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DIFFUSION INDUCED GRAIN BOUNDARY MOTION IN THE
IRON-ZINC SYSTEM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By

Venkata Subramanian Iyer, B.Tech., M.S.

* * * *

The Ohio State University
1986

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CHAPTER I
INTRODUCTION

It has now been reported by several authors that in many binary systems, diffusion of a solute into or out of a polycrystalline sample can induce the grain boundaries in the sample to migrate (1-35). These migrating boundaries leave behind them regions that are either enriched or depleted in solute depending on whether the solute is going into or out of the specimen. This phenomenon has come to be known as "Diffusion Induced Grain Boundary Migration" (DIGM). Fig 1 shows a schematic sketch of this process, with Fig 1(a) corresponding to the solute coming into the specimen and Fig 1(b) showing the solute leaving the specimen.

DIGM has been observed and documented in well over twenty binary systems. Most of the systems have a substitutional element as the solute, e.g. Zn going into Cu or Fe (1,17). However DIGM has also been reported in the Ni-C system, in which carbon is an interstitial solute (26). It was initially thought that DIGM was
ALLOYED ZONE  
DE-ALLOYED ZONE  

INITIAL BOUNDARY POSITION AT $t=0$

BOUNDARY POSITION AT $t=t$

(a) $J_{in} > J_{out}$

(b) $J_{out} > J_{in}$

Fig 1 Schematic Illustration of "Diffusion Induced Grain Boundary Motion"

a. Solute coming into the sample
b. Solute leaving the sample

[After Reference 27]
restricted to low temperatures where lattice diffusion is essentially frozen out. However recently it has also been observed at higher temperatures where there is appreciable lattice diffusion (10). DIGM is an important phenomenon because it can result in significant alloying or de-alloying, i.e. mass transport at low temperatures. Furthermore it is not restricted to just diffusion from the vapor phase, but has been observed in fields as diverse as diffusion in thin solid films (14), liquid phase sintering (36-39), sputtering of heated alloy targets (11,12) and the irradiation of alloy materials (40).

The salient features of DIGM are as follows:
1. The concentration of solute in the region swept out by the migrating grain boundary is higher than in the bulk. A sharp concentration discontinuity exists across the grain boundary (3,7).
2. Surface relief is often observed to be associated with DIGM. The migrated region is normally higher than the bulk (6,17,21).
3. Not all the boundaries on the sample surface migrate. Those which migrate do so at different rates (14). Sometimes different regions of the same boundary move in different directions (5,9). Often times the same boundary migrates in different directions on either
side of the foil (3). Low angle grain boundaries in general do not migrate (14). Thus it is possible that DIGM is intimately related to the structure of the boundary.

4. New grains often nucleate on the surface of the sample, and as time goes on these new grains can cover the entire surface thus giving rise to a layer of solid solution. This process has been termed "Diffusion Induced Recrystallization" (10).

5. The extent of migration is dependent on the thickness of the specimen. The thicker the foil, the less the chances of DIGM.

There have been several attempts to explain these features on the basis of a model. All these attempts have met with only partial success. There is no one single model that can explain all the observations and which is universally accepted as an explanation for this phenomenon. The goal of the present research is to seek out the best model from those suggested for this process, and to learn more about the process itself. In this dissertation, the following questions are addressed for the Fe-Zn system.

1. What are the different morphological changes that accompany DIGM in this system and how do they evolve?
2. Is DIGM reversible? Will the boundary return to its original position when the source of zinc is removed?

3. Is DIGM reproducible? Will the same boundary show the same kind of migration under identical circumstances?

4. Which model can best explain the observations of this and other work on this system?

In order to answer these questions, three sets of experiments were done. The results of these experiments form the subject matter of this report. The iron-zinc system was chosen for this investigation because of the ease of observation of DIGM in this system under a wide range of experimental conditions (17-22). Work done in the past on the iron-zinc system and on some other systems and the various models that have been proposed over the last few years are reviewed in Chapter II.

All the previous work done on this system involved the observation of DIGM in the iron after exposure to the zinc vapor for a fixed time. These studies revealed little on the evolution of the observed structures. It was hence decided to observe the same regions after successive anneals. In this way, the growth of the structures right from the initial stages were followed.
Several interesting morphological features were observed. To shed more light on the mechanism of DIMG, it was thought to be necessary to test the reversibility and the reproducibility of the observed phenomena. Indeed, if the same boundary did the same thing under the same conditions it would strongly suggest that there existed a relationship between the grain boundary structure and the migration (type and extent) observed. Accordingly we tried to cycle the zinc in and out of the iron in an attempt to check the reproducibility of the process. The results of these investigations are presented and discussed in Chapter III.

To supplement the results obtained from the experiments in which the zinc was put into the system first, we repeated the experiments for the case where the zinc was removed first. Accordingly, we started with an iron-10%zinc alloy (which is entirely one phase at the annealing temperature) and tried to cycle the zinc in and out of it. Several different morphological changes were observed. The results of this work are presented and discussed in Chapter IV.

The work done in both the above cases yielded interesting results. In order to gain more information
on the relationship between the boundary structure and
the type of motion observed we obtained both electron
channeling patterns in an attempt to find the
relative misorientation across the various boundaries.
These misorientations were then compared with the type of
DIGM shown. The results of this work are reported in
Chapter V.
CHAPTER II
LITERATURE SURVEY

The first observation of Diffusion Induced Grain Boundary Migration (DIGM) was made by Rhines and Montgomery (1). They found that the grain boundary in bi-crystalline copper moved when it was exposed to a zinc vapor from alpha-brass. The next observation was made only in 1972 by Den Broeder in the W-Cr system. Since then there have been a large number of reports on DIGM in various binary metallic systems. The occurrence of DIGM has become more the rule rather than the exception in binary metallic systems though it has not been observed in at least three systems [Cu-Mg, Cu-Ag (43,44) and Cu-Al (45)]. It has also been seen in some ceramic systems (24,26) and there has also been one observation in a system where the solute is interstitial (29).

The systems on which the most work has been done are the Cu-Zn, Au-Ag, Au-Cu, Fe-Zn and some ceramic systems. The observations in these systems and the five models that have been put forward to explain them are also discussed along with their strong points and shortcomings.
2.1 REVIEW OF THE OBSERVATIONS OF DIGM IN VARIOUS SYSTEMS

2.1.1 THE COPPER-ZINC SYSTEM

The copper-zinc system is possibly the most comprehensively investigated of all the binary systems surveyed (3-9), and has been studied using a wide variety of solute sources and in a large number of temperature regimes. Butrymowicz et al (9) used 3.9% to 30.5% Zn-Cu sources in their study using color metallography. Tsai (3) worked mainly with a 15% Zn source while Mishra (4) worked mainly with 30% Zn alloy. The main difficulty in this system is the existence of a large number of annealing twins on the copper. The main observations of the Cu-Zn system may be summarized as follows:

1. Faceted growth of the migrating region was observed, especially when a source with a larger zinc content (30%) was used (3,4).

2. The incoherent part of twin boundaries often migrated when a high zinc source (30%) was used (3,4).

3. The same region on either side of a foil 50 microns thick sometimes showed different behavior (3). This could be a result of grain boundary inclination or it could be because DIGM is a purely random process, or due to the relative availabilities of zinc.
4. New grains nucleating on the surface of the Cu foil grew with a higher zinc content than was found in the DIGM swept regions (4,6).

5. The zinc content within the region swept by the boundary was found to vary (6,7), but all authors report that there was a sharp change in concentration at the initial and final positions of the boundary.

6. Corrugations and pits are often seen in the migrated regions (5). This suggests that the grain boundary diffusivity of zinc is higher than that of copper.

7. Limited orientation work done suggests that there is no relation between the misorientation across a boundary and whether or not it shows any migration, except for the fact that low angle boundaries do not migrate. (4).

8. Jerky motion of the boundary was often seen (4).

9. There was no appreciable difference in the twin densities found on the copper foils before and after the anneal in a zinc rich vapor (4). There are however reports of twinning taking place in the migration area and where no existing twin boundary was originally present (4).

10. The migration rate increases with the zinc content of the source used (4,6).
11. The migration morphology (the direction and extent of motion) changed on successive annealing (4). This could be due to a change in the structure of the boundary on migration, or due to a critical dependence of the morphology observed on the experimental conditions.

12. On electropolished specimens, it was noted that several small zinc rich regions had developed on the surface after annealing in a zinc rich atmosphere (6). These were equiaxed new grains of a Cu-Zn alloy. Sometimes however, every new grain that nucleated on the same grain extended or grew in a characteristic direction.

13. In this system it was found that the value of $D_b$ for migrating boundaries was at least two orders of magnitude more than than the corresponding value along stationary boundaries (6).

Often times in this system, it has been observed that the grain boundary stops migrating after it has advanced a small distance (6,3). One possible explanation for this observation was suggested by Shewmon (41) who said that the boundary stops after a while because of a buildup of stresses in the migrated region because of solute addition. This argument is substantiated by the
fact that DIGM does not occur in thick foils (19). Another explanation stems from the work of Mishra (4) who observed changes in the migration morphology on successive annealing. This suggests that the boundary structure changes when DIGM occurs and that after a while the boundary adopts a low mobility configuration.

Garke and King (8) reported that the grain size of the copper foil before the DIGM treatment had an important effect on the migration process. It was found that the "average zinc content" of the foils was a constant independent of the initial grain size. This suggested that the smaller grain size played an important role in inhibiting DIGM, otherwise, the higher grain boundary area in these samples should give rise to more alloying.

The same authors also reported (47) on the effect of prior cold work on the motion. They found that the extent of alloying was constant for anneals ranging from one to seven hours, but after that it decreased. The rate of decrease was inversely proportional to the amount of prior cold work. They interpret these results in terms of the dislocation content, by saying that the higher dislocation density of the samples with more cold work
generated more grain boundary dislocations and hence caused a decrease in the deceleration of the boundary.

2.1.2 THE GOLD-SILVER AND GOLD-COPPER SYSTEMS

Pan and Balluffi investigated the Au-Ag and the Au-Cu systems using transmission electron microscopy (14). They used polycrystalline gold as their substrate and deposited silver or copper thin films on them. These were then annealed to induce boundary motion in the gold. After the DIGM anneal, the Ag (or Cu) layer was dissolved away by acid etching and the alloyed regions were observed using the TEM. They used (001) tilt boundaries for the Au-Cu system and (111) tilt boundaries for the Au-Ag system. Their major results may be summarized as follows:

1. DIGM occurred by the formation and expansion of bulges in the boundary which grew into the adjacent grains in opposite directions. The migration thus occurred against the curvature of the boundary in opposition to capillary forces.

2. The alloyed region formed by each bulge was a single crystal region having the same orientation as the bulging grain. The initial position of the migrated boundary consisted of an array of low angle
dislocations to account for the lattice parameter mismatch. The final position of the boundaries consisted of dislocations to accommodate the normal crystal misorientation in addition to the lattice parameter mismatch. Step-like discontinuities in composition were observed at both these interfaces.

3. Boundaries were often observed to facet during DIGM. No clear evidence was found for the effect of faceting on the DIGM kinetics.

4. DIGM did not occur at low angle tilt boundaries where the boundaries consisted of discrete lattice dislocations.

5. Migration rates were quite erratic and appreciable differences were found in the migration rates of similar boundaries.

6. DIGM was considerably reduced for certain special boundaries with a high density of coincident lattice sites. It was negligible for boundaries corresponding to coherent $\Sigma = 3$ (111) twins. This could be because the diffusion rate along such boundaries is not very much faster than through the bulk lattice.

Butrymowicz et al (15) studied DIGM in the Au-Ag system and also in a system [60% Au 40% Ag (which has the same lattice parameter as Au) and an Au solute] where the
lattice parameter mismatch is essentially zero. They found that DIGM occurred very easily in this system, and concluded that the coherency strain mechanism for DIGM suggested by Hillert (31) (this will be discussed later in Section 2.2.3) is not applicable.

Grovenor's study of the Au-Cu system (16) was unique in that he was the first to study DIGM in-situ in the transmission electron microscope. He worked with thin film bi-metallic couples containing well defined tilt boundaries. His major observations were as follows:

1. The process of grain boundary migration showed two well defined temperature regimes. DIGM occurred exclusively at temperatures below 200 C. Above 200 C both DIGM and DIR were seen.

2. There was an incubation time for DIGM which varied from a few minutes to a few hours depending on the misorientation of the boundary.

3. Boundaries did not migrate at a constant velocity. They moved in discrete jumps during which the boundary velocity was between 1 and 10 microns/minute. Most of the time however the boundaries were immobile. The intermediate positions of the boundary (the location after every jump) consisted of arrays of dislocations that had the character of low angle boundaries. There
was no significant discontinuity in the solute content across these arrays and so the dislocations were obviously not misfit dislocations present to account for any lattice parameter change. The properties of these dislocations (their Burgers vector, their line direction etc.) were however not reported.

Grovenor also discussed the mechanisms by which the boundary was able to move in discrete jumps. According to his theory, the boundary dissociates at every step into a highly mobile interface and a boundary of essentially no mobility. The mobile interface then migrates leaving behind the low angle boundary. As it migrates it interacts with the dislocations in the lattice and thus loses its mobility. A subsequent dissociation restores its mobility once again. This mechanism agrees with the work of Mishra (4) who reported the morphology of migration changed with every successive anneal since it could be interpreted to mean that the structure of the boundary changes everytime it moves. However it does not agree with the work of Tsai et al (5), who found that the orientation of the migrated region was uniform, and was the same as the growing grain, i.e the structure of the boundary was the same before and after DIGM.
2.1.3 THE IRON-ZINC SYSTEM

The first investigation of DIGM after the work of Den Broeder on the W-Cr system was done by Hillert and Purdy (17) on the iron-zinc system. They worked with 3 mm discs annealed with Fe-11.3 wt% Zn alloys at temperatures ranging from 545 to 600 °C. They also used transmission electron microscopy in their work. Their main results were as follows:

1. At the temperatures studied, the zinc transport into the specimen is achieved almost entirely by grain boundary motion coupled with grain boundary sweeping. The swept regions showed 8-10% Zn.

2. The original position of the boundary is marked by a remnant wall of dislocations. These are misfit dislocations present to account for the lattice mismatch between the iron and the adjacent iron-zinc alloy region. This also could suggest that the structure of the boundary at the initial and final position are not the same.

3. Dezincification of an Fe-11.3 wt% Zn alloy revealed similar DIGM effects with the region swept by the boundary containing less zinc than the original grain. No mention was made of the zinc content in the migrated region.
They then went on to suggest that the driving force for the motion is purely chemical in nature, and that the mobility of the boundary is independent of the size of the driving force. They also suggested that grain boundary diffusion is greatly enhanced by the motion of the boundary and that it is necessary to distinguish between the static and dynamic structures of the boundary; in other words, the structure of the boundary changed on migration.

Yu and Shewmon (18) worked on this system using thin (40 micron thick) foils. They used two kinds of thin sheets, decarburized sheet steel and high purity iron sheet as their substrate and high zinc (65 or 75%) brass as their source of zinc. Their annealing temperatures were between 550 and 630°C. Their main results were as follows:

1. There were essentially two types of structures at the boundary. One had the appearance of a faceted hillock. This hillock was highest on the side of the original position of the boundary. The other was a more or less even migration along a longer piece of the boundary. There was little difference in the surface relief and alloying contents between the two kinds of iron used.
2. Since the foils used were relatively thin, the boundary remained essentially straight and migrated uniformly across the thickness of the foil.

3. The higher the temperature and zinc concentration of the source the higher the migration rate that occurred. The zinc content of the migrated regions however remained constant at between 7.2 and 9.5 % in the migrated regions.

4. After one hour at 600 C, there were "precipitates" on the surface of the foil that contained 27-30 wt% Zn. They were located on the region of the foil closest to the source. These precipitates stood out like poles and after two hours, they were dissolved as more zinc was mixed into the foil. It may be noted that the equilibrium solubility limit of zinc in iron at this temperature is about 15 % (61).

5. From the shape change accompanying the diffusion of zinc into the iron foil, they concluded that $D_b(Zn) \gg D_b(Fe)$.

Shewmon and Yu (19) did similar experiments on thicker foils to assess the effect of size and internal stress on the motion of the boundary. They used 127 micron thick iron samples and also sheet that was several millimeters thick. The foils were notched in the center
and then pulled to fracture to provide a gradient in the thickness. The same alloy source (65% Zn-Cu) was used.

After half an hour, they saw DIGM only in the thinnest regions of the foil. After an hour however there was DIGM all over the foil and these regions extended to depths of about 30 microns within the foil. There were small precipitates that formed on the surface of the foil, and after three hours these were replaced by grains of zinc rich ferrite. These grains were in turn covered by the iron-zinc intermetallic after 12 hours. Both the solid solution layer and the intermetallic layer contained the equilibrium concentrations of zinc at the annealing temperature. The solid solution layer thickened linearly with time, while the intermetallic layer thickened roughly as the square root of time. The iron sheet several millimeters thick showed no DIGM even after a week. No solid solution layer was seen, but the intermetallic formed on the surface.

These authors explained the observations by noting that since the foils were thick, the plastic strain associated with the selective alloying process of DIGM prevented it from occurring through the thickness of the foil. Instead, a uniform new grain layer nucleated and
grew on the surface by the process of DIR. The same argument was used to account for the lack of any DIGM in the sheet that was several millimeters thick.

Blendell et al (20) conducted an investigation of DIGM in this system using 25 micron thick foil, and an Fe-10%Zn alloy as the source. They used two temperatures 830 K and 870 K. Their main result was that at the lower temperature, the migrating boundaries remained parallel to the original boundary over long sections and at the higher temperatures, they bulged out in many hemispherical caps in both directions from the original boundary location. In several of the samples, the boundary moved in discrete steps. Within each step, the zinc content of the swept region was uniform. The difference in the morphology at the two temperatures was attributed to the changes in the rates of boundary diffusion and boundary migration. At lower temperatures, the concentration of zinc atoms in the boundary was not depleted since the jump into the lattice (of the zinc atoms) was slow compared to diffusion down the boundary. Thus the entire boundary was able to migrate. At the higher temperatures, the jumps into the lattice were fast and as a result there was a higher zinc content at the surface. This caused local migration of the boundary
Li and Hillert (21) have conducted a detailed study of DIGM in this system. They also used the vapor transport method from Fe-Zn alloys of various compositions and annealed in the temperature range 450–650 C. They reported the same results as the previous workers and the following new ones:

1. At 600 C they found that often times the boundaries seemed to stop before the whole grain was swept. Some boundaries even started to move back.

2. Some boundaries were found to oscillate about a mean position rather than migrate in a particular direction.

3. At 650 C a fine grained surface layer of zinc rich ferrite formed on the surface. Surface roughness promoted the formation of this layer and it was not commonly seen on foils that were electropolished prior to the exposure to the zinc. This fine grained surface layer migrated into the thickness of the foil preferentially along the grain boundaries. Later the surface layer was replaced by large zinc rich grains, i.e. a kind of abnormal grain growth occurred.

They were also able to estimate the value of the diffusion coefficient along migrating grain boundaries.
and found that this was several orders of magnitude higher than that along stationary grain boundaries (for pure iron). Finally they also suggested a model for the thickening of the surface layer. They assume that the solid solution consists of a columnar array of grains that thicken. Diffusion along the boundaries that form the walls of these cylinders causes them to lengthen by the migration of the base of the cylinders. The zinc transport down these grain boundaries was mathematically related to the thickness variation with time and was found to be in good agreement.

2.1.4 DIGM IN CERAMIC SYSTEMS

The first attempt to study DIGM in ceramic systems met with little or no success (22). Handwerker et al (22) investigated DIGM in various ceramic systems (NiO-MgO, MnO-MgO, NaCl-KCl ). In most of their work, the bi-crystalline substrate ceramic was annealed with a powder of the diffusing ceramic. They found none of the microstructural and compositional changes characteristic of DIGM. However they did observe DIGM like morphologies in a set of hot-forged KBr samples that were stored at room temperature for six years. In this case, they postulated that the diffusing (solute) species was either OH\(^-\) or O\(^2-\). The probable causes for the absence of DIGM
in these systems are as follows:
1. Annealing temperatures were either too high, or too low to observe DIGM in the time period studied.
2. There could have been a change in the boundary structure at the high temperatures studied leading to a decoupling of diffusion and motion of the grain boundaries.
3. Solute impurities could have precipitated out at the grain boundaries and inhibited migration.
4. There was an improper choice of systems.

Another important aspect was brought out by Cahn et al (23), who suggested that to maintain charge neutrality when ions are added at the grain boundary, both cations and anions must be added in correct proportions. The migrating rates of these species however differ significantly in some systems and consequently, DIGM is limited by the slower diffusing species. Thus DIGM will not be easily observed in some ceramic systems.

Parthasarathy and Shewmon (24) were the first to observe DIGM/DIR in ceramic systems. They worked with NiO prepared by oxidizing pure Ni foils in air at 950 C. The NiO was then encapsulated with a piece of pure Ni in an evacuated capsule and annealed for various lengths of
time. This experiment involved the reduction of NiO within its stoichiometric range. On reduction a grainy structure was produced on the initial faceted surfaces of the NiO grains. These grains however did not have any epitaxial relationship with the old grains. The reduced NiO samples were subsequently annealed in air i.e. oxidized and, at 1200 C new grains were produced on the surface. All the grains were faceted and it was thus shown that new grains could be produced during both the reducing and oxidizing parts of the cycle. The depth of penetration of the recrystallized grains was determined by looking at the cross-section of the foils, and the layer was found to extend to about ten microns. They were however unable to see diffusion induced motion of prior boundaries.

The copious nucleation of new grains is not very different from the nucleation of new grains on Fe or Cu when exposed to a zinc atmosphere. But as Parthasarathy and Shewmon point out, the free energy available in the case of Fe or Cu is about one or two orders of magnitude larger than that is available for NiO. However since there is a negligible volume change when one goes across the stoichiometry range of NiO a lower driving force may be enough to drive DIR in this case. These authors
finally suggest that the phenomenon may be common in ceramics that have a large stoichiometric range. Compounds like Al₂O₃ and MgO should not show this phenomenon. No experiments on DIGM or DIR have been attempted with these ceramics.

Pfeiffer et al (25) contested the interpretation of the surface phenomena observed by Parthasarathy and Shewmon (24) in NiO. Working with CoO, they found cavities on the surface of their foils when the O/Co ratio was reduced from air saturation to some lower value. They maintain that these results could be interpreted to be the result of bulk vacancy relaxation processes. They also suggest that due to the higher defect concentration in CoO, DIGM and related processes should be more readily observable than in the NiO case.

Parthasarathy and Shewmon (26) were however able to obtain results in CoO similar to those in NiO. The only difference was that the grain size of the recrystallized CoO was much smaller than that of NiO i.e. DIR was indeed easier in CoO than in NiO. They thus contend that recrystallization did occur due to oxygen diffusion and DIGM had to be invoked to account for these phenomena.
2.2 REVIEW OF THE PROPOSED MECHANISMS FOR DIGM

Any model that claims to explain DIGM has to do the following:
1. Provide a driving force that is large enough to drive the boundary.
2. Provide a method of coupling this driving force with the motion of the boundary.
3. Explain all the observations in the various systems.

There have been several attempts to suggest a model that will provide all these three ingredients, and it is worth going through them briefly, as the implications of the results of the present work on these models will be discussed in the following chapters. The models are essentially of two types: the boundary structure sensitive models (dislocation climb and shear modulus effects) and those that consider only energy effects (classical coupling, coherency strain, surface energy).

2.2.1 THE GRAIN BOUNDARY DISLOCATION CLIMB MECHANISM

The only "mechanistic" model that has been suggested for DIGM is the grain boundary dislocation climb model proposed independently by Balluffi and Cahn (27) and Smith and King (28). These authors start out by asserting that the ideal part of the free energy of
mixing (which is purely entropic) cannot be the driving force for DIGM. They suggest a hypothetical experiment of the mixing of two isotopes. Isotope diffusion along the boundary will not be able to move it (no experiment to prove this has however been done) and so the ideal free energy of mixing cannot move the boundary. The excess free energy in systems showing DIGM can be either positive or negative. The assumption that DIGM is caused by this non-ideal part of the free energy of mixing would predict no DIGM on alloying for positive deviations since the energy that has to be supplied to mix the alloys must come from the entropy of mixing, and no DIGM on dealloying for negative deviations for similar reasons. They conclude that the free energy change alone cannot drive DIGM. The basic features of the model as suggested by them are:

1. Different species diffuse at different rates along the grain boundary. i.e. there exists a grain boundary Kirkendall effect.

2. This divergence of the fluxes of the two diffusing species causes the grain boundary dislocations (GBDs) to climb (by the creation or annihilation of vacancies).

3. The climb of the GBDs cause the grain boundaries to migrate by the motion of the steps that are
intrinsically associated with the GBDs.

The model is schematically illustrated in Fig 2. for the symmetric tilt boundary. If the grain boundary dislocation in Fig 2 (a) absorbs a vacancy it will climb upwards by a distance \( s \), three atoms will be removed from Crystal 2, and two atoms will be added to crystal 1. In this manner two atoms are transferred from crystal 2 to crystal 1, one vacancy is destroyed and Crystal 1 grows at the expense of Crystal 2.

The driving force they assert is not the free energy of mixing but the difference in the diffusivities of the two diffusing species. The reason for the lack of DIGM in some systems would be the absence of a divergence in diffusion flux. This scheme however has several problems: 1. The observation of DIGM in the Ni-C system (29) cannot be explained by this model. Carbon is an interstitial atom, and interstitials cannot cause GBDs to climb. To explain this, it has been suggested that the rapid diffusion of carbon down Ni grain boundaries causes a concentration gradient of Ni. The back diffusion of Ni causes the GBDs to climb thus moving the boundary.
Fig 2. Schematic Illustration of the Grain Boundary Dislocation Climb Model for DIGM
a. Before the climb
b. After the climb

[ After Reference 27 ]
2. This model would imply that a boundary can move only in one direction under a given set of experimental conditions as DIGM is closely associated with the grain boundary dislocation structure. Yet there are several observations of DIGM in which different sections of the same boundary have moved in opposite directions in regions where the structure is about the same (4,14). Again, Hillert and Chongmo (6,21) have reported that some boundaries moved in one direction stopped and then came back. Some boundaries oscillated about a mean position.

2.2.2 THE SHEAR MODULUS EFFECT

Partha Sarathy (35) has suggested that DIGM could be related to the change in the shear modulus on alloying. His model was born out of a mechanism proposed by him for grain boundary migration during discontinuous alloying. He starts out by asserting that since grain boundaries are known to be composed of dislocations, a mechanism by which dislocation migration can occur should in principle be applicable to grain boundary motion.

Due to the image forces present at an interface between two regions of differing shear moduli, a dislocation present there will experience image forces
tending to repel it away from the region of higher shear modulus. In most cases ordering causes an increase in the shear modulus. Thus if an ordered phase nucleates on a boundary, then a random fluctuation in the position of the boundary will cause the dislocations present there to experience image forces pushing them away from the original position. As the dislocations in the boundary glide (or climb) the boundary motion is sustained by the wake of ordered phase of higher shear modulus. The grain boundary motion could thus transform the disordered grain into an ordered one.

Parthasarathy then states that the model could be extended to DIGM if alloying could cause an increase in the shear modulus. In several alloy systems which show DIGM, this is indeed the case, a notable exception being the Cu-Zn system. Again the only way the model could be extended to systems which show DIGM during both alloying and dealloying (e.g. Fe-Zn) is if the solute raises the shear modulus of the system up to a certain concentration and then decreases it on further addition of the solute. To account for the lack of DIGM, we would need the shear modulus to remain constant on alloying in systems that do not exhibit the phenomenon.
This model is thus plausible for many DIGM systems but is not applicable to all. Also a lot more work on the measurement of the effects of alloying on the shear modulus is necessary to establish the model.

2.2.3 THE COHERENCY STRAIN MODEL

The coherency strain model suggested by Hillert (31) and later substantiated by Tashiro and Purdy (32) assumes the existence of volume diffusion even at the low temperatures at which DIGM is known to occur. The salient features of their model are as follows:

1. Lattice diffusion occurs ahead of the grain boundary and solute is mixed in this diffusion zone.
2. The lattice parameter mismatch due to the solute sets up strain gradients in this region.
3. The motion of the boundary would relax these strain gradients and so the boundary moves.

Handwerker et al (38,39) have tested this model for Liquid Film Migration during the liquid phase sintering of alloy powder compacts. They developed an equation based on thermodynamics for the migration velocity of the film. This was expressed in terms of diffusion across a liquid film due to a concentration gradient arising from equilibria with solids on both sides of the film at
different levels of compositional stress. The coherency strain was thus related to the rate of migration. These workers then varied the coherency strain by changing the temperature and composition of Mo-Ni base ternary alloys. The observed change in the migration velocity was consistent with the expected value of the coherency strain. In particular, when the coherency strain was made zero, no migration was observed. They concluded, that the coherency strain energy was thus the driving force for liquid film migration.

They then suggested, that the model can be extended to DIGM, by simply replacing the liquid film by a grain boundary. There are however difficulties in doing this, as the liquid phase serves as a sink for the compositional changes unlike the grain boundary. The model they assert is not that simple, but the qualitative predictions are the same.

The driving force for motion is thus the strain associated with the lattice mismatch. This model however has several flaws:

1. DIGM has been observed in the Ag-Au system by several authors (14,15). In this system the lattice mismatch is of the order of just 0.19% an amount that is
hardly sufficient to cause appreciable strain. It has also been observed in a system where the lattice mismatch was made zero (15).

2. DIGM has been known to occur even when substantial lattice diffusion occurs. The effect has been observed at temperatures where lattice diffusion is fast enough to prevent the establishment of strain gradients (10).

3. DIGM occurs even in very low temperature regimes where \( D/v \ll 1 \), i.e. there is low lattice diffusion.

2.2.4 SURFACE ENERGY EFFECTS

Louat et al (33) have proposed a model wherein they try to prove that DIGM is connected with the energy changes associated with the interaction of the solute with grain boundaries. A similar model has been suggested for discontinuous precipitation by Meyrick (34). The basic assumption of this model is that the interaction energy between the solute and the grain boundary is a function of the concentration of solute at the boundary. A concentration gradient would cause the boundary to move to reduce its energy. Such a concentration gradient exists naturally (in a direction normal to the boundary) during DIGM, and thus the grain boundary migrates to minimize its energy by moving up or
down the gradient. From expressions for the grain boundary energy in terms of the interaction energy, Louat et al were able to derive specific equations for the force on the boundary as a function of its concentration and position. The sign of the force was positive for alloying and negative for dealloying.

This model considers only energy effects and does not bother how the solute atoms increase or decrease the boundary energy. The other chief drawback of this model is that it requires the same species to both increase and decrease the grain boundary energy to account for DIGM during the cases of alloying and dealloying.

2.2.5 THE CLASSICAL COUPLING APPROACH

The classical approach suggested by Parthasarathy and Shewmon (35) was derived from the old concepts of grain growth. In this model the boundary fluctuates back and forth about an average position, but is ratcheted forward because each time it moves into a solute free grain the incremental volume swept out by the boundary has solute mixed in it. A fluctuation of the boundary of the boundary backward into the alloyed region will not cause a decrease in free energy due to mixing. Hence the largest decrease comes from the fluctuations that drive
the boundary in one direction. The driving force for the motion is thus the decrease in the free energy associated with the mixing of solute into or removal of the solute from the foil.

The "classical coupling" theory has little direct evidence to support it, but indirect evidence is provided by the observation of "Diffusion Induced Dislocation Glide" (DIDG) (30). Shewmon et al (30) argue that if the free energy of mixing can drive boundaries, dislocations can be driven by diffusion in the same way. To nucleate a coherent twin a series of glissile partial dislocations all of the \((a/6)[\overline{1}12]\) type must be nucleated and one such dislocation must be moved on each plane of a parallel set of glide planes. In the Cu-O and Ag-O systems, they found that twin boundaries can nucleate and grow during DIGM. Since these twin structures are quite different from those observed after anneals in the absence of DIGM (anneals in an inert atmosphere) and the chemical driving force is capable of exerting stresses that are enough to nucleate and drive these dislocations, they argue that it is indeed the decrease in the chemical free energy of mixing that drives the boundary.
Li and Rath (62) in their paper considered how the motion could originate. They suggested that the initial motion may start as a consequence of a pre-existing curvature in the boundary, or an asymmetric exchange of diffusing species with the host atoms at grain boundary ledges, or other processes that can create local free energy differences across the boundary. Once the process has started the difference in chemical potential across the boundary sustains the motion.

This concept was discarded by Balluffi and Cahn (27) when they presented their dislocation climb model. Their argument about the inability of the free energy of mixing to drive the grain boundary has already been discussed in Section 2.2.1. Parthasarathy and Shewmon however argue that since the isotope experiment has not been done, and that there is no evidence to the contrary, this model is indeed the correct one. The other drawbacks with this classical coupling approach are:
1. There is no way to couple the driving force with the actual motion of the boundary.
2. This model does not explain the observations that boundaries can stop and come back, or even oscillate about their final position.
None of the five different models presented above can account for all the different observations made in the different systems that have been studied. The free energy of mixing model comes closest to at least qualitatively explain all the observations, but is still not very convincing. Thus there may not be one single model that operates all the time. Some of the suggested models may operate at different times, and it is also possible that different models may operate at the same time. More work is clearly necessary in order to establish the mechanism and its relation to the various characteristics of the phenomenon. It is hoped that the present investigation will provide information towards this end.
CHAPTER III

ZINCIFICATION AND DEZINCIFICATION OF IRON FOILS

3.1 INTRODUCTION

Diffusion Induced Grain Boundary Migration in the iron-zinc system has been studied quite extensively in the past (17-21). However in all these investigations only the morphological changes produced during single anneals of iron foils in a zinc atmosphere for selected times have been reported. In the present work, an attempt has been made to follow the evolution of these changes by observing the same boundary at intervals during successive anneals. These foils which contained zinc, were then subjected to dezincification to check the reversibility of the process. After all the zinc was removed, the foils were annealed again in a zinc rich atmosphere in an attempt to see whether the same changes occurred. The boundaries however did not migrate during the second anneal.

The various structures observed during the first DIGM anneal, the results obtained from the
dezincification experiments along with some possible explanations for the inability of the boundary to move again after the dezincification process and the implications of these observations on the various suggested mechanisms for DIGM are presented and discussed in this chapter.

3.2 EXPERIMENTAL PROCEDURE

High purity iron foil, 75 microns thick was used to conduct this investigation. The composition of the iron was (in ppm) C-12, S-2.6, O-60, N-10. Small specimens were cut from the foil and annealed for 24 hours at 1000°C in flowing hydrogen, and then furnace cooled. The pieces were then electropolished in a mixture containing by volume 6 parts perchloric acid and 94 parts acetic acid. The voltage was maintained at 25 Volts and the current density was 0.35 A/cm². The foils were washed repeatedly in methyl alcohol and distilled water to get a good clean surface. A Cu-70%Zn alloy was used as the zinc source. The alloy was prepared by melting together weighed amounts of Cu and Zn in an evacuated Vycor tube.

The electropolished iron was then encapsulated along with the zinc source in a Vycor tube. The encapsulation
was done by evacuating with a mechanical forepump, back filling with hydrogen, evacuating again and then sealing with a low pressure of hydrogen (a third of an atmosphere) inside the tube to prevent oxidation of the specimen. The annealing treatment done after the encapsulation was almost always done at 600 C, but some anneals were also done at 500 C.

Initially a few anneals were done for very short times (15-30 minutes) until it was established that the morphological changes evolved consistently with time. After that most experiments involved two successive anneals. The first had a duration of one hour. Following this anneal, the foils were etched with a 3% Nital solution and examined using the light microscope. The second anneal was two hours long and the specimens were examined as exposed (without etching). Both optical and scanning electron microscopy (JEOL 35 microscope equipped with a 9100 Energy Dispersive Analyzer) were used for this observation.

To find out how the microstructure varied beneath the surface of the foil, some samples were mounted using double sided adhesive tape and then polished mechanically using 0.3 micron alumina powder. At intervals they were
etched and observed. The structure was followed until about half the thickness of the sample was polished away.

To assess the reversibility of the process, samples (which had been exposed to the zinc vapor) were dezincified by annealing in flowing hydrogen for various times. The samples were then examined using the SEM as before. To find out the position of the boundary, electron channelling patterns were obtained from different regions after the dezincification process.

To evaluate the reproducibility of the process, these dezincified foils were then annealed with the same 70%Zn–Cu alloy source to see if the same morphology was observed. Sometimes the surface relief accompanying the DIGM process was removed by polishing the dezincified samples mechanically prior to the second diffusion anneal. To supplement these experiments on the reproducibility, some foils that showed DIGM after about 10–15 minutes were electropolished to remove the surface DIGM layer, and then reannealed using a similar source. In these experiments, a fixed weight of a powdered source was used, and the specimen geometry, (the distance from the source to the specimen ) was maintained constant.
Thus the experimental work consisted of trying to cycle the zinc in and out of the iron foil to verify whether the same structure was produced in every cycle.

3.3 RESULTS

Typical microstructures obtained from a sample annealed at 600°C for fifteen minutes are shown in Fig 3. As will be discussed later, these structures grew consistently i.e. they became larger as time went on but showed no fundamental morphological change. DIGM was observed on samples annealed for fifteen minutes or more and various morphologies and behavior were observed. These can be classified into the following types:

1. Boundaries showing no migration.
2. Boundaries showing normal motion, i.e. growth of one grain at the expense of the other.
3. Boundaries showing a new grain on one side of the boundary and normal motion on the other.
4. Boundaries showing two new grains one on each side of the boundary.
5. Nucleation of pyramidal shaped zinc rich "new grains" with zinc contents within the solubility limit of zinc in iron at the annealing temperature
Fig. 3 Typical DIGM microstructures obtained after 15 minutes at 600 C (etched).
away from the boundary. i.e. within the parent grain.

6. Formation after three hours of annealing of new grains on the surface with zinc contents in excess of the solubility limit at the annealing temperature.

The different types of structures that were seen at grain boundaries were well distributed over the surface of the foil, i.e., the different kinds of motion were not confined to particular regions on the surface. Zinc rich regions that form away from the boundaries with a zinc content below the solubility limit at the annealing temperature were seen in almost all the grains after 3 hours.

There were approximately an equal number of boundaries that showed the three different structures. Specifically, out of forty-five boundaries that showed motion in two different samples, twelve showed normal motion, sixteen showed normal migration and a new grain, while seventeen showed the formation of two new grains after three hours. However, the same boundary always showed the same kind of structure after both the one hour anneal and the subsequent two hour anneal.
3.3.1. BOUNDARIES SHOWING NO MOTION:

Not all boundaries showed DIGM after one hour. There were several boundaries in a foil that did not migrate after the first hour when other regions on the same sample showed significant migration. However after the subsequent two hour anneal some of these boundaries showed migration. Thus it is possible that these boundaries needed more time to move, i.e. there was some incubation time for the motion.

3.3.2. BOUNDARIES SHOWING NORMAL MIGRATION:

Fig 4(a) shows a typical normal migration structure after one hour. As is clearly illustrated different sections of the same boundary advanced in different directions. At X for example, grain "A" grew at the expense of grain "B". Again at Y, grain "B" grew at the expense of grain "A". This type of migration is common in DIGM and has been well documented by several authors. The boundary is straight to start with, and the characteristic curvature associated with DIGM is developed. The same region is shown after the subsequent two hour anneal in Fig 4(b). The boundaries continued to migrate in the same directions they started out in. This is typical of all boundaries and no evidence of the boundary stopping and reversing its path
Fig. 4 Optical micrograph of a region showing normal migration of the boundary

a. After 1 hour (etched)

b. After 3 hours (as exposed)
Fig. 4 (contd) SEM micrographs of the same region as Fig 4(b)
(as has been reported by some authors \((6,21)\)) was seen. Fig 4 (c)\&(d) show SEM micrographs of the same region. They show the surface relief and clearly indicate the directionality of the motion.

3.3.3. BOUNDARIES SHOWING NORMAL MIGRATION ON ONE SIDE AND A NEW GRAIN ON THE OTHER:

Along with normal migration often times a new grain was found to nucleate on one side of the boundary. The boundary migrated on the other side at the same time. Fig 5(a) is an example of this type of behavior. Three triangular shaped new grains have nucleated on the right while the boundary has shifted to the right. The evolution of the structure after three hours is illustrated in Fig 5(b). The boundary has moved further, while the new grains have grown in all directions except that in which the boundary moved. The surface relief from this type of structure is illustrated better in the SEM micrograph of Fig 5(c). The new grain produced is generally triangular, but sometimes rectangular grains were also seen. Fig 5(d) shows such rectangular grains on one side of the boundary.

The nucleation of these new grains caused much more surface relief than did normal migration. As time went
on, these grains joined together to form one large grain. Thus all the grains that nucleated on the same boundary had the same orientation. Fig 5(e) is a excellent example of this. We thus produced three orientations where only two existed. Electron channelling patterns from the different regions also indicated that the new grains had the same orientation.

3.3.4. BOUNDARIES THAT PRODUCED TWO SETS OF NEW GRAINS ONE ON EACH SIDE OF THEM

The third type of change did not involve motion of the boundary. Instead, two sets of new grains formed along the grain boundary; one set grew into one grain while the second set grew into the other. As in the second type of change, the grains of each set ultimately joined together to form two new grains one on each side of the boundary. These new grains then advanced in opposite directions along two irregularly shaped fronts. Fig 6(a) shows such behavior as seen under the optical microscope, while Fig 6(b) shows the surface relief associated with this process as seen under the SEM.

A light polish followed by an etch which removed the surface relief showed three boundaries where only one had existed. Fig 6(c) is an example. Several attempts were
Fig. 5 Optical micrographs of a region showing a new grain on one side and normal DIGM on the other at 600 C.

a. After 1 hour (etched)

b. After 3 hours (as exposed)
Fig. 5 (contd) SEM micrographs of a region showing a new grain on one side and normal DIGM on the other after 3 hours at 600 C (as exposed)

c. Triangular Shaped Grain
d. Rectangular Shaped Grain.
Fig 5(Contd) e. SEM micrograph indicating that all the new grains on the same side of the boundary have the same orientation.
Fig. 6 Micrographs of a region showing two new grains one on each side of the boundary after 3 hours at 600 C.

a. Optical micrograph (as exposed)

b. SEM micrograph (as exposed)
Fig 6 (contd) c. Micrograph showing three Boundaries where only one existed (polished and etched)

d. Electron Channelling Patterns from the labeled regions of Fig 6(b)
made to examine the orientations of these new grains by electron channelling. The patterns obtained clearly showed the existence of four grains; however presumably due to the strain, the surface relief and the change in the lattice parameter as we go into the foil the quality of the pattern was too poor to get a precise misorientation measurement. Fig 6(d), despite the poor quality of the patterns from the new grains, does illustrate that we have four orientations where there were initially only two.

3.3.5. NUCLEATION OF "NEW GRAINS" AWAY FROM THE BOUNDARY

The next type of change occurred not at the boundary but within the grain. Fig 7(a) shows two such grains. The pyramidal shaped structure on the right was the more commonly observed of the two. It is shown in Fig 7(b) at a higher magnification. Stereopairs of such regions showed that these features were raised above the surface of the foil; another fact which stood out was that topographic features such as scratches were retained across this area. Channelling patterns taken from this region were again poor, but indicated that it had an orientation that was very close to the parent crystal. Fig 7(c) shows patterns taken from the points marked "A" and "B" on Fig 7(b). They clearly show that no high
angle boundary exists between the pyramid and the parent matrix. Superimposition of the negatives of the channelling patterns also showed that the parent crystal was within 1-2 degrees of the zinc rich region. Also, the zinc rich region is more distorted compared to the parent crystal.

3.3.6 FORMATION OF AN ALLOYED REGION WITH A SOLUTE CONTENT IN EXCESS OF THE SOLUBILITY LIMIT

During the second anneal, often times the DIGM regions on the sample surface were covered by spotty new grains. These new grains had an excess of 20% Zn in them. Fig 8(a) is an illustration of this phenomenon. The region within the migrated region but outside the high zinc region shows the normal zinc level (8-10%) associated with DIGM. Fig 8(b) shows the variation of the zinc content in this region.

This type of structure is also seen on the sample surface away from the DIGM regions. Fig 9(a) illustrates this type of structure far away from the grain boundary after two hours. This region again has a zinc content in excess of 20% while the surrounding region is essentially pure iron. On annealing for 4 hours the high zinc new grains spread almost entirely over the surface of the
foil. Fig 9(b) shows another region after four hours. No evidence of the iron-zinc intermetallic (a phase with about 60% Zn) was seen even after six hours.

When the experiment was repeated at 500 °C the same phenomenon was seen. The zinc content (17%) was however lower corresponding to the lower temperature, but there was no significant change in the kinetics. Fig 9(c) illustrates this phenomenon at 500 °C.

A light polish of the surface (after about 2-3 microns are polished away) results in a complete loss of zinc from the surface. The DIGM regions however show up around the boundaries with the usual amount of zinc associated with them (about 8-10%). The high zinc new grains are thus very shallow, and there is no penetration of zinc beneath them. These regions were at least a micron thick, because we were able to get distorted but distinct electron channelling patterns from them. Thus, the EDS measurements were from the new grains and we were not getting background signals from the iron substrate.

3.3.7 SUCCESSIVE POLISHING

The results of the successive polishing experiments established the fact that DIGM occurred through the
thickness of the foil in one hour. Fig 10 illustrates how the microstructure of a region with a rectangular new grain on one side and normal migration on the other side of the grain boundary varies with depth. As the plane of polish progressed inward the size of the new grain diminished but it remained rectangular. Eventually it became triangular and after the last view in the sequence it disappeared. Further polishing showed an increase in the migration distance, thus indicating that we had polished away more than half its thickness. Fig 11 shows how the structure of the two new grains at the boundary varied beneath the surface of the foil. The new grains became smaller as we went deeper into the foil, but their crosssection remained the same. A similar observation was made for the pyramids that were seen on the surface. Micrometer measurements indicated that after the fourth polish we had traversed half the thickness of the foil. Thus the topographical changes extended to depths two or three times their width at the surface. As mentioned earlier the surface of the foil had between 8 and 10% zinc in the alloyed region with a negligible zinc content in the bulk. As the foil was traversed this zinc content decreased monotonically till it dropped to just 3% at the center of the foil.
Fig. 7 a. Region showing zinc rich regions away from the boundary after 1 hour at 600 C.
Fig. 7(contd.) b. Zinc rich region on the right of Fig 7(a) (Magnified)

c. Electron channelling patterns taken from the region the regions shown in Fig 7(b)
Fig. 8  a. Micrograph showing DIGM and high zinc new grains after 3 hours at 600 C.
b. Concentration Profile of the Region marked "A" in Fig 8 (b)
Fig 9  a. Micrograph showing zinc rich grains away from the boundary after 2 hrs at 600 C
b. Micrograph showing complete coverage of the surface by high zinc new grains after 4 hrs at 600 C.
Fig 9. (contd) c. Micrograph showing complete coverage of the surface by high zinc new grains after 4 hrs at 500 C.
Fig. 10 Variation of the microstructure below the surface of the foil of a zinc rich new grain at the boundary after three hours at 600 C.
Fig. 11 Variation of the microstructure below the surface of the foil of two zinc rich new grains at the boundary after three hours at 600 C.
3.3.8 DEZINCIFICATION FOLLOWED BY REZINCIFICATION

Several samples which were initially exposed to the zinc vapor were dezincified by annealing in flowing hydrogen. As before the initial zinc content of the alloyed region was 8 to 10%. After twenty-four hours of dezincification the surface topography remained unchanged while the zinc content dropped to zero. Fig 12 (a) & (b) show the same area before and after dezincification respectively. The surface relief is the same both at the grain boundary and also at the zinc rich region away from the boundary. A light polish removed the surface relief from both regions. No evidence of any porosity was seen on the surface before or after the polish. A subsequent etch revealed that only one boundary was present. Thus the boundary had moved back, the zinc was removed but the surface relief was still intact.

Samples that were successively dezincified for one three and three hours showed a continuous decline of the zinc content near the free surface. After seven hours it was only 3%. Fig 13 shows a micrograph and electron channelling patterns from regions that were dezincified for seven hours. During the zincification process, normal DIGM had occurred with the boundary migrating into the grain "A" through the region "B". On dezincification
the boundary goes back to its original position. This is evident from the channelling patterns of the three regions. As "A" and "B" are the same (superimposition of the negatives confirms that no misorientation exists) and "C" is quite different, the boundary has migrated back. EDS measurements show there is still 3 to 4% Zn in the region "B". Thus the boundary returns to its original position long before the zinc is removed. The contrast seen in Fig 13 is due only to the zinc composition difference. These experiments indicate that DIGM is not reversible in the sense that the boundary does not remove the zinc as it returns to its original position. Rather it returns rapidly and the zinc is then slowly evolved.

When these dezincified foils were then annealed with the same 70%Zn-Cu alloy used initially, it was found that the boundaries did not move the second time. No DIGM was seen on the foil even after three hours, while DIGM was seen in fresh samples in less than one hour. To ensure that the conditions were right for DIGM, a fresh Fe foil was annealed along with the dezincified foil in the same tube along with the 70%Zn-Cu alloy. The virgin sample showed copious DIGM (all the forms reported earlier), while the dezincified sample showed none.
Fig 12 Conservation of the surface relief following dezincification at 600 C of a region showing two new grains

a. Before dezincification

b. After dezincification
Fig 13 Micrographs and electron channelling patterns illustrating the return of the boundary to its original position after dezincification
Fig 14(a) shows a region with DIGM, Fig 14(b) the same region after dezincification, a light polish and etch and a second exposure to zinc. This clearly indicates that the boundaries lose their ability to migrate after dezincification. The polishing treatment to remove the surface relief could not have been responsible for the lack of motion. Fig 14(c) shows a DIGM region before the dezincification treatment and Fig 14(d) shows the same region after a second exposure to zinc following dezincification. Again, there is clearly no evidence of any change in the topography that is characteristic of DIGM.

If dezincified samples were treated for prolonged periods of time in a zinc vapor, high zinc precipitates with zinc contents in excess of the solubility limit at the annealing temperature (discussed in Section 3.3.6) were formed on the surface, but the boundaries remained immobile.

Several attempts were made to restore the mobility of the boundary by annealing at higher temperatures (800 C for 24 hours) in flowing hydrogen after dezincification and before the second diffusion anneal. These attempts however were not successful, and the boundary did not
Fig. 14 Micrographs illustrating the loss of the ability of the boundary to migrate following dezincification

a. Before dezincification

b. after dezincification a light polish and a second anneal
Fig 14 (contd) Micrograph illustrating the loss of the ability of the boundary to migrate following dezincification

c. Before dezincification
d. after dezincification and a second exposure to zinc
migrate after the second exposure to the zinc vapor. These experiments thus did not yield any results on the reproducibility of DIGM.

3.3.9 TWO EXPOSURES OF THE SAME BOUNDARY TO ZINC

Since dezincification did not yield a boundary that was capable of DIGM, we decided to test the reproducibility of DIGM in a different way. This method consisted of polishing away (electrolytically) the DIGM layer after a brief DIGM anneal and re-exposing the thinned sample to zinc.

Fig 15(a) shows a boundary after a brief exposure and Fig 15(b) shows the same boundary after the second exposure. It is clear that the behavior is not the same everytime, and this boundary shows normal migration after the first anneal and normal motion plus a new grain after the second. All combinations of structures were seen after two exposures. Some boundaries however did show the same structure after both treatments. Fig 16 is an example. There were also times when the same boundary did not move after the first exposure, but did so after the second. Thus DIGM is clearly not reproducible in the sense that the same boundary does not show the same behavior under identical situations. However it may be
Fig 15. a. Micrograph showing DIGM after 15 minutes.

b. Micrograph showing the same region after a polish and a second exposure to zinc
Fig. 16 Micrographs illustrating a boundary that showed the same structure after two different anneals.
noted that the entire boundary is saturated with solute after the first anneal. In that sense, the same conditions were not present during the two anneals. However this observation illustrates the fact that DIGM is a random process and may not be as intimately related to the grain boundary structure as was earlier believed.

3.4 DISCUSSION

3.4.1. MORPHOLOGICAL CHANGES AT THE BOUNDARY

When an iron foil was exposed to zinc vapor from a 70%Zn-Cu alloy source, there were three distinct types of changes that were observed for the boundaries that migrated. The first was normal DIGM in which long portions of the boundary migrated into one or other of the adjoining grains. The characteristics of this process were in accordance with those reported in several of the previous observations in the Fe-Zn system (17-21) and were basically akin to those seen in other binary systems (6,11,13). In the second type of behavior, distinct new grains were seen on one side of the boundary. These new grains usually had characteristic triangular or rectangular shapes. These new grains also had the same orientation and coalesced together as time went on to give one large grain on one side. At the same
time the boundary moved on the other side, and we eventually got three orientations as is shown in Fig 17(a). In the third type we got two sets of new grains, one on each side of the boundary. These sets again had characteristic shapes and joined together rapidly to produce four orientations as shown in Fig 17(b).

A possible explanation for the formation of these structures is the "S" mechanism which has been used to explain both discontinuous precipitation (48) and DGM. This is shown schematically in Fig 17(c). In this approach the boundary is assumed to bulge locally into one grain in the opposite direction to that in which its neighboring parts migrated (bulged). Continued migration of this bulge along with its lateral movement along the original position of the grain boundary would cause it to be isolated and left behind at the free surface within one of the grains. The chief drawback of this model is that it is unable to produce a third or fourth orientation where only two previously existed. As the schematic sketches indicate it is not possible to account for either the new orientations or the regular shapes of the new grains. The "S" model also cannot explain the surface relief of the new grains which is much more than that for normal DGM. Again the mechanism should have
Fig. 17 Schematic illustration of the second and third type of morphological change on DIGM.

a. Second type

b. Third type
Fig 17 (contd) c Schematic illustration of the "S" mechanism used to explain DIGM and discontinuous Precipitation
progressed to different stages at different distances within the foil. Successive polishing and etching experiments however do not reveal this. Though it may apply to the case of normal DIGM, the "S" mechanism is thus clearly unable to account for the other changes.

A more attractive explanation is that some boundaries are able to dissociate as a result of the large driving force available from alloying. There are ample observations of grain boundary dissociation in the literature (49,50). Goodhew et al. (49) observed the dissociation of <110> tilt boundaries in gold. They obtained a twin (Σ=3), and another high angle grain boundary when these boundaries dissociated. Fionara et al (50) followed the dissociation of high angle boundaries in aluminium. These boundaries dissociated into "special" boundaries and a low angle boundary, or two "special" boundaries. "Special" boundaries refer to those boundaries in the CSL orientations with Σ =3,11,17 etc. Both these authors assert that this dissociation is possible only if the sum of the energies of the two resultant boundaries is less than that of the original boundary. More recently Grovenor (16) has also observed the dissociation of boundaries during DIGM in the Ag-Au system.
Grain boundaries are known to combine under the conditions of normal grain growth where the driving force is the reduction in grain boundary area. If two boundaries can combine together to form one grain boundary, it is feasible that if the conditions are right, the same boundaries could dissociate into two or three different units which could then move apart. In this manner we could create three or four orientations from just two.

In the two examples cited above, the driving force available is much less than the free energy change available during the DIGM process. Thus it is possible, that grain boundaries which would not dissociate under normal circumstances (the resulting two boundaries may have higher energy than the parent boundary) would do so under DIGM conditions. The free energy change derived from alloying would compensate for the increased energy of the two boundaries.

Fig. 6(a) & Fig. 7(a) clearly show that dissociation occurs locally at certain preferred sites at the boundary. The second type of change involves the dissociation of the boundary into two parts, one mobile and the other immobile. At the sites where dissociation
did not occur the boundary moves into the grain away from that in which the mobile boundary is formed. The original boundary can thus move laterally to leave the new grain isolated within one of the old grains. In the third type of change the boundary dissociates into three parts, one immobile and two mobile. The two mobile parts then migrate on opposite sides of the boundary providing four orientations.

Grain boundary dissociation thus provides a ready explanation for the generation of new orientations. It is also consistent with the fact that members of each set of new grains have the same orientation. In the published results, faceting of the boundary is a common occurrence. The characteristic shapes of the new grains may be a result of similar reasons.

3.4.2 MORPHOLOGICAL CHANGES AWAY FROM THE BOUNDARY

In other work done in the Fe-Zn system, Li and Hillert (21) found that a fine grained surface layer of an Fe-Zn alloy formed on the surface of the iron foil after one hour. This layer then grew inwards into the foil as a uniform front and after fifteen hours, the whole foil was converted into an alloy. They however used Fe-Zn alloys as their zinc source.
In our experiments zinc rich regions were obtained away from the boundary, but these were isolated and had characteristic shapes. These pyramidally shaped regions grew to depths several times their width at the surface. Topographical features were conserved across them and they possessed orientations very close to that of the parent grain. Since the regions were not bounded by high angle grain boundaries, the grains could not have nucleated on the surface and then grown by DIGM since low angle grain boundaries generally do not migrate by DIGM.

A more interesting possibility is a mechanism akin to that proposed by Eshelby (52) and Frank (53) for the growth of whiskers on metals. If it is supposed that zinc can diffuse into the iron by way of pipe diffusion along dislocations, at a rate much faster than the iron can diffuse out, the vacancy flux thus generated can cause the dislocations to climb. By a combination of climb and glide, these dislocations could spiral upwards. This process is attractive because it would account for the surface relief, the depth of the region and also for the lack of any orientation change across the boundary.

There are however a couple of drawbacks in this model. Firstly, to spiral, the dislocations would need
to have near screw orientation and the pipe diffusion down such dislocations is rather slow. Secondly, the width of the new grains are of the order of 5 microns at the surface, and it is difficult to imagine the formation of a pyramid with just one dislocation. Presumably we would need a group of dislocations which would have to spiral. The mechanistic details of the process are however unclear.

3.4.3 FORMATION OF REGIONS WITH ZINC IN EXCESS OF THE SOLUBILITY LIMIT

The limit of the solid solubility of zinc in iron at 600 C is about 15% (59). After three hours of annealing we sometimes found new grains with 20% Zn or more which is way above the limit of the one phase field at the annealing temperatures. Besides the work of Li and Hillert (21) cited earlier, Shewmon and Yu (19) have studied the growth of the intermetallic layer and the solid solution layer on iron when it is exposed to a zinc vapor. They report the formation after four hours of a saturated solid solution having a zinc content equal to the solubility limit, and on top of it the iron-zinc intermetallic which has about 70% Zn. There is a definite interface between these two layers where the
zinc content changes abruptly. In our samples however, we could not find the intermetallic on the surface of the foil even after six hours.

We believe that the new grains on the surface that contain 20% Zn have the crystal structure of alpha-ferrite and grow by the formation and sweeping motion (possibly repeated sweeping) of new grain boundaries. The two questions that need to be addressed are why these grains form with such a high zinc content and why they do not penetrate into the foil.

The reason for the high zinc content is that the first iron-zinc intermetallic phase, delta, nucleates very slowly and hence does not form. It is well known that in thin film solid diffusion couples, only one intermetallic forms (54). This idea may be extended to solid vapor couples and thus if the first intermetallic does not form, we get a zinc content of 20% rather than 15%. If the iron-zinc alloy comes to equilibrium with the 70%Zn-Cu source, the activity of zinc in the 70 at%Zn-Cu alloy at 500°C is 0.585 (55). This works out to an activity of 0.597 at 600°C. (See Appendix A). The activity of zinc in the 20 at%Zn-Fe alloy at 893°C is 0.491 which works out to a value of 0.598 at 600°C
assuming that we still have a solid solution. Thus the Cu-Zn alloy has the potential to alloy the iron up to 20 at% (which is about 23wt%) at this temperature. The lower activity of zinc in the source causes a lower zinc content at 500°C, but the results are similar. (See Appendix A). Abbas (56) has also observed the higher zinc content in Fe-Zn solid diffusion couples. Looking at the cross-section he found that the high zinc region penetrated to a depth of tens of micrometers. This observation and our thermodynamic calculation clearly indicate that we have a high zinc region on the surface and not a two phase mixture we are unable to resolve.

The reason for the small penetration of these grains below the surface of the foil is unclear. In the Fe-Zn system, DIGM is known to occur to 20 micrometers or more below the surface (Section 3.3.7.). Pyramids and new grains that often form on the surface of the foil away from the boundary and which contain 8-10% Zn also penetrate to these depths. Presumably the higher zinc content and hence the greater amount of strain associated with the penetration of these new grains, is responsible for the fact that they remain shallow. Lattice diffusion cannot be responsible for these new grains. From the data of Richter and Feller-Kniepmein (57) the diffusion
coefficient of zinc in iron-zinc alloys with 10% Zn is about $10^{-14}$ cm$^2$/sec at 600°C. For a diffusion time of 3 hours (roughly $10^4$ seconds), the penetration depth works out to $10^{-5}$ cm or a tenth of a micrometer. The observed penetration depths are at least an order of magnitude greater than this value.

The nucleation of these zinc rich zones could stem from the strain developed in the surface layer by the lattice diffusion of zinc in from the vapor. The change in volume on diffusing in enough zinc to raise the composition of the layer to 20% is about 20%. Since the diffusion layer is fully coherent with the bulk sample, this volume change will lead to substantial plastic deformation of the surface layer (58). The dislocations generated in this layer, could glide and create new grains within it. The boundaries of these grains could be driven by DIGM to generate the high zinc regions seen on the surface.

It was impossible to get any definite orientation relationship between these new grains and the matrix using electron channelling because the patterns were distorted. Grovenor (16) has reported that new grains formed during "Diffusion Induced Recrystallization" (DIR)
in Au-Cu foils have either the <110> or <100> directions lying normal to them. He does not report the solute content of these grains, but the Au-Cu system shows complete solid solubility. In our samples, we get new patterns from these new grains but the patterns are unclear. They however demonstrate that we do indeed have new grains on the surface.

3.4.4 DEZINCIFICATION FOLLOWED BY REZINCIFICATION

When the foils that had been exposed to the zinc vapor were annealed at 600 C in flowing hydrogen, the process did not repeat itself. Instead the boundaries returned rapidly to their original positions. The zinc was then removed slowly, without disturbing the surface relief. The zinc leaves the foil presumably by a combination of lattice diffusion to the boundary and boundary diffusion out of the foil.

Speich (42) has calculated the diffusion coefficient of zinc in iron both in the bulk and in the boundary. He reports values of $1.2 \times 10^{-6}$ cm$^2$/sec in the boundary and $5.0 \times 10^{-14}$ in the bulk at 600 C. Using these values the relaxation time for the alloy would be 55 seconds based on just grain boundary diffusion and $1.125 \times 10^7$ seconds based on only lattice diffusion (See Appendix B). In our
experiments, we found the relaxation time to be 24 hours. Thus some combination of lattice and grain boundary diffusion is responsible for the removal of zinc. How exactly this occurs is however unclear.

The boundary however returned to its original position long before the zinc was removed. The interesting fact is that the boundary does not move even though it is in contact with a zinc rich zone. In the case where new grains form on both sides of the boundary, the boundary has zinc on both sides of it. Yet it does not move again even though Fe-Zn alloys are known to undergo dezincification by DIGM (21, Ch. 4 of this report).

Because of experimental difficulties associated with the sensitivity of the etchant (nital) to zinc concentration there is some uncertainty with respect to the speed with which the boundaries move back. They certainly returned much faster than they initially moved out by DIGM. Evidently, when the source of zinc is removed the boundaries that were being driven out by DIGM can return to their original positions by normal grain boundary migration, possibly by the reduction in grain boundary area. This motion occurs too rapidly for an appreciable reduction in concentration to take place while the boundary traverses the alloyed region.
Though it has been reported in the literature, we did not observe the grain boundary stopping and reversing its path during DIGM. Assuming that the boundary cannot move back during DIGM, a possible explanation for these observations would be that if a boundary is capable of moving in one direction to produce solute enrichment, it cannot move in the same direction to reduce the solute content. The existence of a preferred direction is not predicted by a random racheting mechanism as suggested by Parthasarathy and Shewmon (29), but would be predicted by mechanistic models such as those suggested by Balluffi and Cahn (27) and Smith and King (28). This is because the direction of climb of the grain boundary dislocations (in the mechanistic models) would depend on the creation or annihilation of vacancies i.e. dealloying or alloying. However, this may not be the case as the same boundary can show different behaviour under similar conditions.

These experiments also have other interesting implications with respect to the mechanisms that have been proposed for DIGM. When DIGM is taking place, the driving forces moving the boundaries must exceed those forces that move the boundaries back when the source of solute is removed. For the Fe-Zn system, these latter
forces are capable of moving the boundary without the aid of a composition change. This suggests that the coherency strain energy near the boundary (31) is not of major significance in this system, as otherwise the boundaries would remain anchored at the discontinuity in composition. The motion of the grain boundary back, would leave a strained layer behind it. A similar conclusion can be made for grain boundary energy effects (33,34) and also for the shear modulus effects (35). However the free energy of mixing and the dislocation climb models require continued diffusion of solute along the boundaries to maintain DIGM. In these cases removing the source of solute immediately removes the means of overcoming the restraining forces.

When these dezincified foils were annealed again in a zinc rich atmosphere under conditions that were right for DIGM, the boundaries did not move again and no alloying had occurred after three hours. There could be at least two reasons for this lack of migration:

The first reason is that the grain boundary is pinned by an array of pores which inhibit its motion. When a boundary undergoes DIGM, the volume change is accommodated by a surface upheaval of the alloyed region.
When the zinc is now removed, the surface relief is not destroyed. The system thus needs away of accommodating the volume change on dealloying. The only way this change could be accounted for is by the creation of voids or pores at the boundary or in the region surrounding it. These pores were however not detected by the SEM. It is possible that the pores were too fine to be detected. Attempts were made to sinter these pores and restore the mobility of the boundary by annealing at a higher temperature. This anneal however did not cause the boundary to migrate again.

A second reason for the lack of motion, is a change in the structure of the boundary. Hillert and Purdy (17) have reported the existence of a wall of dislocations at the original position of the boundary after DIGM has occurred. They say that these are misfit dislocations present in order to accommodate the change in lattice parameter. When the boundary returns to its original position on dezincification, it meets this array of dislocations. These additional dislocations could change the structure of the boundary. It is not clear how this change in structure relates to the mobility of the boundary. More transmission electron microscopy work needs to be done, to evaluate this structural change, and
find out mechanistically whether or not it could stop the boundary from migrating.

These experiments which were designed to check the reproducibility of the DIGM process were however inconclusive. The dezincification results were thus consistent with both the dislocation climb model and the free energy of mixing model. It is clear that we did not have the same situation during both anneals. The only method to get this kind of information would be to anneal identical boundaries in the same atmosphere. This was attempted and the results are discussed in the next section.

3.4.5. TWO EXPOSURES OF THE SAME BOUNDARY TO ZINC

When a sample that showed DIGM after 15 minutes was electropolished and re-exposed to zinc, the same boundary showed two different types of behavior. At least two of the models suggested for DIGM, the dislocation climb mechanism suggested by Balluffi and Cahn (27) and the shear modulus effect suggested by Parthasarathy (35) require the same boundary to show identical behaviour under the same conditions. The results of our experiments indicate that this may not the case, as the same boundary showed a different behaviour during the
second anneal. The only variable changed was the thickness of the foil which was reduced from 60 microns to 40 microns after the electropolish. This should not significantly affect the results.

However the other mechanisms that consider DIGM to be the result of a biased fluctuation in the position of the boundary appear to be possible as they do not require the boundary to move in one particular manner everytime. This conclusion is also supported by the observations of Tsai (3). Working with the Cu-Zn system, he found different behavior on either side of the same foil. It is possible that the vapor pressure of zinc controls the type of motion seen, but the type of motion shown is definitely not an intrinsic property of the boundary. There have been no experiments on DIGM in which the solute vapor pressure is critically controlled, and we believe that such a study will shed more light on the reproducibility of the process.

Another possible explanation for this behavior stems from the work of Grovenor (16) and from our previous discussion on grain boundary dissociation. In Grovenor's observations of in-situ DIGM in the Ag-Au system, he observed the boundary moving in an intermittent manner.
He suggested that the boundary dissociated and left behind a low angle boundary at every step in its motion. It is possible that more than one mode of dissociation is possible, and what mode occurs is purely the result of the first perturbation of the boundary. The same boundary is thus capable of different kinds of motion.

From the above discussion, it appears that it is difficult to reconcile the observations with the Balluffi-Cahn model. The classical coupling approach along with grain boundary dissociation however can explain all these observations. Though it does not specifically provide a coupling between the driving force and the motion, it agrees at least qualitatively with all the observations made in this study.

3.5 CONCLUSIONS

1. Diffusion induced grain boundary migration in the Fe-Zn system results in four distinct types of topographical changes:
   a. Normal migration of the boundary.
   b. Nucleation of a new grain on one side of the boundary and normal migration on the other.
   c. Nucleation of two new grains one on each side of the
boundary

d. Nucleation of pyramidal shaped new zinc rich regions with a zinc content within the solubility limit of zinc at the annealing temperature within parent grains away from the boundary.

e. Nucleation of new zinc rich grains that contain zinc in excess of the solubility limit at the annealing temperature.

2. On dezincification (of foils showing DIGM), the boundary returns rapidly to its original position without removing any appreciable amount of zinc and leaving the surface relief intact. i.e. DIGM is not reversible.

3. The grain boundary loses its ability to migrate after the dezincification process.

4. The same boundary need not show the same kind of behavior after two anneals under identical conditions i.e. DIGM is not reproducible.

5. The classical coupling approach along with grain boundary dissociation is the only model that is consistent with all the observations in this work.
CHAPTER IV

DEZINCIFICATION AND ZINCIFICATION OF IRON -ZINC ALLOYS

4.1 INTRODUCTION

The last chapter dealt with the morphology, reversibility and reproducibility of DIGM in Fe foils exposed to a zinc rich atmosphere. The reversibility and reproducibility experiments had interesting implications on the models put forward for DIGM; specifically the classical coupling approach of Parthasarathy and Shewmon (35) was found to be the only model that was consistent with all the observations. In order to test this hypothesis, we thought that it was necessary to repeat similar experiments starting with Fe-Zn alloys. Hence an Fe-Zn alloy that was in the one phase region at the annealing temperatures (and had a zinc content close to the amount of alloying obtained by DIGM of pure iron) was made, and zinc was cycled in and out of it, to see whether or not the results obtained when we started with pure iron foils were reproduced. The results of these experiments are presented and discussed in this chapter.
Fe-10% Zn alloys were prepared by annealing weighed amounts of pure iron (in the form of 75 micron thick foil) and granulated zinc in an evacuated vycor tube with a hydrogen back pressure of about a third of an atmosphere. The annealing was done at 800°C for five days. The relaxation time at this temperature was calculated to be 96 hours. The foils were mechanically polished with 0.3 micron alumina to obtain a clean observable surface. EDAX measurements confirmed that we had a uniform concentration all over the surface of the foil.

The foils were then annealed at 600°C in flowing hydrogen in a tube furnace. The temperature gradient in the furnace was enough to cause the zinc to be removed from the surface of the foil and to cause DIGM. The annealing treatment was done for various times, but typical anneals were for one hour. The foils were examined using both optical microscopy and the SEM. An energy dispersive analyzer was used to analyze for zinc. Some of the foils were polished and etched with a 3% nital solution prior to the observation. After observation, the foils were annealed with a 70% Zn-Cu
alloy to get the zinc back into them. Following the second anneal, electron channeling was used to locate the position of the boundary (because of the sensitivity of the etching treatment to zinc). Finally the foils were annealed again in hydrogen to see if the boundary moved again.

4.3 RESULTS

Figs 18 and 19 illustrate the structure that is obtained following dezincification for one hour at 600 C. The boundary shows distinct migration and the region within the migrated region shows ghost lines which indicates the intermittent motion of the boundary. The zinc content of the migrated region was uniformly between 7 and 8% and no obvious step in the zinc concentration was observed across the ghost lines within the migrated regions. The bulk showed almost no zinc loss. The other striking fact about DIGM on dezincification is that the boundary generally moves only in one direction, and the characteristic "S" shaped morphology is not frequently seen. Fig 20 shows another boundary that has migrated into one grain and not the other. After a light polish and etch, the DIGM regions show up clearly along the boundary, but without the ghost lines within the migrated
regions. Fig 21 is a good illustration of this.

When these samples were reannealed (following dezincification) with a 70% Zn-Cu source, the boundaries moved back to their original positions quite rapidly. However, the zinc content of the regions that were swept by the boundary did not increase. Instead, small grains with zinc contents of about 20% (of the type reported in Section 3.3.6) nucleated both near the boundaries and away from them. Fig 22 shows a micrograph and channelling patterns illustrating the return of the boundary to its original position on zincification. The etching contrast is due to the difference in the zinc content.

When these samples were again subjected to dezincification by annealing in flowing hydrogen, (after a light polish to remove the high zinc new grains) the boundaries did not migrate a second time. We did not however have the same situation during both anneals, as the region around the boundary was depleted in zinc. Fig 23(a) shows a boundary after the first dezincification treatment, while Fig 23(b) illustrates the same region after the second dezincification treatment. Before the
Fig. 18 DIGM after dezincification of an Fe-10% Zn alloy after 1 hour at 600 C.
Fig. 19 DIGM after dezincification of an Fe-10% Zn alloy after 1 hour at 600 C.
Fig 20. Micrograph illustrating motion in only one direction of a boundary in an Fe-10% Zn alloy after 1 hour at 600 C.
Fig. 21. DIGM after dezincification of an Fe-10% Zn alloy after 1 hour (polished and etched).
Fig. 22 Micrograph and channelling patterns illustrating the return of the boundary to its original position on zincification with a 70% Zn-Cu alloy at 600°C.
Fig. 23 Micrograph illustrating the inability of the boundary to migrate after zincification

a. After the first dezincification treatment
b. After the second dezincification treatment
second anneal, the boundary was at its original position and it remained in the same position even after the second dezincification treatment.

4.4 DISCUSSION

4.4.1 MORPHOLOGICAL CHANGES

The morphological structures obtained after dezincification are quite different from those obtained after DIGM during zincification. During dezincification, the boundary moved in distinct jumps, with each intermediate position clearly visible under the microscope. The surface relief on dezincification is clearly less than that obtained on zincification. Again, the boundaries moved in only one direction. We did not see the same boundary moving in two different directions, (the "S" shaped morphology) or the dissociation of the boundary into two new grains, or the formation of solute free new grains on the surface.

The main reason for all these differences has to be associated with the fact that the zincification process uses 10% Zn while the dezincification removes only 2-3% Zn from the region swept by the boundary. Thus the free energy of mixing (or demixing) used to drive the process...
is much less. This argument could clearly account for the intermittent motion of the boundary, as the lower driving force would find it more difficult to move the boundary, and would do so in steps rather than in one continuous motion. As has been discussed earlier, Grovenor (16) also reported that the boundary moves intermittently during his observations of in-situ DIGM in the Au-Ag system. He does not however report the solute content of the migrated region. This model is also consistent with the small surface relief in the migrated region, as the volume change is much less when 2% of the solute is removed rather than 10%. The reason for all the boundaries moving only in one direction would be that the lower free energy of mixing would be unable to support the larger curvature of the boundary, if it moved in two directions. The boundaries do migrate away from their center of curvature, but do so as a uniform front. Blendell et al (20) have also reported a similar difference in morphology when they annealed their iron with the same Zn source (Fe-10%Zn) at two different temperatures. At the lower temperature, they found migration along a broad front but at the higher temperature, they found the same boundary moving in two different directions (the "S" shaped morphology). They correlated their observations to the jump frequencies at
the two different temperatures. However in our experiments, the difference in morphology was seen at the same temperature (600 C) for two different solute contents. Again, the two temperatures reported by Blendell et al differed by only 40 C. The jump frequencies would not be much different at these temperatures, while the free energy of mixing would be more. Thus, it is more likely that the lower free energy of mixing at the lower temperature was responsible for the difference in morphology reported by these authors. The free energy of mixing is also not enough to cause the grain boundary to dissociate, or to cause new grains to nucleate on the surface.

The free energy of mixing argument as suggested by Parthasarathy and Shewmon (35) can clearly account for all the differences in the morphological features that are seen on dezincification. There appears to be a threshold value for the amount of solute to be mixed into the substrate to cause the "S" shaped morphology of classical DIGM, grain boundary dissociation and new grain nucleation. An experiment to test this hypothesis, would be to make the driving force as small as possible by using say a 1%Zn-Fe alloy as the source for DIGM in a pure iron foil and see whether or not the structures
reported in the previous chapter are reproduced. A systematic study of the effect of the solute content on the morphology would also be helpful.

4.4.2 REVERSIBILITY

The results clearly indicate that the DIGM process is not reversible in the sense that the boundary does not move back because of zinc diffusion into the system. Rather, because there is no sink for the removal of zinc, it moves back quickly to reduce its area, under the forces of normal grain growth. This effect is similar to that when zincification was the first step, and has similar implications on the models for DIGM. The interesting aspect however is that the region around the grain boundaries never attain the old zinc content of 10%. Instead, new high zinc regions of the type discussed in Section 3.3.6 are formed on the surface of the foil. Obviously the source used for the zincification treatment had the potential to alloy the surface above the 10%Zn that we started with. There is no way of preferentially alloying the zinc depleted regions around the boundary.

During the second dezincification treatment however, the boundaries did not migrate. This is consistent with
the observations made previously, but in this case, the boundary already had a zinc depleted region around it. The situations during the two different anneals was not the same, as the first anneal had a uniform 10%Zn around it, while in the second case, it had 10% on one side and 8% on the other. However, in view of the observations made in the previous chapter, the inability of the boundary to migrate is no surprise.

4.5 CONCLUSIONS

1. The morphological features obtained on DIGM during dezincification of Fe-Zn alloys are different from those obtained on zincification of pure Fe. The differences were explained by the lower free energy that is used to drive the boundary on dezincification.

2. DIGM on dezincification of Fe-Zn alloys is not reversible. The same results were obtained in the zincification experiments. This conforms the hypothesis that the free energy of mixing (classical coupling) is the best model for DIGM.
CHAPTER V
RELATION BETWEEN GRAIN BOUNDARY MISORIENTATION AND DIGM

5.1 INTRODUCTION

The last two chapters yielded interesting results on the morphology of DIGM in the Fe-Zn system. Also, it was shown that the same boundary was capable of different kinds of motion when exposed to the same atmosphere. This observation could not be reconciled with the dislocation climb model for DIGM. In the present chapter, misorientations across a boundary that showed DIGM were measured using electron channelling. An attempt was made to see whether there was any correlation between the boundaries that showed the various types of DIGM and the misorientation across them.

There have been in the past two attempts to obtain a relationship between the misorientation across the boundary and whether or not it migrated. Mishra (4) attempted such a study in the Cu-Zn system but was unable
to correlate the two. Pan and Balluffi (14) were also unable to get any significant relationship in the Au-Ag system. In the present work, an attempt was made to obtain a relation between the type of motion and the misorientation in the Fe-Zn system rather than between the misorientation and just the occurrence of migration. Such a relationship would tend to support the grain boundary dislocation climb model while the lack of such a relationship would lend more credence to the classical coupling approach (29).

5.2 THEORY

A grain boundary possesses five main degrees of freedom. These are the angle of misorientation / axis of misorientation pair (θ/hkl), and the boundary normal plane. The axis of misorientation is the direction in the two crystals that has the same crystallographic indices and about which, a rotation of one crystal describes the relative orientation of the two crystals. In the definition of the axis / misorientation pair, three degrees are specified. The other two are specified by the physical position of the boundary. The geometrical structure of grain boundaries (specially high angle grain boundaries) is best given by the Bollmann 0
lattice theory (61), which includes the coincidence site lattice approach.

Coincidence site lattices (CSL) occur at specific values of \( \Theta /hkl \), which give rise to a continuous set of structure sites across the boundary. E.g. (60° about the <111> corresponds to one in three sites being common in cubic materials, and is called a \( \Sigma =3 \) boundary). According to the Bollmann 0 lattice approach, any boundary that deviates from the CSL orientation by a small angle (<5°) may be represented by periodic arrays of secondary grain boundary dislocations superimposed on the CSL structure. These dislocations are derived from the DSC lattice. The DSC lattice is defined as the coarsest lattice that contains the two crystal lattices in the particular coincidence orientation and position, and is characteristic of the coincidence site lattice that the boundary is close to. The structure of high angle grain boundaries far removed from the special CSL orientations is however unclear.

5.3 EXPERIMENTAL PROCEDURE

Bulk (75 micron thick) iron foils were used to obtain the various DIGM structures by exposing them to a
70% Zn-Cu alloy at 600 °C. Electron channelling patterns were obtained using both the JEOL 35 SEM and the JEOL 200X STEM in the SEM mode. Since it was difficult to get patterns from the migrated (zinc rich) regions, the patterns were obtained from the interior of the grains away from the boundary. In the SEM, a 9° rocking angle was used (due to the limitation of the instrument), while in the STEM two rocking angles 15 and 10 were used. An accelerating voltage of 35 kV was used for the SEM while 160 kV was found to be the best for the STEM. In all eighteen boundaries were studied: six for each of the structures obtained on DIGM. i.e. boundaries that showed normal migration (Type 1), boundaries that showed normal migration on one side and a new grain on the other (Type 2) and boundaries that showed two new grains one on either side of the boundary (Type 3).

The electron channelling patterns were solved using the computer programs provided by Heilmann et al (60). Several different sets of lines were considered till a consistent solution (which agreed to a degree) was generated. The misorientations were compared with a table of exact coincidence orientations presented by Bollmann (61). The deviation of the misorientations away from any particular coincidence orientation were then
calculated, and an attempt was made to correlate these deviations with the type of motion shown.

5.4 RESULTS AND DISCUSSION

The first result that was seen was that the patterns obtained were distorted and the lines were blurred. The lines were not straight, and this made the patterns more difficult to solve, as the angles and distances between the lines were not clearly defined. The reasons for these difficulties are the following:

1. Surface oxide layers, since some of the samples that were used were stored for several days after the DIGM treatment. The electron channelling signals come off the top one micron of the sample.

2. Iron is a ferromagnetic material, and it distorts the field of the electromagnetic lenses in the SEM. The problem is more acute in the STEM, as the specimen is immersed in the field of the objective lens.

The type of patterns obtained are illustrated in Fig 5.2. These patterns were obtained from a boundary that showed normal migration, shown in Fig 5.1. The misorientations obtained across the various boundaries are shown in Table 1 along with the type of motion that
Fig. 24 Micrograph of the region showing normal DIGM from which the channelling patterns of Fig 25 were obtained.
Fig. 25  Electron Channelling Patterns Obtained from the regions shown in Fig. 24.
Table 1 Relation between the type of motion shown and the misorientation across the boundary

<table>
<thead>
<tr>
<th>Boundary Number</th>
<th>Migration Type</th>
<th>$\theta$/&lt;hkl&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>44.27/.999 .021 .015</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>33.86/.586 -.562 -.583</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>64.38/- .847 -.530 .014</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>44.37/.300 -.033 .953</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>39.20/.418 -.132 .898</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>33.58/.599 .491 .632</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>32.83/.697 .721 .024</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>42.63/- .100 .875 .471</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>24.19/.727 .557 .400</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>61.34/- .917 .381 .114</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>46.39/.318 .371 .872</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>39.57/- .832 -.396 .387</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>37.84/.887 -.460 .012</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>62.97/- .605 -.571 .553</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>17.13/.031 .711 .553</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>35.30/- .100 .876 .472</td>
</tr>
<tr>
<td>17</td>
<td>3</td>
<td>27.27/.721 .692 -.008</td>
</tr>
<tr>
<td>18</td>
<td>3</td>
<td>59.81/.426 -.894 .132</td>
</tr>
</tbody>
</table>
Table 2 Relation between some of the boundaries and the nearest Coincident Site Lattice

<table>
<thead>
<tr>
<th>Boundary #</th>
<th>Nearest CSL</th>
<th>$\theta' / h' k' l'$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Sigma, \theta/&lt;hkl&gt;$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>29, 43.6/&lt;100&gt;</td>
<td>6.32/.0115 .0251 .0268</td>
</tr>
<tr>
<td>2</td>
<td>39, 32.2/&lt;111&gt;</td>
<td>9.26/.033 -.005 -.026</td>
</tr>
<tr>
<td>7</td>
<td>27, 31.59/&lt;110&gt;</td>
<td>8.14/ .0109 .0317 .0284</td>
</tr>
<tr>
<td>14</td>
<td>3, 60/&lt;111&gt;</td>
<td>10.60/ .0599 .0326 .0396</td>
</tr>
<tr>
<td>17</td>
<td>19, 26.53/&lt;110&gt;</td>
<td>5.92/.025 .0016 -.0094</td>
</tr>
</tbody>
</table>
the boundaries showed. As can be seen from Table 2 five
boundaries were within 10° of exact coincidence
orientations. All these coincidence orientations were
different, and the secondary grain boundary dislocations
that describe the boundary are different. The remaining
grain boundaries were not near any coincidence
orientation.

From the relatively small sample studied, there does
not appear to be a relation between the type of motion
and the misorientation across the boundary for boundaries
that are far from any CSL orientation. Thus grain
boundaries that were far away from the coincidence
position are capable of all the three kinds of motion.
Also grain boundaries close to CSL orientations were seen
to show different kinds of behaviour. It may however be
noted, that all the parameters that define the boundary
were not considered. The grain boundary normal, which
fixes the exact position of the boundary in the lattice
was not found. This could have some bearing on the type
of motion shown. However, the observation of the lack of
a relation between the misorientation and the type of
motion shown by the boundary is consistent with the fact
the the same boundary is capable of different types of
motion under the same conditions. This observation is
also consistent with the work of Mishra (4) who found no relation between the misorientation of the boundary and whether or not it moved. The only difference is that we have one low angle boundary (17°) that showed Type 3 motion (formation of two new grains). The authors cited earlier found that in general low angle boundaries with a misorientation less than 20° did not show any motion. There does not appear to be an explanation for this observation. The present observations are difficult to reconcile with the GBD climb model. The free energy of mixing approach coupled with grain boundary dissociation can however can explain these observations.

5.5 CONCLUSIONS

1. There is no relationship between the type of motion that a boundary shows on DIGM and the misorientation across it. This observation cannot be reconciled with the grain boundary dislocation climb model.

2. The classical coupling approach is the model that can best account for the observations in this work.
CHAPTER VI
SUMMARY OF PRINCIPAL OBSERVATIONS AND CONCLUSIONS

In this work, Diffusion Induced Grain Boundary Motion in the Fe-Zn system has been studied. On zincification of iron foils the following changes occurred.

a. Normal migration of the boundary.

b. Nucleation of a new grain on one side of the boundary and normal migration on the other.

c. Nucleation of two new grains one on each side of the boundary

d. Nucleation of pyramidal shaped new zinc rich regions with a zinc content within the solubility limit of zinc at the annealing temperature within parent grains away from the boundary.

e. Nucleation of new zinc rich grains that contain zinc in excess of the solubility limit at the annealing temperature.

On dezincification (of iron foils showing DIGM), the boundary returns rapidly to its original position without removing any appreciable amount of zinc and
leaving the surface relief intact. i.e. DIGM is not reversible. The grain boundary loses its ability to migrate after the dezincification process. The same boundary need not show the same kind of behavior after two anneals under identical conditions i.e. DIGM is not reproducible.

On dezincification of Fe-10%Zn alloys the morphological features of DIGM that were obtained are quite different from the zincification case. The differences can be explained by the lower free energy that is used to drive the boundary on dezincification. DIGM on dezincification of Fe-Zn alloys is also not reversible.

There is no relationship between the type of motion that a boundary shows on DIGM and the misorientation across it. This observation implies that the grain boundary structure is not as intimately related to DIGM as was previously thought to be.

The above observations are best explained by the classical coupling approach that was suggested by Parthasarathy and Shewmon (29)
Appendix A

The thermodynamic activity is converted from one temperature to the other assuming regular solution behavior i.e. by use of the formula

\[ T_1 \ln Y_1 = T_2 \ln Y_2 \]  

(1)

where \( Y_1 \) and \( Y_2 \) are the activity coefficients at the temperatures \( T_1 \) and \( T_2 \) respectively.

Thus for a 20 at% Zn-Fe alloy which has an activity coefficient \( Y_1 \) of zinc of 2.455 at 793°C we have the activity coefficient \( Y_2 \) at 600°C given by

\[ \ln Y_2 = \left( \frac{1066}{873} \right) \times \ln (2.455) \]

\[ Y_2 = 2.99 \]

The activity of zinc in the Fe-Zn alloy at 600°C is thus

\[ 0.2 \times 2.99 = 0.598. \]

The activity of the 70% Zn-Cu alloy at 600°C is similarly obtained. This alloy has an activity coefficient \( Y_1 \) of zinc of .835 at 500°C.
From Equation 1 we get

\[ T_1 \ln Y_1 = T_2 \ln Y_2 \]

i.e. The activity coefficient at 600 C is given by

\[ \ln Y_2 = \left( \frac{773}{873} \right) \times \ln (0.835) \]

\[ Y_2 = 0.854 \]

The activity of zinc in the Cu-Zn alloy at 600 C is thus

\[ 0.7 \times 0.584 = 0.597. \]

The Cu-Zn alloy source thus has the capability to alloy the Fe up to 20 at % or 23 wt%.

A similar calculation was made for the DIGM process at 500 C, and the values of the activities were found to be consistent.
Appendix B

The diffusion time $t$ can be assumed to be given by

$$ t = \frac{x^2}{16D} $$

where $D$ is the diffusion coefficient

$&$ $X$ is the diffusion distance

Thus from the data of Speich (42), we have this value given by (for grain boundary diffusion)

$$ t = \frac{75 \times 10^4}{16 \times 1.2 \times 10^{-6}} $$

$$ = 55 \text{ seconds} $$

For lattice diffusion, this becomes

$$ t = \frac{75 \times 10^{-4}}{16 \times 5 \times 10^{-16}} $$

$$ = 1.125 \times 10^8 \text{ seconds} $$

Thus the removal of zinc occurs by a combination of lattice diffusion and grain boundary diffusion.
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