DETERMINATION OF THE NATURE OF LIQUID STEEL – ALUMINA INTERFACIAL INTERACTIONS FROM SESSILE DROP MEASUREMENTS: CASES OF Fe-Ti AND Fe-P ALLOYS

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Abstract

The wettability of alumina by binary and ternary alloys of the system Fe-Ti-P has been investigated using sessile drop experiments conducted under inert gas atmosphere in the temperature range of 1550 to 1620°C. The surface and interfacial structures have been explored by scanning electron microscopy and energy dispersive X-ray spectroscopy.

Substantial additions of titanium are known to induce steel melts to wet alumina due to the formation of a titanium rich reaction product at the alloy/ceramic interface, but the present work has shown that even low titanium concentrations can induce a reactive wetting process leading to an improvement of the wettability of alumina by Fe alloys.
The contact angle of molten steel containing phosphorus on alumina decreased with increasing P content. The improvement of the wetting behaviour in this system was attributed solely to the adsorption of P on the alumina side of the interface without formation of a reaction product layer.
The addition of phosphorus as a ternary alloying element to the system Fe-Ti proved to be beneficial to the wetting behaviour. The measured contact angles were much lower than those in the binary systems Fe-Ti and Fe-P. It was concluded that the effect of P consists in enhancing the activity of Ti in the ternary system and dismantling the interfacial hercynite layer.
According to experimental observations, it turns out that the wettability of liquid Fe based alloys, when an Al_2O_3 surface is present is not only a property of the metal/oxide couple but is also dependent on the oxygen partial pressure, whereas temperature variations bring about a comparatively small effect.

The results of this work are of interest in understanding the phenomena pertaining to inclusion engineering and steel/refractories interactions, such as the blockage of submerged entry nozzles by agglomerated alumina particles.

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1. Introduction

An understanding of iron alloy/refractory material interactions is of great significance due to their extensive application in a number of metallurgical processes. Typical examples related to the continuous casting process are the collision and agglomeration of non metallic inclusions in the steel melt, the removal of inclusions from the melt by flotation or filtration, the entrapment of inclusions at the refractory interface, which can eventually lead to the clogging of the submerged entry nozzle, as well as the local corrosion of refractory linings at the metal/slag boundary as a result of the Marangoni convection [1].

Reactions between molten iron alloys and alumina based materials have been the subject of a number of investigations [2, 3, 4, 5, 6]. However, most of the efforts have been focused on pure Fe/Al$_2$O$_3$ systems or on Fe alloys containing extremely high concentrations (up to 30 mass percent and more) of the alloying element. The aim of this study was to establish the effect of titanium and phosphorus on wetting in the Fe alloy/Al$_2$O$_3$ system on samples reasonably close to commercial steel compositions. The ultimate goal – not part of this work - being to determine the role played by wetting properties of Fe alloys in the nozzle clogging mechanisms during the continuous casting of steels.

The motivation for the choice of alumina as substrate material was twofold: first, Al$_2$O$_3$ is an interesting ceramic material which constitutes one of the major components of the submerged entry nozzle used in the continuous casting process of steels; secondly, non-metallic inclusions formed in Al-killed steels are mainly composed of Al$_2$O$_3$. An understanding of the phenomena underlying the reactions in the Fe alloy/Al$_2$O$_3$ system would, therefore, be useful in optimising the continuous casting process.

Titanium and phosphorus contents were chosen as the experimental variables of the steel, since literature [7, 8] and operational experience show that the presence of those elements tends to exacerbate the problem of nozzle clogging during the continuous casting of Al-killed steels bearing Ti and / or P.

The investigation of wetting through sessile drop tests will allow a characterisation of surfaces and the interaction of substrates with liquid Fe alloys, since the wetting process depends on the surface properties of a solid substrate and its interactions with the liquid metal.

1.1 Fundamental equation of wetting

A liquid placed on a solid substrate forms a droplet which has a specific equilibrium shape and wetting (contact) angle. The equilibrium wetting angle, **Fig. 1**, which is a quantitative measure of the ability of a liquid to wet the substrate can be described by Young's equation [9], which is the result of balancing the horizontal force components at the three-phase line:

$$\gamma_{sg} - \gamma_{sl} - \gamma_{lg} \cdot \cos\theta = 0 \tag{1}$$

A contact angle $\theta < 90°$ indicates that the solid is wet by the liquid, and $\theta > 90°$ identifies a non-wetting behaviour, with the limits $\theta = 0°$ and $\theta = 180°$ defining complete wetting and complete non-wetting, respectively [10,11]. Thus, the degree of interaction between the liquid and the substrate material increases as the contact angle decreases [12].
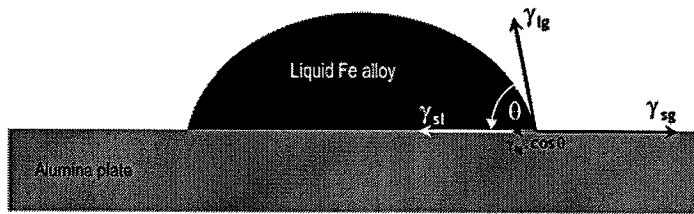
Figure 1. Schematic drawing of a liquid drop resting on an Al_2O_3 substrate in a partial wetting situation. θ is the equilibrium contact angle; γ_{sg}, γ_{lg}, and γ_{sl} represent solid/gaseous, liquid/gaseous, and solid/liquid interfacial tensions, respectively.

1.2 Factors affecting the wetting process

Following **Eq. (1)** an improvement in wetting can result either from a decrease of γ_{sl} only or from a decrease of both γ_{sl} and γ_{lg}. The following parameters contribute to a change in interfacial tensions, and thus in the wetting behaviour of the system Fe alloy/Al_2O_3.

1.2.1 Adsorption

The surface and interfacial tensions can be extremely lowered by the presence of minute amounts of adsorbed species on substrate and metal melt surfaces and at substrate/metal interfaces [13].

A distinguishing factor between interfacial (e. g. surface tension, wetting angle) and bulk properties (e. g. viscosity) is that small concentrations of surface active elements (e.g. O, S,...) can cause dramatic changes in both the surface (or interfacial) tension and its temperature dependency [14, 15]. It is worth pointing out that interfacial properties depend on the soluble O or S, and not the total contents, as inclusions have any influence on surface tension [16]. Since most steels contain elements like Al, Si, Mn, Cr or Ti, with a stronger affinity to O than Fe, they react with O and reduce the soluble O to very low levels. However, during the melting process (prior to wetting tests) in the tube furnace, other phenomena [13] contribute to some increase of the dissolved O in the liquid metal, viz.: the dissolution of Al_2O_3 at the interface or the adsorption of O from the furnace atmosphere, **Fig. 2.**
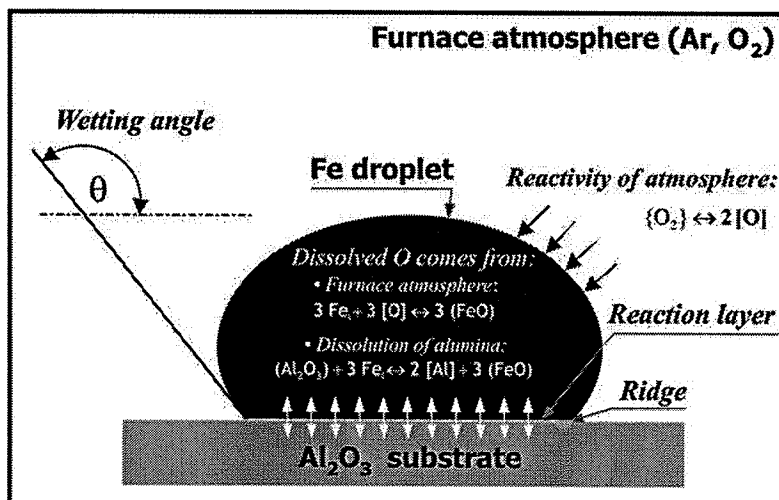
Figure 2. Schematic illustration of the mechanisms taking place in the furnace during the wetting experiments of pure Fe on Al_2O_3. The presence of a non-wetting reaction

product at the Fe/Al$_2$O$_3$ interface inhibits the spreading process. As a result, obtuse contact angles are registered.

Actually, a decrease of θ at very low O$_2$ partial pressures has been reported [17, 18] in the system Fe/Al$_2$O$_3$. It was attributed to the increase in the Al dissolved in the Fe melt consecutive to the dissolution of the Al$_2$O$_3$ substrate which caused strong changes in γ_{sl} and γ_{lg}. Since, in equilibrium with Al$_2$O$_3$, the lower the O content, the higher the dissolved Al content, this effect could explain the drop in contact angle as the pO$_2$ decreases.

1.2.2 Influence of alloying elements

When an iron melt is alloyed, both its surface tension and the metal/solid interfacial tension are affected, especially if the alloying elements tend to segregate at the liquid surface and at the solid/liquid interface [19]. This behaviour can be explained using **Eq. (2)** [10], which relates the change of surface tension $\partial\gamma$ to the activity a$_i$ of a solute i in the melt, as follows:

$$\left(\frac{\partial\gamma}{\partial a_i}\right)_T = -\frac{RT\Gamma_i}{a_i} \qquad (2)$$

It states that when a surface active element i enriches itself at the interface, its surface excess concentration Γ_i becomes positive and therefore $\dfrac{\partial\gamma}{\partial a_i}$ negative. This leads to a decrease of the surface tension. At a constant concentration of the element i, an increase of temperature dT acts in a similar manner. On the other hand, when a solute avoids the interface, the surface tension increases upon adding that element.

Most additions to steel produce a decrease of the interfacial tension, their influence being more pronounced in the following order: Ni, Mn, Cr, Mo, Si, P, C, V, and Ti. Unlike that group, W belongs to the few elements that contribute to an increase of the interfacial tension between Fe alloys and oxide substrates [20].

1.2.3 Ridge formation

For most high temperature systems, the temperatures during the experiment are typically $\geq$ 0,5T$_m$, where T$_m$ is the melting point of the substrate material, and therefore, local atomic diffusion can occur [21, 22]. This provides conditions for ridge formation even for hard substrates like alumina [23]. If ridges are formed, however, spreading requires motion of the triple line both horizontally and vertically, so that one has to differentiate between microscopic and macroscopic angles. The microscopic angles are the dihedral angles ϕ_s, ϕ_l, ϕ_g, and the macroscopic angle is the Young's equilibrium wetting angle [23]. The presence of a ridge can constitute a barrier to the spreading process, and hence have an influence on the value of the equilibrium wetting angle [22, 24].

1.3 Interfacial reactions

Interfaces between metals and ceramics are divided into *non-reactive* and *reactive* systems. In a non-reactive system, the nature of the ceramic substrate is not significantly modified by its contact with a metal melt. The wettability is only the result of receiving chemical equilibrium bonds, which are achieved by the mutual saturation

of the free valences of the contacting surfaces and acting van der Waals forces [13, 25]. Therefore, the interaction of liquid metal with the ceramic does not lead to the formation of new phases. In reactive systems, however, wetting, chemical reactions, and solute segregation are interactively coupled [26]. The liquid metal is not in direct contact with the initial unreacted substrate, but with the new compound formed at the metal/ceramic interface due to the chemical reaction accompanying the wetting process [14, 18]. In this case, the final wetting angle θ_f may be expressed by the Young's equation applied to the reaction product/liquid/gaseous system [13]:

$$\cos\theta_f = \frac{\gamma_{pg} - \gamma_{pl}}{\gamma_{lg}} \tag{3}$$

in which θ_f represents the equilibrium wetting angle on the reaction product p.

Obviously, the wetting in reactive systems is governed by the final interfacial chemistry at the triple line rather than the intensity of interfacial reactions [27, 28, 29]. That means that even a very thin reaction layer may profoundly affect the wetting behaviour.

2. Experimental method

The sessile drop technique was used in the present study to measure the contact angles of molten steel alloys containing Ti and P on solid Al_2O_3 substrates as a function of the steel chemistry at temperatures ranging from 1550 to 1620°C.

2.1 Sample preparation for wetting tests

In order to reduce the contamination of the steel alloys with oxygen to minimal levels, the master alloys were prepared using a novel method consisting in a combination of vacuum induction melting and air induction melting with a $CaO-SiO_2-Al_2O_3$ protective slag, as well as a sampling done under inert gas atmosphere.

Table.1 shows the chemical composition of all Fe-Ti and Fe-P alloys as analysed by Leco® for oxygen and nitrogen and by Spectrolab for the other elements.

Table 1. Chemical compositions of the Fe alloys used in the wetting experiments

(a) Titanium samples									
Sample	Chemical composition of steels [mass %]								
	C	Si	Mn	P	S	Al	Ti	Otot	N
Ti01	0.0265	0.0046	0.0462	0.0047	0.0070	0.0055	0.0030	0.0035	0.0044
Ti02	0.0266	0.0059	0.0242	0.0038	0.0046	0.0050	0.0062	0.0067	0.0067
Ti03	0.0321	0.0042	0.0243	0.0028	0.0054	0.0060	0.0089	0.0078	0.0053
Ti04	0.0308	0.0036	0.0625	0.0036	0.0047	0.0075	0.0198	0.0067	0.0077
Ti05	0.0355	0.0040	0.0291	0.0042	0.0100	0.0096	0.0320	0.0057	0.0044
Ti06	0.0257	0.0043	0.0242	0.0045	0.0035	0.0083	0.0410	0.0025	0.0067
Ti07	0.0241	0.0070	0.0268	0.0029	0.0048	0.0092	0.0524	0.0039	0.0053
Ti08	0.0253	0.0032	0.0399	0.0039	0.0043	0.0098	0.0763	0.0024	0.0044
Ti09	0.0245	0.0032	0.0242	0.0047	0.0050	0.0096	0.0885	0.0027	0.0067
Ti10	0.0333	0.0083	0.0282	0.0033	0.0047	0.0081	0.0989	0.0087	0.0030
Ti11	0.0266	0.0039	0.0242	0.0047	0.0031	0.0316	0.1060	0.0049	0.0067
Ti12	0.0275	0.0049	0.0242	0.0050	0.0032	0.0473	0.1740	0.0046	0.0067

(b) Phosphorus samples								
Sample	**Chemical composition of steels [mass %]**							
	C	**Si**	**Mn**	**P**	**S**	**Al**	**Ti**	O_{tot}	**N**
P01	0.0381	0.0021	0.0499	0.0034	0.0043	0.0011	0.0013	0.0080	0.0038
P02	0.0265	0.0014	0.0462	0.0047	0.0070	0.0014	0.0030	0.0045	0.0037
P03	0.0258	0.0024	0.0322	0.0148	0.0087	0.0013	0.0016	0.0045	0.0043
P04	0.0387	0.0079	0.0567	0.0181	0.0040	0.0014	0.0015	0.0076	0.0045
P05	0.0156	0.0019	0.0316	0.0291	0.0095	0.0013	0.0018	0.0045	0.0045
P06	0.0381	0.0012	0.0574	0.0335,	0.0037	0.0010	0.0019	0.0066	0.0046
P07	0.0383	0.0018	0.0593	0.0454	0.0035	0.0012	0.0021	0.0091	0.0049
P08	0.0102	0.0019	0.0314	0.0502	0.0086	0.0015	0.0022	0.0045	0.0046
P09	0.0399	0.0064	0.0380	0.0733	0.0047	0.0011	0.0014	0.0052	0.0042
P10	0.0159	0.0042	0.0381	0.0751	0.0288	0.0012	0.0026	0.0045	0.0052
P11	0.0382	0.0068	0.0388	0.0952	0.0042	0.0009	0.0014	0.0049	0.0041
P12	0.0128	0.0011	0.0429	0.1060	0.0090	0.0009	0.0041	0.0045	0.0056

(c) Ti + P samples								
Sample	**Chemical composition of steels [mass %]**							
	C	**Si**	**Mn**	**P**	**S**	**Al**	**Ti**	O_{tot}	**N**
Ti+P01	0.0402	0.0074	0.0537	0.0034	0.0049	0.0035	0.0102	0.0076	0.0039
Ti+P02	0.0408	0.0078	0.0625	0.0035	0.0047	0,0071	0.0198	0.0067	0.0077
Ti+P03	0.0395	0.0072	0.0611	0.0035	0.0044	0.0084	0.0390	0.0063	0.0040
Ti+P04	0.0348	0.0033	0.0641	0.0224	0.0042	0.0028	0.0445	0.0061	0.0044
Ti+P05	0.0418	0.0069	0.0649	0.0221	0.0039	0.0022	0.0838	0.0060	0.0040
Ti+P06	0.0267	0.0085	0.0083	0.0223	0.0031	0.0032	0.1016	0.0049	0.0058
Ti+P07	0.0278	0.0087	0.0086	0.0220	0.0032	0.0073	0.1427	0.0046	0.0034
Ti+P08	0.0381	0.0063	0.0391	0.1230	0.0042	0,00510	0.0038	0.0079	0.0043
Ti+P09	0.0383	0.0087	0.0399	0.1230	0.0043	0,00410	0.0148	0.0084	0.0042
Ti+P10	0.0386	0.0054	0.0525	0.1230	0.0038	0.0096	0.0378	0.0064	0.0050
Ti+P11	0.0391	0.0094	0.0410	0.1230	0.0046	0,00610	0.0427	0.0078	0.0039
Ti+P12	0.0397	0.0023	0.0487	0.1230	0.0038	0.0833	0.0903	0.0080	0.0045

A further step in the preparation saw the master alloys being cut to cylindrical steel samples weighing 1,6 to 1,7 g which were polished, washed in acetone and cleaned in an ultrasonic bath for 5 minutes. After the drying process, the specimen was placed on a clean alumina substrate before being introduced in the furnace. Thereafter, the system was sealed and flushed with Ar gas at a flow rate of 250 cm^3/min until the oxygen content as measured by means of a mass spectrometer on the gas flow exiting the tube furnace reached values under 10 ppm.

To eliminate the influence of surface roughness, high purity alumina substrates (99.98 mass % Al_2O_3, R_a=0,2 µm) were used throughout the experiments.

2.2 Experimental set-up and procedure

The wetting experiments were conducted in a laboratory horizontal tube furnace, **Fig. 3** under a well controlled atmosphere of ultra high purity Ar gas. The latter, initially containing 2 ppm of O_2 and H_2O, was further purified to less than 10 ppb O_2 by being passed through an *oxisorb*® refining system prior to entering the reaction chamber of the furnace.
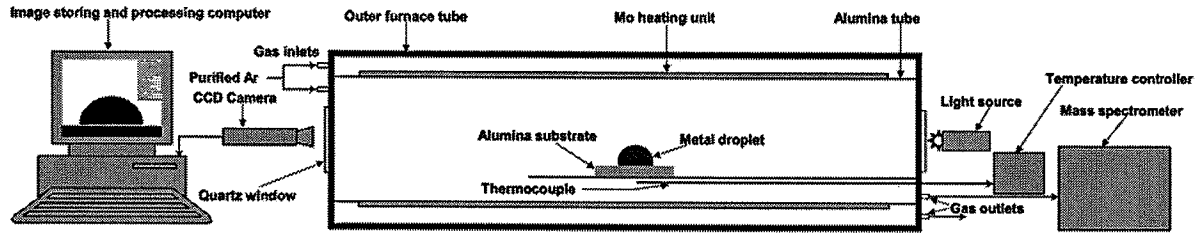
Figure 3. Schematic sketch of the drop shape analysis unit for high temperature wetting measurements. '

The heating process was linear at a rate of 15°C/min. A holding time of 10 min at 1620°C was followed by the cooling down at a rate of 10°C/min. The temperature was measured by a type B (Pt30Rh-Pt6Rh) thermocouple located in the immediate vicinity of the sample.

Once the sample was melted, the measurements of the contact angle as a function of temperature and time started. They consisted in a continuous monitoring of the shape of the sessile drop by a digital video camera (25 frames per second) connected to a computer, enabling automatic image analysis on the basis of a commercial software. The characteristic dimensions of the droplet (contact angle θ, drop base radius R and height H) were extracted with an accuracy of ± 2° for θ and ± 2 % for R and H [30].

2.3 Microscopic analysis of the interface

At the end of the wetting experiments, the samples were taken out of the furnace and the interfacial region was analysed microscopically in order to get information on the nature of interaction between the substrate and the liquid melt, and the possible formation of reaction products. The chemistry, morphology and microstructure of both sides (metal and substrate) of the interfacial area were determined using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) facility.

3. Results

The results of the wetting measurements in the Fe–Ti/Al_2O_3 system are presented in **Fig. 4**. It is clearly seen that the wetting angle decreases greatly with increasing Ti contents most notably in the low concentration range. This is in good agreement with the results of earlier works [31, 32, 33], but does not accord with a recent paper [34], in which the effect of Ti on the wettability of steels was found to be weak at 1575°C and 1600°C and negligible at 1550°C.
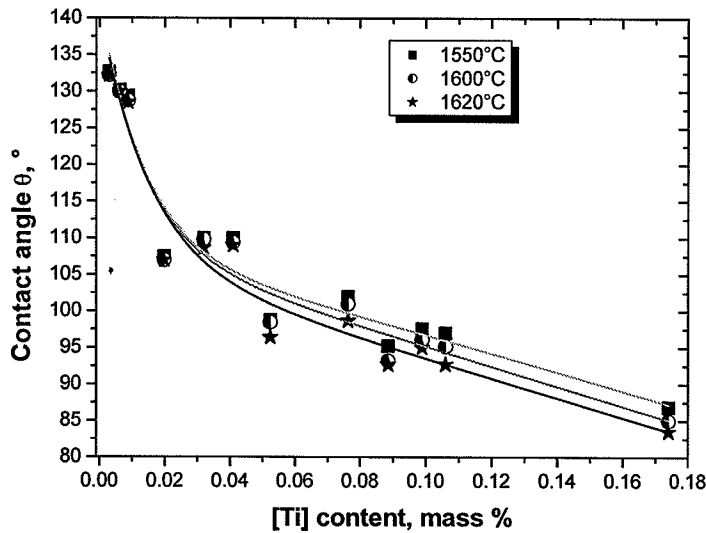
Figure 4. Effects of [Ti] contents on the wetting angle between Fe-Ti alloys and Al_2O_3 substrates as a function of temperature.

As expected, droplets of Fe alloys without Ti did not wet alumina, the measured contact angles being greater than 130°. Additions of up to 0,10 mass % Ti led to a remarkable decrease in the steady contact angle to about 90°, and at [Ti] contents greater than 0,15 mass % the Fe alloys were found to become wetting (i.e., θ < 90°). The non-wetting behaviour observed at very low [Ti] contents is a consequence of the formation at the Fe–Ti/Al_2O_3 interface of an oxide layer. For the oxygen contents expected in the Fe drop, the stable interfacial phase will be hercynite ($FeAl_2O_4$) which is formed according to the reaction:

$$Fe + [O] + Al_2O_3 = FeAl_2O_4 \qquad (4)$$

$$\Delta G^0 = -328,348 + 82,044T \; [J.mole^{-1}] \quad (T \geq 1809K) \; [35].$$
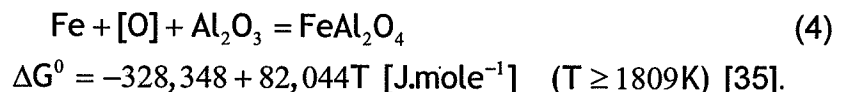
After the wetting experiments, the substrate surface under the droplet was completely covered with the reaction product layer, **Fig. 5 (a)**. Nevertheless, the solidified droplet detached easily from the substrate. This implies that the formed hercynite layer is not wetted by liquid steel. Hence, the equilibrium contact angle θ at the Fe alloy/$FeAl_2O_4$ interface is an obtuse one. An SEM examination of the contact surfaces revealed that after experiments of Fe-Ti alloys with Ti contents < 0,1 mass % and low [O] contents, the reaction layer between the droplet and the substrate was rather very thin and consisted only in $FeAl_2O_4$, while in the case of the experiments under high [Ti] contents that layer was thicker and rich in Al, O, Fe and Ti. In the latter case, the removal of the droplet from the substrate was made difficult by the increase in adhesion, which is another clear indication that a reaction between the droplet and the substrate occurred. Furthermore, a ridge formed at the spreading front at low [Ti] contents, **Fig. 5 (b)**.
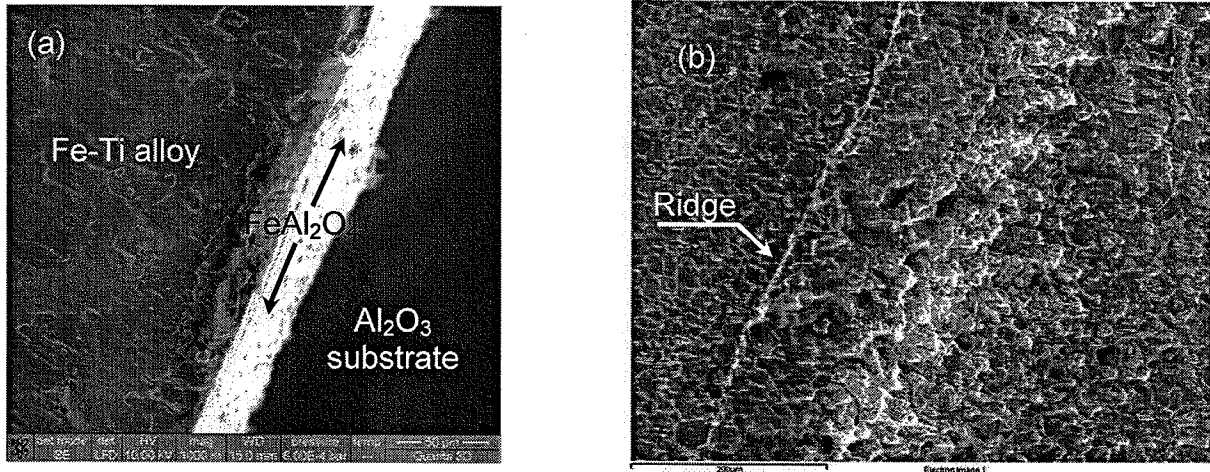
Figure 5. SEM images of the interfacial zone after a wetting experiment of the sample TiO2 with 62 ppm total O and 67 ppm [Ti]. The formation of a hercynite layer **(a)** and of a ridge **(b)** are established.

Although the measurement results show that the influence of temperature on the wetting behaviour in this system is not very significant, it is interesting to notice that it is less pronounced at lower [Ti] contents as illustrated in **Fig. 4**. As a general trend though, a slight improvement in wettability is registered at higher temperatures.

As for the spreading kinetics, it was observed that the equilibrium contact angle θ_f was reached within very few seconds for Fe-P samples, whereas for Fe-Ti samples it took up to 60 seconds to attain the value of θ_f, **Fig. 6**.
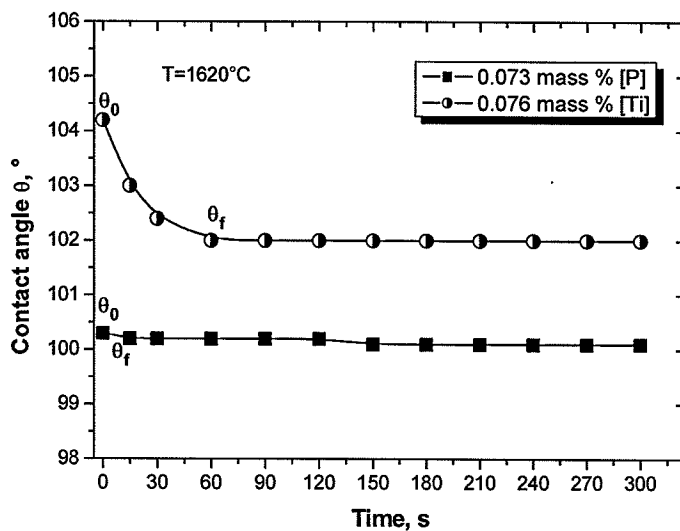

Figure 6. Variation of contact angle with time for Fe alloys on Al_2O_3 at 1620°C.

In the case of Fe-P samples, it was found that the wetting angles exhibited a marked decrease with increasing [P] concentration in the melt composition, **Fig. 7**, but the improvement of wettability was moderate as compared to that observed in the Fe-Ti series. Additional alloying to [P] contents above 0,10 mass % could not contribute to any further decrease of the contact angle which remained obtuse in the investigated concentration range.
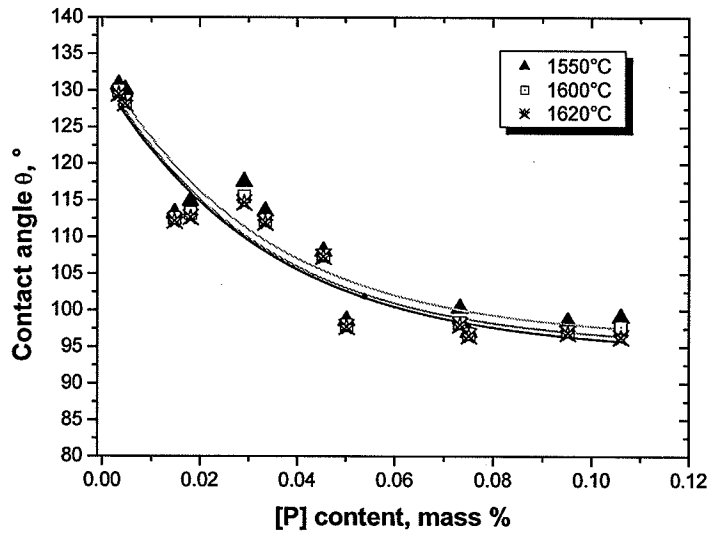
Figure 7. Effects of [P] contents on the wetting angle between Fe-P alloys and Al_2O_3 substrates as a function of temperature. The temperature influence on the wetting behaviour is constant for all investigated temperature values.

The SEM analysis of the P samples after the experiments showed that, like in the case of Ti, there was a hercynite reaction layer between the droplet and the substrate at very low [P] contents. The layer was, however, thinner compared to the one formed during the experiments with Ti. At high [P] contents (0,1 mass %), no hercynite layer was detected at the substrate.
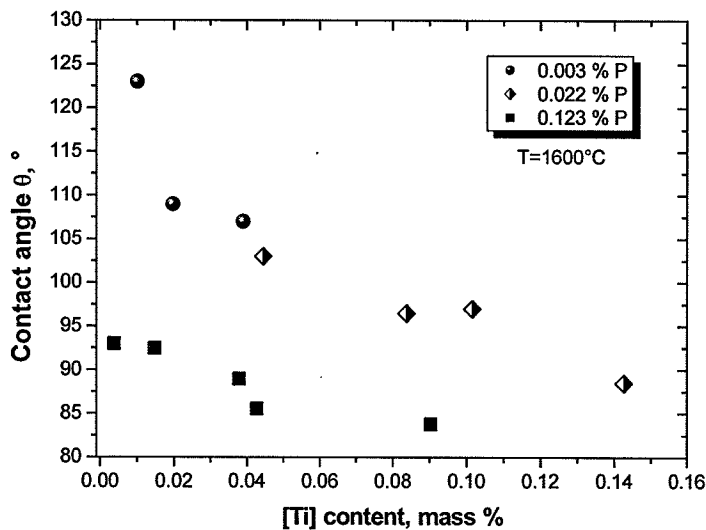
Figure 8. Combined effect of [Ti] and [P] contents on the wetting angle between Fe-Ti-P alloys and Al_2O_3 substrates at 1600°C.

Finally, the combined effect of Ti and P on the wetting behaviour in steel melts was found not to be additive. The curves in **Fig. 8** clearly show that at low [P] contents in the Fe alloy, changes in contact angle follow almost the pattern observed in **Fig. 4**, in which the θ values decreased exponentially with increasing [Ti] contents irrespective of [P] concentrations. At high P contents, however, the wettability depends largely on the [P] concentration in the melt, as will be discussed later.

With regard to the SEM/EDS analysis, the results obtained after the experiments with samples containing Ti and P did not show any presence of an interfacial hercynite layer.

4. Discussion and interpretation of results

Due to the addition of small amounts of Ti (<0,2 mass %) a decrease in the final contact angle from 133° to 85° was observed in our experiments, **Fig. 4**. It has been suggested that the addition of reactive elements such as Ti to the liquid Fe alloy improve the wetting on ceramics due to the formation of an interfacial reaction layer [13], which was confirmed in this work.

In the liquid Fe-Ti/Al$_2$O$_3$ system, reactivity depends critically on the concentrations of titanium and oxygen in the alloy, as the actual O$_2$ potential is determined by the kinetics of the reaction between Ti and O and the evaporation of the Al$_2$O$_3$ substrate [36]. The equilibrium in the droplet must fulfil the following condition:

$$Al_2O_3 \rightleftarrows 2[Al] + 3[O] \tag{5}$$

As the O$_2$ partial pressure is reduced in the system, Al$_2$O$_3$ will dissociate, contributing to an increase in [Al] in the melt. This is a potential mechanism that drives reactive wetting in a low O content gas atmosphere where the steel droplet wets alumina due to reaction (5). Thus, at low [Ti] concentrations, reactivity consists in some but limited dissolution of Al into the alloy, whereas at high [Ti] contents, Ti reacts with Al$_2$O$_3$ to form wettable TiO$_x$ layers of the order of some microns in thickness at the interface. The change in the type of alloy/substrate interface, from Fe-Ti/Al$_2$O$_3$ to Fe-Ti/TiO$_x$, leads to a pronounced change in wetting (from contact angles much higher than 130° to contact angles in the 80 – 90° range). The spreading rate is found to depend strongly on Ti activity in the alloy, indicating a reaction-induced process. The experimental results are in good agreement with the approach to reactive wetting proposed in [13], according to which both the final degree of wetting and the spreading rate are controlled by the interfacial reaction product. This was confirmed by the observation of the wetting kinetics through the examination of videos taken during the experiments. During the first few seconds, no spreading of the alloy was observed while the temperature was raised at a constant rate of 15°C/min. The contact angle of about 130° observed at this stage is typical of non-reactive metal/oxide systems [13]. The sudden spreading appears to be triggered by Ti attaining the triple line by diffusion from the top of the droplet.

From thermodynamic considerations, it was concluded [37] that Ti exists in the form of a binary TiO$_x$-Al$_2$O$_3$ phase in the inclusions observed in Ti-bearing Al-killed low carbon steels. The TiO$_x$-Al$_2$O$_3$ inclusions are reported to be wetted more easily by the liquid steel compared to the pure Al$_2$O$_3$ inclusions [38]. In the case of TiO$_x$ (i.e. Ti oxides of varying oxidation states), reported values of the contact angle for TiO$_2$ with liquid Fe vary between 84° [17] and 80° [39]. As a result of those low θ values, the separation of TiO$_x$ inclusions at the steel/slag interface is unlikely.

The results of SEM analysis revealed that the titanium oxides segregated at the surface of the steel droplet and at the interface between the droplet and the alumina substrate, **Fig. 9**, causing dramatic decreases in the contact angle. This suggests that those oxides are surface active with respect to Fe melts.
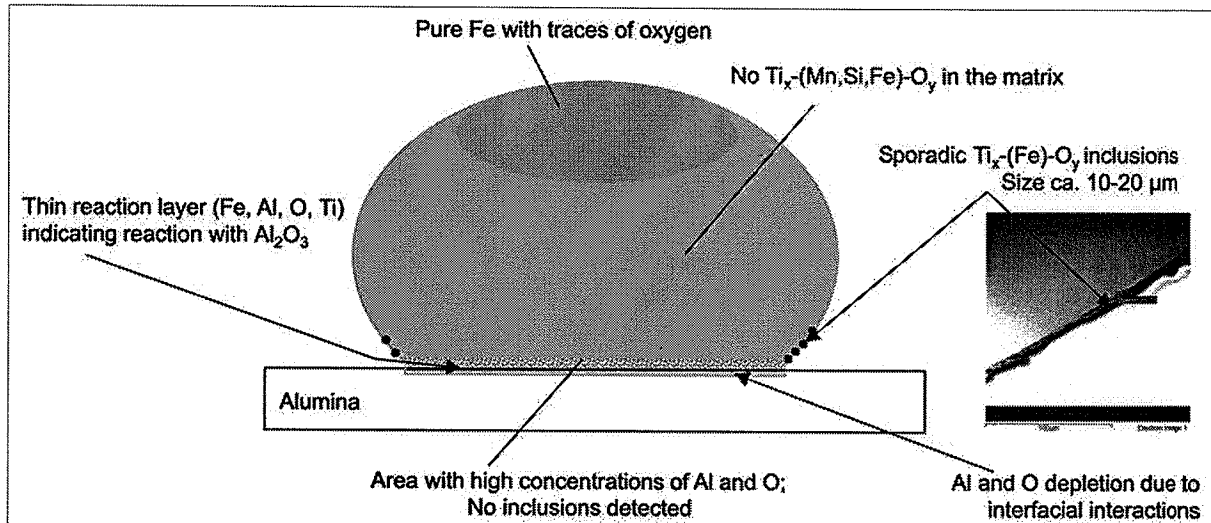
Figure 9. Summary of findings of SEM examination of the droplet-alumina system after wetting experiments on Fe-Ti alloys. The presence of a layer of complex oxides at the interface is confirmed.

Considering the influence of P, the improvement in the wetting behaviour of P bearing Fe alloys on alumina substrates cannot be attributed to a formation of a continuous reaction product layer at the metal/alumina interface. At investigated P contents, a decrease in contact angles with increasing [P] contents was registered but no reaction layer containing P was observed. Instead small islands of the reaction product rich in P close to the triple line were detected. This supports the theory which focuses on the adsorption of the alloying element at the solid/liquid interface before the reaction can take place. The rate determining process for wetting would then not be the formation of a reaction layer. Furthermore, the decrease in contact angle could be explained by these adsorption effects, since metallographic studies revealed that P segregates at the metal/ceramic interface.

The time dependence of the contact angle shows that the stable values of θ are established within seconds. This suggests that we deal with a non-reactive system.

During the experiments on Fe-Ti-P melts, it was found that the effect of Ti and P on the wetting behaviour is not additive. Ti being the most surface active element, enriches itself at the interfaces and contributes, consequently to a decrease of γ_{sl} and /or γ_{lg}. As the experimental results showed, at least at high [P] contents (> 0,1 mass %) an increase in [Ti] content does not contribute significantly to wetting in spite of the precipitation of Ti at the interface. The positive effect of P on wetting is due to its role in enhancing the Ti activity and dislocation of the previously formed interfacial hercynite layer, allowing this way a direct contact of Fe-Ti with the Al_2O_3 substrate.

5. Conclusion

This paper has provided a systematic study of the wetting behaviour of Al_2O_3 by Fe-Ti und Fe-P alloys as a function of steel chemistry, temperature and time. The main findings can be summarised as follows:

- In light of our experimental data, it is expected that the wetting behaviour of Fe-Ti and Fe-P melts will depend on both the identity and quantity of the alloying element and the abundance of dissolved oxygen.

- In binary Fe-Ti alloys, wetting increases considerably with increasing Ti content, and moderately with temperature. The alloys react with Al_2O_3 at the interface forming a complex layer of oxides composed of $FeAl_2O_4$ and TiO_x. The slight variation of wetting angles with time results from the high interfacial reactivity due to the presence of Ti which is a reactive metal.

- The $Fe-P/Al_2O_3$ system is a non-wetting one in which the wetting angles decrease substantially with increasing P concentrations. The initial transient wetting angles do not significantly vary with temperature and time, and the final equilibrium is built between the Fe-P melt and the initial Al_2O_3 substrate.

- The effect of Ti and P on the wetting behaviour of Fe alloys on Al_2O_3 is not additive. The effect of P on Ti bearing steels is rather to enhance the activity of Ti in the melt. Moreover, P contributes to a decomposition of the interfacial hercynite layer.

Cleary, this research has only been able to touch on some aspects of the complex topic of high temperature wetting. In order to validate the work carried out, a more in-depth investigation into the role of P is needed.

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