JOURNAL OF MATERIALS SCIENCE **37** (2002) 1061 – 1066

# Kinetics of interfacial reaction between solid iron and molten aluminium

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## 1. Introduction

Interfacial reaction in the Al-Fe system has been widely studied due to its technical and scientific importance and also practical implications in many manufacturing processes including aluminizing [1], permanent mold casting and solidification [2–4], and bi-metals fabrication [5]. The introduction of advance composite materials and particularly composites with intermetallic constituents [6, 7] has increased the importance of such reaction even further.

In order to study the interfacial reaction between liquid aluminum and solid iron, tests have been carried out in both static and dynamic conditions, where for the static test, an iron coupon was simply immersed into a stationary molten aluminum bath, as for example in the work reported by Komatsu *et al.* [8] or Bouche *et al.* [9]. For dynamic tests, however, iron discs were rotated within the molten aluminum [10–14]. In both cases, the formation of a very thin layer of intermetallic compounds was reported at the beginning of each test, but the subsequent growth of such newly formed interface layer was found to be different.

The growth rate is generally high for the stationary tests, from the start, as for instance reported for aluminizing [15–24]. For the dynamic situation, however, the growth rate is very much dependent on the state of molten aluminum with regard to the dissolution of the iron disk and its degree of saturation with iron atoms [11–13]. Generally, the initial growth rate is low but increases with the degree of saturation of molten aluminum with iron. As for the mechanism responsible for growth of the interfacial layer, volume diffusion was reported as the rate controlling mechanism [25], other factors such as chemical reaction, nucleation and wetting of iron test bars with molten aluminium have a lesser effect in progressing the reaction [11]. Taking volume diffusion into consideration, based on a theoretical approach, a general parabolic equation was proposed [9, 26], $d = Kt^{1/2}$, where $d$ is the thickness of the interfacial layer at time $t$ and $k$ as a constant, but deviation was reported from this ideal situation in experimental works [9, 11, 18, 22–24].

The current investigation was set up, as part of a wider study on the fabrication of net or near net-shaped iron-based aluminide components [27], to examine the kinetics of the Fe-Al reaction in a systematic fashion. This is because, a thorough knowledge of kinetics is critically important in devising appropriate experimental parameters. The literature however lacks any systematic study in this field, although there are reports of a positive or negative deviation from the parabolic law for shorter or longer exposure times, respectively [25].

## 2. Experimental procedures

In order to investigate the kinetics of interfacial reaction for the solid iron-liquid aluminum couple, rectangular iron coupons were submerged in a molten aluminium bath using the experimental set-up shown in Fig. 1.

Rectangular iron coupons, 60 mm long, 20 mm wide and $(1.7 \pm 0.2)$ mm thick, were ground and polished down to 0.5 $\mu$m using diamond paste, degreased, pickled and washed in alcohol before immersion into the molten aluminium. A 200 g commercially pure aluminium was melted in a graphite crucible under COVERAL flux and an argon atmosphere and three sets of temperatures, 700, 800 and 900°C, were employed. Table I gives the composition of both aluminium and iron samples. The iron test pieces were preheated to 700, 800, and 900°C for 60 seconds for each respective set of tests, i.e. kept 60 seconds inside the argon atmosphere furnace and above the molten aluminum crucible before being lowered into the molten aluminum, and held for 90 to 3000 seconds, i.e. 90, 185, 375, 750, 1500, and 3000 s, before quenching the whole crucible to room temperature in water.

The as-quenched test bars were sectioned transversally half way through immersion depth, cold mounted and ground and polished down to 3 $\mu$m diamond paste

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TABLE I Chemical analysis of iron and aluminum specimens used in this investigation (in Wt%)

| Specimen | C | Mn | Si | Cr | Ni | Cu | Fe | Zn | V | Ti | Mg | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Iron coupon | 0.111 | 0.348 | 0.1 | 0.028 | 0.023 | 0.029 | Bal. | – | – | – | – | – |
| Molten aluminium | – | 0.03 | 0.2 | – | 0.03 | 0.04 | 0.13 | 0.04 | 0.05 | 0.03 | 0.03 | Bal. |

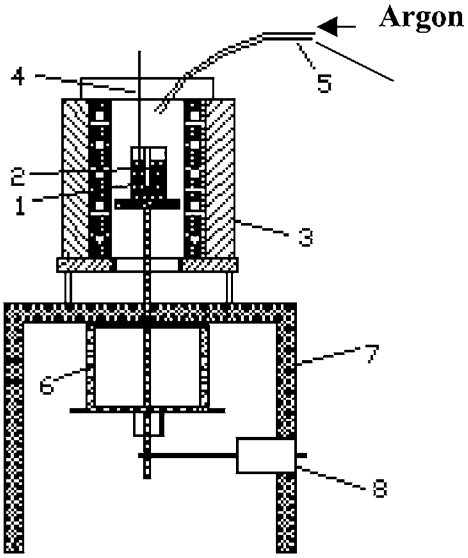


*Figure 1* Schematic diagram of the experiment setup; 1) Liquid aluminium 2) Iron coupons 3) Furnace 4) K-type thermocouple 5) Argon gas inlet 6) Water tank 7) Table 8) Crucible movement unit.

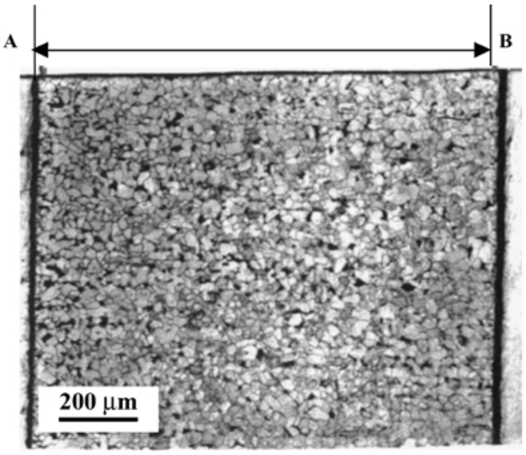
for microstructural analysis. Both etched and unetched specimens were examined using light and electron microscopes to measure the thickness of interface layer. A Cambridge S-360 SEM with EDAX and Lieca 200 image analysis attachments was employed. A total of forty measurements were taken for each test to measure the interface thickness accurately. The etchant was 3% nital solution.

## 3. Results

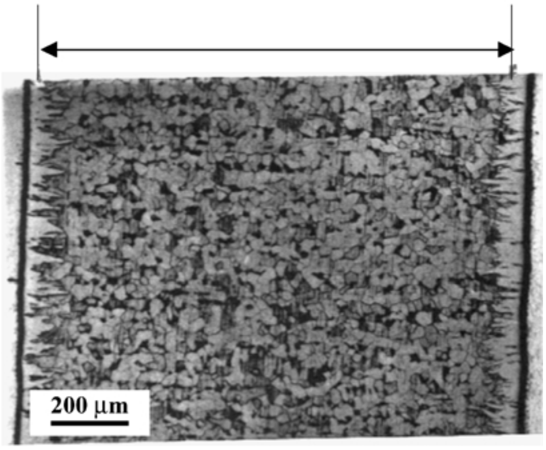
The light micrographs presented in Fig. 2 show the progress of interfacial reaction at different times and temperatures. The line AB represents the original thickness of the iron coupon. As can be seen, the thickness of the interface layer increases continuously with time for both 700 and 800°C tests. The initial thickness of iron coupon, however, increases up to 1500 and 750 seconds for 700 and 800°C respectively but decreases afterwards. For 900°C, however, the situation is slightly different in that the thickness of the interface layer increases only up to 375 seconds but decreases afterwards. Parallel to this, the initial thickness of the iron coupon decreases continuously from 185 seconds and disappears completely, i.e. dissolves within molten aluminium, after 3000 seconds.

The details of the interface layer microstructure is reported elsewhere [28]; it comprises $Fe_2Al_5$ as the major constituent and $FeAl_3$ as the minor phase.

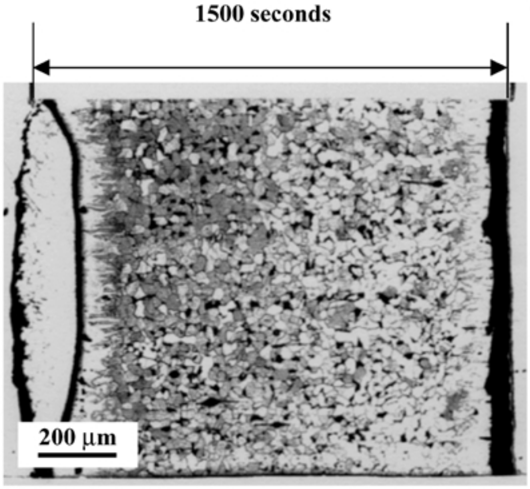
In order to examine the interface layer in more detail, a combination of scanning electron microscopy and image analysis techniques was used to reveal that the growth of the interface layer is initially towards the molten aluminium side, but changes direction towards the iron as the thickness of interface layer increases, see Fig. 3. The MK line in Fig. 3 represents the original interface between iron and molten aluminium. As will be discussed later, this may be due to diffusion of aluminium and iron atoms within the intermetallic layer.



95 seconds



1500 seconds

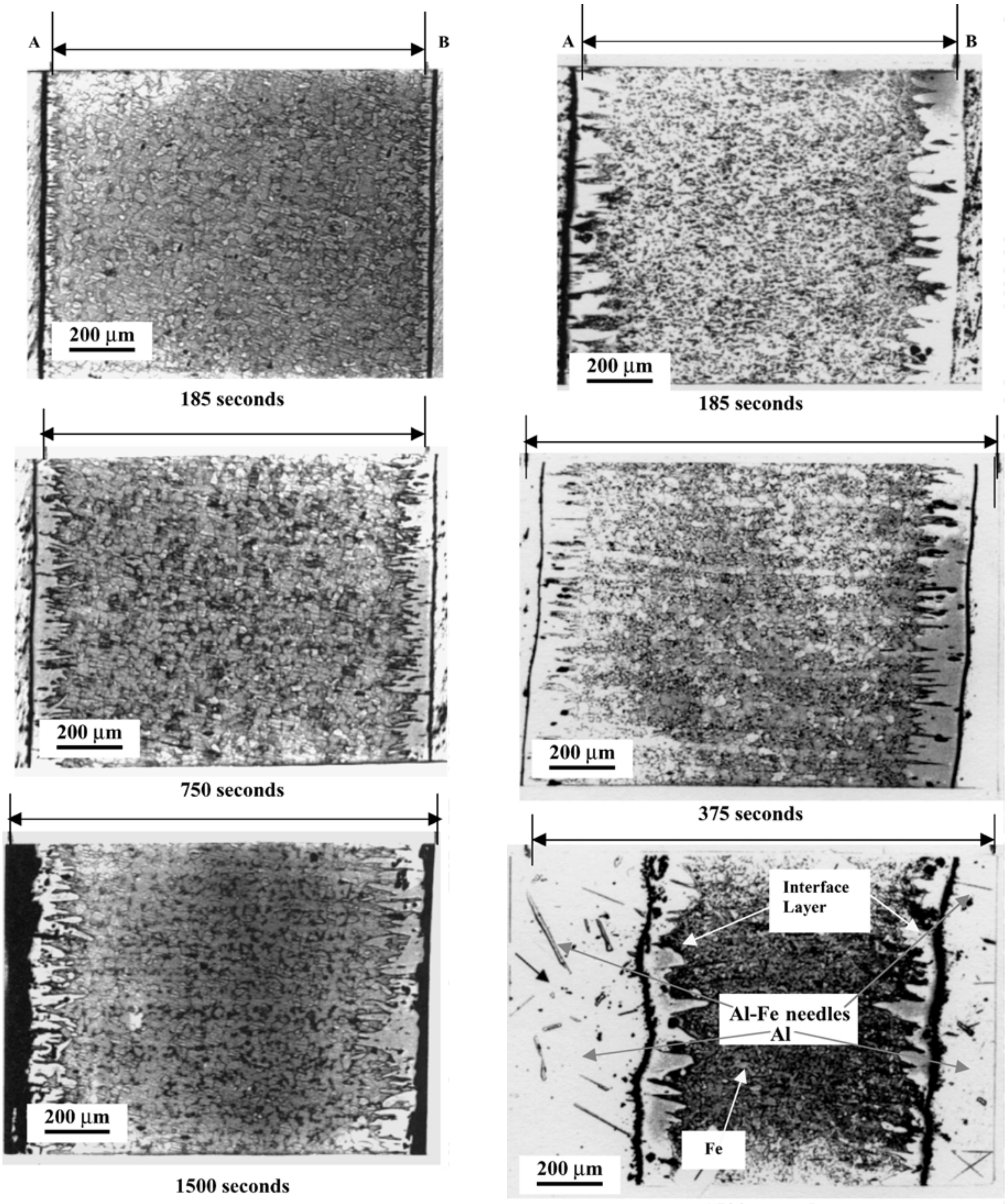


3000 seconds

(a) 700 °C

*Figure 2* Optical micrographs to show the interface layer formation and growth with time and temperature. (AB is the original thickness of Fe-coupons). (*Continued.*)

The average thickness of interface layer and its standard error values are given in Table II and plotted in



(b) 800 °C

(c) 900 °C

*Figure 2* (*Continued.*)

TABLE II The mean thickness of interface layer measured at different times and temperatures

| Temperature | 700°C | | 800°C | | 900°C | |
|---|---|---|---|---|---|---|
| Time (sec) | *d* (μm) | Std. Err. | *d* (μm) | Std. Err. | *d* (μm) | Std. Err. |
| 95 | 35 | 2 | 46 | 2 | 147 | 5 |
| 185 | 48 | 2.5 | 62 | 2 | 172 | 7 |
| 375 | 66 | 2.5 | 93 | 3 | 186 | 8 |
| 750 | 84 | 3 | 123 | 5 | 158 | 7 |
| 1500 | 101 | 4.5 | 145 | 8 | 113 | 5 |
| 3000 | 139 | 5 | 176 | 10 | *– | *– |

*Specimen dissolved completely.

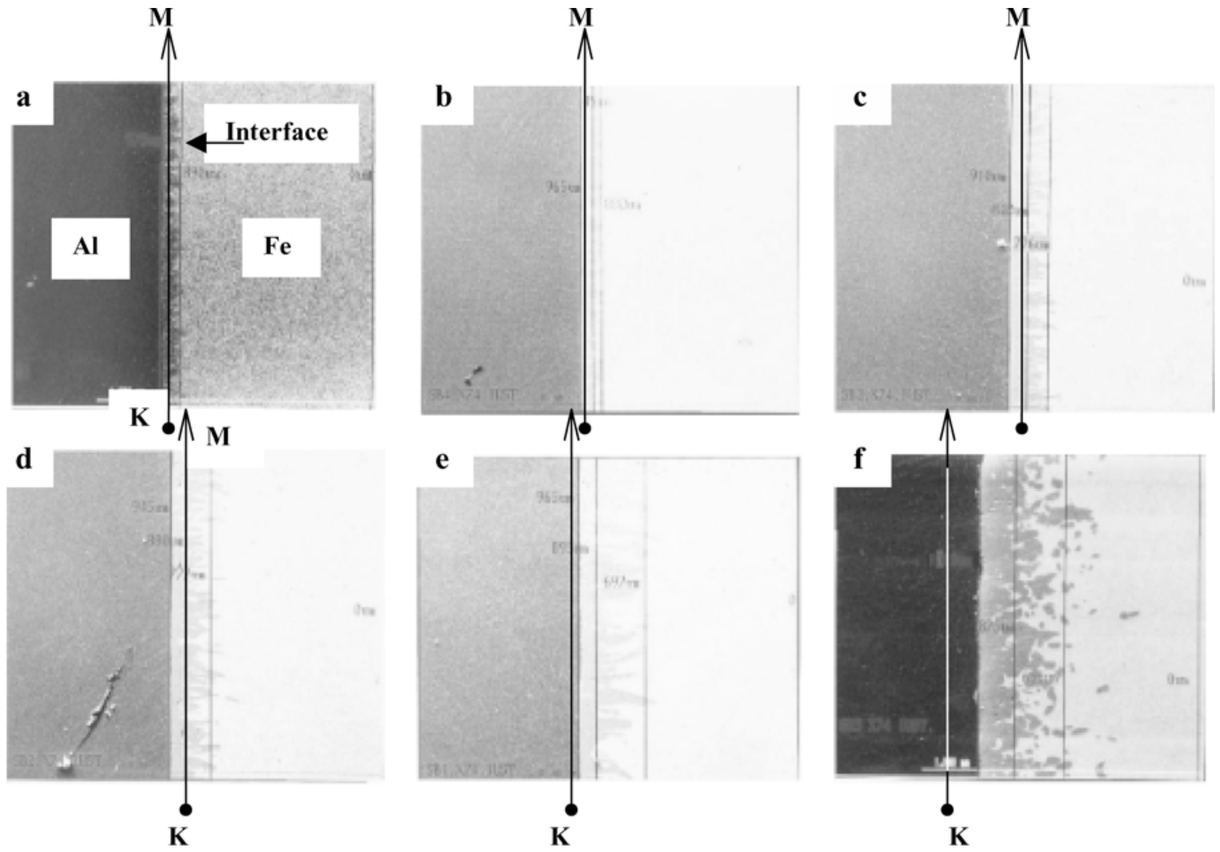


*Figure 3* SEM-Image analysis micrographs of the interface region to show the growth direction of the interface layer at 800°C. MK represents the position of Fe-Al interface before reaction. (a) 95 s, (b) 185 s, (c) 375 s, (d) 750 s, (e) 1500 s, (f) 3000 s.

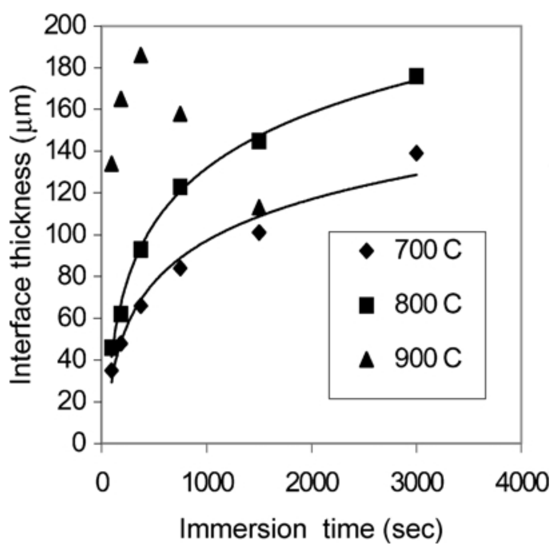
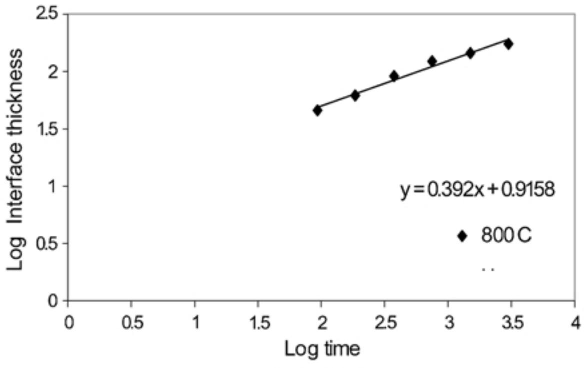
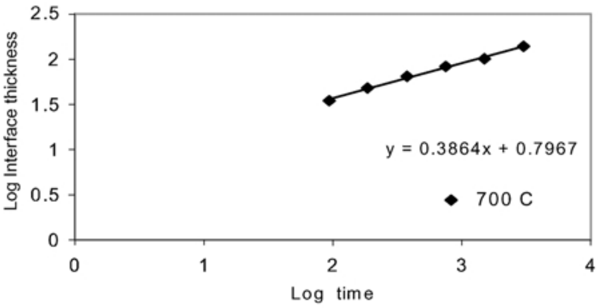


*Figure 4* The thickness of interface layer is plotted versus immersion time at different temperatures.



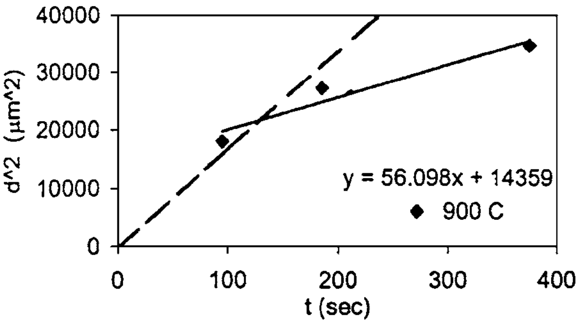
**(a) 800°C**



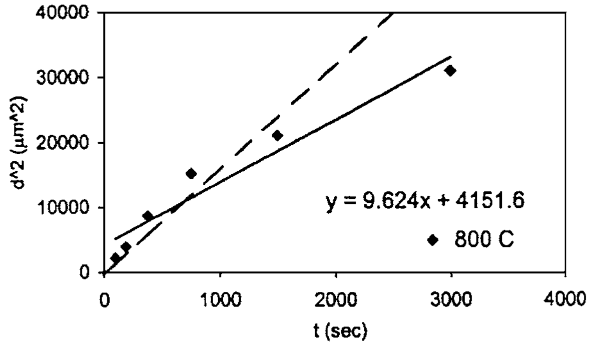
**(b) 700°C**

*Figure 5* The mean thickness plotted against time for (a) 800°C and (b) 700°C tests.

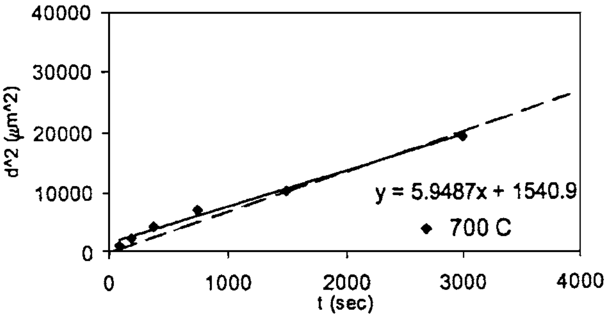
Fig. 4 for different times and temperatures. As it is evident, the initial thickness is higher at higher temperatures, and the rate of growth, i.e. the slope of each graph, is also higher in the early stages, but decreases with time. For the 900°C test, however, the trend changes after about 375 seconds, after which time the slope is negative. As will be discussed in the next section, this may be attributed to dissolution of the iron coupon within the molten aluminum. Table II is also plotted on a log-log scale, Fig. 5, to calculate the time exponent at each temperature. The time exponent for 700 and 800°C, ($n \approx 0.4$), is close to $n = \frac{1}{2}$ and thus may support the previous report that the reaction follows a parabolic law [9, 25]. For 900°C, however, both the time exponent and constant ($k$) are different, which may be attributed to the dissolution of iron coupon as mentioned before.



(a) 900°C



(b) 800°C



(c) 700°C

*Figure 6* The square of interface layer thickness plotted against time for tests at (a) 900°C (b) 800°C and (c) 700°C. (Note: Reaction constant, $k$, calculated from the solid lines).

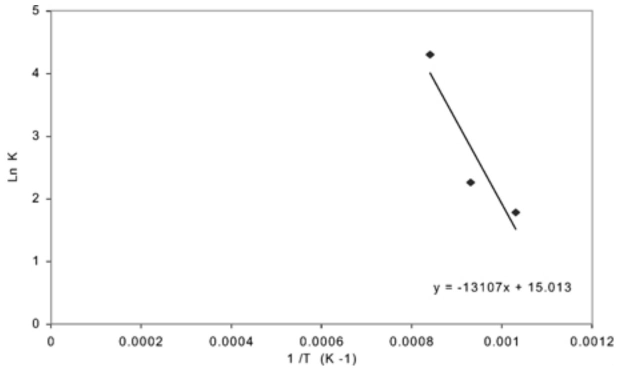


*Figure 7* Ln values of reaction constant, $k$, plotted versus inverse of temperature.

In order to investigate the rate controlling mechanism of such reaction, the square of interface thickness is plotted against time, $d^2 \propto t$, in Fig. 6 from which the $k$ values were calculated (solid line). The logarithm, (ln) of $k$-values are then plotted against the inverse of temperature, $\frac{1}{T}$, in Fig. 7 and the activation energy is calculated to be 109 $\text{kJ} \cdot \text{mol}^{-1}$. It is noted that the first three points of the 900°C test only were considered as the other points showed a different trend at this temperature.

## 4. Discussion

The initial growth of the interface layer into aluminium may be attributed to the ease of diffusion of iron atoms into molten aluminium. As the intermetallic layer is formed, $Fe_2Al_5$ [28], further growth is dependent on diffusion of iron and/or aluminium atoms within $Fe_2Al_5$. As reported before [25], the activation energies for diffusion of aluminium and iron within $Fe_2Al_5$ are 107 and 171 $\text{kJ} \cdot \text{mol}^{-1}$ respectivelyand therefore easier diffusion of aluminium is expected and thus the intermetallic phase grows towards the iron rich section as schematically depicted in Fig. 8. The activation energy calculated for these tests, 109 $\text{kJ} \cdot \text{mol}^{-1}$, is close to the energy needed for bulk diffusion of aluminum within $Fe_2Al_5$, and thus the change of growth direction for $Fe_2Al_5$ should be expected after the early stages of reaction.

As is evident from the light micrographs in Fig. 2, there are two processes of growth and dissolution of the interface layer active during the course of this experiment. The growth itself may be dominated by reaction, particularly in the early stages of the test, and diffusion. The fact that the growth is near parabolic with positive and negative deviations at the early and later stages of the test respectively clearly suggests that diffusion is not the only process active and therefore any deviation from the ideal situation should be attributed to reaction and dissolution. This is in support of work reported by Bouche *et al.* [9], who have also emphasised the effect of reaction and dissolution on the final thickness of the interface layer.

In order to identify the dominance of any process at any stage during the test, broken lines are drawn through the origins in Fig. 6 noting that dissolution of the iron coupons starts at about 1500, 750, and 185 seconds for 700, 800, and 900°C respectively. As dissolution should result in a negative deviation, it should be possible to identify the dominance of reaction at any temperature from Fig. 6. As is evident, the mechanism of growth for $Fe_2Al_5$ is reaction controlled, giving positive deviations, up to about 1000, 700, and 100 seconds for 700, 800 and 900°C respectively, but changes to diffusion, ($d = Kt^{\frac{1}{2}}$), a mixture of diffusion and dissolution, (a negative deviation), and finally to complete dissolution as in case of the tests at 900°C. The magnitude of the deviation from the parabolic distribution is an indication of the severity and dominance of any of the processes active during the course of interface growth.

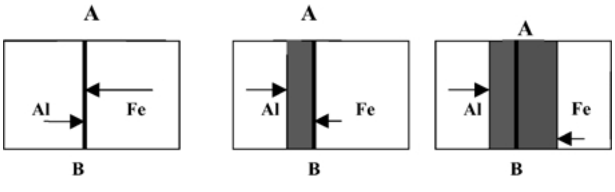


*Figure 8* Schematic diagrams to show intermetallic growth within iron and aluminium. (AB = initial interface, length of arrows is a measure of rate of diffusion of Al and Fe into respected phases).

In other words, the order or sequence of processes responsible for interface growth may be summarized as;

$$\text{Reaction} \rightarrow \text{Diffusion} \rightarrow \text{Diffusion} + \text{Dissolution} \rightarrow \text{Dissolution}$$

Such a scheme is clear for 900°C and that is why the 900°C data in Fig. 4, appear anomalous to the other temperatures.

The quantitative results reported here are in agreement with those reported by Bouche *et al.* [9] for temperatures of 700 and 800°C, but do not fully support their results at 900°C. Although they are similar for short times, but at longer holding times the results diverge. Bouche *et al.* [9] showed that there is continous increase in $Fe_2Al_5$ thickness even after 15 minute (900 seconds) at 900°C, and this was not found in this work.

## 5. Conclusions

It has been shown that the rate of growth for the interface layer in liquid aluminium-solid iron system follows a near parabolic distribution, but temperature plays an important role. At higher temperatures, e.g. 900°C, iron dissolves in molten aluminium after about 3000 seconds. The mechanisms responsible for the interfacial reaction are dominated by reaction, diffusion, diffusion and dissolution and finally dissolution. If reaction is the dominant mechanism, the interface layer thickness has a positive deviation to that predicted by the parabolic law, i.e. faster growth. The parabolic law is only valid if diffusion or more precisely bulk diffusion is the only mechanism responsible for interface growth. For diffusion and dissolution or dissolution only, however, the deviation from parabolic law is negative and becomes more negative with the domination of dissolution.

## Acknowledgments

H. R. S is grateful to the ministry of mines and metals of Iran for providing financial support towards his Ph.D. studies. Special thanks go to Mr. R. Ashraf-Semanai, acting deputy minister for his continuous support during the course of this study. Dr. Aboutalebi, head of DMSE-IUST is acknowledged for providing research facilities. Dr. Ghomashchi is grateful to Prof. S. Priest for granting him leave of absence to work at DMSE-IUST. Technical assistance provided by Mr. Shahamat and Mrs. Salehpoor is gratefully acknowledged.

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*Received 8 March 2000*
*and accepted 9 October 2001*