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SUBMITTED TO Proceedings - Materials Research Society Meeting
Boston, MA
November 1990

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FREE ENERGY SIMULATION OF GRAIN BOUNDARY SEGREGATION AND THERMODYNAMICS IN $Ni_{3-x}Al_{1+x}$

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ABSTRACT

The free energy simulation method is employed to study segregation to $\Sigma5$ and $\Sigma13$ (001) twist grain boundaries and their free energies in ordered $Ni_{3-x}Al_{1+x}$. In the temperature range studied (300 - 900K), it is shown that there is almost no segregation, strong Al segregation, and weak Ni segregation to the grain boundary for the stoichiometric, Al-rich, and Ni-rich bulk compositions respectively. It is also shown that the segregation is limited to a few (002) planes around the grain boundary and its magnitude decreases with increasing temperature. For Al-rich bulk composition, it is demonstrated that segregation at low temperature substantially lowers the grain boundary free energy.

INTRODUCTION

There has been, in recent years, some atomistic simulation studies of the properties of grain boundaries in the intermetallic ordered alloy Ni_3Al [1-4]. These studies [2,3] were aimed at explaining the brittle fracture behavior of the Ni_3Al in the polycrystalline phase. It has been shown [3] that the cohesive strength of grain boundaries in Ni_3Al is increased by doping with boron when the boundaries are Ni-rich than when they are either stoichiometric or Al-rich. This energy increase suggests that boron doping of the grain boundaries should decrease the tendency for brittle fracture in polycrystalline Ni_3Al. Most of these calculations have been carried out at zero temperature for the stoichiometric bulk composition. Monte Carlo simulation studies of the same system have shown that introduction of boron atoms into the boundary does not induce any chemical disorder at grain boundaries [4] as speculated based on $T=0$ studies [3].

In the following study, we address the effect of temperature and bulk composition on the chemical, structural, and thermodynamic properties of grain boundaries in ordered Ni_3Al within the framework of the newly developed free energy simulation method for binary alloys [5]. The simulation method is briefly described in the following section and its application to (001) twist grain boundaries with misorientation angles of 36.9 ($\Sigma5$) and 22.6 ($\Sigma13$) in $Ni_{3-x}Al_{1+x}$ ($x=-0.016$, 0, and 0.015)are presented in the following section.

METHOD

The local harmonic (LH) model has been applied with considerable success to perfect and defected single component solids [6,7]. In this model, the classical vibrational contribution to the free energy for a single component system is given by

$$A_v = k_b T \sum_{i=1}^{N} \sum_{\beta=1}^{3} \ln\left[\frac{\hbar\omega_{i\beta}}{2\pi k_B T}\right] \tag{1}$$

where k_B is the Boltzmann constant, and ω_{i1}, ω_{i2}, and ω_{i3} are the three vibrational eigenfrequencies of atom i. These frequencies may be determined in terms of the local dynamical matrix of each atom $D_{i\alpha\beta}$ $(\partial^2E/\partial x_{i\alpha}\partial x_{i\beta})$, where the $x_{i\beta}$ correspond to atomic displacements of atom i in the β direction. Diagonalization of this 3x3 matrix yields the three vibrational frequencies for atom i. As described in reference [6], the approximations of the LH model reduces the calculation of the vibrational contribution to the free energy from one of diagonalizing a 3Nx3N dynamical matrix to the calculation of N determinants of 3x3 matrices, where N is the number of atoms in the system.

In order to study binary alloys within the frame work of the LH model, an effective atom is assigned to each atomic site which has the effective mass of $m_i = x_a(i)m_a + x_b(i)m_b$. Here, $x_a(i)$ is the probability that atomic site i is occupied by an atom of type a and correspondingly $x_b(i) = 1 - x_a(i)$ is the probability that the same atomic site is occupied by atom of type b. The vibrational contribution to the free energy is determined from the appropriately averaged local dynamical matrix (for details see reference [5]). The configurational entropy is written using the point approximation as

$$S_c = -k_b \sum_{i=1}^{N} \{x_a(i) \ln[x_a(i)] + x_b(i) \ln[x_b(i)]\} \qquad (2)$$

In the simulations described below, we employ a reduced Grand Canonical ensemble, where the total number of atoms remains fixed but the relative amounts of each atomic species varies. The appropriate thermodynamic potential for this type of ensemble is the Grand potential and is given by

$$\Omega = A + \Delta\mu \sum_{i=1}^{N} x_a(i) = E + A_v - TS_c + \Delta\mu \sum_{i=1}^{N} x_a(i) \qquad (3)$$

where A is the Helmholtz free energy, E is the potential energy (obtained via an interatomic potential), and $\Delta\mu$ is the difference in chemical potential between atoms of type a and b. Given $\Delta\mu$, the equilibrium concentration at each site can be determined by minimizing Ω with respect to those concentrations.

Defect free energies, in this ensemble is defined as the difference in grand potential energies between the system with the defect and the defect-free system at the same chemical potential difference and temperature.

The simulation cell set-up used here has been described in detail elsewhere [7]. Briefly, the grain boundary is embedded in a perfect crystal at the desired temperature and composition. In the plane of the boundary, periodic border condition are enforced. Normal to the boundary plane the simulation cell is bounded by two infinite, mobile but rigid blocks of structurally perfect crystal. The extent of the grain boundary region between the two blocks of perfect system is increased during the course of the simulation to a size such that the free energy and other properties of the grain boundary remained unchanged within the predetermined values. The interatomic interactions employed in this study were the embedded atom method type potentials developed by Voter and Chen[8].

Depending on the chemical arrangement of the terminating (002) planes of the two crystals at the interface there are three distinct types of grain boundaries which correspond to different stacking sequence of (002) planes; $\alpha\beta\alpha\beta|\alpha\beta\alpha\beta$, $\beta\alpha\beta\alpha|\alpha\beta\alpha\beta$, and $\alpha\beta\alpha\beta|\beta\alpha\beta\alpha$ where α and β are planes of pure Ni and ordered 50% Ni, respectively. These different types of boundaries correspond to the stoichiometric, Ni-rich, and aluminium rich composition in the grain boundary region which have been denoted as 50/100, 100/100, and 50/50, respectively in Ref. [2]. Simulations of the $\Sigma 5$ and $\Sigma 13$ structures at zero temperature showed that the 50/100 type boundary has the lowest grain boundary energy. In the present study, we concentrate on the properties of the 50/100 type grain boundaries as a function of temperature and composition.

In order to isolate the effect of segregation on the grain boundary properties from that due merely to atomic structural relaxation, we have performed two types of simulations for each temperature and bulk composition. In the first, the composition of each atomic site remains fixed at a value corresponding to the sublattice composition in the perfect crystal (no segregation) and the free energy is minimized with respect to the atom positions. In the second, the composition of each site is allowed to vary along with atom positions to reach the minimum free energy

RESULTS

The free energy minimization method, described above, was used to investigate the compositional changes in the vicinity of $\Sigma5$ and $\Sigma13$ (001) twist grain boundaries in $Ni_{3-x}Al_{1+x}$ ordered alloys for three different bulk compositions, namely 73.5, 75.0, and 76.6 Ni atomic percent. These compositions are within the stability range of Ni_3Al phase as predicted by the model using the present interatomic potentials [8]. The experimental stability range for Ni_3Al phase is approximately 74-76 atomic percent. The effect of temperature on grain boundary segregation was determined by performing different simulations at 300, 600, and 900 K for the above three bulk compositions.

The equilibrium concentration profiles of the (002) planes for $\Sigma5$ and $\Sigma13$ grain boundaries at the 73.5 % Ni bulk composition (Al-rich) are shown in Figures 1a and 1b for 300 and 900K temperatures. The geometrical grain boundary plane was originally between planes 0 and 1. The averaged concentration on each (002) plane is normalized by the concentration of the appropriate (002) plane in the bulk. For $\Sigma5$ at T=300 K, planes 0 and +1, which were initially almost pure Ni and 50% Ni, respectively, are enriched with Al by about 20% whereas planes +2 and -1 are slightly enriched with Ni. When the temperature is raised to 900K, plane 0 returns to almost pure Ni whereas plane +1 still remains enriched with Al. For $\Sigma13$ at T=300K (Fig. 1b), plane +1 is strongly (34%) enriched with Al whereas plane 0 is enriched by only 6%. When the temperature is increased to 900K Al enrichment on plane +1 is reduced to about 18% and plane 0 becomes nearly bulk-like.

Simulations performed at stoichiometric composition for the three temperatures showed no significant segregation of either Al or Ni to the $\Sigma5$ and $\Sigma13$ grain boundaries studied in the present work.

In Figure 2, we show the calculated concentration profiles for the $\Sigma5$ grain boundary at the 300 and 900K for a bulk composition of 76.6% Ni. At T=300K planes -1 and +1 which were initially at about 50% Ni concentration have been enriched by 9 and 13% Ni, respectively, and planes -3 and +3, which were similar to planes -1 and +1 are slightly enriched in Al. When the temperature is increased to 900K the Ni enrichments on planes -1 and +1 are reduced to less than 2%. We observed similar behavior for the $\Sigma13$ grain boundary.

A measure of the overall compositional changes in the grain boundary is the integral of the excess concentration of Ni (or Al) over the (002) planes. Figure 3 shows the total segregation of Ni as a function of Ni bulk composition at T=300K for the $\Sigma5$ and $\Sigma13$ grain boundaries. For the Ni bulk composition of 73.5%, the total or net Al segregation to the $\Sigma5$ and $\Sigma13$ grain boundaries are equivalent to the addition of 25 and 32% of an (002) monolayer of Al, respectively. The total Ni segregation to the $\Sigma5$ and $\Sigma13$ grain boundaries at the bulk composition of 76.6% Ni are equivalent to 10 and 6% of an (002) monolayer of pure Ni, respectively. There is no significant net segregation of either Ni or Al to the grain boundaries at the stoichiometric bulk composition.

The effect of temperature on the net segregation to the $\Sigma5$ and $\Sigma13$ boundaries is shown in Figures 4 for the Al-rich and Ni-rich compositions. In both cases, the net segregation monotonically decreases towards zero with increasing temperature. At the Al-rich bulk composition, the total amount of segregation to the $\Sigma13$ grain boundary decreases from 32% to 13% of a (002) pure Al plane when temperature is raised from 300 to 900K. For the same grain boundary structure, at the Ni-rich bulk composition, the decrease in the total Ni segregation is from 6 to 2% of an (002) Ni monolayer over the same temperature range.

Although, the above results suggest that some site disordering is taking place in the grain boundary region, especially at low temperatures, detailed site concentrations profiles show that the grain boundaries are still highly ordered. Figure 5 shows the equilibrium site concentrations of two (002) planes just above and two (002) planes below the $\Sigma13$ grain boundary for the Ni rich bulk composition at 300 K. In this figure, the small circles represent atomic sites where the degree of grayness changes from white to black corresponding to a change in site concentration from 100% Ni to 100% Al. The big solid circles in Figure 5, indicate which atomic sites have changed from being initially almost pure Ni to almost nearly pure Al. The sites indicated by broken circles have changed to 60% Al from initially almost pure Ni.

The effect of segregation on the grain boundary free energy at 300K, as a function of bulk composition, is shown in Fig. 6. The dashed line is the grain boundary free energy when no segregation is allowed (concentration at all sites are kept fixed at values corresponding to the appropriate sublattice concentration in the bulk) and the solid line is the free energy where segregation is allowed to occur. For the Al-rich bulk composition, there is a pronounced free energy decrease (about 20%) for both $\Sigma 5$ and $\Sigma 13$ grain boundaries upon segregation, whereas for the Ni-rich bulk composition, there is only a very small decrease in free energy for the $\Sigma 5$ boundary and almost no change for the $\Sigma 13$ boundary. The free energy change at the stoichiometry composition is insignificant for both grain boundaries. The segregation effect on the grain boundary free energy at 900K is less than that at T=300K but with a similar trend (Figure 6b).

Figures 7a and 7b show the temperature dependence of the grain boundary free energy at the Al-rich and Ni-rich bulk compositions for the two grain boundaries, respectively. As in Figure 6, the dashed lines represent the case where no segregation is allowed. With increasing temperature, the free energy curves corresponding to segregation and no segregation approach each other. For the Ni-rich bulk composition, there is almost no difference in the free energies in the temperature range of 300 to 900K for the $\Sigma 13$ grain boundary with and without segregation. There is a small decrease (2%) in the free energies for the $\Sigma 5$ grain boundary with and without segregation at low temperatures which vanishes at high temperature. It is interesting to note that the slopes of the free energy curves in Figure 7a, which is the grain boundary entropy, changes sign when segregation is allowed.

DISCUSSION AND CONCLUSIONS

The free energy minimization method was used to study the properties of (001) twist grain boundaries ($\Sigma 5$ and $\Sigma 13$) in ordered $Ni_{3-x}Al_{1+x}$ alloys. For the stoichiometric bulk composition, ($300K \leq T \leq 900K$) there was no significant segregation of either Al or Ni to the grain boundary region. There was also no observable site disordering in the grain boundary region for either of the boundaries in the temperature range studied here. This is consistent with a recent Monte Carlo simulation results [4] on a $\Sigma 5$ tilt grain boundary where the same EAM type potential [8] was used.

At the Al-rich bulk composition (73.5% Ni), the composition profile at 300K (Figure 4) shows significant Al segregation to the boundary region which decreases with increasing temperature. The role of configurational entropy at low temperature is not significant and segregation to the grain boundaries is mainly controlled by the grain boundary enthalpy which, in turn, is controlled by the bond energies. Although, at low temperatures, a significant amount of Al segregation to the grain boundary has been observed examination of the site compositions on different (002) planes shows very little site disordering and the segregation is due mainly to the replacement of Ni with Al atoms at some sites on the two (002) planes immediately adjacent to the grain boundary plane, see Figure 5. This indicates that the strong ordering tendency in the Ni_3Al system is well represented by the EAM-type potential [8] used here. With increasing temperature, the Al segregation to the grain boundary decreases but the site disordering in the grain boundary region, relative to that at low temperature, increases. This site disordering, which is less than 2% for most of the sites, is essentially due to the configurational entropy that generally tends to move the system towards a disordered phase at high temperature.

For the Ni-rich bulk composition (76.6% Ni) at 300K we observed a weak tendency for Ni atoms to segregate to the grain boundary region. As can be seen from Figure 4, the total amount of Ni segregation is much less than the total amount of Al segregation to the boundary for Al rich composition at the same temperature and there is almost no segregation at 900K . This highly asymmetric segregation tendency is partly due to the predicted stability of the Ni_3Al phase over a much wider composition range on the Ni-rich side than is seen experimentally. This shortcoming of the EAM-type [8] potential employed here, makes it difficult to assess the effect of the segregation on the grain boundary properties for the Ni-rich side of the Ni_3Al phase field because the sites at the grain boundary region belonging to the Al sublattice can accommodate much more Ni atoms than one would expect according to the experimental phase diagram.

The effect of temperature on the grain boundary free energy is strongly related to the net segregation. Segregation is strongest at low temperature for the Al-rich bulk composition and it is there that the grain boundary free energy is the lowest. The cohesive energy of Al atoms is greater than that of Ni atoms and thus Al segregation to the boundary lowers the grain boundary free energy but this energy change is less than 10% of the total decease in the grain boundary free energy. This suggests that the interaction between segregated atoms and the boundary structure is the dominant factor in decreasing the grain boundary free energies and therefore making them more stable.

In summery, we employed the free energy simulation method to study segregation to the grain boundaries of $\Sigma 5$ and $\Sigma 13$ and their free energies as a function of temperature and bulk composition. It was shown that in the temperature range of 300 to 900K that there is almost no segregation, strong Al segregation, and weak Ni segregation to the grain boundary corresponding to the stoichiometric, Al-rich, and Ni-rich composition of the bulk, respectively. It is also shown that the segregation is limited to a few (002) planes around the grain boundary and its magnitude decreases with increasing temperature. For Al-rich bulk composition, it is demonstrated that segregation at low temperature substantially lowers the grain boundary free energy.

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Figure 1. Composition profiles of (002) planes plotted as a function of plane number from interface for the (a) $\Sigma 5$ and (b) $\Sigma 13$ grain boundaries at the Al-rich bulk composition. x^b_{Ni} the Ni concentration on the corresponding plane in the bulk.

Figure 2. Composition profiles of (002) planes in the $\Sigma 5$ boundary plotted as a function of plane number from the interface for the Ni-rich bulk composition

Figure 3. Net Ni segregation plotted as a function of Ni bulk concentration at T=300 K.

Figure 4. Net Ni segregation plotted as function of temperature for the Al (solid line) and Ni (dashed line) rich bulk compositions.

Figure 5. Atomic site concentration on four (002) planes around the $\Sigma 5$ grain boundary for the Al-rich bulk composition at 300 K. The darker the circle, the higher the Al concentration at the site. The circled sites have undergone a large change in concentration (see text).

Figure 6. Grain boundary free energy as a function of Ni bulk concentration. Solid and dashed lines represent the calculations with and without segregation, respectively, at (a) T=300 K and (b) T=900K

Figure 7. Grain boundary free energy as a function of temperature for (a) the Al-rich bulk composition and (b) the Ni-rich bulk composition. Solid and dashed lines represent the calculations with and without segregation, respectively.

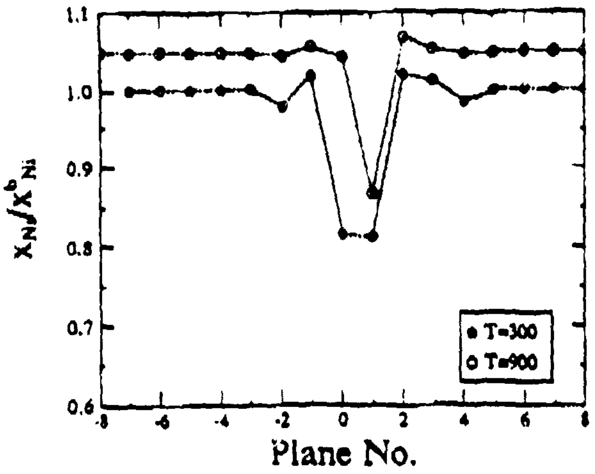


Fig 1a

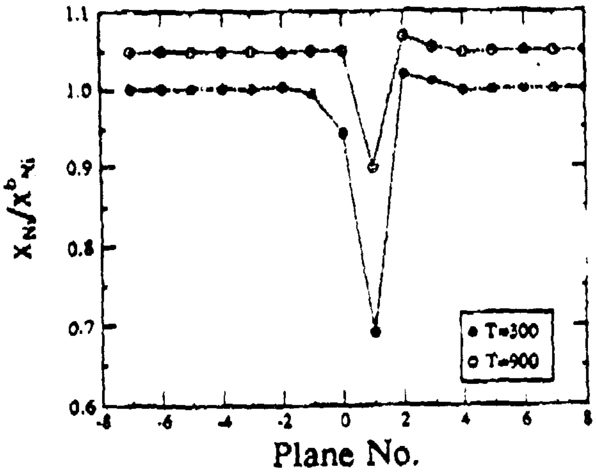


Fig. 1b

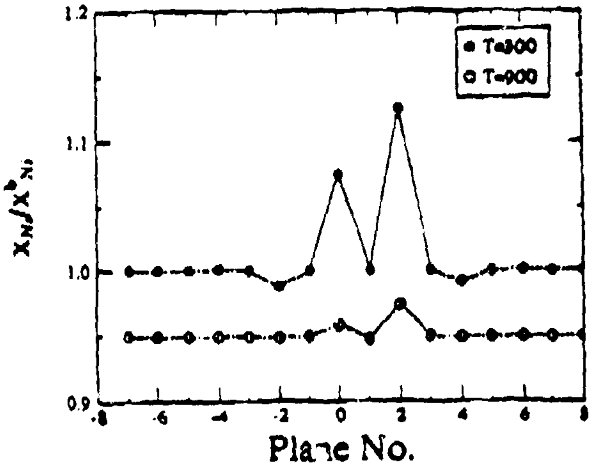


Fig 2

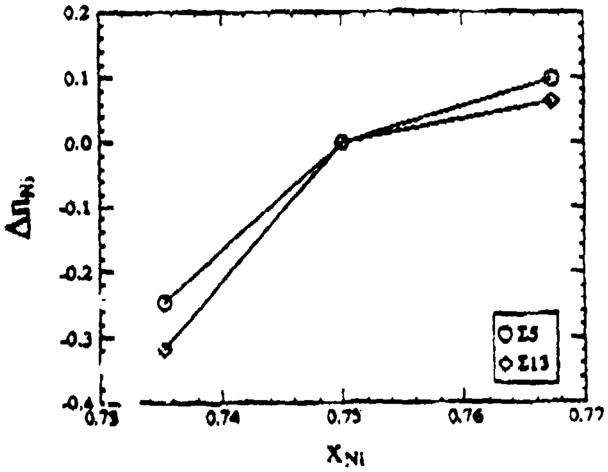
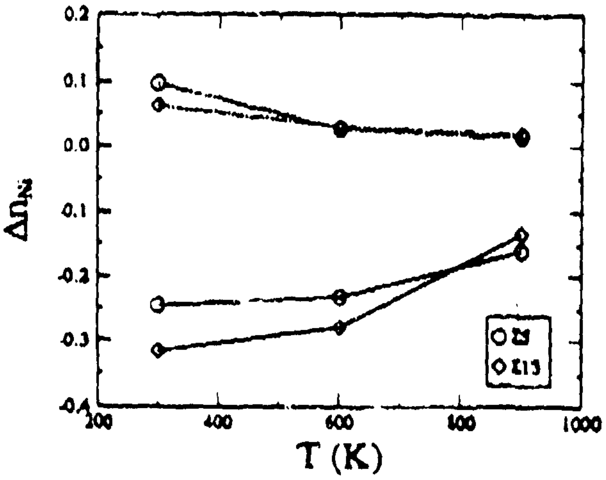
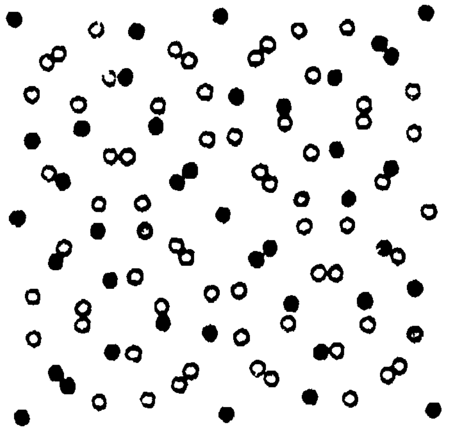


Fig. 3





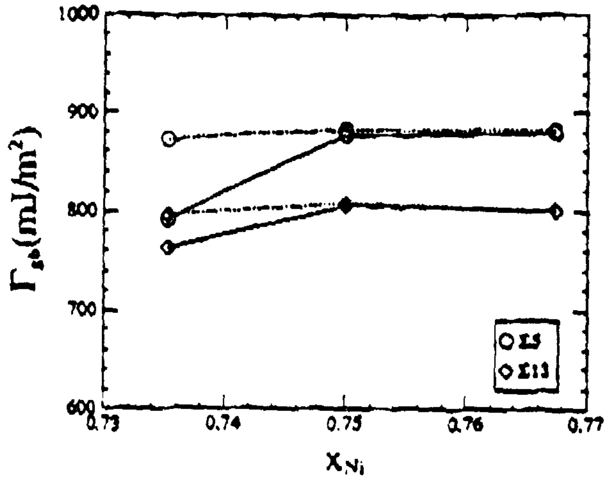


Fig 6.b

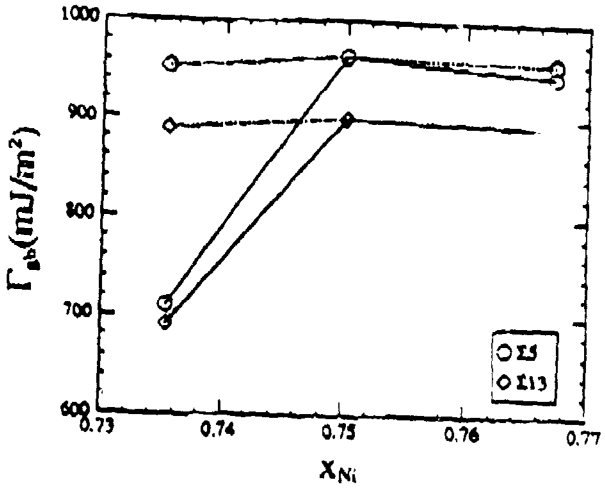


Fig.6.a

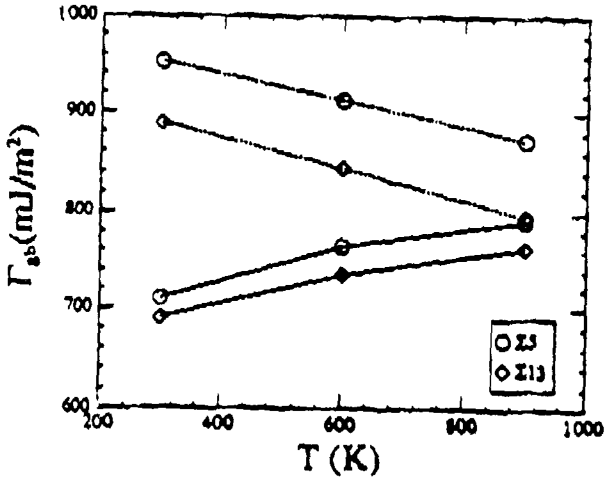


Fig 7.a

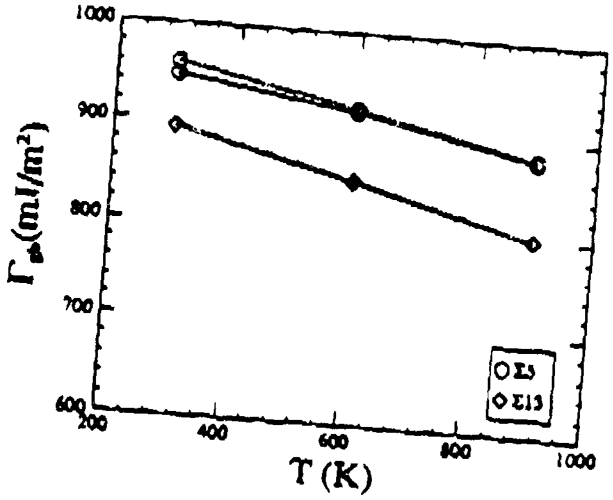


Fig 7.b