combine with these impurity elements thus preventing their segregation to grain boundaries. This study was undertaken to assess the influence of lanthanides as a way to minimize temper embrittlement in 2 1/4% Cr - 1% Mo steels. Special effort was made in comparing the effects of combined lanthanide additions as mischmetal or as individual lanthanide elements such as cerium, lanthanum and neodymium. The analytical technniques employed include transmission electron microscopy (TEM), STEM-EDS quantitative microanalysis of thin-foil and carbon-extraction replica specimens and atom probe field-ion microscopy (APFIM).

TUESDAY, AUGUST 19, A.M. PIER 4

SESSION III – Inclusion Characterization

Chairman - J.D. Boyd, CANMET, Ottawa, Ontario.

9:00 – Paper III-1 (18.1)
"Microscopical Characterization and Finite Element Method Analysis of Residual Inclusions in Carbon Steels"
F. Gordoninejad, R.G. Reddy and S.D. Cromwell, University of Nevada Reno, Reno, Nevada.

Residual inclusions in industrial carbon steel samples of calcium-treated, continuous-cast, rolled products of rods and plates were characterized using scanning electron microscope. SEM and Edax analysis showed that the residual inclusions in the rods are of endogenous type. More massive segregation of calcium-manganese-silicate inclusions is observed close to the surface than the center of the steel plates and rods. Effect of these residual inclusions on physical properties of carbon steel using finite element analysis of steel and oxide inclusions was studied. The effect of Poission's ratio on stress distribution around inclusions in different location of the plate was considered. Numerical results for the stress and displacement distribution around the inclusions, and the whole plate are presented. The practical implications of the results are discussed.

9:30 – Paper III-2 (18.2)
"Assessment of Non-Metallic Inclusions in Steels by Automatic Image Analysis"
M.T. Shehata and J.D. Boyd, CANMET, Ottawa, Ontario

Software-based image analysis systems with facilities for pattern recognition and image amending can produce a more complete assessment of non-metallic inclusions in steels than manual methods. In addition to rapid determinations of volume fractions of different types of inclusions, their complete distributions of size, shape and spacings can be obtained. it is shown that such quantitative information is necessary to determine the effects of inclusions on various properties of steels. Examples are given of inclusion assessments which illustrate the effects of inclusions on the toughness of weld metal, hydrogen-induced cracking of line-pipe steels, machinability of free-machining steels and wear properties of rail steels.

10:00 – Paper III-3 (18.3)
"Sulphide Inclusions in Ti-Bearing Steels"
W.J. Lui, S. Yue and J.J. Jonas, McGill University, Montreal, Quebec

The morphological and chemical compositional variations of sulphide inclusions in a series of hot-rolled, Ti bearing steels containing 0.05, 0.11, 0.18 and 0.25% Ti were investigated by microscopical and microanalytical techniques. The results indicated that the inclusions were modified to Mn-Ti sulphides, the Mn-Ti ratios of which varies with the Mn-Ti ratio of the alloy, although their chemical compositions were by no means homogeneous. It was also observed that, as the Mn-Ti ratio decreased, the elongation of the inclusions in the as hot-rolled plates also decreased, the inclusions remaining essentially undeformed below a certain Mn-Ti ratio.

10:30 - 10:45 – Break

10:45 – Paper III-4 (18.4)
"Inclusions and Machinability"
S.V. Subramanian and D.A.R. Kay, McMaster University, Hamilton, Ontario.

Chips formed during the machining of low and medium carbon steels over a wide range of cutting speeds exhibit ductile fracture. The concept of cumulative damage to fracture is used to rationalize the behaviour of these steels in metal cutting. The influence of calcium deoxidation and microalloying additions is discussed in the context of high productivity machining.

11:15 – Paper III-5 (18.5)
"The Effect of MnS Inclusions in AISI 1215 Free-Machining Steels on Shear Band Formation under High Strain Rate Torsional Tests"
H. Yaguchi, Inland Steel Co., East Chicago, IN, K.A. Hartley, Bell Laboratories, Holmdel, NJ, J. Duffy and R.H. Hawley, Brown University

High strain rate torsional tests were carried out in a torsional Kolsky bar to investigate shear band formation in three AISI 1215 low-carbon resulfurized free-machining steels having different sulfide inclusion morphology and machinability. Formation of multiple shear bands was observed in one of the steels, but not in the other two. The steel that formed multiple bands was the one with the highest inclusion aspect ratio and the poorest machinability. The fractography reveals a large number of deep holes containing sulfide inclusion fragments in the steel with multiple bands. In the other two, only shallow dimples and shattered inclusions were observed. Different behaviours of shear band formation and fractography are discussed in terms of the relative hardness of the sulfide inclusions.

11:45 - Paper III-6 (18.6)
"The Influence of Inclusion Shape on the Hot Ductility of Steels"
D.N. Crowther, British Steel Corp., Sheffield Laboratories, and B. Mintz, The City University, London, England

It is well established for plate steel with elongated MnS inclusions that the reduction of area values obtained in tensile tests at room temperature are dependent on the position the tensile samples are taken from in the plate. Through thickness R. of A. values are often very low and transversely tested samples generally have slightly lower R. of A. values than samples taken from the plate in the rolling direction.

The present work was carried out in order to establish whether similar trends exist when plate is tensile tested in the temperature range 600 to 1100°C. Hot rolled plates of a C-Mn-Al and C-Mn-Nb-Al steel containing elongated MnS inclusions were tensile tested in this temperature range in both the rolling and transverse directions at a strain rate of 3×10^{-4} sec^{-1}. Transversely tested samples gave inferior hot ductility compared to longitudinal samples. Modification of the sulphides by calcium treatment removed this difference.

TUESDAY, AUGUST 19, P.M. PIER 4

Session IV – Effect of Inclusions on Properties

Chairman – D. McCutcheon, Stelco Inc., Hamilton, Ontario.

14:00 – Paper IV-1 (26.1)
"The Role of Inclusions on Steel Properties: A New Approach"
F. Moussy and C. Quennevat, IRSID, St. Germain en Laye, France.

The influence of inclusions on various mechanical properties of steels is quite well known, but the physical mechanisms are not always understood. In the last years, the attention was focused on the behaviour of holes initiated on inclusions. A damage concept and damage mechanics were established. In this paper, we present some results obtained by using two specific experimental techniques: density change measurements and ion beam polishing. We observe that:

– Often, an "initial damage" initiates on second phase particles. It is due to the hot or cold working and so pre-exists before final cold working operations.
– The growth of holes depends on the initial cavity shape and stress state.
– Coalescence and fracture involve locally a second submicroscopical damage, revealed only by using the ion polishing.

These considerations are elaborated with the use of two modern techniques. They contribute to a better comprehension of cold forming operations. Fatigue and toughness behaviour will also be qualitatively explained.

14:30 – Paper IV-2 (26.4)
"Effects of AOD Refining Upon Inclusions and Mechanical Properties of Low Alloy Steel"
L.J. Hagerty, Union Carbide Corp., Tarrytown, NY, R.J. Andrieni and S. Yaguchi, Earle M. Jorgensen Co., Seattle, Washington.

The effects of AOD processing upon inclusions and mechanical properties in low alloy steel forgings at Jorgensen Steel is reviewed. The vigorous mixing with lime based slags provided by AOD results in excellent desulphurization and a high degree of oxide shape control. The ability to desulfurize to below 30 ppm sulphur virtually eliminates manganese sulphide inclusions. Oxide inclusions are modified by residual calcium and are small and widely dispersed in the forged product. The amount, distribution and shape of the non-metallics result in near- isotropic mechanical properties.

15:00 – Paper IV-3 (26.5)
"The Influence of Inclusions on the Formability of D & I Tinplate"
T. Waram and D.J. Harris, Stelco Inc., Hamilton, Ontario.

Steel cleanness is of prime importance for the successful manufacture of drawn and ironed (D&I) beverage cans. Large inclusions present in D&I tinplate sheets can be used to estimate the inclusion content of D&I coils, and therefore, predict their forming behaviour in the can plant.

Analysis of these inclusions allowed prediction of their source during the continuous casting operation. This led to the development of a clean steel practice which significantly reduced the main inclusion types causing defects in the finished product.

15:30 – 15:45 – Break

15:45 – Paper IV-5 (26.6)
"The Effect of Deoxidation and Innoculation Practice on the Fracture Toughness of an As-cast Alloy Steel"
Z. Meka, D.T. Baddeley and K.D. Lakeland, Queensland Institute of Technology, Brisbane, Australia.

An alloy steel based on IN646, was deoxidized and innoculated using three separate treatments. The amounts of aluminum, rare earths, FeTi and CaSiMn, as well as the addition sequence were varied. Test specimens were tempered at three different temperatures after receiving the same homogenizing and normalizing heat treatment. The Double Torsion test method was used to determine the fracture toughness of the as-cast plates. Deoxidation and innoculation procedure, as well as tempering temperature, produced a significant effect on the fracture toughness.

16:15 – Paper IV-6 (26.7)
"The Effect of Innoculants on the Mechanical Properties of As-Cast Mild Steel"
A.H. Downing, A.B. Michael, D.T. Baddeley and K.D. Lakeland, Queensland Institute of Technology, Brisbane, Australia.

A series of commercial heats of mild steel were innoculated after deoxidizing with aluminum. Innoculants used included compounds containing Ce, SiMn and Ca. The results were compared to AS2074-C3. Normalized and as-cast specimens met the mechanical property requirements, with the exception of the Charpy impact values for as-cast heats. However, those heats treated with Ca or Ce compounds, had 21°C Charpy values of 25J and 30J respectively as-cast. As-cast microstructures generally contained both blocky and acicular ferrite, with the latter appearing to have nucleated at higher temperatures. Work is continuing to determine any effects of inclusion type, distribution, etc., on the nucleation and morphology of ferrite microstructures. The aim is to produce castings for use without subsequent heat treatment, and to improve the inherent as-cast ductility of large steel castings.

SESSION I

CONTROL OF INCLUSIONS

Chairman: G.A. Irons

Department of Materials Science and Engineering
McMaster University, Hamilton, Ontario, Canada

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CONTENTS (continued)

THE EFFECT OF WATER VAPOUR ON THE RATE OF OF OXYGEN TRANSFER ACROSS A $CaO-Al_2O_3-SiO_2$ SLAG

J. Speelman and K.G. Leewis

Technical University of Nova Scotia
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Abstract: - Oxygen transfer is limited by the rate of electron transport through ionic slags; reducing this constraint allows the rate of oxygen transfer to increase by two to ten orders of magnitude. To date this has been achieved by providing either an external electrical path around or through the slag. This work provides evidence that the rate of oxygen transfer is also significantly increased by the addition of water vapour to the furnace atmosphere. An electrochemical mechanism for this enhanced rate is proposed, and the industrial implications of the coupling of oxygen and hydrogen transfer are discussed.

INTRODUCTION

The object of this experimental series was to investigate the effect of water vapour on the rate of transfer of oxygen across a lime-alumina-silica slag. In general the limit to such transfer in ionic slags is the transport of electrons from one electroneutral surface to the other ie. from the slag-metal interface to the gas-slag interface (1). Recently, Sasabe demonstrated that the addition of 0.2 wt.% of Fe_2O_3 raised the rate of oxygen transfer across a lime-silica-alumina slag by ten orders of magnitude (10^{-18} to 10^{-8} moles of O_2/cm^2 sec.) (2). The increase in oxygen transfer was directly related to the increased current flow through an electrical circuit.

External circuits have been used by Caley (3), Winnecki (4), and others (5,6) to confirm that the current passed was equal to the number of moles of oxygen ions transferred between the gas and metal interfaces. The classic external circuit was described by Wagner (7) in his explanation of Ramachandran and King's (8) classic work on electroneutral interfaces.

Internal electrical short circuits to enhance oxygen transfer have also been used by Caley (3), Ilschner-Gensch (5), Pal (6), and Leewis (9). The first three used systems that produced liquid oxidation or corrosion products while Leewis had SO_2, as the oxidation product. In each of these systems the oxygen uptake was essentially the formation of oxide corrosion products. However, the rate of oxygen transfer was limited by the gas kinetics at the slag-gas interface and not by the formation of the oxidation product, although the nucleation of a gas phase product in the work of Leewis et al (1) required a considerable supersaturation of oxygen dissolved in the liquid silver matte.

These internal electrical short circuits were caused by the insertion of either platinum or iridium wires and foils. This was a parallel technique to Sasabe's addition of iron oxide for the purpose of changing the slag from a fully ionic medium to a semiconducting electrolyte (2).

For the present work the silver-sulphide originally used by Leewis et al was replaced by pure carbon (10). The carbon provided the oxygen sink while pure oxygen, rather than carbon dioxide provided the source, both were separated by the lime-alumina-silica slag acting as the electrolyte. Unlike systems that produce solid or liquid oxidation products where the slag remains quiescent, the formation and perculation of a gas product through the slag adds to the transport of oxygen by the mechanism of mechanical stirring. Thus one would expect that diffusion gradients were reduced by gas bubbling.

Gas evolution in similar systems has been described by Gosh and King (11), Schenck (12) as well as the author (1). Their observations confirmed that the spike evolution and slow decay typical of both the gas analysis curves and the electromotive potential plots did indeed indicate the nucleation and growth of a gaseous reaction product below the slag electrolyte.

Method

The apparatus used has been described previously (9,10). Briefly 7 gms of slag (50% CaO, 43% SiO_2, 7% SiO_2) and approximately 1 gm of spectrographically pure carbon as a disk 1.2 cm in diameter and 0.3 cm tall were placed in a

99.8% Al_2O_3 crucible (16 cm x 3.0 cm). A notched alumina rod wedged the graphite into the bottom of the crucible and prevented it from floating. This assembly was located inside a sealed 30 mm diameter alumina tube. The oxygen or carbon dioxide was saturated with water vapour by bubbling through distilled water at room temperature before being passed through an ice water bath to condense out the excess moisture. The gas mixtures were jetted onto the slag surface from a height of 30 mm and at a flow rate of 45 ml/min. Finally the reaction products were lead from the closed system to a calibrated infared analyser located adjacent to the furnace.

Results

Background values are given in figure 1, where % CO_2 is presented as a function of time. There was no attempt to provide an electrical path between the carbon and the slag/gas interface, and no evolution of CO_2 with the system under argon was noticed. After oxygen was introduced, the characteristic peaks of CO_2 evolution were observed, with the rate of CO_2 evolution peaking steadily at 0.14%. After three hours the gas flow was diverted to saturate the oxygen with water vapour at 0^oC. At this point the rate of CO_2 evolution doubled, rising steadily to 0.28% until replaced by dry oxygen two hours later. The evolution of CO_2 returned to previous values once dry oxygen replaced the water saturated oxygen.

A typical result using a platinum foil to enhance electron transfer from the graphite to the slag gas interface is presented as figure 2. To ensure good electrical contact with the graphite, the foil was inserted into a groove before melting and was sufficiently tall to extend above the slag-gas interface. Under argon there was essentially no oxygen transfer. However introduction of oxygen to replace the argon resulted in a dramatic increase in the rate of oxygen transfer. During this period the CO_2 evolution was regular, peaking to 0.8%. The introduction of water saturated oxygen at 0^oC again increased the evolution of CO_2, with the peaks increasing to almost 1.0%. The rate of CO_2 evolution as measured by comparing the areas under the curves was approximately doubled.

Similar results were obtained at three other electrode geometries and in all cases the CO_2 evolution doubled. These results are plotted in figure 3. As before, the reaction was controlled by the gas-phase-kinetics at the slag-gas interface, the critical parameter being the perimeter of the metallic conductor providing the short circuit between the carbon and the gas-slag-conductor interface.

As a comparison to previous work, one experiment was done using silver sulphide and CO_2. The SO_2 evolution was measured and is presented as figure 4. The evolution of SO_2 followed the typical curve established in the earlier work (1,9) with periodic peaks and a large SO_2 evolution. The introduction of water saturated carbon monoxide doubled the rate of SO_2 evolution, ie. A vs. B. These two points are plotted in figure 3. The experiment (point A) duplicated the original results within experimental error.

DISCUSSION

The formation of the CO_2 reaction product was explained using the following model (10):

$$O_2 + 4e^- = 2O^= \qquad - 1$$

$$2O^= = 2O^* + 4e^- \qquad - 2$$

Pure oxygen in the presence of the electrons released in equation 2 entered the slag as oxide ions. These oxide ions migrate from the gas-slag interface at the high oxygen potential, to the carbon surface at the low oxygen potential. Since oxygen cannot dissolve in the solid graphite, the formation of an activated species was suggested accompanied by the release of four electrons. The electrons were conducted through the platinum to the site of reaction 1 at the perimeter of the metal electrode. Supersaturation of O^* drives

$$2O^* + 2C = 2CO \qquad - 3$$
$$2CO + O_2 = 2CO_2 \qquad - 4$$

the nucleation and growth of carbon monoxide ie. reaction 3. After perculating through the slag, the CO oxidizes in reaction 4 to CO_2. Thus for every mole of O_2 transferred across the slag one mole of CO_2 was observed and four electrons were transferred along the platinum electrode. This rate of oxygen transfer was shown in Figure 3 as the dashed line. The dependence on electrode perimeter at the gas-slag interface reconfirmed that the rate limiting step was the availability of electrons.

The present work has been summarized as the solid line in figure 3 where the experimental conditions remained identical except for this addition of water vapour. Figures 1 and 2 showed typical dramatic increases observed in the CO_2 concentration for this change. The following model offers an explanation for the increase of oxygen transfer from 0.66×10^{-7} to 1.32×10^{-7} moles O_2/cm^2 = sec cm of perimeter.