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Periodic Formation of FeSi Bands in Diffusion Couples Fe(15 wt.% Si) – Zn

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During the reaction in Fe(15 wt.% Si)-Zn diffusion couples at temperatures between 623 and 723 K thin regularly spaced parallel bands containing very small FeSi precipitates are observed throughout the δ and ζ reaction layers.

The periodic nature of this effect is strongly reminiscent of the well-known Liesegang phenomenon. A detailed analysis of our results with respect to the principles underlying the Liesegang mechanism, however, shows that such a mechanism cannot explain the observed phenomenon in our case.

A more probable explanation is found in the action of shear and tensile stresses in the diffusion couple which lead to a periodic release of the continuously formed FeSi precipitates from the Fe(15 wt.% Si) substrate. Preliminary results obtained with substrates of varying thicknesses are strongly in favour of the latter explanation.

Periodische Bildung von FeSi-Bändern in Fe(15 Masse-% Si)-Zn Diffusionspaaren

Während der Reaktion in Fe(15 Masse-% Si)-Zn Diffusionspaaren bei Temperaturen zwischen 623 und 723 K wurden in regelmäßigen Abständen durch die δ- und ζ-Reaktionsschichten dünne parallele Bänder von sehr kleinen FeSi-Ausscheidungen beobachtet.

Die periodische Natur dieses Effektes ist dem wohlbekannten Liesegang-Phänomen sehr ähnlich. Eine detaillierte Analyse unserer Ergebnisse unter Berücksichtigung der Prinzipien, die dem Liesegang-Mechanismus zugrunde liegen, zeigte jedoch, daß ein solcher Mechanismus in unserem Fall nicht zutreffen kann.

Vielmehr muß die Erklärung unserer Ergebnisse gesucht werden in der Wirksamkeit von Schub- und Zugspannungen in den Diffusionspaaren, die dazu führen, daß die kontinuierlich gebildete FeSi-Ausscheidungen periodisch vom Fe(15 Masse-% Si)-Substrat gelöst werden. Vorläufige Versuche mit Substraten unterschiedlicher Dicke sind zugunsten dieser letzten Erklärung ausgefallen.

This investigation is part of an extensive investigation into the influence of silicon present in iron on the reaction between iron and zinc. The role of silicon during the reaction between iron and zinc has been the subject of many investigations[1][2]. Because of the tremendous effect that very low silicon concentrations in iron have on this reaction all former investigations were dealing with these low (0.07 to 0.3 wt.%) silicon concentrations.

In order to obtain a more complete understanding of the role that silicon plays we have extended the concentration range to higher concentrations; up to the solubility limit of silicon in iron: i.e. 15 wt.%. The experiments have been carried out by means of the diffusion couple technique in which solid Fe(Si) – solid Zn and solid Fe(Si) – liquid Zn couples were studied at 623, 668 and 723 K, respectively. Because of the very peculiar observations we made on the Fe (15 wt.% Si)-Zn couples we decided to publish the work on these couples as an intermediate result.

Experimental

As starting materials we used electrolytic iron lumps (99.9 %, Highways International), silicon rod (99.9 %, Hoboken Belgium), zinc sheet (used for solid-liquid couples, 99.99 % Budelco B. V. Holland) and zinc rod (used for solid-solid couples, 99.999 %, Koch Light Laboratories, England). The Fe-15 wt.% Si alloy was prepared by repeated argon arc melting. The solid-solid diffusion couples were made by thoroughly clamping the mechanically ground (up to 600 Grit) slices of the couple halves. The couples were then heated in sealed evacuated silica capsules at 623 K or 668 K for appropriate times.

The solid-liquid diffusion couples were made by hot-dipping the Fe-15 wt.% Si slices in a zinc bath (saturated with iron) at 723 K. Before dipping the slices were degreased, pickled in 6N HCl (5 min) and wet-fluxed for 5 min in a solution of $ZnCl_2$ and NH_4Cl (1 M) at 353 K. Subsequently they were dried during 10 min in a furnace at 383 K.

After the reaction the diffusion couples were quenched and subsequently embedded, ground and polished. After etching in a 3 % nital solution (HNO_3 in alcohol) they were examined microscopically.

Concentration profiles in the couples were measured using an electron probe X-ray microanalyser (Jeol Superprobe 733). Point measurements were carried out and iron, zinc and silicon pulses were counted. The intensity data were converted into concentration units by using the Magic 3B computer program, developed by J. W. Colby. By grinding the diffusion couples in a plane perpendicular to the diffusion direction the various phases present in the couples could be exposed one by one and identified by means of X-ray diffraction techniques.

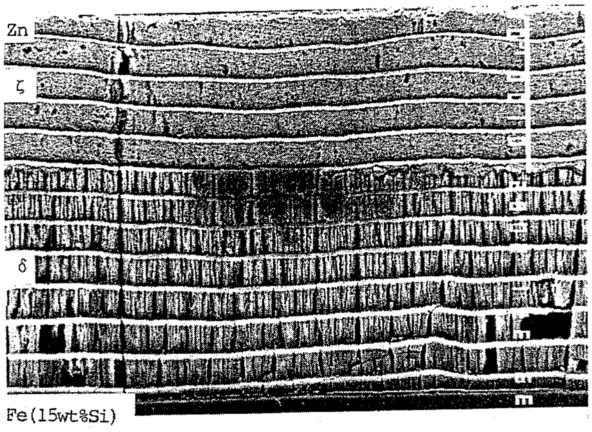

Fig. 1. Diffusion couple Fe(15 wt.% Si)-Zn annealed for 24 h at 668 K. The holes between the grains of the δ layer are due to the prolonged etching of the couple. The white bar indicates 100 μm (Back scattered electron image).

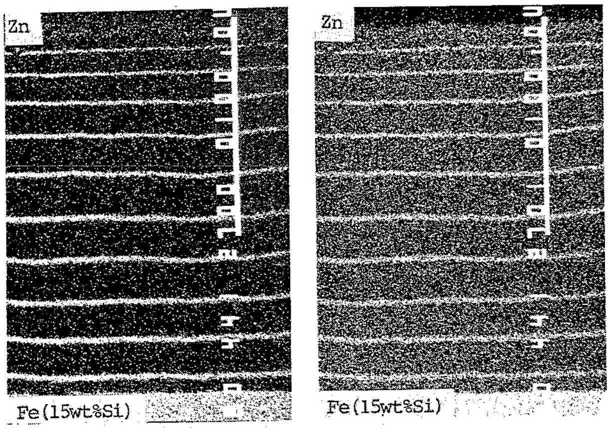

Fig. 2a and b. Si-Kα (a) and Fe-Kα (b) distribution map of an Fe(15 wt.% Si)-Zn diffusion couple annealed for 20.5 h at 668 K. The white bar indicates 100 μm.

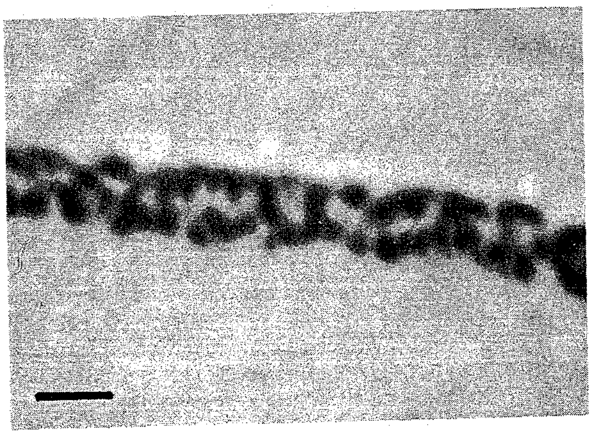

Fig. 3. FeSi band in an Fe(15 wt.% Si)-Zn couple at a large magnification. The bar indicates 1 μm (Back scattered electron image).

Table 1. Total layer thickness and number of FeSi bands in the Fe(15 wt.% Si)-Zn diffusion couples as a function of annealing time at 668 K.

Annealing time in h	total layer thickness in μm	number of bands in the reaction layer
1	25	–
4	60	4
20.5	170	11
64	290	16

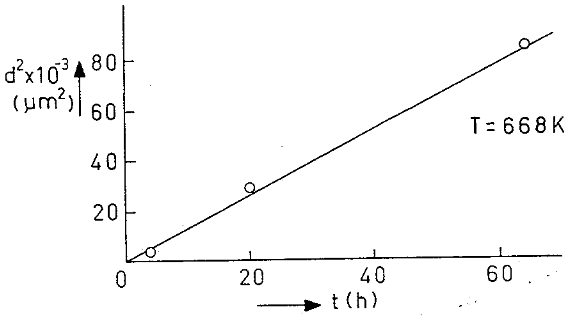

Fig. 4. Total layer thickness in the Fe(15 wt.% Si)-Zn diffusion couples for different annealing times at 668 K.

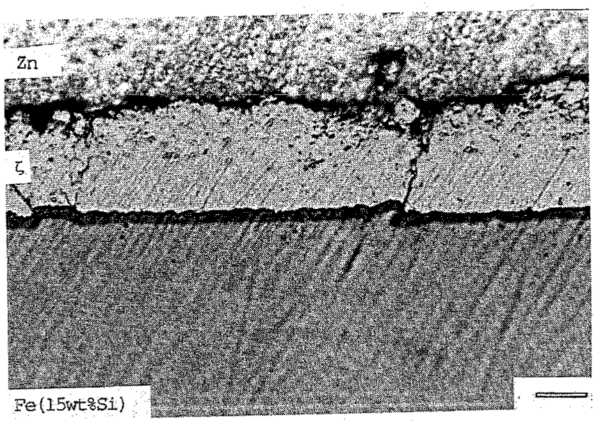

Fig. 5. Diffusion couple Fe(15 wt.% Si)-Zn annealed for 1 h at 668 K. At this annealing time δ isn't visible yet. The bar indicates 10 μm.

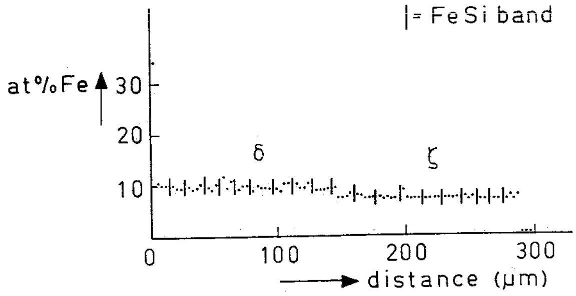

Fig. 6. Fe-concentration profile of an Fe(15 wt.% Si)-Zn diffusion couple annealed for 64 h at 668 K.

Table 2. Calculated spacing coefficients for an Fe(15 wt.% Si)-Zn diffusion couple, annealed for 139 h at 668 K. A photomicrograph of the couple is shown in fig. 7.

Bandnr.	X_n/X_{n-1}	Bandnr.	X_n/X_{n-1}	Bandnr.	X_n/X_{n-1}
1	–	13	1.09	25	1.04
2	1.79	14	1.08	26	1.04
3	1.53	15	1.08	27	1.04
4	1.35	16	1.08	28	1.04
5	1.31	17	1.07	29	1.04
6	1.25	18	1.07	30	1.04
7	1.19	19	1.06	31	1.04
8	1.17	20	1.06	32	1.04
9	1.15	21	1.05	33	1.03
10	1.14	22	1.05		
11	1.13	23	1.05		
12	1.10	24	1.04		

Results

Morphology

Figure 1 gives an example of the layer morphology in a solid-solid diffusion couple annealed at 668 K for 24 h. What strikes immediately in this couple is the presence of thin parallel bands with a very regular spacing in both reaction layers. From fig. 2a and b we must conclude that these bands are richer in iron and silicon than the adjacent matrix. By examining the bands more closely (fig. 3) we can see that they are not compact layers but contain many very small precipitates.

By means of X-ray diffraction (CoKα, Fe filter) we were able to identify these precipitates as FeSi. The two other reaction layers turned out to be the δ ($FeZn_{10}$) and ζ ($FeZn_{13}$) phases of the binary Fe-Zn system as expected. This phenomenon of bands containing FeSi precipitates at regular distances from each other was not restricted to the temperature of 668 K. It was also observed at lower temperatures (e.g. 623 K) and higher temperatures (e.g. 723 K, i.e. above the melting point of zinc). This latter observation indicates that the physical state of the zinc has no influence on the presence of bands in this temperature range.

Kinetics

Table 1 and fig. 4 show the result of some preliminary measurements on the kinetics associated with this phenomenon at 668 K. At short annealing time ($<$1 h) no band with FeSi precipitates is observed in the reaction layer. At these short annealing times we do observe such a band at the Fe(15 wt.% Si) substrate (fig. 5).

From fig. 4 we see that the total layer thickness follows a parabolic growth law, indicating a diffusion controlled growth mechanism.

The distance between the bands is not constant but varies between approximately 20 μm for bands at the iron-side of the couple to approximately 15 μm for bands at the zinc side of the couple.

Microprobe analysis

Figure 6 gives the measured Fe concentration profile for a Fe(15 wt.% Si)-Zn diffusion couple annealed for 64 h at 668 K. The profiles we measured were very similar to those in pure Fe-Zn-couples with an exception for the δ layer where we did not find the δ_c sublayer-concentration (Fe concentration 11 to 12 at.%). The average composition of a band was found to be 37 at.% Fe, 33 at.% Si and 30 at.% Zn. By means of the microprobe we also studied the relation between the distance of the last formed band from the Fe(15 wt.% Si)-substrate and the composition of the substrate in the vicinity of the phase boundary. This was done in order to verify whether a periodic depletion in Si took place in the substrate near the phase boundary. No such effect, however, could be observed.

Discussion

At first sight it would seem tempting to describe the observed phenomenon in terms of the well-known Liesegang mechanism3)4). This mechanism, although mostly found in electrolyte-gelatin systems, has also been observed in solid systems5)6). A closer inspection of the facts, however, shows that the resemblance between both phenomena is only superficial, mainly because of the following considerations:

- The FeSi band formation does not obey the spacing law (Jablczynski7)) which states that x_n/x_{n-1} is a constant, where x_n is the distance of the n^{th} band from the Zn/reaction layer boundary. Table 2 shows these calculations for a diffusion couple annealed for 139 h at 668 K. A photomicrograph of this couple is given in fig. 7.

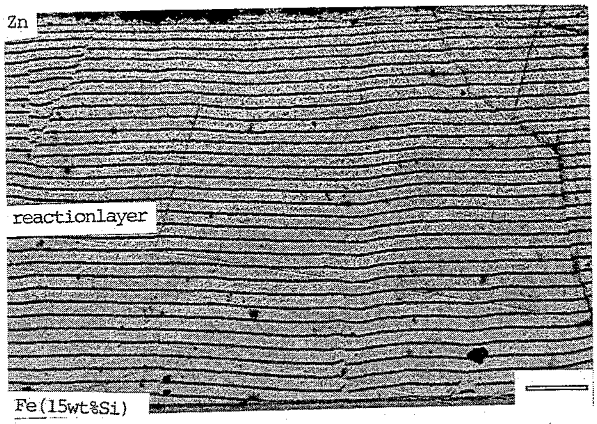

Fig. 7. Diffusion couple Fe(15 wt.% Si)-Zn annealed for 139 h at 668 K, used for spacing coefficient calculation of table 2. Because of the light etching the distinction between the δ and ζ layers isn't visible. The bar indicates 100 μm.

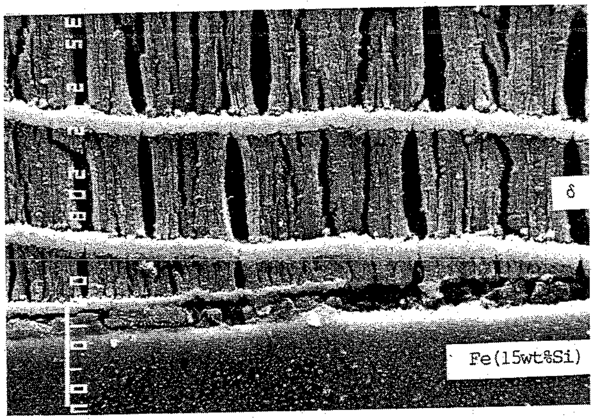

Fig. 8. Fe(15 wt.% Si)/reaction layer boundary of the diffusion couple shown in fig. 1. The white bar indicates 10 μm. (Back scattered electron image).

- According to the supersaturation theory of Ostwald8), which has been commonly accepted as the explanation for the Liesegang mechanism, one would expect the band formation to be discontinuous in nature; a new band not being produced until a critical supersaturation is reached. In our case the process is obviously continuous as fig. 8 clearly shows that a new band is immediately formed after the previous one has been released from the substrate.

In our opinion the most likely explanation for the observed phenomena must be sought in the operation of shear and tensile stresses which frequently occur in diffusion couples. These stresses build up as a result of volume changes during the diffusion process. In the Fe(15 wt.% Si)-Zn system Zn diffuses into the substrate to form Fe-Zn diffusion layers with the result that the substrate is depleted in iron and a layer of porous FeSi is formed. We believe that this process is accompanied by a gradual build-up of tensions at the interface, eventually leading to a lift-off of the FeSi layer from the substrate. The periodic nature of this process is reflected in the constant thickness of the FeSi bands. Normally the stresses built up in a diffusion couple can be accomodated by means of stress-relaxation in the substrate or the diffusion layers itself. In our case, however, both the brittleness of the substrate and the couple preparation (in a clamp) would stand in the way of such a relaxation process.

If this stress theory applies it would be expected that a change in mechanical properties of substrate and/or diffusion layer would have its influence on e.g. the spacing and thickness of the FeSi bands. As the mechanical properties of the diffusion layer can hardly be influenced from the outside it is obvious that the only way to test our theory is to vary the properties of the substrate and to choose a different way of couple preparation. In practice the first point can be tested by reducing the thickness of the substrate as in a thin substrate the possibilities for stress relaxation by plastic deformation are greatly enhanced.

The second point can be realised by abandoning the clamp in the couple preparation and choosing instead a vapour-deposited layer of zinc as the zinc source.

Preliminary experiments with such thin-substrate-couples indeed showed a marked change in the spacing and thickness of the FeSi bands, thus substantiating our stress theory. More work to this effect is being carried out at the moment.

In particular, various other ternary systems are being tested for the same phenomena. In this context it is interesting to say that preliminary experiments in the Fe(Ge)-Zn and Co(Si)-Zn systems indeed showed the expected periodic band formation.

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