# *The use of transmission $^{57}$Fe Mössbauer spectroscopy to study the kinetics of hot-dip aluminizing of iron*

A previous communication [1] indicated that the kinetic interactions between solid iron and molten zinc can be successfully studied by means of transmission Mössbauer spectroscopy. This involves the measurement of the quantity of iron converted to intermetallic phases by areal evaluation of specific absorption peaks. The use of this analytical mode for the study of the iron-aluminium system should result in a more prominent Mössbauer effect than for iron–zinc because the intermetallic compounds produced during the aluminizing of iron are richer in iron, and hence $^{57}$Fe, than the corresponding phases formed during the galvanizing of iron. However, under commercial operating conditions (approximately 450 and 700° C for galvanizing and aluminizing respectively), the reaction rate in aluminizing is much faster than in galvanizing. This means that the thin iron substrates required for transmission Mössbauer spectroscopy can only be dipped for short times (less than 10 sec) otherwise complete conversion to intermetallic phases, followed by solution in the molten aluminium will occur.

The fully annealed iron foil (nominal purity 99.6% Fe) used in this study was 0.045 ± 0.005 mm thick. Prior to immersion in the aluminium (99.99%), foil samples were given a surface treatment to ensure elemental contact between the reactants. This was accomplished by hydrochloric acid pickling and aqueous fluxing using a saturated solution of 30% KCl; 30% NaCl and 10% each of LiCl, NaF, KBr and KI [2]. After drying, so that a thin layer of solid flux covered each specimen, the iron foils were aluminized for specific times at 670 and 685° C. The estimated maximum temperature variation was ± 2° C whilst the error in time was less than ± 1 sec. The aluminized specimens were examined using a commercial constant acceleration Mössbauer spectrometer with 25 mCi of $^{57}$Co diffused into a rhodium matrix as a source of $\gamma$-photons. Counts were stored in a 512 channel multi-channel analyser.

Fig. 1 shows that the normal six peak ferromagnetic iron spectrum is modified after aluminizing: extra absorption maxima arising from Fe–Al intermetallic compounds appear between peaks "3" and "4". Neglecting saturation effects and assuming that the recoil-free fraction of Fe–Al intermetallic phases is equivalent to that of $\alpha$-Fe, then the quantity of iron in a specific environment is directly proportional to the area encompassed by the absorption peak of that environment. Thus the percentage of total iron converted to Fe–Al intermetallic compounds, $\alpha$, is given by:

$$\alpha = \left[\frac{[(A_4+A_7+A_8)-A_3]}{[A_1+A_2+2A_3+A_5+A_6]+[(A_4+A_7+A_8)-A_3]}\right] \times \frac{100}{1}$$

where $A_j$ is the area under the $j$th peak.

Evaluation of $\alpha$ as a function of both time and temperature enables the early stage kinetic interactions between iron and aluminium to be evaluated. Linear regression fitting of the extent of

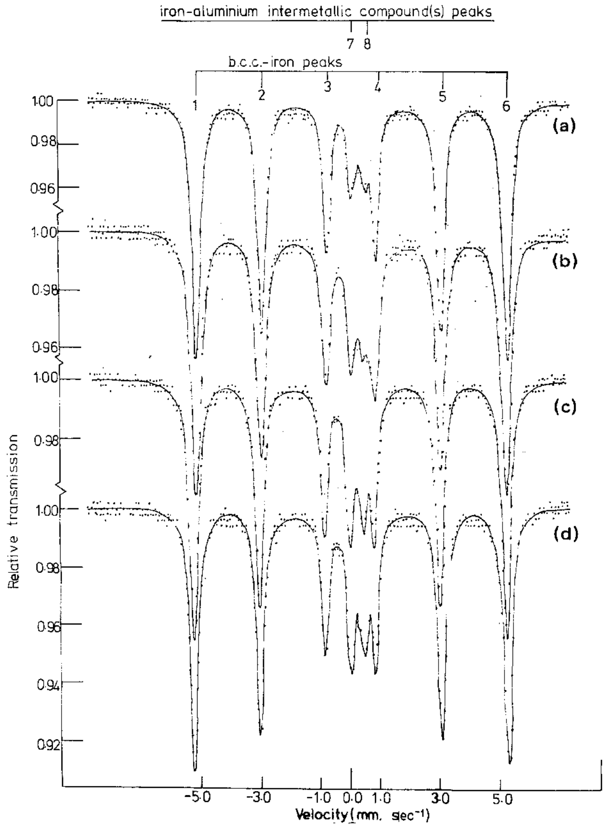

*Figure 1* Transmission Mössbauer spectra of the annealed iron foils hot-dip aluminized at 670° C for (a) 2 sec; (b) 4 sec; (c) 7 sec; (d) 10 sec.

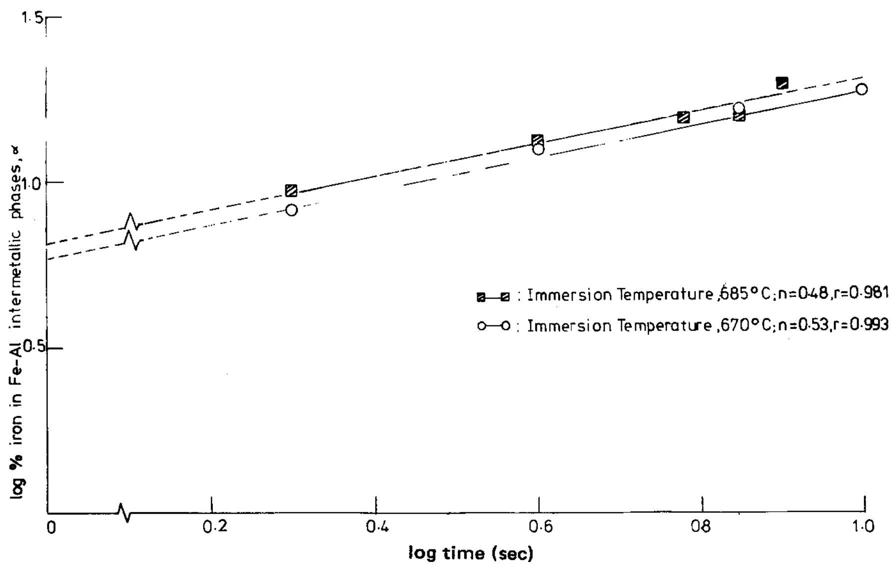

*Figure 2* Hot-dipping kinetic interactions between iron and aluminium at 670 and 685° C.

reaction, $\alpha$, to a power law of the form:

$$\alpha = Kt^n,$$

where $K$ is the reaction rate constant, $t$ the time and $n$ a temperature independent constant, yields time exponents of 0.53 at 670° C and 0.48 at 685° C (Fig. 2), which are close to 0.50, the value predicted theoretically for a volume diffusion controlled reaction. Since Mössbauer spectroscopy gives a true measure of the extent of interaction, this finding contrasts with the work of Heumann and Dittrich [3], who were unable to obtain a parabolic time evolution for growth when they measured mean diffusion distances using a metallographic technique. Assuming that the reaction rate constant is governed by an Arrhenius-type temperature dependence, then an activation energy of the order of 140 kJ mol$^{-1}$ can be derived from our data for the rate controlling process in aluminizing. Recent results obtained using a metallographic technique [4] have indicated that the activation energy of the rate determining step in hot-dip aluminizing is of the order of 170 kJ mol$^{-1}$. Although the activation energy reported in this communication is lower, it must, however, be considered a tentative one since it has been derived from data arising from experiments carried out at two temperatures only. A more reliable value could be established by using the Mössbauer technique to evaluate reaction rates at a greater number of temperatures. Nevertheless, the value obtained herein is considerably larger than the previously accepted value of 54 kJ mol$^{-1}$ [3].

In conclusion, this work has shown that transmission Mössbauer spectroscopy can be used to study the early stage kinetic interactions between solid iron and molten aluminium.

## References

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