Study of diffusion and related phenomena by electron probe microanalyser

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Abstract. Interaction of various materials at high temperatures leads to the formation of reaction zones of differing nature ranging from simple solid solutions to multiphase structures. Understanding the diffusion processes leading to the formation of reaction zone and its nature requires an accurate estimation of composition and the distribution of the phases formed. Electron probe microanalyser (EPMA) is an indispensable technique for this purpose, where the quantitative analysis of micron sized layers formed in the diffusion zone is required. Application of EPMA to study the diffusion processes in several metallic systems is dealt in detail. Utility of this technique to study problems related to contact metallurgy in semiconductors and practical problems of joining, particularly to that of diffusion bonding, is also described in this paper.

Keywords. Diffusion reaction; EPMA; diffusion coefficient; interdiffusion; diffusion bonding.

1. Introduction

Electron probe microanalyser (EPMA) is being extensively used in variety of fields including, metallurgy, ceramics, electronics, biology, mineralogy, medicine and geology. Applications related to metallurgy and materials science are essentially, the analysis of inclusions and precipitates, phase identification, phase diagram evaluation, crystallographic studies, fractography and failure analysis and diffusion research. Extensive work related to industrial application of EPMA includes new alloy development, texture studies in steel industry and quality control. EPMA provides unique way to identify localized fine scale structure ($> 1\,\mu m$) and provide information related to quantitative chemistry associated with it. It has contributed significantly in the last three decades in the development of a vast knowledge related to the chemical diffusion in metals and alloys. These studies include interdiffusion in binary, ternary and multicomponent systems, compatibility studies particularly related to nuclear fuel/cladding, interface reactions in metal–ceramic and ceramic–ceramic composites and also in characterizing the reaction zone formed during several joining techniques like soldering, brazing, welding and diffusion bonding. These studies provided an enormous literature leading to the evaluation of diffusion parameters like diffusion coefficient (D), frequency factor (D_0), activation energy (Q) and several parameters related to layer growth kinetics.

2. Electron probe microanalyser

The basis of this technique lies in the emission of X-rays from the surface of a material exposed to the primary beam of electrons of energy range 10–50 keV. A portion of these X-rays is related to the energies of the characteristic of the atom from which they originate. The energy of the X-ray emission is measured by the wavelength dispersive spectrometer (WDS) and/or solid state energy dispersive spectrometer (EDX) with the detectors positioned around the periphery of the microanalytical stage. In addition, scanning electron microscopy (SEM) also forms a part of an integrated EPMA to accurately position the details to be probed by EPMA. Excellent review articles on the working, development and applications are available in literature (Heinrich and Newbury 1991; Cahn *et al* 1993). A detailed working principle of this equipment is shown in figure 1.

Quantitative analysis concerns with the conversion of the X-ray intensity data measured on the samples and the standards to chemical compositions. Extensive research work has been reported in the literature and several schemes have been proposed for quantitative analysis. Standardless analysis, semiemperical methods, the conventional ZAF method and the analysis based on the calculated $\phi(\rho z)$ curves which are effective for the analysis of low atomic numbers are some of the typical correction methods used. Recent developments include the analysis of thin films, where the electron penetration is greater than the thickness of the sample and the relatively new method of Pouchou, Pichoir and Packwood (PAP) is based on the modified $\phi(\rho z)$ curves for the analysis of the surface layers (Cahn *et al* 1993).

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The basic requirement of the exact quantitative analysis involves (i) accurate positioning of the sample and the standard and its flatness to the electron beam, (ii) confirmation that the X-rays are generated and observed in the phase of interest, (iii) optimization of the operating parameters, (iv) information regarding the accuracy of the take off angle (ψ), (v) large counting statistics and (vi) accurate measurement of the peak above the background. It is very difficult to get all the required information and also satisfy these conditions. In general, the elemental sensitivity is order of 100 ppm for WDS analysis and about 1000 ppm for EDS. Analysis can be generally performed in a spot mode at $(1 \ \mu m)^3$ analysed volume or a line profile or in a two-dimensional elemental distribution map. Though EPMA is an extremely powerful technique for studying materials, it requires several techniques like TEM with analytical capability, EELS in conjunction for analysing features whose dimensions are smaller than $1 \ \mu m$.

3. Diffusion studies by EPMA

When the different materials are kept in contact at higher temperatures, they diffuse into each other and depth of diffusion is dependent on the diffusivities of the species and the time of annealing. Diffusion takes place down the activity gradient and Fick's second law is generally used to estimate the diffusion coefficients.

Measurements of diffusion coefficients is based basically on two concepts: (I) Measurement of diffusion length: These studies involve long range diffusion where displacements are more than the interatomic distances, 'd' $[\langle X^2 \rangle^{1/2} \gg d]$. Based on the measurements of the displacement ΔX, diffusion flux (J), and concentration profile $C(x, y, z, t)$ diffusion coefficient are evaluated. The type of diffusion coefficient measured could be self, impurity or chemical diffusion depending on the technique

Figure 1. Block diagram of the working principle of EPMA.

used and (II) Measurement of relaxation phenomena: These studies essentially depend on the measurement of relaxation time of one or more diffusing species. The diffusion coefficient is derived based on this data with a suitable model relevant to the technique. Mostly self diffusion coefficients are measured by these techniques.

Various techniques are available to measure the values of diffusion coefficients. Comparison of these techniques along with their limitations are listed in table 1. It can be seen clearly in the table that EPMA has only spatial resolution of 1–2 μm which will yield a diffusion coefficient in the range of $10^{-12} - 10^{-16} \ m^2/sec$. However, if one needs a better estimate it is essential to use complimentary technique where spatial resolution is better than 1–2 μm. It should be emphasized that EPMA unlike AES or SIMS is non-destructive technique. Moreover, several diffusion controlled processes in metals and alloys are generally high temperature phenomena, where displacements are more than 1–2 μm. EPMA is a powerful technique to study these displacements. A detailed description of these processes is mentioned below.

3.1 Diffusion coefficients in materials

In general, in multicomponent system with 'n' components the species diffuse into each other and flux of the component depends not only on its own concentration gradient but also on the concentration gradients of all other components. The Onsager equation of flux can be written as (Onsager 1945)

$$J_i = \sum_{j=1}^{n-1} -D_{ij}^n \left(\frac{dC_j}{dx} \right),$$ (1)

where D_{ij} is diffusion coefficient and dC_j/dx concentration gradient of the jth component.

These diffusivities are called intrinsic diffusivities and such $n(n-1)$ diffusion coefficients have to be defined. These diffusivities are with respect to the lattice fixed frame of reference which is itself moving with respect to laboratory frame of reference. Diffusion coefficients measured with respect to laboratory fixed frame of reference are called interdiffusion coefficients and there are such $(n-1)^2$ diffusion coefficients to be defined to describe the system completely.

Experimentally impurity diffusion coefficients are measured by allowing the species to diffuse into the matrix. EPMA can be used to measure concentration of diffusing species as a function of distance. EPMA, though has a low spatial resolution can be effectively used for measuring concentration profiles including those for light elements. In these cases diffusion coefficient is independent of composition and error function method is generally used to evaluate it. Recently, the diffusion of
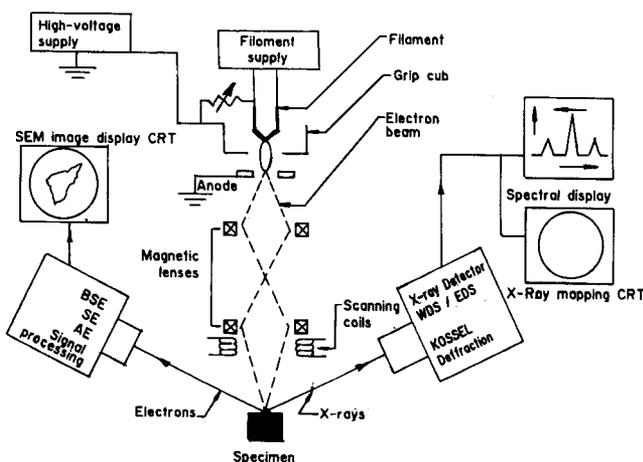
nitrogen in welds of steel has been studied by EPMA (Kucera *et al* 1994).

Chemical diffusion coefficients are measured under the influence of concentration gradient. In this case, two alloys of '*n*' components are annealed at elevated temperature for sufficient time to allow diffusion to occur. The resulting concentration profile is established by EPMA. Diffusion coefficients are evaluated from the experimental profile. Experimental determination of *D* values for binary, ternary and higher order systems are described below.

3.1a *Binary systems*: Simplest of '*n*' component systems is binary system. The concentration profiles across the diffusion zone can be established with the help of EPMA. Interdiffusion coefficients are evaluated by using Boltzmann–Matano method (Boltzmann 1894, Matano 1933) which is a solution of (1):

$$\tilde{D}(C') = -\frac{1}{2t} \left(\frac{dx}{dC} \right) \int_0^{C'} x\,dC, \qquad (2)$$

where $D(C')$ is diffusion coefficient at composition C', t is time of annealing and $(dC/dx)_{C'}$ is concentration gradient at $C=C'$ and $\int_0^{C'} x\,dC$ is area under the curve up to Matano interface.

This method assumes that molar volume of the system remains constant. Interdiffusion studies in Ti–Mo system have been carried out recently (Kale and Patil 1994). In Ti–Mo system it is found that at any plane in the diffusion zone no molar volume change is involved and

hence Boltzman–Matano has been used to estimate *D* values. A more rigorous method for evaluation of diffusion coefficients in systems involving variable molar volume V_m upon mixing was suggested by Sauer and Frecise (1962). The method does not need the explicit calculation of position of Matano interface.

Binary systems with restricted solubility result in the formation of intermetallic compounds in the diffusion zone. The phases grow in the diffusion zone as sequence of layers. Boltzmann Matano method was modified by Heumann (1962) to evaluate average diffusion coefficients of the phase. This method is not useful for the determination of *D* for the phases with narrow homogeneity range or for line compounds. Moreover, the phases sometimes grow with incubation period or some phases grow at the expense of others and hence establishing proper Matano interface is difficult. Sauer and Frecise method, which does not need explicit calculation of Matano interface to evaluate *D* was modified by Wagner (1969). This method is useful for the evaluation of diffusion coefficients for line compounds. Recent studies on Ni–Zr system have indicated that the evaluation of diffusion coefficients by both these methods are comparable (Bhanumurthy *et al* 1990).

3.1b *Ternary and higher component systems*: As seen from (1) there are $(n-1)$ unknowns in equation and as such we need $(n-1)$ independent simultaneous equations to evaluate these unknowns. Typically, in a ternary system we need two independent diffusion profiles which have common concentration at which only diffusion coefficients can be calculated. In order to evaluate dif-

Table 1. Values of diffusion coefficients accessible to different techniques and comparison of various diffusion measuring techniques.

Traditional methods			Non-traditional methods	
Technique	Displacement (ΔX, m)	D (m²/sec)	Technique	D (m²/sec)
Lathe sectioning and grinding	0.1–250×10^{-6}	10^{-19}–10^{-6}	Nuclear magnetic resonance	10^{-20}–10^{-9}
Microtome sectioning	1–10×10^{-6}	10^{-17}–10^{-12}	Neutron elastic scattering	10^{-11}–10^{-9}
Chemical etching	10×10^{-6}	10^{-15}–10^{-13}	Mossbaur effect	10^{-15}–10^{-11}
Electrochemical etching	50×10^{-9}	10^{-20}–10^{-17}	Conductivity	10^{-17}–10^{-10}
Sputtering (auger electron spectroscopy)	5–100×10^{-9}	10^{-22}–10^{-17}	Resistivity (semiconductors)	10^{-20}–10^{-12}
EPMA (electron probe microanalyser)	1–2×10^{-6}	10^{-16}–10^{-12}	Internal friction	10^{-20}–10^{-15}
SIMS (secondary ion mass spectroscopy)	1–100×10^{-9}	10^{-23}–10^{-17}	Magnetic anisotropy	10^{-25}–10^{-21}
RBS (Rutherford back scattering)	1–50×10^{-9}	10^{-20}–10^{-17}		

fusion coefficients at other compositions, other combinations of couples are needed to be made. Apart from this, diffusion paths are generally not linear and it is difficult to predict and plan the experiments. There is also a possibility of development of zero flux planes which cause the reversal of the flux in the diffusion zone. This requires cautious planning of experiments and also careful analysis by EPMA. Ternary diffusion in Fe–Cr–Ni system has been studied (Kale *et al* 1991). The isotherm at 1223 K and intersecting diffusion paths are shown in figure 2. Evaluation of diffusion coefficients in quaternary system by Boltzmann–Matano method and difficulties in its evaluation have been described (Heanley and Dayananda 1986). Average effective interdiffusion coefficient and integrated diffusion coefficient for systems involving higher orders have been defined (Dayananda 1996). Recently, effective diffusion coefficients in multi-component system, Ti/stainless steel, have been evaluated (Kale *et al* 1998). The diffusion coefficients for Ti, Fe, Ni, Cr have been evaluated using Boltzmann–Matano method from these profiles assuming binary system of Fe, Ni and G with Ti. The activation energy for diffusion coefficients of these elements have been evaluated and composition of the plane which controls the total diffusion processes has been established. This simple procedure is helpful in practical problems like diffusion bonding.

4. Diffusion related phenomena

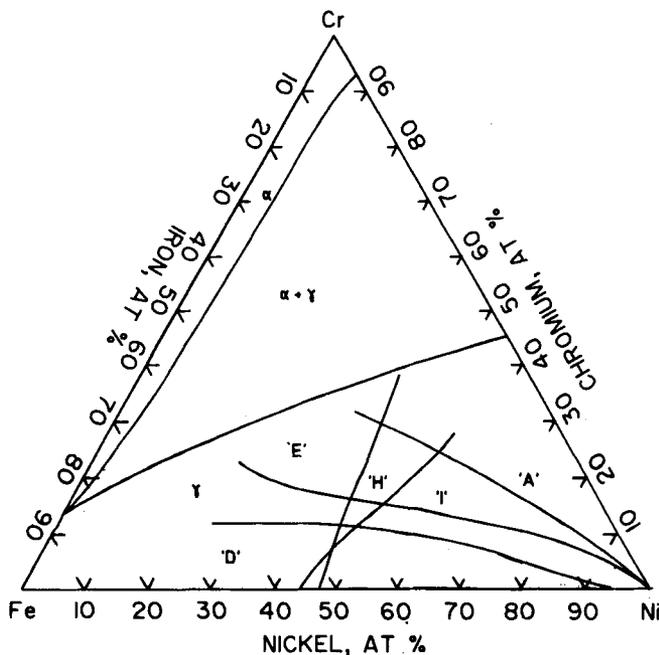There are large number of processes which are controlled by diffusion. Most of the phase transformations are

Figure 2. Phase diagram of Fe–Cr–Ni at 1223 K and the diffusion paths for various couples.

governed by diffusion kinetics. Apart from phase transformation, plastic deformation at high temperature, creep, occur by diffusion essentially due to the movement of lattice defects. Oxidation, carburization, nitriding, sintering, coating, cladding and joining are generally used industrial processes which are possible due to diffusion. In addition, contact metallurgy related to metallic contacts to semiconductor compounds is another diffusion controlled process. In all these processes reactive diffusion between different materials takes place. Basic understanding of reactive diffusion is very important and detailed knowledge of this can be used for controlling these processes. Diffusion bonding is an important method of joining and requires an extensive knowledge of diffusion parameters and also the basic information on the phase formation. Use of EPMA in the study of reactive diffusion, understanding metallic contacts in compound semiconductors and its use in characterizing the reaction zone in diffusion bonded assemblies is discussed below.

4.1 Reactive diffusion

In reactive diffusion, two metals/alloys diffuse into each other, resulting in the formation of intermediate phases in the reaction zone. In principle, all the phases predicted by the phase diagram should form in the diffusion zone. But in practice, it is observed that, even for a simple system like binary system, not all the phases appear in the diffusion zone. Many a times, metastable/non-equilibrium (Philibert 1989), or glassy (Johnson 1986) phases appear. It has also been observed that some phases appear after a incubation time or disappear at higher temperature (Bhanumurthy *et al* 1990). The total nature of diffusion zone depends upon the temperature and time of annealing and also on nature of intermediate phases. The constitution of reaction zone with respect to formation, absence or disappearance of phases have been the subject of interest of many researches (Van Loo 1990; Kale 1995). In spite of extensive work there seem to be many open questions which need to be resolved (Philibert 1997).

Formation of a phase in diffusion zone is controlled by nucleation and growth processes. These processes are essentially governed by thermodynamic and kinetic considerations prevailing in the diffusion zone. Some of these aspects are discussed in detail (Philibert 1997). Several research workers (Walser and Bene 1976; Pretorious *et al* 1993; Bhanumurthy *et al* 1995) have also proposed many theoretical models to predict which phase will nucleate first. Recently, Pretorious model (Pretorious *et al* 1993) has been modified by incorporating congruency factor (Bhanumurthy *et al* 1995). This model predicts correctly the formation of first phase in the diffusion zone in several systems.

4.1a *Analysis of reaction zone by EPMA*: The formation of intermetallic compounds of narrow width in the diffusion zone generally involves steep concentration gradients. It is also possible that there could be deviations in the phase compositions of the compounds compared to the equilibrium values. It is difficult to measure reliable concentration values at a distance smaller than 2 μm from the interface. Some of these problems and the inherent difficulties involved in the correction procedure to arrive at the compositions of a phase, is illustrated in the Ti–Fe and Zr–Ni. In addition, these systems have been chosen as they illustrate interesting results associated with reactive diffusion.

4.1b *Interdiffusion studies in Ti–Fe system*: Interdiffusion in Ti–Fe system has been studied (Kale *et al* 1980). The equilibrium phase diagram of system depicts two phases viz. TiFe and TiFe$_2$. However, experimental results indicate that none of the phases form in the diffusion zone for the couples annealed for all temperatures in which Fe is in γ regime. Whereas, the couple annealed in lower temperatures in which Fe is in the α regime shows the formation of TiFe$_2$ phase in the diffusion zone. Based on flux calculations (see table 2), it was inferred that the phases would not grow even after nucleation, due to unfavourable flux balance. The validity of these calculations were confirmed experimentally (Hirano and Iijima 1984).

4.1c *Interdiffusion studies in Zr–Ni system*: The multiphase diffusion in Zr–Ni has been studied (Bhanumurthy *et al* 1990). A typical concentration profile for the couple annealed at 1169 K is shown in figure 3. It is observed that Ni$_7$Zr$_2$ and Ni$_{10}$Zr$_7$ disappear above 1169 K. Flux balance across the phase is probably responsible for the disappearance of the earlier formed phases at higher temperatures. Assuming that flux is directly proportional to diffusivities, the ratio of these diffusivities with adjoining phases are given in table 3. It is seen from the table that diffusivitiy ratios for these phases decrease gradually with increase in temperature, indicating the tendency to disappear at higher temperatures.

4.2 *Diffusion reactions in ternary systems and relevance to contact metallurgy*

The development of metallic contacts to compound semiconductors like 6H–SiC, which are stable at high temperatures is an essential step in the ongoing miniaturization of high power electronic devices. Diffusion reaction between SiC and various other metals are of vital importance in the development of ohmic and Schottky contacts. In multiphase ternary systems, there is no unique way in which prediction can be made regarding the diffusion path. In general, detailed experiments are essential to have a knowledge of sequence of formation of these phases in the diffusion zone (Van Loo 1990). Based on the detailed experimentation and
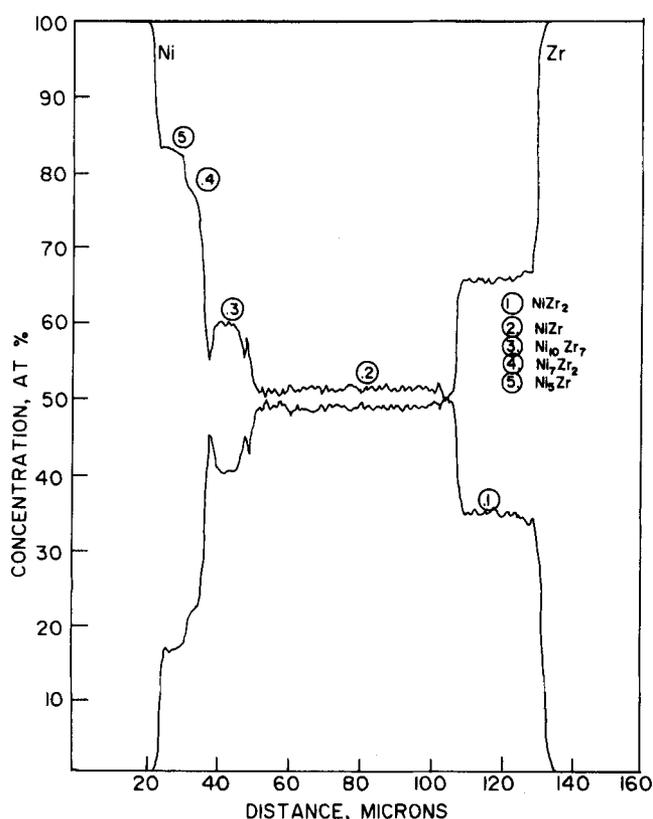
Figure 3. Concentration profiles of Zr and Ni for the diffusion couple Ni/Zr annealed at 1169 K for 24 h.

Table 2. Flux of Fe atoms in Fe–Ti system.

Couple	Temperature (K)	Phase	Flux J_i (atoms/m^2/sec) Entering	Leaving
γFe–βTi	> 1100	TiFe$_2$	$8\cdot4 \times 10^{10}$	$1\cdot4 \times 10^{12}$
		TiFe	$1\cdot4 \times 10^{12}$	$2\cdot0 \times 10^{14}$
αFe–TiFe	< 1100	TiFe$_2$	$1\cdot5 \times 10^{10}$	$2\cdot9 \times 10^7$

Table 3. Diffusivity ratios for intermediate phases to their adjoining phase in Zr–Ni systems.

Temperature (K)	Ni$_7$Zr$_2$	Ni$_{10}$Zr$_7$
1046	3·0	4·17
1115	2·5	3·85
1133	2·33	3·03
1169	2·14	2·86

thermodynamic stability, the necessary inputs for the contact on 6H–SiC could be arrived. Diffusion reactions of Ni, W, Cr, Pd and Ti with 6H–SiC have been investigated (Goessmann and Schmid-Fetzer 1995, Bhanumurthy and Schmid-Fetzer 1996a). These studies confirmed that phase diagrams, diffusion reactions and electrical properties together will lead to the clear understanding of the metal/semiconductor contact formation.

Recently new class of microstructures involving the formation of periodic bands have been reported in many ternary systems (Kao and Chang 1993). The isotherm and diffusion path for the couple 6H–SiC/Ni annealed at 102 K for 24 h is shown in figure 4. Analysis of Si, Ni and particularly C by EPMA in these layers whose thickness is small is very difficult. Several models based on diffusion theory are put forward to satisfactorily explain these phenomena (Kao and Chang 1993). A comparison of these models along with the suggestion that a continuous joining pressure may be required to produce the periodic bands is published recently (Bhanumurthy and Schmid-Fetzer 1996b). However, it is still unclear which model is appropriate to explain all aspects of periodic layer formation.

4.3 *Diffusion bonding*

The information regarding the extent of interdiffusion, dilution and mixing of the phases is prerequisite to optimize the process parameters in several joining techniques like welding, brazing or diffusion bonding. EPMA with its unique capabilities has become an indispensable tool for characterizing the reaction zone formed due to any of the joining techniques. Specific examples related
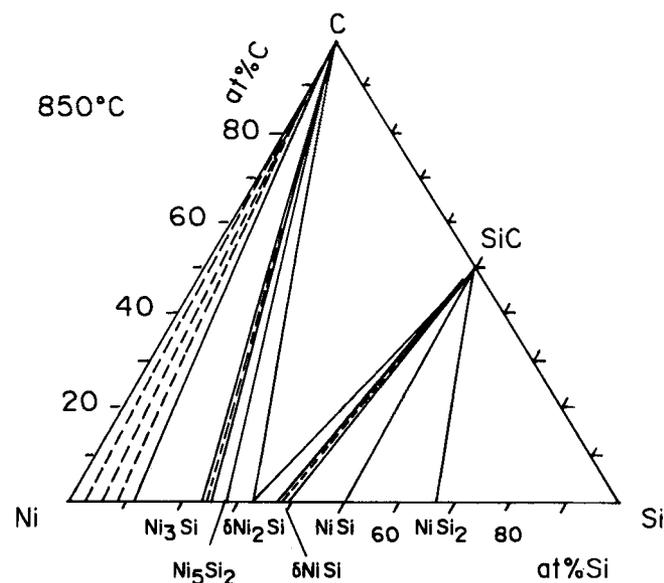
to joining of alloys and ceramic materials by diffusion bonding are discussed below.

4.3a *Diffusion bonding of zircaloy-2 to stainless steel*: Recently joining of zircaloy-2 (Zr-2) to stainless steel by diffusion bonding has been undertaken at the authors laboratory (Bhanumurthy *et al* 1994). The joining of these materials by conventional welding is undesirable because of the formation of intermetallic compounds like $FeZr_2$ and $FeZr_3$. Several intermediate layers consisting of Zr-2/Nb/Cu/Ni/stainless steel have been used to prevent the formation of intermetallic compounds and also minimize the thermal expansion mismatch. Actual assembly of these specimens made by both solid state bonding and also by transient eutectic liquid phase bonding is shown in figure 5.

4.3b *Solid state bonding of HIP–SiC*: Direct bonding of HiP–SiC generally requires high temperature above 1773 K and high pressure. The bonding between SiC is achieved in two stages (Bhanumurthy and Schmid-Fetzer 1996c), (i) the pressureless prereacting of the SiC pieces in a bed of Cr at 1273 K for 3 h to produce the required ternary phase (Cr_5Si_3C) on the SiC surface and (ii) diffusion bonding of the phases using Ni as an intermediate layer at 1213 K for 3 h at a pressure of 15 MPa. A typical back scattered electron image is shown in figure 6. Based on the extent of the reaction zone, optimization of process parameters have been carried out.

5. Conclusions

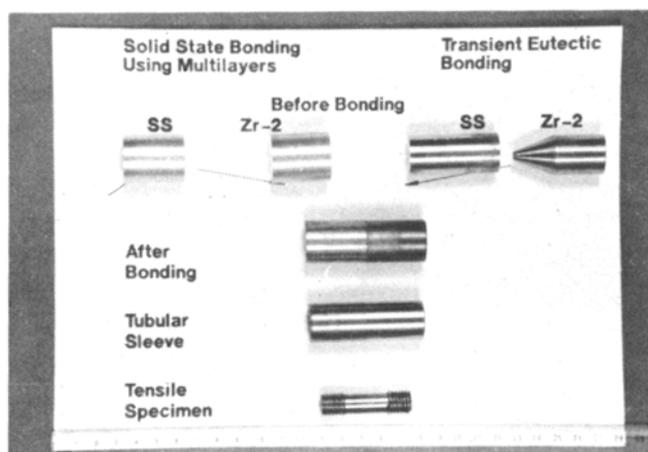Study of diffusion reaction needs accurate estimation of composition of the phases nucleated and grown in the

Figure 4. Phase diagram of Si–C–Ni and the diffusion path for the couple 6H–SiC/Ni annealed at 102 K for 24 h.

Figure 5. Details of the zircaloy-2/stainless steel specimens fabricated by solid state bonding and transient eutectic phase bonding along with tubular sleeves and tensile specimen.
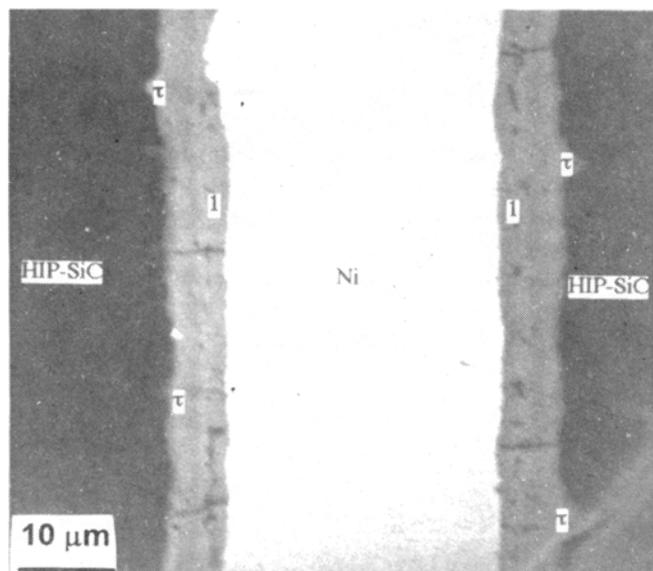
Figure 6. Back scattered electron image of cross section of the diffusion bonded specimen annealed at 1213 K for 3 h. ($\tau = Cr_5Si_3C$ and $1 = Cr_{23}C_6$).

reaction zone. The evaluation of the diffusion coefficients requires the variation of the composition along the diffusion length. Several diffusion controlled processes in metals and alloys at high temperatures involve mass transfer in a dimension more than 1–2 µm. EPMA is an indispensable technique to study these reactions and to analyse the reaction products. The use of this technique for evaluating the diffusion parameters in binary and higher order systems are illustrated in this paper. The utility of EPMA for studies of practical importance such as diffusion bonding and reactive diffusion in contact metallurgy has been discussed.

Acknowledgements

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