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FACTORS CONTROLLING WETTING OF MAGNESIUM OXIDE BY SILICATE LIQUIDS

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Ilhan Arif Aksay
(M.S. Thesis)
March 1969

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FACTORS CONTROLLING WETTING OF MAGNESIUM OXIDE
BY SILICATE LIQUIDS

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REFERENCES
FACTORS CONTROLLING WETTING OF MAGNESIUM OXIDE BY SILICATE LIQUIDS

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ABSTRACT

March 1969

The effect of Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂ additions on the solid-liquid interfacial energy of the magnesium oxide-monticellite (CaO-MgO-SiO₂) system has been studied. The thermodynamic equilibrium of the magnesium oxide-monticellite system is disturbed with R₂O₃ and TiO₂ additions to the liquid. At the liquid-solid interface, reactions occur in order to achieve an equilibrium composition. The degree of wetting is directly proportional to the magnitude of (-) ΔG of this interface reaction. Therefore, the reported contact angles are the steady state angles of a transient reaction stage.

The contact angle of the monticellite liquid on the (100) face of MgO single crystal was in the range of 43-51° at 1550°C. With additions of Al₂O₃ and Fe₂O₃, the angle decreased to a value of 35° and 15°, respectively. Spreading was obtained with Cr₂O₃ and TiO₂ additions.
I. INTRODUCTION

The need for improved refractories is felt in various industries where operating temperatures are constantly increasing. At the present, especially in the steel making industry, the choice of refractories is very limited. The refractory lining of a furnace has to be resistant to chemical attacks by slags. It also has to be rigid enough to hold the furnace structure together without slumping. Magnesite and chromemagnesite refractories have been known, through experience, to meet these requirements. During the last decade, an extensive research has been directed to this area in order to understand and consequently to improve the properties of an already promising system.

The high temperature strength of a material in the presence of a liquid phase is determined by the distribution of this liquid phase between the solid particles.\textsuperscript{1,2} This liquid can either wet the solid particles and form a film around them or stay in isolated pockets when the liquid does not wet the solid. In a compact the distribution of the liquid is indicated by the "dihedral angles,"\textsuperscript{3} shown schematically in Fig. 1(b). At equilibrium, the balance between the solid-liquid interfacial tensions and the grain boundary tension is determined by

\[ s\gamma_s = 2 s\gamma_l \cos(\phi/2) \]  

where \( s\gamma_s \) = solid-solid interfacial or grain boundary energy, \( s\gamma_l \) = solid-liquid interfacial energy, and \( \phi \) = dihedral angle between solid-liquid, measured through the liquid.
Fig. 1a. Equilibrium of forces acting on the periphery of an acute contact angle.

\[(s\gamma_s - s\gamma_l) = 2\gamma_q \cos \theta\]

Fig. 1b. Equilibrium between a grain boundary and two equivalent solid-liquid interphase boundaries.

\[s\gamma_s = 2(s\gamma_l \cos \phi/2)\]
Contact angle measurements with sessile drop experiments also provide useful information on the solid-liquid interfacial energy relative to the solid and liquid surface energies. Under equilibrium conditions, the contact angle, shown in Fig. 1(a), is determined by Young's equation

\[(s \gamma_g - s \gamma_l) = \gamma_g \cos \theta \]  

(2)

where \(s \gamma_g\) = solid-gas surface energy, and

\(\theta\) = contact angle, measured through the liquid phase.

An acute contact angle indicates that the driving force for forming an interface is the lowering of the solid surface energy by the liquid. This force, equal to \((s \gamma_g - s \gamma_l)\), manifests itself as a horizontal force acting on the periphery of the drop. A low contact angle is usually a good indication that the liquid will wet the solid grains in a compact. The final equilibrium distribution of the phases, however, is still determined by the dihedral angle.

The chrome ore used in the production of chrome-magnesite refractories is primarily a solid solution of MgFe₂O₄, MgCr₂O₄, and MgAl₂O₄ spinels. Chrome grains along with periclase grains constitute the solid phases of these refractories in the presence of a calcium, magnesium silicate liquid. The composition of this liquid is best represented by its CaO/SiO₂ ratio. In a periclase-monticellite (CaO⋅MgO⋅SiO₂) model system, the effect of Cr₂O₃, Fe₂O₃, Al₂O₃, and TiO₂ additives on the dihedral angle between the periclase grains has recently been determined.⁴,⁵ The results obtained from this model system have been quite helpful in understanding the role of spinels introduced into a chrome-magnesite system with chrome ore.
The goal of this study is to determine the effect of $\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, and $\text{TiO}_2$ on the solid-liquid interfacial energy of the same periclase-monticellite system. It is hoped that the results of this study will also bring about a greater understanding of the role of interfaces in the development of microstructure.
II. LITERATURE SURVEY

A. Surface and Interface Phenomena

The techniques of measuring surface and interfacial energies at elevated temperatures and the difficulties connected with these techniques have been discussed by Kingery and Humenik, and Kozakévitch. Sessile drop experiments were generally preferred.

Halden and Kingery have studied the liquid iron-Al₂O₃ system with sessile drop experiments in vacuum at 1570°C. The S, O, N, and C additives to the liquid iron were found to adsorb at the surface, and the surface activity decreased in the order: \( S > O > N > C \). Carbon seemed to react with \( \text{Al}_2\text{O}_3 \) at the interface which resulted in a drop in the interfacial energy. The liquid nickel-Al₂O₃ system has been studied by Kurkjian and Kingery with sessile drop experiments at 1475°C. Sn, In, Cr, and Ti were used as additives. Among these additives, only tin and indium changed the surface tension due to adsorption at the surface. Titanium and chromium concentrated at the interface and lowered the interfacial energy. Allen and Kingery have determined surface and interfacial energies in various metal-ceramic systems. The metals used were Fe, Cu, Ni, Co, Sn, Fe-C, Co-C, and Ni-C, and the substrates were \( \text{Al}_2\text{O}_3 \), \( \text{Si}_3\text{N}_4 \), MoSi₂, and SiC.

The understanding of chemical reactions at the interface has been emphasized by Kingery as a major task for the fabrication of cermet bodies. Economos and Kingery have investigated the interfacial reactions in metal oxide systems at elevated temperatures and classified them under four groups: (a) formation of a new phase at the interface, (b) corrosion of the oxide by the metal, (c) penetration along the grain.
boundaries and diffusion into the bulk, and (c) no physical alteration at
the interface. Humenik and Kingery have determined surface tensions
and work of adhesion in metal-ceramic systems with sessile drop experi-
ments. They found that the wetting tendency and work of adhesion were
increased whenever interfacial reactions occurred. The increase in the
wetting tendency and work of adhesion was attributed to a decrease in the
interfacial energy caused by a change in the composition of the metal at
the interface. The wettability and work of adhesion were also found to
increase with low surface tension of the metal and high metal-oxide bond
strength. Furthermore, Kingery has determined the interfacial and sur-
face energies of the Ni-Al$_2$O$_3$, Ni-ZrO$_2$, and Fe-Al$_2$O$_3$ systems. In the
Fe-Al$_2$O$_3$ system, with small additions of Si to Fe, chemisorption of Si at
the interface was explained on the basis of a greater stability of Si-O
bonds as compared to Fe-O bonds.

Armstrong, et al. have performed sessile drop experiments with
(Ni-Ti) and (Ni-Cr) alloys on Al$_2$O$_3$ at 1500°C. In the (Ni-Ti)-Al$_2$O$_3
system, the interfacial energy decreased approximately 600 ergs/cm$^2$ when
the Ti content of the alloy was increased from 0.2 to 2.0%. In the
(Ni-Cr)-Al$_2$O$_3$ system, this drop in the interfacial energy was about 750
ergs/cm$^2$ when the Cr content was increased from 1 to 10%. In each case
the drop in the interfacial energy was due to the selective adsorption of
Ti and Cr atoms at the interface where in the (Ni-Ti)-Al$_2$O$_3$ system the
formation of α-Ti$_2$O$_3$, and in the (Ni-Cr)-Al$_2$O$_3$ system only the diffusion
of Cr into Al$_2$O$_3$ were observed. Armstrong, et al. have also studied
interface reactions in SiO$_2$-refractory metal (Ta, V, Nb and Mo) systems
at 1650°C and in MgO-Fe alloy systems at 1550°C. In the SiO$_2$-refractory
metal systems, the metals reacted with SiO₂ to form metal oxides at the interface. The changes in the interfacial energies could not be determined due to the irregularities in the shape of the sessile drops. Similar oxide formation reactions were evident in the MgO-Fe alloy systems in vacuum. The dissociation of MgO, followed by the oxidation of iron, resulted in reduction of the liquid surface tension and the solid-liquid interfacial energy. Further reduction of the solid-liquid interfacial energy was observed in air when complete oxidation of Fe took place to form FeO. They pointed out that the system in vacuum was at pseudo-equilibrium since the oxidation of Fe was dependent upon other rate controlling steps. However, in air firing, the oxidation was rapid, and the true equilibrium state was attained immediately.

Kozakévitch⁷ has shown that when a CaO·Al₂O₃·SiO₂ slag is in contact with iron containing 0.7% sulfur at 1500°C, the interfacial energy drops from 800 ergs/cm² to less than 5 ergs/cm² and then increases back to 800 ergs/cm². He argued that this sudden drop of the interfacial energy was due to the diffusion of Fe⁴⁺ S⁻ units (or couples) through the interface since the lowering of the interfacial energy due to a pure adsorption process could probably not account for such a drastic effect.

The effect of interface reactions on interfacial energy in the Cu-Al₂O₃ system has been studied by Chaklader, et al.⁸ At 1230°C, with CuO additions to Cu, a decrease in the contact angle resulted due to CuAlO₂ formation at the interface. In air, complete wetting was obtained.

On metal-glass bonding, Pask and Fulrath¹⁰ proposed a theory which states that chemical bonding at the interface occurs when there is a balance of bond energies across the transition zone between metal and
glass which occurs when the phases at the interface are saturated with the metal oxide. This concept was later discussed by Pask in more detail. Pask and Borom further pursued this theory on glass-metal bonding. They concluded that if the thermodynamic equilibrium does not exist at the interface, then a driving force exists for reactions at the interface to achieve such an equilibrium, the success of which is dependent upon the kinetics of the reactions. This analysis provides an explanation for the pseudoequilibrium conditions discussed by Armstrong, et al. 

B. Distribution of a Liquid Relative to Solids

The principles governing the spatial distribution of a liquid phase in a polyphase system were first established by Smith. He showed that the spatial distribution of the liquid phase relative to solids depends only on the equilibrium dihedral angle. When $\phi < 60^\circ$, the liquid extends along the grain edges; when $\phi = 0^\circ$ the liquid extends along the grain faces; when $\phi > 60^\circ$ but $< 120^\circ$ the liquid is at the grain corners, and finally, when $\phi > 120^\circ$, there is no liquid present. The application of these principles in ceramic systems has been illustrated by Van Vlack and White.

In the $\text{SiO}_2$-iron oxide system Van Vlack has shown that $\text{SiO}_2$ grains maintain a solid-solid contact at elevated temperatures and the oxidizing character of the atmosphere does not have any noticeable effect on the dihedral angle. The microstructure of magnesioferrite in the presence of a liquid phase containing $\text{MgO}$, $\text{FeO}$, and $\text{SiO}_2$ has also been studied by Van Vlack and Rieger. Contrary to the $\text{SiO}_2$-iron oxide system, the degree of solid-solid contact was quite poor in this system. However, in the presence of a second solid phase, $\text{FeAl}_2\text{O}_4$, $\text{FeFe}_2\text{O}_4$, or $\text{MgFe}_2\text{O}_4$, the degree of contact between the grains improved. These spinel-type phases
formed bridges between the magnesiowustite grains, which they interpreted as a lower interfacial energy between unlike solid phases than that between two identical phases.

Riegger, et al.\textsuperscript{25} have shown that in MgO-liquid systems, under the steel-making variables, a calcium silicate liquid penetrates between the periclase grains more than calcium ferrite and calcium aluminoferrite liquids. They have further suggested two factors for this contrast between the silicate liquids and the ferrite liquids: (a) a solid-liquid interfacial energy is low when the composition of the liquid is closer to that of the solid, and (b) adjustments at the boundaries in atomistic scale are more permissible in open atomic packing than in close atomic packing. The composition of silicate liquids is closer to that of periclase than the composition of ferrite liquids since the solubility of MgO is relatively high in the former liquids. Furthermore, the open framework of silicates would form a relatively low energy interface with the periclase grains. The formation of low energy grain boundaries between unlike grains was again observed in this study in the presence of a second solid phase.

Riegger, et al., and Van Vlack and Madden\textsuperscript{26} have also studied the growth of solid phases in the above systems. They concluded that the presence of a second solid phase inhibits grain growth, and the growth is proportional to the square root of firing time.

Buist, et al.,\textsuperscript{27} and Stephenson and White\textsuperscript{28} have performed similar grain growth experiments in one solid+liquid and two solids+liquid systems. Grain growth was inhibited with the presence of a second solid phase which was in agreement with the observations of Riegger, et al.,
and Van Vlack and Madden. However, they found that the grain growth was proportional to the one third power of the firing time which differed from the former investigators' results.

A study of the factors controlling bonding in the periclase refractories has been performed by Jackson, et al., and Jackson and Ford. In a periclase-monticellite system Cr₂O₃, Fe₂O₃, Al₂O₃, and TiO₂ were used as additives. It was concluded from these studies that among these additives only Cr₂O₃ additions increased the dihedral angle, promoted the degree of direct bonding between the solids, diminished the firing shrinkage, and inhibited grain growth of the periclase grains. Fe₂O₃, Al₂O₃, and TiO₂ additions were found to have a reverse effect on these properties. The appearance of a spinel phase was found to promote the degree of direct bonding since the spinel-periclase interfacial energy was low, and the spinel precipitates tended to form bridges between the periclase grains. Furthermore, as the CaO/SiO₂ ratio of the liquid was increased from 0.5 to 2.0 both the dihedral angle and the degree of solid-solid bonding increased.

C. Physical Properties in the Presence of a Liquid Phase

1. At Elevated Temperatures

The high temperature tensile strength of chrome-magnesite refractories has been investigated in the temperature range of 1290-1575°C by Ford, et al. They showed that the tensile strength improved progressively as the extent of the direct bonding between the magnesite grains and between the chrome and magnesite increased. They also mentioned a temporary gap formation between the chrome and the periclase grains which could be due to either migration of the silicate liquid between the grains.
at an intermediate stage or to the diffusion of iron oxide and chromic oxide from the chrome grain to the periclase.

Baker and Schroth\textsuperscript{29} have reported that in chrome-magnesite and magnesia refractories the grain boundary spinel bond and the fused grain bond which is basically a spinel bond at the MgO solid-solid grain boundaries are the most effective ones for attaining high temperature strength.

In silica refractories the existence of a high strength at elevated temperatures has also been attributed, by Van Vlack,\textsuperscript{2} to the formation of a solid skeleton between silica grains.

Kriek and Segal\textsuperscript{30} have determined the high temperature strength of chrome-magnesite and magnesite refractories with torsion technique in the temperature range of 1300-1500\degree C. The lowest strength of the magnesite refractories corresponded to a CaO/SiO\textsubscript{2} ratio of 1.0. With a CaO/SiO\textsubscript{2} ratio of 2.0, the maximum strength was obtained which was higher than the strength of the direct bonded chrome-magnesite refractory. Thus, they concluded that in the achievement of high temperature strength the nature of the liquid phase is also as important as the direct bond formation of the chrome-magnesite refractories.

Hayhurst and Laming,\textsuperscript{31,32} in heat treatment studies of the chrome-magnesite refractories, have shown that in the temperature range of 1500-1700\degree C the silicate liquid generally surrounds the solid grains. The direct bond which is observed at room temperature studies, therefore, is a result of precipitation during slow cooling in production. They observed that upon slow cooling, spinel and forsterite precipitated out between the periclase grains and formed an interlocked structure. The
observations of Konopicky\textsuperscript{33} were also in agreement with these studies.

As indicated by Ford, et al. earlier, a gap containing a thin film of silicate was also observed by Hayhurst and Laming between a chrome grain and periclase envelope surrounding it. Recently, Brezny and Smutny\textsuperscript{34} have shown that this gap, which hinders the direct bond formation, is due to the rapid diffusion of iron cations from chrome grains to periclase grains to achieve an equilibrium structure. They showed that by adding Fe\textsubscript{2}O\textsubscript{3} into the periclase grains, thus reducing the iron concentration gradient between the chrome and the periclase grains, the rate of direct bond formation could be increased.

2. At Low Temperatures

In cermet systems, Humenik and Parikh,\textsuperscript{35} and Parikh and Humenik\textsuperscript{36} have shown that the presence of a continuous liquid film between the solid grains is desirable for achieving improved mechanical properties at low temperatures. A continuous liquid film which is undesirable at high temperatures was found to improve the hardness and impact resistance of titanium carbide base cerments upon solidification.

D. Sessile Drop Experiments in the MgO-Monticellite System

Raju and Pask\textsuperscript{37} have recently initiated a program in order to understand the fundamental factors involved in the distribution of silicate liquids in multiphase magnesia and forsterite (Mg\textsubscript{2}Si\textsubscript{O\textsubscript{4}}) systems. As part of this program, they determined the contact angle of monticellite on (100) faces of MgO single crystals at 1550°C. The contact angle for the MgO-monticellite system was 45°. They have also investigated the effect of Cr\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} additions to the liquid on the contact angle. Spreading of the liquid was observed with Cr\textsubscript{2}O\textsubscript{3} additions in excess of 3%. 
The contact angle decreased to a constant value of 15° with Fe₂O₃ additions in excess of 3%. It was proposed that in each case a reaction taking place at the interface could contribute to the lowering of the contact angle. The nature of these reactions, however, was not clearly understood.
III. EXPERIMENTAL PROCEDURE

The experimental procedure, in short, consisted of measuring the contact angles of premelted liquids on (100) faces of magnesium oxide single crystals and then studying the polished cross sections of the interface with an optical microscope and an electron microprobe analyzer.

The liquids were prepared with reagent grade MgO, CaCO₃, SiO₂ and additive oxide Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂ powders. The chemical analyses of these powders are given in the appendix. The batches were dry mixed and melted in platinum crucibles in air, at temperatures approximately 25-75° higher than the subsequent test temperature.

The magnesium oxide single crystals were obtained from the Muscle Shoals Electrochemical Corporation.* The spectrographic analysis of an average sample is given in the appendix. Substrates of approximately 1/2" x 1/2" and 1/8" thick were cleaved from approximately 1" x 1" x 1" single crystal boules. First, these substrates were polished in boiling H₃PO₄ acid before the sessile drop experiments. Later this step was omitted since the same results could be obtained with experiments repeated on freshly cleaved substrates cleaned with ethanol.

Two types of furnaces were used: (a) a gas/air fired Bickley model 2150 furnace, for temperatures higher than 1550°C, and (b) a quench type furnace with MoSi₂ heating elements. The Bickley furnace was monitored and controlled by a Honeywell-Radiamatic recorder-controller. The quench furnace was monitored and controlled by a Leeds and Northrup Speedomax-H recorder-controller. A sketch of the quench furnace has been given by Blank.33

*P.O. Box 87, Tuscumbia, Alabama
The sessile drop experiments were performed at 1550°C in air. Some experiments, which will be discussed in the following sections, were performed at 1700°C. A small piece of premelted liquid was placed on a MgO single crystal which was covered with either a platinum or magnesia crucible to prevent any contamination from the furnace. The specimens were held at the test temperature for approximately 3 hours. Firings for shorter (1 hour) or longer (up to 5 hours) periods did not alter the results. Subsequently, the power was shut off, and the specimens were cooled in the furnace.

Contact angles were measured at room temperature using a telescope equipped with a filar-micrometer eyepiece. This apparatus has been described by Brennan. The specimens were then cut with a diamond saw perpendicular to the interface, polished, and were subjected to metallographic examination. The polishing was done on 1, 1/0, 2/0 and 3/0 emery papers followed with a short polishing step with 0.3μ Al₂O₃ on a lap.

The electron microprobe analyses were done on the same specimens. Carbon was vacuum-deposited, and the portions around the interface were coated with a slurry of carbon in ethanol in order to improve the surface conductivity. The areas of interest were scanned with an electron beam of 20KV and a specimen current of approximately 0.03μA, and the excited Kα x-radiations were counted with spectrometers. The oscilloscope traces of the relative intensities were then used to analyze the specimens semi-quantitatively.

*Analyzer was a Materials Analysis Company model 400 type.
IV. RESULTS AND DISCUSSION

A. Contact Angle Measurements

The results of the sessile drop experiments which show the effect of Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂ additions to monticellite at 1550°C are shown in Fig. 2. The measurements which are indicated with solid marks are those of Raju and Pask. The contact angle of the monticellite liquid without any additions on MgO was found to be in the range of 43-51°. A photomicrograph of the cross section of a typical monticellite-periclase interface is shown in Fig. 3. The average 47° angle of the monticellite-periclase system decreased to a constant value of 35° with addition of more than 5% Al₂O₃ to the liquid. The decrease of contact angle was more pronounced with Fe₂O₃ (15°) and Cr₂O₃ (0°, spreading) additions. Again, the angles became constant after about 3% R₂O₃ addition. Spreading was observed with 30% TiO₂ addition although the sample with 5% TiO₂ had a contact angle of 16°.

Table I. Wetting of MgO by Cr₂O₃ Containing Silicate Liquids

<table>
<thead>
<tr>
<th>Drop Composition</th>
<th>Test Temp. (°C)</th>
<th>Time at Temp. (hrs.)</th>
<th>Contact Angle</th>
</tr>
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<tbody>
<tr>
<td>4% MgCr₂O₄ + 96% CaO·MgO·SiO₂</td>
<td>1550</td>
<td>3</td>
<td>16-18°</td>
</tr>
<tr>
<td>&quot;</td>
<td>1700</td>
<td>4</td>
<td>15°</td>
</tr>
<tr>
<td>20% Cr₂O₃ + 40% MgO + 40% CaO·SiO₂</td>
<td>1700</td>
<td>3</td>
<td>Spreading</td>
</tr>
</tbody>
</table>

In Table I, the results of the experiments with Cr₂O₃ containing liquid compositions other than the ones shown in Fig. 2 are given. The
Fig. 2. Effect of $R_2O_3$ and $TiO_2$ additions to monticellite on contact angle after 3 hours at 1550°C.
Fig. 3  Photomicrograph of the cross section of a monticellite sessile drop on magnesium oxide, held 3 hours at 1550°C.
experiment with 4% MgCr$_2$O$_4$ addition to the monticellite was performed both at 1550° and 1700°C which showed finite contact angles of 16-18° and 15°, respectively. The experiments with 20% Cr$_2$O$_3$, however, could only be performed at 1700°C since a minute amount of liquid formed below this temperature. Spreading was observed in this latter experiment.

In sessile drop experiments the adsorption of additives either at the solid-liquid interface or the liquid surface has an important effect on the equilibrium value of the contact angle. The observations of Halden and Kingery, and Kingery on the liquid iron-Al$_2$O$_3$ system when S, O, N, or C adsorbed at the surface and when Si adsorbed at the interface were good illustrations of the adsorption phenomenon. Similarly, Kurkjian and Kingery illustrated the effect of adsorption on the contact angle in the liquid nickel-Al$_2$O$_3$ system when Sn and In adsorbed at the surface and Cr and Ti adsorbed at the interface.

On the other hand, if the liquid drop and the solid are not at a thermodynamic equilibrium, a redistribution of the components between the liquid and the solid will take place. An equilibrium contact angle will form only after this thermodynamic equilibrium is achieved. The phenomena which would occur during this transient redistribution or the reaction stage, however, are not clearly understood. In metal-ceramic systems, the wetting tendency increased whenever interfacial reactions occurred, according to Humenik and Kingery. They concluded that this increase in the wetting tendency was due to a decrease in the interfacial energy caused by a composition change at the interface. The lowering of the interfacial energy in the metal-ceramic systems studied by Armstrong, et al., and Chaklader, et al. was attributed to the formation of a
stable phase at the interface. Finally, the drastic drop observed by Kozakévitch in the interfacial energy of the CaO-Al₂O₃-SiO₂-iron system was attributed to the diffusion of Fe²⁺ S²⁻ units through the interface.

In the monticellite-periclase system of this investigation, monticellite itself is at a chemical equilibrium with MgO at 1550°C, by a slight precipitation of MgO in the liquid, according to the phase diagram drawn by Osborn and Muan. However, with the addition of Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂, this equilibrium will be disturbed, and the liquid and the substrate will react to attain a thermodynamic equilibrium. An examination of the equilibrium phase diagrams corresponding to these systems will lead to the understanding of the nature of these reactions.

B. Phase Diagrams

In the literature, sufficient data were available to construct the equilibrium phase diagrams of the R₂O₃-MgO-CaO-SiO₂ systems. The work of the author was merely to make use of these data in order to draw the diagrams presented in the following sections.

1. The Al₂O₃-MgO-CaO-SiO₂ System

The Al₂O₃-MgO-CaO-SiO₂ equilibrium diagram is shown in Fig. 4. The details of the MgO-Al₂O₃ joint of this system are from the work of Roy, et al., and of Alper, et al. The details of the MgO-CaO-SiO₂ joint and the Al₂O₃-CaO-SiO₂ edge are from the diagrams drawn by Osborn and Muan. On the MgO-CaO-SiO₂ joint the compounds CaO·MgO·SiO₂ and 2CaO·MgO·2SiO₂ are represented as CMS and C₂MS₂, respectively. El-Shahat and White have recently worked on the MgO·Al₂O₃-CMS joint, and their results have been found to be essentially in agreement with an earlier work by Osborn, et al. This latter work was used to complete the rest
Fig. 4. $\text{Al}_2\text{O}_3$-$\text{MgO}$-$\text{CaO}$-$\text{SiO}_2$ equilibrium phase diagram.
of the diagram.

The overall compositions of the drops used in this study varied along the dash line connecting Al₂O₃ to CMS. An approximate 1550°C isotherm is shown with long dash lines in the spinel and periclase primary fields. When additions of up to 10% Al₂O₃ are made to CMS at 1550°C, the liquid is at equilibrium not with pure MgO, but with a MgO-Al₂O₃ solid solution. Thus, when this liquid is in contact with a MgO substrate, it will react with the substrate to form an equilibrium solid solution structure. With additions in excess of 10% Al₂O₃, the liquid becomes deficient in MgO. The liquid will then dissolve MgO from the substrate to reach an equilibrium composition along the 1550°C isotherm. If the Al₂O₃ content of the drop is high enough to saturate the liquid with respect to MgO-Al₂O₃ (spinel), the nature of the interface reactions becomes more complicated since the liquid might now also react with the substrate to form spinel.

During cooling, the liquid drop probably behaves independently due to fairly rapid cooling rates (~50°C/min.). After passing through the peritectic point "J", the last portion of the liquid should freeze at the eutectic point, at 1390°C, where only the spinel, monticellite, and melilite phases would be present under equilibrium conditions.

2. The Cr₂O₃-MgO-CaO-SiO₂ System

The Cr₂O₃-MgO-CaO-SiO₂ equilibrium diagram is shown in Fig. 5. The MgO-Cr₂O₃ joint of this system has been determined by Alper, et al., and Wilde and Rees. The Cr₂O₃-CaO-SiO₂ edge is from the work of Glasser and Osborn. El-Shahat and White's work on the MgO-Cr₂O₃-CaO-MgO-SiO₂ joint has provided all the information needed for this study. Although Ford and Rees showed that MgO-Cr₂O₃ joins to both
Fig. 5. Cr$_2$O$_3$-MgO-CaO-SiO$_2$ equilibrium phase diagram.
2CaO·MgO·2SiO₂ and CaO·SiO₂, the details of the rest of the diagram still remain to be determined. Again, the behavior of the liquid and the nature of the reactions between the liquid and the substrate are the same as those in the Al₂O₃-MgO-CaO·SiO₂ system. The main difference is that here only a small amount of Cr₂O₃ is needed to saturate the liquid with respect to MgO·Cr₂O₃.

3. The Fe₂O₃-FeO-MgO-CaO·SiO₂ System

The Fe₂O₃-MgO-CaO·SiO₂ system is somewhat more complicated than the former ones since, with the loss of oxygen, Fe₂O₃ dissociates in the FeO direction. In this case, therefore, one actually deals with a quaternary system. An attempt has been made to draw this system as shown in Fig. 6 after an original quaternary drawing of El-Shahat and White.⁴⁴ The MgO-Fe₂O₃-FeO section of the diagram is from a recent work of Willshee and White.⁴⁹ The MgFe₂O₄-CMS joint has been investigated by El-Shahat and White. Although Berezhnoi⁴⁰ has determined that MgFe₂O₄ joins to both 2CaO·MgO·2SiO₂ and CaO·SiO₂, the details of these joints have yet to be determined.

In this system, for example, any composition along the dash line between Fe₂O₃ and CMS at room temperature will correspond to some other composition at high temperatures in the plane outlined by the dash lines and Fe₂O₃-FeO axis. The liquid at point "a" will be at equilibrium with a magnesiowustite solid solution as given by the upper border of the MgO-D magnesiowustite solid solution field. It will also be at equilibrium with a MgFe₂O₄ spinel solid solution as given by the line MgFe₂O₄-E-Fe₃O₄. The liquids corresponding to a point on the liquidus passing through MgO, L, a, and J will be at equilibrium only with a magnesiowustite solid solution.
Fig. 6. $\text{Fe}_2\text{O}_3$-$\text{FeO}$-$\text{MgO}$-$\text{CaO}$-$\text{SiO}_2$ equilibrium phase diagram.
wustite solid solution. The liquidus passing through Fe₃O₄, L, a, and J will contain liquids which will be at equilibrium only with a spinel solid solution. The behavior of the liquid drops on MgO and the nature of the interface reactions will again be similar to those of the previous systems.

4. The MgO-R₂O₃ Solid Solutions

In Fig. 7, the MgO-R₂O₃ solid solution portions of the MgO-R₂O₃ binary systems are superimposed for a direct comparison of the solid solubility limits. The MgO-Al₂O₃ and MgO-Cr₂O₃ sections are from the diagrams drawn by Alper, et al., and the MgO-Fe₂O₃ section is from the diagram drawn by Willshee and White. At elevated temperatures, the MgO-Fe₂O₃ system indicated here is not a binary system but a projection of the MgO-Fe₂O₃-FeO ternary system on the MgO-Fe₂O₃ axis. At 1550°C, the solid solubility limits are 9% and 50% of Cr₂O₃ and Fe₂O₃(-FeO), respectively, and almost 0% of Al₂O₃ in MgO. Thus, at this temperature, when a drop containing Fe₂O₃ is placed on a MgO substrate, most of the iron will diffuse into the MgO. Since the mass of the drop is smaller than that of the substrate, the drop will never have enough iron to saturate both the liquid and the substrate. At equilibrium the system will always be undersaturated. However, with Al₂O₃ and Cr₂O₃ additions, one could expect to attain the saturation of the whole system if enough R₂O₃ is added to the liquid initially.

5. The TiO₂-MgO-CaO·SiO₂ System

Sufficient data are not available in the literature to construct a ternary diagram similar to those given above. According to Berezhnoi,
Fig. 7. MgO-R$_2$O$_3$ solid solution regions of the MgO-MgCr$_2$O$_4$, MgO-MgAl$_2$O$_4$, and MgO-MgFe$_2$O$_4$ systems.
with 5% TiO₂ addition to CaO·MgO·SiO₂, the overall drop composition would be inside the CaO·TiO₂-2CaO·MgO·2SiO₂-CaO·MgO·SiO₂-2MgO·SiO₂ composition tetrahedron. Thus, any of these solids can coexist in equilibrium with the liquid portion of the drop. Due to the incongruent melting of CaO·MgO·SiO₂ one would expect the MgO primary field to extend into this composition tetrahedron. Then, at temperatures above the peritectic reaction temperature, MgO can also coexist in equilibrium with the liquid. The peritectic temperature of the MgO-CMS system is 1502°C (Fig. 4).

This temperature would be lowered below 1502°C when TiO₂ is added to the system. Therefore, since the 1550°C test temperature of this investigation would be above the peritectic temperature, any liquid placed on the MgO substrate would either be in or at the boundary of the MgO primary field after equilibrium is achieved. If the liquid composition is outside this primary field initially, it will dissolve MgO from the substrate surface to attain this equilibrium composition. With 30% TiO₂ addition to CaO·MgO·SiO₂, the first liquid to form would definitely be outside the MgO primary field since the overall drop composition is now in another composition tetrahedron, and the MgO primary field would not extend into this tetrahedron. According to Berezhnoi's diagram, this new composition tetrahedron would be CaO·TiO₂-CaO·MgO·2SiO₂-2CaO·MgO·2SiO₂-2MgO·SiO₂.

TiO₂ and MgO react to form the compounds 2MgO·TiO₂, MgO·TiO₂, and MgO·2TiO₂ as shown in the MgO-TiO₂ equilibrium phase diagrams of Massazza and Sirchia,⁴⁰ and Coughanour and DeProsse.⁴⁰g No solid solution of TiO₂ in MgO is indicated in these diagrams. Alper⁴¹ points out that Ti⁺, which is the stable state in an air atmosphere, is very insoluble
in MgO even at high temperatures. Thus, only a negligible amount of TiO$_2$ in the liquid may react with the substrate to form a solid solution. Furthermore, at the liquid-solid interface, there would be no compound formation since the primary fields of the compounds indicated above are not in the composition tetrahedrons.

C. Optical Microscope and Electron Microprobe Studies

The optical microscope and electron microprobe studies were in agreement with the equilibrium diagrams presented in the previous section. Although all of the samples were examined, only the typical examples of various combinations will be discussed to avoid repetition.

1. Al$_2$O$_3$-MgO-CaO·SiO$_2$ System

In Fig. 8, the interface of the sample with an original drop composition of 1% Al$_2$O$_3$ + 99% CMS is shown. At 1550°C, the liquid portion of the drop is in the MgO primary field. Thus, the only interaction between the liquid and the substrate is the formation of MgO-Al$_2$O$_3$ solid solution at the interface. According to the equilibrium phase diagram, at room temperature the drop will contain spinel, monticellite, and melilite but no periclase. However, since the cooling rates are fast, a non-equilibrium structure is frozen in. The oscilloscope trace of the same sample is shown in Fig. 9 where the white areas indicate the presence of the corresponding element. In the liquid only the MgO particles containing a high magnesium concentration and some aluminum in solid solution can be identified distinctly. The MgO which constitutes the solid portion of the drop was present in the liquid at 1550°C (light color, round particles, in Fig. 8), whereas the remaining dendrites formed during cooling. Some segregation is observed in the matrix due to the precipitation
in MgO even at high temperatures. Thus, only a negligible amount of TiO$_2$ in the liquid may react with the substrate to form a solid solution. Furthermore, at the liquid-solid interface, there would be no compound formation since the primary fields of the compounds indicated above are not in the composition tetrahedrons.

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Fig. 8  Solid-liquid interface of the sample with an original drop composition of 1% Al$_2$O$_3$ + 99% CMS, held 3 hours at 1550°C.
Fig. 9  Oscilloscope trace of the solid-liquid interface of the sample with an original drop composition of 1% Al₂O₃ + 99% CMS, held 3 hours at 1550°C.
of monticellite and spinel. The voids in the drop appear as the dark areas in Fig. 8. In the MgO substrate some aluminum could be detected, although most of it was due to the background.

2. Cr₂O₃-MgO-CaO·SiO₂ System

The liquid-solid interface of the sample containing an original liquid composition of 4% MgCr₂O₄ + 96% CMS is shown in Fig. 10. The structure of the drop observed at room temperature is not the equilibrium structure of spinel, monticellite, and akermanite, but a non-equilibrium structure of a frozen-in matrix containing MgO solid solution particles, similar to the previous sample. The liquid of this sample at 1700°C contains only particles of MgO with Cr₂O₃ in solid solution. These particles appear as the light gray, round particles. The oscilloscope trace of this same sample, shown in Fig. 11, verifies the existence of chromium in those particles which showed a high magnesium concentration with some chromium. The matrix shows a very low chromium concentration. As shown in Fig. 7, the maximum solubility of Cr₂O₃ in MgO at 1700°C is about 13%. Thus the liquid will be losing some of its chromium to the substrate. In Fig. 11, the diffusion layer of chromium in the substrate appears to be about 60μ.

3. Fe₂O₃-MgO-CaO·SiO₂ System

The experiment with an original drop composition of 56% Fe₂O₃ + 44% CMS illustrates a case in which the premelted liquid is not at equilibrium with MgO but is at equilibrium with spinel. At 1550°C, the liquid portion of this drop will correspond to a composition on the liquidus surface passing through Fe₃O₄, L, a, and J, in Fig. 6. The solid portion of the drop will be a MgFe₂O₄-Fe₃O₄ solid solution. When this drop is in
Fig. 10 Solid-liquid interface of the sample with an original drop composition of $\frac{1}{4}\% \text{MgCr}_2\text{O}_4 + 96\% \text{CMS}$, held 4 hours at 1700°C.
Fig. 11 Oscilloscope trace of the solid-liquid interface of the sample with an original drop composition of 4% MgCr₂O₄ + 96% CMS, held 4 hours at 1700°C.
contact with a MgO substrate, the substrate can react with the liquid at
the interface to form either a spinel or a magnesiowustite solid solution.
At the same time the liquid will dissolve MgO from the surface to reach
equilibrium with the substrate. As a result, the liquid composition will
shift towards the "LaJ" boundary line. During cooling, the liquid will
follow this boundary line, while both magnesiowustite and spinel will pre-
cipitate out. All the magnesiowustite in the liquid should disappear at
the peritectic point "J" before the liquid moves along the monticellite-
spinel boundary line. However, since the cooling rates are fast, some
magnesiowustite will also be seen at room temperature.

A photomicrograph of the liquid-solid interface of this sample is
shown in Fig. 12. In the liquid drop, the angular white particles are
the MgFe₂O₄ solid solution while the round gray ones containing small
spinel particles are the magnesiowustite solid solution. Some spinel
apparently precipitates out during cooling inside the magnesiowustite
particles. The remaining portion of the drop is primarily monticelllite
(dark gray) and the final portion of the liquid which freezes at the
invariant point. An iron diffusion layer of about 400µ is also apparent
in the Fe-Kα trace.

4. TiO₂-MgO-CaO·SiO₂ System

As indicated in the discussion of the TiO₂-MgO-CaO·SiO₂ system, with
additions of TiO₂ the liquid dissolves MgO from the substrate to reach
saturation with respect to MgO. Only a very small amount of TiO₂ in the
liquid may react with the substrate to form a solid solution, while no
compound formation at the interface will take place. With 5% TiO₂
addition any of the solids, CaO·TiO₂, 2CaO·MgO·2SiO₂, CaO·MgO·SiO₂,
Fig. 12 Solid-liquid interface of the sample with an original drop composition of 58% Fe₂O₃ + 44% CMS, held 3 hours at 1550°C.
Fig. 13 Oscilloscope trace of the solid-liquid interface of the sample with an original drop composition of 50% $\text{Fe}_2\text{O}_3 + 44\%$ CMS, held $3$ hours at $1550^\circ\text{C}$. 

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2MgO·SiO₂, and MgO can be expected to coexist with the liquid. With 30% TiO₂ addition, CaO·MgO·2SiO₂ replaces CaO·MgO·SiO₂. In Fig. 14 a photomicrograph of the sample with 5% TiO₂ containing liquid is shown. A comparison of this micrograph with the oscilloscope traces of the elements given in Fig. 16(a) shows that the white angular particles in the liquid contain only calcium and titanium. Thus, the white particles correspond to the CaO·TiO₂ phase. The light gray, round particles concentrated close to the liquid-solid interface indicate only the presence of magnesium, and thus, they will be the MgO phase. The dark gray sections, which constitute the main portion of the liquid, indicate all the elements but titanium. These are probably the CaO·MgO·SiO₂ primary phase. According to Berezhnoi's composition tetrahedron, the CaO·MgO·SiO₂ primary field will be next to the MgO primary field, and the CaO·MgO·SiO₂ phase will precipitate out during cooling as the liquid moves along the MgO-CaO·MgO·SiO₂ boundary line. The rest of the liquid, where a fine eutectic structure is observed, is the portion of the drop which freezes at the invariant point.

The photomicrograph of the sample of 30% TiO₂ containing liquid is shown in Fig. 15. Again, from a comparison of this micrograph with the oscilloscope traces of the elements given in Fig. 11(b), the white regions are identified as the CaO·TiO₂ phase. The dark gray regions appear to be the 2MgO·SiO₂ phase since they contain no calcium and titanium. The rest could not be identified clearly. In both of these samples some titanium in the substrate could be detected, although as in the Al₂O₃-MgO-CaO·SiO₂ system, most of this would be due to the background effect.
Fig. 14 Solid liquid interface of the sample with an original drop composition of 5\% TiO₂ + 95\% CMS, held 3 hours at 1550°C.
Fig. 15 Solid liquid interface of the sample with an original drop composition of 30% TiO₂ + 70% CMS, held 3 hours at 1550°C.
Fig. 16 Oscilloscope traces of the solid liquid interfaces of the samples with original drop compositions of (a) 5% TiO₂ + 95% CMS, and (b) 30% TiO₂ + 70% CMS, held 3 hours at 1550°C.
D. Nature of Interface Reactions and Their Effect on Contact Angle

The interface reactions discussed in the preceding sections can be classified under three general groups:

(a) The liquid dissolves MgO from the substrate surface when it is unsaturated with respect to MgO,

(b) If the liquid is saturated with respect to MgO•R₂O₃, but not with MgO, the MgO of the substrate reacts with the R₂O₃ of the liquid to form spinel, and

(c) The MgO of the substrate reacts with R₂O₃ or TiO₂ of the liquid to form a solid solution.

A hypothetical R₂O₃-MgO-CaO•SiO₂ ternary phase diagram, shown in Fig. 17, will be used to discuss the nature of these interface reactions. Although the iron oxide-MgO-CaO•SiO₂ system is a quaternary system, the use of this simplified diagram will not alter the discussion on the interface reactions. Furthermore, in this R₂O₃-MgO-CaO•SiO₂ system, the discussion of the behavior of a drop composition "L₁" on the MgO substrate will be sufficient to cover all the different cases encountered in this study.

At a temperature "T₁," the premelted drop of the composition "L₁" contains solid particles of MgO•R₂O₃ and a liquid of composition "L." When this drop is on a pure MgO substrate, the liquid composition will shift from L to L' by dissolving MgO from the substrate surface. The liquid composition will next tend to move into the MgO primary field along the T₁ isotherm as it loses some of its R₂O₃ to the substrate since all of the R₂O₃'s formed solid solution with MgO. However, if the spinel particles of the drop can make up for this loss by dissolving in the
Fig. 17. Hypothetical $\text{R}_2\text{O}_3$-$\text{MgO}$-$\text{CaO}$-$\text{SiO}_2$ equilibrium phase diagram.
liquid faster than the substrate can react with the $R_2O_3$ of the liquid, the composition should stay at $L'$ until all of the spinel in the drop is depleted. The liquid composition will then shift into the MgO primary field only after the excess spinel of the drop is depleted.

The overall composition of the drop-substrate system can be represented by a point "0" on the line joining $L_T$ to MgO. This point will be closer to the MgO side since the mass of the substrates used was considerably larger than that of the drops. As the overall drop composition changes from $L_T$ to $L'$ and subsequently moves into the MgO primary field, the overall substrate composition moves towards a saturated solid solution composition represented by point D for temperature $T_1$. During this adjustment period, the liquid and the substrate compositions will be joined by the dash line which rotates with point 0 as a fulcrum. This adjustment will cease when the activity of $R_2O_3$ in the substrate becomes equal to that of the $R_2O_3$ in the liquid. At equilibrium, the substrate and the liquid will then be represented by equal $R_2O_3$ activity compositions $S$ and $T$, respectively. In this study the equilibrium for the whole system was never attained since the time allowed for the diffusion of $R^{3+}$ or $R^{2+}$ cations into the MgO substrate was not long enough to attain the equilibrium structure. In the experiment with 56% $Fe_2O_3$ + 44% CMS liquid composition, for instance, the diffusion layer constituted only 20% of the substrate.

Although the system as a whole needs a long time to attain an equilibrium composition, the interface region itself can reach a transient equilibrium state rapidly. In the $L_T$-MgO system, for instance, if the interface reaction is not the rate controlling step, the substrate at the
interface will correspond to the saturation composition of D while the liquid is at L'. Then the interface region can be thought of as an isolated system containing equal amounts of liquid and substrate phases. The overall composition of this interface region will be represented by point I.

The liquid L' can coexist in equilibrium with the MgO solid solution phase of composition D and with the spinel phase. If the liquid is in the spinel primary field, however, it reacts with the MgO solid solution to form more spinel. If the MgO solid solution is unsaturated, this liquid now reacts with the unsaturated MgO solid solution to form either spinel or saturated MgO solid solution, as given by the following reactions:

\[
\begin{align*}
R_2O_3({\text{in liquid}}) &+ MgO-R_2O_3({\text{subst., unsat.ss}}) \rightarrow MgO-R_2O_3({\text{sat.ss}}) \quad (3) \\
R_2O_3({\text{in liquid}}) &+ MgO-R_2O_3({\text{subst., unsat.ss}}) \rightarrow MgR_2O_4({\text{spinel}}) \quad (4)
\end{align*}
\]

The magnitude of \(-\Delta G\), in both cases, is directly proportional to the degree of undersaturation of the MgO-R2O3 solid solution. Thus, one would expect \(\Delta G_3\) and \(\Delta G_4\) to be the same. In sessile drop experiments, when the substrate at the interface is an unsaturated solid solution and the liquid is in the spinel primary field, both of these reactions can take place. The growth rate of the products, however, will determine which one of these two phases will grow at the interface.

Once the liquid reaches L' and begins to move into the MgO primary field, the liquid and the substrate can react to form only the saturated MgO solid solution phase as given by reaction (3). The \(-\Delta G\) of the reaction now decreases as the liquid composition changes to a lower R2O3 content.
Under equilibrium conditions, the contact angle in Young's equation is determined by a balance of interfacial and surface tensions acting on the periphery of the drop. Under non-equilibrium conditions, however, the use of this equation becomes inappropriate since the interfacial and surface tensions will be changing continuously as the whole system adjusts itself towards a lower free energy configuration. The nature of the interface reactions now plays a very important role in the behavior of the liquid.

If the liquid is in the spinel primary field, under unsteady state conditions the ΔG for reactions (3) and (4) will have a high negative value immediately after the first portion of the liquid forms on the substrate. This is due to the initial high undersaturation of the substrate. As the reaction proceeds, the degree of undersaturation of the substrate, and consequently, the driving force of the reaction will decrease. Around the periphery of the drop, however, where the liquid is next to an undersaturated MgO-R2O3 solid solution, the liquid will advance further to react with more MgO. When the driving force for this reaction is high, the liquid can wet the substrate completely before the steady state conditions are attained. If the kinetics are such that the substrate surface around the periphery of the drop can approach the saturation composition rapidly, the driving force for the reaction becomes low. The liquid then stops at a finite steady state angle when the liquid surface cannot be stretched any further.

The steps which might play an important role in the kinetics of this wetting phenomenon are:
(a) Dissolution of spinel in the liquid,

(b) Diffusion of $R^{3+}$ or $R^{2+}$ cations in the liquid,

(c) Interface reaction,

(d) Diffusion of $R^{3+}$ or $R^{2+}$ cations in the substrate, and

(e) Dissolution of MgO in the liquid.

The diffusion of $R^{3+}$ or $R^{2+}$ cations in the liquid will not be expected to be a rate controlling step because the diffusion in the liquid will be much faster than that in the substrate. If (a) is the rate controlling step, the $R_2O_3$ content of the liquid around the periphery will be depleted as diffusion into the substrate continues. Once the liquid reaches L' and subsequently becomes undersaturated with respect to MgR$_2$O$_4$, reaction (3) will be the only possible interface reaction. The magnitude of $(-)\Delta G$ for this reaction will now decrease as the liquid approaches a pure CMS composition. If the interface reaction is the rate controlling step, the substrate will always be undersaturated while the liquid stays saturated. The magnitude of $(-)\Delta G$ will then be high. The magnitude of $(-)\Delta G$ will become low again if the diffusion of $R^{3+}$ or $R^{2+}$ cations in the substrate is the rate controlling step since now, the interface region of the substrate also becomes saturated. Finally, if the dissolution rate of MgO in the liquid is low, the above argument still applies unless the dissolution rate of spinel in the liquid is also slow. Then, as the liquid becomes depleted of $R_2O_3$, it will move along an almost constant MgO direction instead of following the T$_{1}$ isotherm.

In the Al$_2$O$_3$-MgO-CaO-SiO$_2$ and Fe$_2$O$_3$-FeO-MgO-CaO-SiO$_2$ systems in excess of 3% $R_2O_3$, the steady state contact angles would be 35° and 15°, respectively. On the other hand in the Cr$_2$O$_3$-MgO-CaO-SiO$_2$ and
TiO₂-MgO-CaO-SiO₂ systems, the steady state contact angles become very low as the amount of Cr₂O₃ and TiO₂ are increased. These angles are indicated as zero in Fig. 2 since, in each case, the substrate was wetted completely. Attempts were later made to determine this very low contact angle with Cr₂O₃ additions at 1550°C. The biggest MgO substrates available were used while the size of the drops was decreased considerably. After 3 hours a contact angle of 7° was obtained for the system with 3% Cr₂O₃ + 97% CMS liquid composition. With the 5% Cr₂O₃ + 95% CMS liquid, the angle was 6° after 6 hours of heating. The contact angle could not be measured when the 15% Cr₂O₃ + 85% CMS liquid was fired on MgO for 3 hours since the drop segregated into very small segments around the trace of the original drop. Apparently, as the Cr₂O₃ content of the drop was depleted, the liquid tried to pull back, and during this process it formed small segments. With the 3% and 5% Cr₂O₃ containing liquids, the drops must also have spread first and pulled back as the Cr₂O₃ content in the drop decreased. In both cases the original drop traces were visible. For practical purposes, then, the liquids containing in excess of 3% Cr₂O₃ can be considered to spread on MgO. Yet this spreading was not obtained in the system with 4% MgCr₂O₄ + 96% CMS drop composition (Table I).

At this stage, one more step must be added to the five rate controlling steps listed above, namely the solution of R₂O₃ from the MgO-R₂O₃ solid solution in the liquid. This step plays an important part if the amount of MgO-R₂O₃ solid solution particles in the liquid is high and the solution rate of R₂O₃ at the (MgO-R₂O₃)-liquid interface is slow. In the 4% MgCr₂O₄ + 96% CMS liquid, the percentage of MgO-Cr₂O₃ solid
solution particles at test temperature is slightly higher than that in the 3% Cr₂O₃ + 97% CMS liquid. Although the former system, as a whole, contains more than 3% Cr₂O₃, the percentage of Cr₂O₃ in the liquid portion is actually less than that of the latter system. This percentage will decrease further after the liquid forms if the solution rate of Cr₂O₃ at the (MgO-Cr₂O₃)-liquid interface is slow. Thus, a finite steady state contact angle corresponding to a liquid composition less than 3% Cr₂O₃ is obtained instead of spreading.

In the literature, unfortunately, only limited data are available on the kinetics of the possible rate controlling steps outlined above. The diffusion rate of Fe²⁺ cations in MgO has been determined by Tagai, et al. and Blank. Tagai, et al., and recently Greskovich and Stubican have determined the diffusion rate of Cr³⁺ cations in MgO. No data could be found on the kinetics of aluminum cation diffusion in MgO. Furthermore, the kinetics of the other steps still remain to be investigated.

According to Tagai, et al., at 1600°C Fe²⁺ and Cr³⁺ cation diffusivities in MgO are 3.1 x 10⁻⁹ and 1.3 x 10⁻¹¹ cm²/sec., respectively. If the diffusion of cations in MgO is the rate controlling step within the first second of the diffusion, the activity profiles of Fe₂O₃ and Cr₂O₃ in MgO will be as shown in Fig. 18. In order to plot these activity profiles, the concentration profiles of Fe₂O₃ and Cr₂O₃ in MgO were first determined using Tagai, et al.'s diffusivity data. Assuming that the MgO-Fe₂O₃ and MgO-Cr₂O₃ solid solutions are ideal, the activities can be obtained directly from the concentration profiles. A comparison of these profiles shows that for a given time the interface region of the substrate around the periphery in the Fe₂O₃ containing systems would
Fig. 18. Activity profiles of Fe$_2$O$_3$ and Cr$_2$O$_3$ in MgO solid solution, after 1 sec at 1600°C.
reach saturation much faster than it would in the Cr$_2$O$_3$ containing systems. If an effective interface region of 100 Å can be assumed, $\Delta G_3$ and $\Delta G_4$ at the interface will have a higher negative value in the Cr$_2$O$_3$ containing systems than it will in the Fe$_2$O$_3$ containing systems. Under these conditions, then, one would expect the Cr$_2$O$_3$ containing liquids to spread more on a MgO substrate.

The kinetics of aluminum cation diffusion in MgO is yet to be determined. A fast aluminum cation diffusion in MgO could be a contributing factor to the relatively high steady state contact angle observed. The microscope studies, however, indicated that the dissolution rate of MgAl$_2$O$_4$ spinel in the liquid could also be an important factor to consider. In Fig. 19, the periphery region of a drop with an original composition of 30% Al$_2$O$_3$ + 70% CMS is shown. The angular particles are MgAl$_2$O$_4$ spinel. It appears that the periphery region of the liquid is almost completely depleted of excess spinel after 3 hours at 1550°C. This phenomenon which was not observed in the other systems would be due to a slow dissolution rate of MgAl$_2$O$_4$ spinel in the liquid. Thus, at steady state the contact angle corresponds to a finite value since the $(-)\Delta G$ of the interface reaction around the periphery region will be low. Similarly, in the TiO$_2$-MgO-CaO-SiO$_2$ system the formation of a solid solution at the interface would be a contributing factor to the lowering of the contact angle. In this case, since the liquids dissolve MgO from the surface, the driving force for this reaction may also contribute to the decrease in the contact angle. Apparently with 5% TiO$_2$ containing liquid, this dissolution step was short since the presence of MgO particles in the drop indicates that the liquid was already at equilibrium.
Fig. 19 Periphery region of the sessile drop with an original composition of 30% Al₂O₃ + 70% CMS, held 3 hours at 1550°C.
with MgO after 3 hours.

The macroscopic nature of the experiments in this study was the primary cause for the delay in reaching the final equilibrium states. In a compact, however, where the solid particles are usually micron size, the equilibrium configuration will be readily achieved. The dihedral angle measurements of Jackson, et al. \(^4\) and Jackson and Ford \(^5\) in the periclase-monticellite system corresponded to this equilibrium configuration. In their studies, a firing period of one hour was adequate to reach equilibrium. Finite dihedral angles were obtained between the MgO grains. If shorter firing periods corresponding to the non-equilibrium stage were used, either the dihedral angles would have been very low or the MgO grains would have been completely surrounded by the liquid. This transient wetting stage would be due to the reactions at the solid-liquid interface.
V. CONCLUSIONS

The contact angle of monticellite (CaO·MgO·SiO₂) liquid on (100) faces of magnesium oxide at 1550°C was determined to be in the range of 43-51°. The Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂ additions to the liquid, in each case, resulted in a decrease in the contact angle. Spreading was obtained with Cr₂O₃ and TiO₂ additions (Fig. 2).

The equilibrium structure of the monticellite-magnesium oxide system is disturbed with additions of Al₂O₃, Cr₂O₃, Fe₂O₃, and TiO₂. The system then goes through a transient non-equilibrium stage. During this stage, a driving force exists for reactions at the liquid-substrate interface to achieve an equilibrium structure. The degree of wetting is directly proportional to the degree of this driving force, or the magnitude of (-)ΔG for the reaction. Spreading is obtained when the magnitude of (-)ΔG for the reaction is high resulting in a wetting driving force that exceeds the surface tension of the liquid.

The wetting phenomenon in this transient stage is affected by the kinetics of: (a) dissolution of spinel in the liquid, (b) diffusion of additive cations in the liquid, (c) interface reaction, (d) diffusion of additive cations in the substrate, and (e) dissolution of MgO in the liquid.

The goal of this study which was to determine the effect of Cr₂O₃, Fe₂O₃, Al₂O₃, and TiO₂ on the solid-liquid interfacial energy of the equilibrium periclase-monticellite system was not achieved. The final equilibrium compositions could not be attained due to the macroscopic nature of the experiments. Therefore, the reported contact angles are not the equilibrium contact angles but the steady state angles of a
transient reaction stage. In order to measure the equilibrium contact angles, one then has to perform the sessile drop experiments on substrates that are initially at equilibrium with the liquid.

Nevertheless, the results of this study are quite valuable since they provide a greater understanding of the role of interface reaction kinetics in sessile drop experiments. It is felt that the kinetics of interface reactions would play an equally important role in the microstructure development of a compact.
ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation for the patient guidance of Professor Joseph A. Pask.

The counsel of Professor Leo Brewer was very helpful during the course of this research project.

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The author's research was supported by the United States Atomic Energy Commission.
APPENDIX

1. The Chemical Analysis of MgO Powder

Baker and Adamson Reagent No. 1917

<table>
<thead>
<tr>
<th>Substance</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assay (MgO) (after ignition)</td>
<td>99.0</td>
</tr>
<tr>
<td>Insoluble in dilute HCl</td>
<td>0.020</td>
</tr>
<tr>
<td>Soluble in water</td>
<td>0.40</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2.0</td>
</tr>
<tr>
<td>Ammonium hydroxide precipitate</td>
<td>0.020</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>0.010</td>
</tr>
<tr>
<td>Nitrite (NO₃)</td>
<td>0.005</td>
</tr>
<tr>
<td>Sulfate and sulfite (as SO₄)</td>
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<tr>
<td>Barium (Ba)</td>
<td>0.005</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
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<tr>
<td>Heavy metals (as Pb)</td>
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<tr>
<td>Iron (Fe)</td>
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<tr>
<td>Manganese (Mn)</td>
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<tr>
<td>Potassium (K)</td>
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</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.50</td>
</tr>
<tr>
<td>Stroniu.rn (Sr)</td>
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</tr>
<tr>
<td>Silica (SiO₂)</td>
<td>0.040</td>
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2. The Chemical Analysis of CaCO₃ Powder

Baker and Adamson Reagent No. 1506

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<th>Substance</th>
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<tbody>
<tr>
<td>Assay (CaCO₃)</td>
<td>99.0</td>
</tr>
<tr>
<td>Insoluble in dilute HCl</td>
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<tr>
<td>NH₄OH precipitate</td>
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</tr>
<tr>
<td>Chloride (Cl)</td>
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<tr>
<td>Oxidizing substance (as NO₃)</td>
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<tr>
<td>Sulfate (SO₄)</td>
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<tr>
<td>Ammonium (NH₄)</td>
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<tr>
<td>Barium (Ba)</td>
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</tr>
<tr>
<td>Stronium (Sr)</td>
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<tr>
<td>Magnesium (Mg)</td>
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<tr>
<td>Potassium (K)</td>
<td>0.01</td>
</tr>
<tr>
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<td>0.10</td>
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<tr>
<td>Heavy metals (as Pb)</td>
<td>0.001</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.002</td>
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3. SiO₂ Powder

Ottawa Silica Flour

<table>
<thead>
<tr>
<th>Substance</th>
<th>Wt. %</th>
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<tbody>
<tr>
<td>Silica (SiO₂)</td>
<td>99.8</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>0.1</td>
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<tr>
<td>Iron oxide (Fe₂O₃)</td>
<td>0.02</td>
</tr>
<tr>
<td>Calcium oxide and magnesium oxide (CaO, MgO)</td>
<td>0.1</td>
</tr>
</tbody>
</table>
4. The Chemical Analysis of Al₂O₃ Powder

Baker Analyzed Reagent No. 0536

<table>
<thead>
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<th>Substance</th>
<th>Wt. %</th>
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<tr>
<td>Assay (Al₂O₃)</td>
<td>99.5</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.3</td>
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<tr>
<td>Chloride (Cl)</td>
<td>0.005</td>
</tr>
<tr>
<td>Sulfate (SO₄)</td>
<td>0.003</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>0.0005</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.001</td>
</tr>
</tbody>
</table>

5. Cr₂O₃ Powder

Baker Analyzed Reagent No. 1616. A chemical analysis was not performed.

6. The Chemical Analysis of Fe₂O₃ Powder

Baker Analyzed Reagent No. 2024

<table>
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<th>Substance</th>
<th>Wt. %</th>
</tr>
</thead>
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<tr>
<td>Assay (Fe₂O₃)</td>
<td>99.5</td>
</tr>
<tr>
<td>Insoluble in HCl</td>
<td>0.04</td>
</tr>
<tr>
<td>Phosphate (PO₄)</td>
<td>0.02</td>
</tr>
<tr>
<td>Sulfate (SO₄)</td>
<td>0.04</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.003</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.03</td>
</tr>
<tr>
<td>Substances not precipitated by NH₄OH (as SO₄)</td>
<td>0.003</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.003</td>
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</tbody>
</table>
7. The Chemical Analysis of TiO₂ Powder

Baker Analyzed Reagent No. 4162

<table>
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<th>Substance</th>
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<tr>
<td>Water soluble salts</td>
<td>0.01</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.0001</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.001</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.008</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>0.005</td>
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8. The Spectroscopic Analysis of MgO Single Crystals

<table>
<thead>
<tr>
<th>Substance</th>
<th>Wt. % Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium (Mg)</td>
<td>Principle Constituent</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.015</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>0.007</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.002</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>Not detected</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.01</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>0.001</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

* The analysis was performed by the American Spectrographic Laboratories, Inc., 557 Minna Street, San Francisco, California
REFERENCES


(b) E. F. Osborn and A. Muan, Figure 630, ibid.

(c) W. F. Ford and W. J. Rees, Figure 924, ibid.

(d) A. S. Berezhnoi, Figure 927, ibid.

(e) A. S. Berezhnoi, Figures 930 and 934, ibid.

(f) F. Massazza and E. Sirchia, Figure 269, ibid.

(g) L. W. Coughanour and V. A. DeProsse, Figure 270, ibid.

44. R. M. El-Shahat and J. White, "Phase-equilibrium relationships in spinel-silicate systems, II, The pseudo-systems MgAl₂O₄ - MgCr₂O₄ - CaMgSiO₄, MgFe₂O₄ - MgCr₂O₄ - CaMgSiO₄, MgAl₂O₄ - MgFe₂O₄ - MgCr₂O₄ - CaMgSiO₄," Trans. Brit. Ceram. Soc., 65 [6] 309-36 (1966).
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