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EFFECTS OF SURFACE OXIDATION ON VACANCY DEFECTS
IN BETA NICKEL-ALUMINUM ALLOYS

BY

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ABSTRACT

EFFECTS OF SURFACE OXIDATION ON VACANCY DEFECTS IN BETA NICKEL-ALUMINUM ALLOYS

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Transmission Electron Microscopy and Auger Electron Spectroscopy has been used to make observations of the oxidation process in β -NiAl alloys annealed under controlled conditions of temperature and oxygen partial pressure. Binary Ni-Al alloys, with nominally 47.5, 50.4 and 52.5 at.% Al, were examined. The Auger spectroscopy analysis showed that the predominant oxide formed on these alloys is Al_2O_3 , with a possible thin intermediate layer of spinel. Bulk oxidation experiments indicate that the oxide grows by outward diffusion of cations to the oxide/gas interface.

As a result of this diffusion, a counter-flow of vacancies occurs, and these vacancies are injected into the substrate. The vacancy injection results in formation and growth of interfacial voids and growth of existing vacancy dislocation loops and internal voids in thin foil samples. Vacancy loop growth rates increase with annealing time and also increase as the oxygen partial pressure is increased - in accordance with a vacancy injection model. This vacancy injection takes place in the alloys tested here, at temperatures above about 600°C, even in ultra high vacuum ($<10^{-8}$ torr) annealing atmospheres. An exception was found in the case of samples annealed at $T > 850^\circ\text{C}$ in UHV. In these samples the oxidation mechanism seems

to change from cation diffusion to anion diffusion and as a result, vacancy defects shrink, rather than grow, in these samples.

In addition to vacancies injected by oxidation, vacancy defects are also formed from retained thermal vacancies. From quenching and ageing experiments, and using electron microscopy, an estimation of 1.45 ± 0.2 eV was made for the formation energy of a pair of vacancies, one on each sublattice. Large concentrations of thermal vacancies can be generated as a result of this low vacancy formation energy, and can be retained in the alloy even during slow cooling due to the impervious oxide formed.

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1. INTRODUCTION

Oxidation is a phenomenon of wide ranging consequence and concern in metallurgy. At elevated temperatures, metals and alloys react with the gases in given environments, leading to deterioration of their properties. This can happen in a number of ways. Firstly, the metal is converted to an oxide, which has less desirable properties. Secondly, internal oxide formation and grain boundary penetration of oxygen can affect the structural integrity. Thirdly, oxidation can introduce defects into the material, which might have an effect on physical and mechanical properties. Fourthly, selective oxidation of one constituent of an alloy could deplete the material of important alloying elements. Thus oxidation is not just a surface problem but can have serious consequences on bulk properties as well.

Superalloys are one group of materials where the problem of oxidation is of particular concern. These alloys retain their high strength at elevated temperatures but can be rapidly degraded by oxidation. To increase the oxidation resistance of superalloys, aluminide coatings have been used successfully. As a result, a fair amount of research has been carried out on the behavior of these coatings under simulated environmental conditions.¹⁻⁵ One of the most important phases constituting these coatings is β -NiAl, which is very oxidation-resistant at high temperatures. This compound has been the subject of much fundamental and applied research. It has a well known defect structure where constitutional vacancies can exist on the nickel sublattice depending on the composition. The presence of this defect structure seems to play an important role in the mechanical and physical properties of the compound.

In addition to the constitutional defects, it has been clearly shown that a high concentration of vacancies can easily be introduced into the

compound, even during its preparation and fabrication. While vacancy loops and voids have been observed by many investigators, the source of such high vacancy concentrations is in considerable dispute. It was initially proposed that the large number of vacancy defects found in quenched and aged NiAl were formed as a result of a relatively low vacancy formation energy and a relatively high activation energy for motion of vacancies.⁶ This proposal was supported by other investigations and it was further suggested that the reason for the low vacancy mobility was interaction of vacancies with impurities.^{7,8} On the other hand, work⁹ on annealing of single crystals of NiAl seems to indicate that surface oxidation provides the source of vacancies. Vacancy dislocation loops and voids were found to grow in thin foils of slowly-cooled NiAl upon annealing in vacuum and this was explained in terms of vacancy injection by surface oxidation, similar to that proposed in hexagonal metals.¹⁰⁻¹⁴ It was therefore suggested that the source of vacancies is surface oxidation during preparation, fabrication and heat treatment of these compounds and not necessarily the low formation energy for vacancies. However, more recent work¹⁵⁻¹⁸ indicates that the vacancy formation energy may indeed be low and in one case,¹⁶ anomalously high rates of loop growth near the surfaces of thin foils was attributed to loss of aluminum by evaporation. This prompted the comment¹⁹ that there are likely to be at least two ways of introducing vacancies into NiAl - as thermal vacancies and as vacancies injected by oxidation. But it has been argued recently that much of the evidence quoted in support of vacancy injection by oxidation is capable of alternative explanation and that induced stresses in metal substrates during oxidation could cause growth of voids by the Hull-Rimmer mechanism.²⁰ Also, the growth of loops in thin foils has been attributed to "sealing-in" by an oxide film of high temperature vacancies during cooling.²⁰⁻²² Lastly, in the course of inves-

tigations on the oxidation of Ni_3Al ²³ and Ni-Cr-Al alloys,²⁴ void formation in the alloy has been attributed to the Kirkendall effect. Indeed, diffusion data for β -NiAl alloys shows a pronounced variation of the ratio of the intrinsic diffusivities of Ni and Al with composition.²⁵ The selective oxidation of one constituent of the alloy could result in a counter-flow of vacancies due to the Kirkendall effect and cause nucleation and growth of loops and voids.

There is therefore a lack of agreement and understanding regarding the source of vacancies in β -NiAl. The aim of the present project is to develop a better understanding of vacancy generation which appears to occur during oxidation of the compound. As mentioned before, the commercial use of the compound is based on its oxidation resistance. It has been shown in many cases that one of the most common reasons for spalling of the oxide and the resulting loss of oxidation protection is void formation in the metal-oxide interface. Vacancies therefore have an important role to play in oxidation processes. Furthermore, in NiAl, vacancies could also profoundly affect the physical and mechanical properties of the compound as for example in Ni and Ni-Cr alloys.²⁶ It is therefore very important to determine the mechanisms of vacancy generation and oxide formation of β -NiAl. This thesis is aimed at understanding these phenomena by annealing specimens under controlled oxidation conditions of temperature and pressure and making observations of the oxidation process using Transmission Electron Microscopy and Auger Electron Spectroscopy.

2. BACKGROUND RESEARCH

It is now well recognized that vacancies can play an important role in the overall processes occurring during high temperature oxidation of a metal or alloy. When an oxide scale grows on a metal by the outward diffusion of cations, the transfer of atoms from the metal to the oxide may result in vacancy generation at the interface. These vacancies can have a profound effect not only on the corrosion behavior of the metal or alloy but also on its mechanical and physical properties. In a recent review Gibbs and Hales,²⁷ for example, showed that while the effects of vacancy supersaturations on oxidation kinetics may be small, annihilation of these vacancies can often lead to breakdown of the scale-metal interface and loss of scale adhesion. Vacancy condensation can also change the reaction product from a single layer of compact oxide, to a duplex porous layer often leading to increased oxidation rates. Similarly, Hancock²⁶ has shown that the mechanical properties of nickel and Ni-Cr alloys is significantly affected by vacancies generated during oxidation. Precipitation of voids during growth of even thin oxide films caused a pronounced reduction in creep rupture life and tensile ductility. He also showed that in some cases, the vacancies can cause strengthening at low strains and attributed it to cluster hardening at low temperatures and grain boundary pinning by voids at high temperatures and suggested that these effects also influence creep, yield stress and recrystallization. Vacancy generation during oxidation is therefore an important phenomenon and has been the subject of a fair amount of research.

The earliest work suggesting that scale separation is due to vacancy condensation seems to be that of Dunnington, Beck and Fontana.²⁸ Wires and rods of iron were oxidized and it was found that the roughly cylindrical scale around the wire or rod was adherent on one side but loose and separated

from the iron on the other side. The explanation was that vacancies generated by outward diffusion of Fe atoms need sinks. The sink is provided by a void formed by scale separation on one side, to which all vacancies diffuse. As a result, the rest of the oxide remains adherent until all the metal is consumed. Similar experiments on oxidation of iron were done by Engell and Wever,²⁹ who found that if metal diffusion predominated, voids were formed between the scale and the metal or the oxide layer was porous. There was further confirmation of vacancy condensation during oxidation of iron in the work of Tylecote and Mitchell³⁰ who were able to maintain adhesion of the scale for a longer time by drilling holes on the surface of the metal, which acted as artificial vacancy sinks. The holes were found to be enlarged after oxidation.

Effects similar to those seen in iron, have since been shown to occur in other metals as well. Hancock and Fletcher³¹ found a large number of voids at grain boundaries in oxidized nickel and attributed them to vacancy diffusion from the metal-oxide interface. This was confirmed by Hales and Hill,³² who investigated the effect of changing the surface geometry and the surface-to-volume ratio on the oxidation of Ni. Their results showed that agglomeration of vacancies into voids maintained the shape of the interface whereas annihilation of vacancies at dislocations or grain boundaries caused shrinkage of the metal. The strength of the oxide determined whether or not it deformed plastically to follow the metal and voids were found to form more easily if the oxide was strong. Vacancies have also been shown to migrate into copper, which like nickel, oxidizes by cation diffusion. Jaenicke et al³³ found voids at Cu_2O -Cu interfaces which diffused into the metal and precipitated at internal defects. Appleby and Tylecote³⁴ investigated the sources of stress which exist in oxidized Cu and identified the movement of vacancies into the bulk metal as one of the stress sources.

Vacancy agglomeration during oxidation has also been shown to occur in alloys. Howes³⁵ investigated Fe-Cr alloys with 16-38 % Cr and found all of them with voids developed at the metal-oxide interface after oxidizing. In fact, the area of contact of the metal and the oxide was found to decrease as the Cr content increased. Two reasons were given for this. Firstly, the rate of oxidation was higher for the higher Cr alloys - therefore more vacancies would be generated. Secondly, Cr diffusion in these alloys is known to be slower as the Cr content is increased - hence vacancy mobility and dispersion within the lattice would be less and vacancy agglomeration at the interface would be favored. In the 16% and 19% Cr alloys, Howes also observed that a discontinuous inner oxide layer was formed in addition to the compact outer layer. This duplex nature of scales formed on Fe-Cr alloys with less than 20% Cr was confirmed by Cox et al,³⁶ who found a compact layer above the original metal surface and a porous inner layer below the original metal surface. They claimed that the voids in the inner layer were due to vacancies injected by the formation of the outer layer and that these vacancies remain in solution until they reach a critical concentration and then condense out as voids. Duplex layers were also found on Ni-Cr alloys with about 10% Cr by Douglass,³⁷ with NiO scales overlaying Cr_2O_3 . Above 900°C, it was found that the Cr_2O_3 was formed as a continuous film and this presumably restricted vacancy transfer because massive voids occurred at the NiO- Cr_2O_3 interface. In general, as stated by Scott,³⁸ duplex oxide layers are very commonly formed on metals and alloys and their structure and morphology is often determined by the behavior of vacancies produced in the surface regions. He also pointed out that while it is generally accepted that vacancies are produced in the surface regions when oxides grow by cation diffusion, the subsequent behavior of these vacancies is not well understood.

In particular, there is disagreement concerning the possible injection

of these vacancies into the substrate. Besides, vacancies could also originate from other sources. Evidence for this comes from work on oxides growing inward by diffusion of oxygen ions. It would be expected that vacancies, rather than being created, would be destroyed at the oxide-gas interface as a result of such anion diffusion in the oxide. But Tien and Pettit³⁹ found large voids and cavities in an oxidized Fe-25% Cr-4% Al alloy, where the predominant oxide Al_2O_3 was found to grow inward, presumably by anion diffusion. The adherence of the oxide was very much improved by small additions of yttrium, scandium or a dispersion of Al_2O_3 particles. It was explained that the rare earth atoms formed complexes with vacancies and the dispersion of Al_2O_3 particles (or YAlO_3 and ScAlO_3 particles) also acted as sinks for vacancies. While the origin of these vacancies was not known to them, they said that in the absence of these traps, vacancies conglomerated at the interface leading to poor oxide adherence. Very similar work was also done on Ni_3Al ²³ and Ni-Cr-Al²⁴ alloys by Douglass and his co-workers. Here again the oxide was predominantly Al_2O_3 , formed presumably by grain boundary diffusion of oxygen, and again the oxide adherence was much improved by Y additions. The voidage at the interface in the base alloy was attributed to the Kirkendall effect - since Al_2O_3 was being formed, the surface regions of the alloy would be depleted in Al and the composition gradients would cause diffusion of Ni or Ni + Cr inward and a counter diffusion of Al toward the surface. Since in Ni-rich Ni-Al alloys, Ni has been shown to diffuse much faster than Al,²⁵ vacancies would therefore have to diffuse along with Al atoms, from the interior towards the surface. It is these vacancies, according to them, that condense and form voids at the alloy-oxide interface. But this mechanism cannot be universally applicable for alumina forming alloys because for Ni-Al alloys rich in Al, it has been shown that Al diffuses much faster than Ni.²⁵ β -NiAl alloys also mainly

form Al_2O_3 , and Hutchings and Loretto⁴⁰ have recently found evidence for vacancy generation during oxidation of these alloys on either side of stoichiometry. They found that the oxidation kinetics (weight gain as a function of time) were much more irregular for electropolished samples than for abraded samples. The electropolished samples were also found to have at least partially spalled oxides, while the abraded samples exhibited no spalling. Interfacial voids were also found all across the electropolished samples.⁴¹ These results seem to indicate vacancy generation in both the Ni-rich and Al-rich alloys and cannot be due to the Kirkendall effect.

In addition to the work discussed so far which investigated the behavior of vacancies during bulk oxidation, transmission electron microscopy (TEM) of thin foils has been used in attempts to demonstrate vacancy injection during oxidation. In the course of observations on faulted vacancy dislocation loops in zinc, Dobson and Smallman found that loops in some areas grew and in other areas, shrank.¹² They proposed that the growth of loops was due to vacancy injection by surface oxidation at room temperature and that the loops that were found to shrink probably lay under discontinuities in the oxide. Similar loops were also found to form and grow in thin foils of quenched Mg during annealing at 150–200°C by Hales et al.¹³ Michell and Ogilvie¹¹ also used x-ray topography and TEM on Zn and Cd to show that dislocation loops and line defects climbed by absorbing vacancies on exposure to air. Hales et al.¹⁴ subsequently found that the growth rate of loops could be correlated to factors which are known to affect the oxidation rate. They annealed Zn and Mg under different partial pressures of oxygen and found that the pressure affected the loop growth rate. But they were unable to explain why in the case of Mg the rate of loop growth increased with oxygen partial pressure while with Zn, the opposite effect was seen. They also

found that small additions of Li, which is known to increase the oxidation rate of Zn, considerably enhanced loop growth, and small additions of Al, which decreases the oxidation rate of Zn, also decreased loops growth rate. Hales et al therefore claimed that their observations confirmed vacancy injection due to oxidation. This was supported by observations of Dobson et al,⁴² who found that prismatic loops grew during annealing at about 200°C in dilute Al-Mg alloys. The rate of growth was found to increase with annealing time and they explained this on the basis of faster diffusion of Mg to the surface to form MgO as more vacancies were injected by oxidation. Increasing the oxygen partial pressure was also found to increase loop growth rates. Indirect support for vacancy injection when oxides grow by cation diffusion (as in all the above cases), also came from the work of Sanders and Dobson.⁴³ They showed that extrinsic faults in Si grew if annealed in air but shrank if the Si was annealed in vacuum. This was consistent with the fact that Si oxidizes by anion diffusion and in such a case, vacancies would be continuously absorbed or interstitials would be produced. More recently, Fraser et al⁹ showed that loops and voids grew in slowly cooled NiAl thin foils during annealing in vacuum and concluded from their observations that vacancy injection by oxidation was the most plausible explanation.

There is therefore a considerable amount of evidence which indicates that vacancy injection occurs during the growth of oxides by cation diffusion. But this is by no means universally accepted. Harris²⁰ argues that most of the evidence quoted to support vacancy injection is capable of alternative explanation. He attributes any flow of vacancies during oxidation to the stresses that are almost always generated because the ratio of volume of oxide formed to the corresponding volume of metal consumed (the Pilling-Bedworth ratio), is usually different from unity. He suggests

that the growth of intergranular voids during oxidation is a consequence of the tensile stresses that are induced leading to void growth by the Hull-Rimmer mechanism - i.e., by removal of atoms from the surfaces of voids and their deposition on suitably oriented grain boundaries to give strain in the direction of the applied stress. Harris also proposes that these induced stresses govern the behavior of loops in thin foils and that changes in loop growth rates upon changing the annealing atmosphere are due to changes in the magnitude of the induced stresses. He also implies that loop growth observed in thin foils is due to vacancies which have been sealed-in by an oxide film - the remnant of the quenched-in population, as reported in his earlier work on quenched Zn and Mg.^{21,22} Doubts are also raised by Stringer,⁴⁴ who concludes that the flow of metal atoms into an oxide does not necessarily result in vacancy injection. He says that vacancy injection to form internal voids would occur only if the system is attempting to maintain metal/oxide adhesion under conditions where the metal would otherwise shrink away from the oxide. Factors such as the strength and plasticity of the oxide, the forces of adhesion and the mechanisms responsible for shape change involved in oxide formation would according to him, dictate the subsequent behavior of any vacancies generated.

Detailed predictions of oxidation mechanisms and vacancy behavior are therefore not possible, even for pure metals. In dealing with alloys, there are other complicating factors as has been seen, such as selective oxidation of some components and the Kirkendall effect. Since this project is aimed at understanding the mechanisms of oxidation of β -NiAl alloys and the behavior of vacancies during annealing, it is now appropriate to review some of the related previous work on Ni-Al alloys particularly the β phase alloys. β -NiAl is an intermetallic compound with the B2 (cesium-chloride) structure. It is stable over a wide composition range (40-55 at % Al) and

apparently remains ordered upto its melting temperature ($\approx 1640^\circ\text{C}$).⁵⁷ The stability of the structure of non-stoichiometric compositions results from the presence of an unusual defect structure. In compounds with an excess of nickel, there is substitution of Ni atoms on the Al sub-lattice while in compounds with an excess of aluminum, the structure is maintained by the presence of vacancies on the Ni sub-lattice.^{58,59}

Wood and his co-workers^{45,46,47} have studied the oxidation of these alloys but only for compositions with less than 20 at. % Al. Pettit⁴⁸ has reviewed in detail the thermochemical data for this system and has compared it with experiment for Ni-Al alloys with upto 25% Al. From these studies it emerges that a continuous film of Al_2O_3 has to be formed in order to significantly lower the oxidation rates and that the minimum Al content has to be roughly in the 10-16% range (depending on temperature) for the formation of such a continuous Al_2O_3 layer. At lower Al contents, an external NiO layer is formed with Al_2O_3 present as internal oxide or as particles in an inner oxide layer. The only work that seems to have comprehensively investigated the oxidation of β -NiAl alloys, is by Hutchings and Loretto⁴⁰ where, as reviewed earlier, it was found that Al_2O_3 was the predominant oxide and signs of vacancy generation were observed.

Vacancy defects in β -NiAl alloys have also been observed by several investigators using TEM. Ball and Smallman⁴⁹ found that polycrystalline NiAl was extremely brittle at temperatures below about $0.45 T_m$ (where T_m is the melting point). But above this temperature there was a marked increase in ductility. Transmission Electron Microscopy studies on annealing behavior of loops that they saw in thin foils showed that at temperatures above $0.45 T_m$, self diffusion becomes significant. More detailed work on quenched and aged samples⁶ showed that large numbers of vacancy loops and helical dislocations were present. These observations were explained in

terms of a low vacancy formation energy and a relatively high activation energy for vacancy motion. This was supported by the observations of Fraser et al,⁹ who found voids in as-grown crystals of NiAl and Yang et al,⁸ who found loops and voids forming spontaneously during annealing at 700-900°C. These defects were thought to be due to a low vacancy formation energy and the trapping of vacancies by solute atoms, and formation of vacancy-impurity complexes was thought to be the reason for the lack of mobility. An estimation of the vacancy formation energy made by Wasilewski⁵⁰ indeed indicates a fairly low vacancy formation energy. He compared data for the thermal variation of the lattice parameter, to dilatometric measurements and deduced a value of about 1.5 eV for the formation of a pair of vacancies - one on each sublattice. On the other hand, Fraser et al¹⁸ found that loop and void growth took place even during annealing of slowly cooled samples of NiAl in which presumably, there was no quenched-in vacancy supersaturation. Using these slowly cooled samples, they were also able to reproduce some of the dislocation climb results which earlier investigators had obtained on quenched and aged samples. This led them to interpret their results on the basis of vacancy injection by surface oxidation and propose that the earlier observations could also be due to vacancy injection and not necessarily because the vacancy formation energy was low. But more recent work seems to lend support to the earlier proposal that the low vacancy formation energy is responsible for the presence of vacancy defects rather than vacancies originating from oxidation. Marshall and Brittain¹⁵ found that impurities in Al-rich alloys in this phase acted as climb sources when the alloys were cooled at rates above 700°C/hour. Large numbers of vacancy loops were found to emanate from these climb sources when the fast cooled alloys were aged at lower temperatures. Further work by them,¹⁶ investigating the effects of different cooling rates, seemed to show

that nearly all the thermal vacancies were retained upon cooling these alloys. They do report seeing anomalously high rates of loop growth near the thin foil surfaces and they attributed this to possible Al evaporation from the surface. Yang and Dodd,⁵¹ in the course work investigating the effect of C content on void formation in NiAl, found large numbers of small voids in quenched and aged samples. Eibner et al¹⁷ examined the annealing behavior of the quenched-in resistivity in NiAl and this, along with TEM observations, certainly indicated that thermal vacancies are formed in large numbers. Acknowledging this fresh evidence, Fraser et al¹⁹ agreed that the vacancy formation energy in NiAl might indeed be low but claimed that their own results on slowly cooled NiAl samples also indicated another source of vacancies - namely, surface oxidation. They commented that it therefore seems likely that there are at least two ways to introduce a high concentration of vacancies into NiAl - quenching followed by ageing, and annealing in an oxidizing environment.

There are other complicating factors which Fraser et al did not consider, and which make it evident that our understanding of oxidation in B2 compounds is far from clear. Firstly, it seems that mainly Al_2O_3 is formed when β -NiAl is oxidized⁴⁰ and work on other alumina forming compounds indicates that it grows by oxygen diffusion.^{23,39} It is difficult to reconcile vacancy injection with an oxide formed by anion diffusion. It is conceivable that in the case of NiAl, the formation of Al_2O_3 might involve at least partial cation diffusion especially since diffusion measurements by Kingery and co-workers^{52,53} showed that Al atoms are more mobile than O atoms in single crystals and coarse grained polycrystals of α - Al_2O_3 . They also showed that oxygen diffusion in alumina is much more dependent on grain size than Al diffusion, leading to the possibility that the Al_2O_3 formed during high temperature oxidation of alloys grows by grain boundary diffusion of oxygen

since it was found to be fine grained. Also, since selective oxidation of Al takes place in NiAl, the effects of the Kirkendall effect on vacancy defects has to be considered. In this connection, it is helpful to refer to some of the work on diffusion in β -NiAl alloys. It was first shown by Berkowitz, Jaumont and Nix⁵⁴ that the tracer diffusion co-efficient of Co in these alloys is very strongly composition dependent, with a deep minimum in the diffusivity near the stoichiometric composition. Hancock and McDonnell⁵⁵ found that the tracer diffusivity of Ni in NiAl varies in a similar fashion but the diffusivity minimum was found to be at slightly Al-rich compositions. Average values for the diffusivity in the β -phase were obtained from layer growth experiments by various investigators and for a few compositions on the Ni-rich side by Janssen,⁵⁶ who suggested that Ni diffuses much faster than Al in NiAl. But Goward and Boone⁵ showed that Ni diffusion may be much more rapid than Al diffusion only in Ni-rich compositions and that in Al-rich compositions the opposite might be true. This was confirmed in the recent comprehensive work of Shankar and Seigle,²⁵ who determined the inter-diffusion co-efficient and the ratio of the intrinsic diffusivities of Ni and Al as functions of composition. The deep minimum in the diffusivity curve was found to be between 48 and 49 at.% Al in the temperature range 950°C - 1150°C. The reason for this off-stoichiometric minimum was not understood. But they found that the ratio D_{Ni}/D_{Al} did change abruptly near the stoichiometric composition at 1100°C. In effect their results show that Ni diffuses much faster (about a factor of 3) than Al in Ni-rich alloys. But beyond 50 at.% Al, D_{Ni}/D_{Al} decreases abruptly from a value of 3 to about 0.1 as the Al content is increased. This obviously implies that profound Kirkendall effects exist in these alloys in the vicinity of stoichiometry. Lastly, the contention of Harris,²⁰ that stresses induced by oxidation rather than vacancy injection could be the reason for loop and void growth, have

to be taken into account. Only after the various theories have been carefully considered in relation to experimental observations, can an accurate prediction be made about the mechanisms of oxidation and vacancy generation in β -NiAl.

3. EXPERIMENTAL PROCEDURE

3.1 SAMPLE PREPARATION

The binary Ni-Al β -phase alloys used in this project were nominally of three different compositions - Ni-47.5 at.% Al, Ni-50.4 at.% Al and Ni-52.5 at.% Al, which will be referred to as the Ni-rich, near-stoichiometric and Al-rich alloys respectively. The near-stoichiometric alloy was obtained in single crystal form whereas the Ni-rich and Al-rich alloys were prepared in polycrystalline form as outlined below. X-ray microprobe analysis was used to roughly estimate the actual alloy compositions - the average values obtained were 52, 49.8 and 47 at.% Ni for the Ni-rich, near-stoichiometric and Al-rich alloys respectively.

3.1.1 Near-Stoichiometric Alloy

Most of the experiments were carried out on single crystals of the Ni-50.4 at.% Al alloy, which were from the same batch as those prepared and used in earlier annealing experiments.⁹ As described by Wasilewski,⁶⁰ polycrystalline NiAl was first prepared by induction melting high-purity Ni and Al and casting into solid copper molds. The castings were then canned in mild steel and impact extruded at 1100°C to 1200°C to 3/8" diameter rod. The steel sheath was then pickled off and the rods converted to single crystals by repeated high frequency induction zone melting in an argon atmosphere containing not more than 5 ppm. of oxygen. After each zone melting pass, the rods were allowed to cool slowly to room temperature. Cylinders cut from the 3/8" dia. rod (with an aspect ratio of about unity) were aligned for deformation along the [001] direction by using the Laue back-reflection X-ray technique, the errors in alignment being approximately $\pm 2^\circ$. Two parallel faces were spark machined perpendicular to the [001] direction for

compressing. The crystals were then deformed about 1% in compression along the [001] direction at about 650°C in air using an Instron testing machine at a strain rate of 10^{-4} /sec. It has been shown that this deformation introduces a high density of vacancy type edge loops into the crystal,⁹ presumably because the contribution of climb to plastic deformation is quite significant at the temperature of the deformation. Slices about 0.015" thick were then cut normal to the compression direction with a diamond saw. From the slices, discs about 3mm. in diameter were spark machined to prepare specimens for electron microscopy. The discs were chemically cleaned and annealed in air at 600-700°C for upto 1 hour in order to relieve stresses and reduce the dislocation density. During the course of these experiments, it was found that a high density of vacancy loops could also be obtained by simply annealing very thin deformed samples (less than .005" thick) in air at around 700°C for about one hour. Standard electropolishing techniques were used to thin samples for electron microscopy. A 50% solution of HCl at 50 volts was used for dimpling both sides of the discs. The final electropolishing was carried out in a mixture made up of 63 parts methanol, 35 parts butyl cellosolve and 2 parts perchloric acid at about 0°C and 63 volts. The electropolishing was discontinued as soon as a perforation appeared at the center of the 3mm. discs. The regions adjacent to the perforation were usually suitable for transmission electron microscopy.

3.1.2 Ni-rich and Al-rich Alloys

Since only the near-stoichiometric alloy was initially available, the Ni-rich and Al-rich alloys had to be made from scratch. Buttons of these two alloys were made by arc melting 99.99% pure Ni and Al on a water cooled copper plate in an argon atmosphere using a non-consummable tungsten electrode. The arc was initially struck on the Ni with the Al being kept at the bottom to prevent any evaporation of Al. After melting the alloy

button each time, it was turned over and re-melted several times to ensure good mixing of the components. The arc-melted alloys were encapsulated in quartz tubes filled with argon, homogenized at 1400°C for 3 days (leading to a coarse-grained structure) and furnace cooled. In order to ensure an equilibrium vacancy concentration, they were subsequently annealed at 900°C for one day and cooled slowly to room temperature at about 5°C/hour. Samples were prepared for electron microscopy using the same techniques as before.

3.2 ANNEALING SYSTEM

In order to be able to do annealing experiments, a system had to be designed in which specimens could be annealed over a wide range of temperatures and pressures. It was decided to build an electron-beam heating system inside a ultra-high vacuum (UHV) chamber. The UHV system used was equipped with sorption pumps and ion pumps and was capable of operating in the 10^{-10} torr range. The system had a poppet valve for isolating the ion pumps in the lower section, from the upper section where the annealing was carried out. While transferring specimens, only the upper section was exposed to the atmosphere. To hasten the attainment of high vacuum, the system was occasionally baked at temperatures upto 200°C. Since only small specimens were to be annealed, electron beam heating seemed to be most appropriate since annealing could be done inside a UHV system without marked deterioration of the vacuum. A tungsten-filament electron beam gun was constructed and fixed to one port in the upper section of the vacuum chamber. Specimens to be annealed were placed on a molybdenum boat which could be manipulated by a bellows-sealed handle outside the vacuum system. Specimen introduction and removal was done from a small side port. Specimens were annealed by focusing a beam of electrons from the gun (at accelerating voltages upto -6 kV), onto one face of the molybdenum boat, which was grounded. A

chromel-alumel thermocouple was spot-welded to the bottom of the boat, the specimens being placed in the close vicinity of the thermocouple. A second thermocouple was initially used to determine the difference between the temperature shown by the spot welded thermocouple and the actual temperature (somewhat lower) of a specimen placed on the boat. Several such calibrating experiments were carried out to ensure that the annealing temperature of a specimen could be determined to within about 5°C . With this system, it was possible to anneal at temperatures over 1000°C .

Provision was made for bleeding high-purity oxygen into the vacuum system through a leak valve at a controlled rate so that annealing could be carried out at any desired partial pressure of oxygen. Annealing was always done under conditions of dynamic equilibrium with a steady input flow of oxygen being balanced by system pumping (with the poppet valve being partially closed if necessary). A fairly constant partial pressure of oxygen was maintained in this way. It usually took less than one minute for the specimen boat to reach the annealing temperature. After being held at the annealing temperature for the required time, the electron beam was turned off and the specimen allowed to cool at a rate of about $300^{\circ}\text{C} - 500^{\circ}\text{C}/\text{min}$. During each anneal there was always a slight rise in pressure due to outgassing of the boat and the specimen - in each case, it is the pressure during the anneal that is reported.

3.3 ELECTRON MICROSCOPY

Transmission electron microscopy was used to examine the effect of annealing under different conditions on vacancy dislocation loops and voids in thin foils of these alloys. Samples were alternately examined in the microscope and annealed in the vacuum system for specific times at desired temperatures and oxygen partial pressures. In this way, it was possible to follow

the effects of prolonged annealing (and the resulting surface oxidation) on vacancy defects in these thin foils, under various conditions. A JEOL JSEM 200 microscope was used in this work, operating at an accelerating voltage of 200kV. Most of the imaging of dislocations and loops was done under the standard "two-beam" conditions with the beam oriented for best contrast and brightness - i.e., with the crystal planes oriented at a small positive deviation from the Bragg condition. For the annealing studies, loops were also usually imaged with the beam direction close to one of the $\langle 101 \rangle$ directions rather than the $[001]$ direction which is close to the foil normal. It was more convenient to follow loop climb in this way because if the $[001]$ beam direction was used, loops with $\vec{b}=[001]$ exhibited only residual contrast and loops with $\vec{b}=[100]$ or $[010]$ could only be imaged on edge. On the other hand, voids were usually imaged with the beam direction close to the $[001]$ direction, but under kinematical conditions for best contrast.

4. EXPERIMENTAL RESULTS

4.1 NEAR-STOICHIOMETRIC ALLOY - FAST COOLED

Annealing experiments were first carried out with the as-received single crystals of this composition (50.4 at.% Al). These were from the same batch as those used in earlier thin foil annealing experiments,⁹ and as mentioned earlier, were made by zone melting polycrystalline rods and allowing them to cool in position. These samples will be referred to as fast cooled NiAl to distinguish them from other samples from this batch, which were subsequently re-annealed at 900°C and cooled to room temperature at much slower rates.

A partial Burger's vector analysis of some typical loops in an as-polished sample is shown in Fig.1. The prismatic edge loops have $\vec{b}=\langle 001 \rangle$ and lie on $\{001\}$ planes. The sides of the square loops also lie along $\langle 100 \rangle$ directions. In general, most loops were not as sharply crystallographic as those in Fig. 1, but had sides lying close to $\langle 100 \rangle$ directions. Fig. 2 shows that the shift in image position on changing the sign of $\vec{g}$, the diffracting vector, is consistent with the loops being vacancy in nature. This test was repeated a number of times, with many samples, and the loops were always found to be vacancy loops.

A series of experiments was first undertaken to determine the effect of annealing temperature on the loops. Preliminary indications were that loop growth occurred at increasing rates as the annealing temperature was increased. To examine this in more detail, a series of isothermal annealing experiments was carried out. Typically, a sample would be examined in the electron microscope, then transferred to the annealing system and annealed for the desired time at a specific temperature and pressure and then removed to be re-examined in the microscope. It would then be annealed again under the

Figure 1 Partial Burger's vector analysis of loops in fast cooled NiAl showing loss of contrast ($\vec{g} \cdot \vec{b} = 0$) for two different $\vec{g}$ vectors, giving $\vec{b} = [001]$. The approximate beam direction and $\vec{g}$ vectors are as marked.

Figure 2 Inside-outside contrast analysis showing that the shifts in images are consistent with the loops being vacancy in nature. The approximate beam direction and the $\vec{g}$ vectors are marked.

same conditions and re-examined. In this way, it was possible to monitor changes in loop size during a prolonged period of annealing. Typical results of such experiments are shown in Fig.3. While some of the loops initially present slipped out of the foil, all the remaining loops grew in size. As can be seen in Fig.3, loop growth is faster at 700°C than at 550°C. Some of the data from these experiments are summarized in Fig.4, and the effects of temperature on the rate of loop growth can be clearly seen. These results closely paralleled previous results⁹ on samples from the same alloy batch and since these samples were not quenched, it seemed that the vacancies were being generated by surface oxidation, even during annealing at ultra high vacuum ($<10^{-8}$ torr). If oxidation was the reason for loop growth, it was felt that changing oxidation rates by changing the oxygen partial pressure would also affect the loop growth kinetics. Experiments were therefore carried out annealing pairs of samples at the same temperature but at different pressures of oxygen, in the range 10^{-4} to 10^{-9} torr. Typical results of such experiments are shown in Fig.5 for one temperature, 550°C. Such results showed that in these samples there were no significant systematic changes in loop growth rates upon varying the oxygen partial pressure. It was difficult to interpret these observations in terms of vacancy injection due to oxidation.

There were other indications that the loop growth in these samples could be due to reasons different from vacancy injection. From Fig.4, it is clear that at 700°C, after annealing for about 2 hours, the loop growth rate has decreased considerably from the initial growth rate. The same sample was then ion-milled and briefly electropolished to remove the surface oxide. Annealing experiments were then repeated at 700°C and it was expected that loop growth rates would correspond to those found in the initial stages for the 700°C sample in Fig.4. Instead, it was observed that there was

Figure 3 Effect of isothermal annealing in fast cooled NiAl at pressures $<10^{-8}$ torr. (a) At 550°C , (b) At 700°C . The annealing times are as marked.

a

$t=0$ min.

$t=300$ min.

b

$t=0$ min.

$t=30$ min.

Figure 4 . Increase in loop size with annealing time, for various temperatures at UHV ($<10^{-8}$ torr) in fast cooled NiAl. The data represent the average growth of several typical loops.

Figure 5 Effect of oxygen partial pressure on loop growth at 550°C in fast cooled NiAl. The pressures are as marked.

very slow growth at rates corresponding to those at the end of the 2 hours of annealing of the same sample in Fig.4. This decreasing rate of loop growth, along with the observations that oxygen partial pressure had almost no effect on loop growth rates, indicated that loop growth in these samples might be due to a supersaturation of thermal vacancies which were somehow retained in these samples during cooling from high temperatures. This was further confirmed by observations on other samples from this batch, in which unusual loop shapes were seen. These observations will now be described.

As mentioned earlier, most of the loops in the fast cooled NiAl samples tended towards a square shape with the sides lying roughly along the cubic directions. But in some specimens, loops were found with the same $\vec{b}=\langle 001 \rangle$ and lying in the same $\{001\}$ planes, but with sides lying along $\langle 110 \rangle$ directions, as shown in Fig.6. This was a surprising observation, in view of the fact that such loops have never been observed before in NiAl and that calculations of predicted loop shape have shown that segments of dislocations of $\vec{b}=\langle 001 \rangle$ on $\{001\}$ planes are elastically unstable in the $\langle 110 \rangle$ directions.^{61,62} In the present study, such loops were found to be very stable, since they retained their configuration even after prolonged annealing and continued to grow with their sides lying along $\langle 110 \rangle$ directions (Fig.6). It was felt initially that some samples had such loops due to an unexpected variation in composition. But electron microprobe analysis revealed that these samples did not differ significantly in composition. Besides, in a few rare cases, the normal $\langle 100 \rangle$ sided loops and these unusual $\langle 110 \rangle$ sided loops were found in the same area of the same sample (Fig.7). In one sample, loops were also seen which had segments along both the $\langle 100 \rangle$ and the $\langle 110 \rangle$ directions (Fig. 9).

As is evident in Fig.6, the loops with the $\langle 110 \rangle$ sides were very stable and showed no signs of slip during annealing. It was therefore possible in

Figure 6 (a) Typical area showing loops with $\vec{b}=[001]$ and sides lying in $\langle 110 \rangle$ directions.
(b) Same area after annealing for 3 hours at 600°C and $<10^{-8}\text{torr}$.

a

b

Figure 7 An area from a sample imaged from two different beam directions (as marked) - loop a has sides lying in $\langle 100 \rangle$ directions, loop b has sides lying in $\langle 110 \rangle$ directions.

these samples to compare the annealing behavior of loops in the middle of the thin foils to those near the foil surfaces, which would have normally slipped out of the foil during annealing. A surprising result of these comparisons, using stereo imaging, was that internal loops grew faster than loops close to the foil surfaces. If oxidation was inducing vacancies, loops closer to the surface would tend to grow more rapidly. These results therefore confirmed that the loop growth in the fast cooled NiAl samples was probably due to thermal vacancies trapped in the samples during cooling.

An effort was made to try and determine why there were stable loops made up entirely of dislocation segments lying in what were thought to be elastically unstable directions. Since the loops showed no tendency to slip, it was felt that the dislocation segments might have split into partial dislocations (with very small separation) on adjacent $\{110\}$ planes as follows:-

$$[001] = 1/2[\bar{1}11] + 1/2[1\bar{1}1] \text{ on } (110) \text{ and}$$

$$[001] = 1/2[111] + 1/2[\bar{1}\bar{1}1] \text{ on } (\bar{1}10).$$

Such a dissociation could possibly explain why the loops were sessile. It was also felt that another possible explanation for this loop configuration could be that while the dislocation seemed to follow a $\langle 110 \rangle$ direction, it might actually be made up of very small zig-zag $\langle 100 \rangle$ segments. Weak-beam microscopy (which is a high resolution imaging technique) was carried out on these loops to see if any splitting into partials or zig-zagging of the dislocation line occurs. However, there was no evidence for this from the weak-beam micrographs (Fig.8). The reason for the occurrence of such loops with $\langle 110 \rangle$ sides is therefore not understood at this time. The electron microscope used here was not particularly suited for high resolution imaging and it is possible that very high resolution microscopy might aid in understanding this problem.

Figure 8 A weak-beam dark-field micrograph of a loop with sides lying in the $\langle 110 \rangle$ directions. Imaging was carried out using the " $\vec{g}-3\vec{g}$ " diffracting conditions.

Figure 9 An area from a fast cooled NiAl sample showing octagonal loops with segments lying in both the $\langle 100 \rangle$ and the $\langle 100 \rangle$ directions.

4.2 NEAR-STOICHIOMETRIC ALLOY - SLOW COOLED

As mentioned in the previous section, the evidence from the annealing experiments on the fast cooled NiAl seemed to indicate an inherent vacancy supersaturation. Since this project was aimed at investigating the possibility of vacancy injection during oxidation, it was necessary to start with samples which did not have a vacancy supersaturation present at the beginning. Blocks of the original single crystal were therefore annealed at 900°C for one day and then slowly cooled to room temperature at about 5°C/hour. It was expected that under these equilibrium cooling conditions, there would be no vacancy supersaturation in solution. If vacancies were trapped inside the sample by an impervious oxide layer, these would also have diffused to and be annihilated at various internal sinks. Annealing experiments on thin foil electron microscope samples from the slowly cooled single crystals were performed in a similar way as with the fast cooled samples.

4.2.1 Vacancy Dislocation Loops

Vacancy dislocation loops were present in the thin foils, very similar to those observed in the fast cooled samples. But in these slow cooled samples, no unusual loop configurations were seen - the loops all had similar shapes, tending towards squares with sides lying close to $\langle 100 \rangle$ directions. Loops were found on all three $\{100\}$ type cube planes. In order to increase the loop density for the annealing experiments, the single crystals of NiAl were usually compressed about 1% along $[001]$ at about 650°C, sliced perpendicular to the compression direction, and annealed at about 650°C for one hour in air to reduce the dislocation density. As a result of this treatment, a majority of the loops lay in the plane of the thin foils, the (001) plane, and a fewer number of loops were found in the (100) and (010) planes. Since they were all edge loops, the corresponding Burger's vectors were always perpendicular to the plane of the loops. A majority of the loops

therefore had $\vec{b}=[001]$, parallel to the foil normal.

Annealing experiments on the thin foils of slowly cooled NiAl revealed that the behavior of loops in these samples was different from that of loops in the fast cooled alloys of the same composition. No signs of loop growth were observed in samples annealed at temperatures below 650°C, clearly indicating that no vacancy supersaturation exists. But when higher annealing temperatures were used, signs of loop climb became evident. Results of a typical annealing sequence are shown in Fig.10. Clear signs of climb can be seen after annealing for 20 minutes at 700°C in 10^{-5} torr of O_2 . While the larger loops in this area remain unchanged in size after 20 minutes, some of the smaller loops are seen to have shrunk. But after 45 min. of annealing, it can be seen that general loop growth is starting to take place. Upon continuing the annealing under these conditions, very marked loop growth can be seen to occur. This can be clearly seen in the micrographs of the area after 65 min. and 95 min. of annealing in Fig.10, in spite of the fact that the image deteriorates due to the formation of inter-facial voids. The formation of such voids will be discussed in a later section.

The general features of loop behavior seen in Fig.10, i.e., an initial period of loop shrinkage followed by loop growth upon continued annealing, were reproduced in many samples. This behavior is more clearly illustrated in Fig.11, which shows an annealing sequence at 750°C in ultra-high vacuum. After 3 min. of annealing, it can be seen that all the loops present have decreased in size. Further annealing upto 13 min. results in continued shrinkage of some loops while others have started to grow. After 20 min. there is no more evidence of shrinkage and loops start to grow rapidly. As mentioned in the previous section, some loops disappear during annealing mainly due to slip along their glide cylinders and sometimes because they intersect the foil surface as they grow.

Figure 10 An annealing sequence from a slow cooled NiAl sample annealed at 700°C and 10^{-5} torr of oxygen. The annealing times in minutes are marked.

$t=0$

5

20

45

65

95

Figure 11 An annealing sequence from a slow cooled NiAl sample annealed at 700°C in UHV ($<10^{-8}$ torr pressure). The annealing times in minutes are marked.

$t=0$

3 m

13 m

20 m

30 m

45 m

Annealing experiments such as these were carried out at temperatures as high as 800°C . At each temperature, the effect of oxygen partial pressure was investigated by annealing one sample in UHV (in the 10^{-9} torr range) and another sample in 10^{-5} torr of oxygen. Some of these results are summarized in Fig.12, where typical loop size changes are plotted as a function of annealing time for 700°C and 750°C in both UHV and 10^{-5} torr oxygen. It can be clearly seen that changing the annealing temperature by 50°C has a profound effect on climb of loops and that to a lesser extent, oxygen partial pressure also affects climb. It is evident, especially at 750°C , that upon annealing, loops initially shrink and eventually start growing as the annealing is continued. The kinetics of this process are very much enhanced when the annealing temperature is raised from 700°C to 750°C . Changing the annealing atmosphere from UHV to 10^{-5} torr oxygen seems to have the effect of causing loop growth in a shorter time of annealing and at a faster rate. The data in Fig.12 represent the average growth of a large number of loops of approximately the same size. As can be seen from the error bars in Fig.12, loops of similar size do not necessarily have the same rates of climb. These differences might be attributed to the probability that loop shrinkage or growth rates will be affected by its position in the foil and its proximity to other vacancy sinks in the foils such as other loops and dislocations. To better understand the kinetics of vacancy diffusion to the loops, it is more appropriate to examine changes in loop area as a function of time since loop area is directly proportional to the number of vacancies in the loop. This has been done in Fig.13, where the change in loop area has been plotted as a function of annealing time for loops of three typical sizes. In all three cases, it can be seen that the rate of increase of loop area continuously increases with time. In other words, vacancies are diffusing to the loops at faster and faster rates as the annealing process

Figure 12 Percentage change in side length of square loops with annealing time in slow cooled NiAl for pairs of samples annealed at 700°C and 750°C, one at UHV ($<10^{-8}$ torr), and the other in 10^{-5} torr oxygen. The data represent the average growth of several loops of approximate initial side length = 1000 Å.

Figure 13 Changes in loop area with annealing time for loops of three different sizes in a slow cooled NiAl sample annealed at 700°C in 10^{-5} torr oxygen.

continues. As mentioned earlier, significant loop growth starts only at about 700°C . At about 800°C and above loops became unstable and the kinetics of shrinkage and growth are so rapid, that it is no longer practicable to study the behavior of vacancies by making observations of climb of dislocation loops. At these higher temperatures, it was therefore decided to use observations of voids instead.

4.2.2 Internal Voids

Voids were found in the thin foils of the near stoichiometric alloy single crystals. As observed by previous investigators,^{7,8} tilting experiments in the electron microscope showed that the voids were in the shape of truncated rhombic dodecahedra, being made up of sections of $\{110\}$ faces truncated by smaller sections of $\{100\}$ faces. These voids were generally in the size range of $500\text{\AA}$ - $2000\text{\AA}$. At the lower annealing temperatures (below 750°C), no change in void size was observed even though significant loop growth took place at those temperatures. This is presumably because changes in void sizes would only result from the diffusion of a much larger number of vacancies. But at temperatures above 800°C , void size change became noticeable. In the early stages of these high temperature annealing studies, experimental difficulties were encountered in the form of contamination of the thin foils. A typical result of such contamination is shown in Fig.14. In this case, a thin foil specimen containing voids was annealed for 10 minutes at 900°C in UHV. The electron micrograph in Fig. 14b shows the as-polished area of Fig.14a, after the annealing treatment. The voids were found to be unchanged in size but impurities seem to have precipitated on the surfaces of the voids. It was felt that these impurities might have originated from the surfaces of the foils because in most cases, as in Fig.14b, there were distinct signs of surface contamination. More detailed examination showed that all areas of the foil which were

Figure 14 Showing the effects of contamination of thin foil samples in the transmission electron microscope. An area is shown from a sample, (a) before, and (b) after annealing for 10 mins. at 900°C and 10^{-8} torr pressure. During the annealing, C from the surface has apparently diffused into the samples and precipitated on the void surfaces.

a

b

exposed to the electron beam in the course of microscopic examination and imaging, were contaminated (Fig.15). In this sample, a clear line of demarcation can be seen between the contaminated region (with the rough appearance), and the clear, non-contaminated region. The contamination shown in Fig.15a is after imaging three times in transmission and annealing for 5 min. at 900°C in UHV after each imaging. The imaging was done only in the regions to the lower right hand corner of Fig.15a and beyond. The clear area in the upper left hand corner of Fig.15a was not exposed to the electron beam until this image was recorded. Having imaged this area, the sample was annealed for 5 more minutes and as a result the clear area in Fig.15a has also become contaminated (Fig.15b). This clearly shows the contaminating effect of the electron beam on the electron entrance and exit surfaces. (Stereo imaging showed the contamination to be on the surfaces of the foils.) In addition, it was noticed that in areas exposed to the beam, voids did not undergo any size changes but only got contaminated as in Fig.14, whereas in the rest of the foil, voids were no longer found after 15 minutes of annealing at 900°C in UHV. It seemed very likely that voids originally present in the areas not exposed to the beam had completely shrunk and disappeared, and that it is the contamination that prevents the same thing from happening to the voids in the areas exposed to the beam. Apparently, upon annealing at temperatures of about 900°C , carbon deposited on the surface due to contamination in the microscope (Auger studies showed that C is the contaminant), diffuses into the thin foils. Some of this C is apparently deposited on the surfaces of the internal voids and prevents vacancy transfer into or away from the voids.

This contamination problem had to be circumvented before any meaningful studies could be made on voids. The carbon presumably originated from two sources - cracking of the diffusion pump oil in the electron microscope

Figure 15 Contamination of areas exposed to the electron beam after imaging and annealing at 900°C in UHV. The areas in (a) towards the bottom right-hand side are shown after imaging and annealing 3 times for 5 min. each time. The areas in (a) to the top left-hand side were not exposed to the electron beam until this micrograph was taken. The same area is shown in (b) after a further 5 min. anneal, showing contamination of the whole area.

a

b

column and contamination left on the sample surfaces after electropolishing. Care was taken to minimize both these sources of contamination. The vacuum in the microscope column was found to be in the 10^{-5} torr range, in accordance with the manufacturer's specifications. It was found that after the microscope and most of the vacuum seals were cleaned and with consistent use of cold traps and a turbo-molecular pump attached to the column, the vacuum was improved by an order of magnitude. Care was also taken to minimize specimen borne contamination by thoroughly cleaning the samples before and after examination in the electron microscope. In addition, during imaging, exposure of the sample to the electron beam was kept to a minimum. Under these improved conditions, it was found that contamination of the voids was no longer a problem.

The behavior of vacancies during annealing at temperatures higher than 800°C was investigated by observations on voids in both UHV and 10^{-5} torr of oxygen. At an annealing temperature of 800°C in UHV, there was no noticeable change in the size of the voids. But UHV anneals at higher temperatures showed that the voids are no longer stable. Figure 16 shows that at 850°C in UHV, all the voids in the micrograph have decreased in size after 3 hours of annealing. There are no longer signs that the surface is acting as a barrier to vacancies diffusing out of the sample as was the case at temperatures below 800°C where vacancy defects were found to grow, not shrink. The shrinkage of voids is more dramatically illustrated in Fig.17 where after only 3 min. of annealing at 950°C in UHV, rapid shrinkage of voids can be seen. Some of the voids have disappeared and the remaining voids were also seen to disappear after a further short annealing period. On the other hand, at annealing temperatures in this range, if the annealing was performed in 10^{-5} torr of oxygen, the behavior of vacancies is very similar to that at lower temperatures. In Fig.18, results of annealing at

Figure 16 An area from a slow cooled NiAl sample with voids: (a) before and (b) after annealing for 3 hours at 850°C and $<10^{-8}$ torr pressure.

Figure 17 An area from a slow cooled NiAl sample with voids: (a) before and (b) after annealing for 3 min. at 950°C and $<10^{-8}$ torr pressure.

a

b

a

b

Figure 18 An area from a slow cooled NiAl sample with voids showing the effects of annealing for 5 min. and 20 min. at 800°C in 10^{-5} torr oxygen.

a

b

c

800°C in 10^{-5} torr of O_2 are illustrated. After 5 min. of annealing, there is no noticeable change in the size of the internal voids, although interfacial voids have nucleated. But after a further 15 min. annealing period, it can be seen that the internal voids and the interfacial voids have all grown in size. Similar growth of internal voids and development of large interfacial voids was seen at 850°C in 10^{-5} torr oxygen (Fig.19). If the annealing temperature is raised above this, observations on internal voids become very difficult due to the formation of large interfacial voids and deterioration of the thin foil samples.

4.2.3 Interfacial Voids

An important feature, generally observed during annealing of the NiAl thin foils, was the formation and growth of interfacial voids. In Fig. 20a, an area from a sample annealed for 1 hour at 725°C, is shown. A uniform distribution of a large number of interfacial voids is formed and these continue to grow as annealing proceeds (Fig.20b). Stereo microscopy on many of these samples revealed that these voids indeed lay on the two surfaces of the thin foils and that there was a thin film overlaying these voids, which was presumably the oxide layer. This was more clearly revealed after the sample in Fig.20b was transferred to an Auger spectrometer and both surfaces were bombarded with Argon ions until the oxygen signal had entirely disappeared. The sample was then examined again in the microscope after removing the oxide layer in this manner. This is shown in Fig. 20c and it can be seen that the voids are still present and are clearly associated with the substrate and not with the oxide. Close examination also showed that there were no more traces of the film covering these voids, strongly indicating that it was indeed a film of oxide. Just as internal voids in NiAl were found to be faceted, the interfacial voids were also very crystallographic.

Figure 19 An area from a slow cooled NiAl sample with voids,
(a) before, and (b) after annealing for 10 min. at
850°C in 10^{-5} torr oxygen.

a

b

Figure 20 Formation and growth of interfacial voids in NiAl, after annealing for (a) 1 hour and (b) 2 hours at 725°C in UHV. In (c), the area in (b) is shown after sputtering away the oxide layer on both sides.

a

b

c

In addition to the profuse formation of interfacial voids in all these samples, other sharply crystallographic features were found to form and grow in the thinnest areas of the foils (Fig.21). At first, the nature of these features was not well understood but later experiments showed that these appeared to be voids which extended throughout the foil thickness - i.e., voids extending from the top to the bottom of the very thin areas and covered by thin layers of oxide on both these surfaces. This conclusion was reached after experiments such as those in Fig.22 where it is shown that interfacial voids are first formed and grow in the course of annealing. When these voids get very large (at $t=50$) in the very thin areas, continued annealing causes them to grow enough to extend right through the foil thickness (at $t=80$). Further annealing then results in further growth of all the voids by vacancy agglomeration. The likelihood that these crystallographic features in very thin areas are voids was further supported by energy-loss spectroscopy. Samples with these features were examined in a Vacuum Generators HB-5 Scanning Transmission Electron Microscope, in which it is possible to study the energy losses suffered by a finely focused electron beam after its passage through a thin foil. In electron energy loss spectra, such as those produced in the VG HB-5, a large peak is always found close to the position of zero loss because the majority of the 100keV electrons, in passing through a thin foil, are pseudo-elastically scattered and lose only a fraction of an eV of their initial energy. In thicker areas of a foil, more electrons are inelastically scattered and this 'zero-loss' peak would be of lower magnitude than in thinner areas of the same foil. The results of the energy loss experiments are summarized in Fig.23. The 'zero-loss' peak with the beam positioned on the 'void' is shown in Fig.23a. Under exactly identical conditions, when the beam is shifted to the matrix adjacent to the 'void' the peak is as shown in Fig.23b. The peak in the latter case is much lower in

Figure 21 Crystallographic features in the thinnest areas near the thin foil edges formed after annealing for 20 min. and 40 min. in 10^{-5} torr O_2 at $750^{\circ}C$.

b

a

Figure 22 Showing that the crystallographic features shown in Fig.21 are developed by growth of interfacial voids. The annealing times in minutes are as marked.

10m

20m

50m

80m

120m

Figure 23 Energy loss spectroscopy on the thin areas containing voids. (a) "Zero Loss" peak in the energy-loss spectrum with the beam positioned on the void. (b) "Zero Loss" peak under identical conditions as in (a) but with the beam positioned on the matrix adjacent to the void. (c) K-absorption edge of oxygen seen in the energy loss spectrum with the beam positioned on a void.

a

b

c

intensity, and clearly, the electron beam has passed through a very much thinner area when it is positioned on the 'void'. This large difference in thickness between two points adjacent to one another, clearly indicates that the crystallographic features in such thin areas are indeed voids, which stereo microscopy shows run all through the thickness of the foil. In addition, the energy-loss spectrum also shows that at 533 eV, corresponding to the K absorption edge for oxygen, an intensity peak can be seen (Fig.23c). This lends support to the earlier indications that the voids are covered by a layer of oxide.

4.2.4 Vacancy Formation Energy

The presence of large numbers of loops and voids in as-prepared samples of this alloy indicated, as suggested by several previous investigators, that the vacancy formation energy (E_f) is low in these alloys. Estimations of E_f have been made before,^{16,50} but are unreliable because only in one case has it been taken into account that there are some restrictions to the formation of vacancies in intermetallic compounds. Wasilewski has considered the formation of thermal defects in compounds with the CsCl structure. He has shown⁵⁰ that since vacancies have to be formed in pairs in these compounds, one on each sublattice, the normal expression for calculating the vacancy formation energy in pure metals, cannot be used for the case of NiAl. If the configurational entropy is calculated under this restriction, he showed that the expression for vacancy formation energy is the following:

$$n/N \approx 1/2\{\exp(-E_f/2kT)\}$$

where n is the number of pairs of vacancies, one on each sublattice, N is the total number of atoms and E_f is the energy of formation for the pair of vacancies. This is clearly different from the expression for vacancy formation energy in a pure metal, which is of the form

$$n/N \approx \exp(-E/kT)$$

But while Wasilewski has used the correct expression, he seems to have made a factor of 2 error in his calculation. In addition, he has equated the number of vacancies exactly to volume change in the sample, without considering any collapse of the lattice around each vacancy.

An attempt was therefore made to calculate a more reliable value for E_f . It was noticed that quenching samples of this alloy from temperatures above 1200°C , followed by ageing at around 500°C , resulted in the formation of a uniform distribution of a high density of voids (Fig.25). As is evident, these voids were also faceted and fairly uniform in size. It was possible therefore to get a good estimation of the vacancy concentration present in the voids. Using standard techniques, it was also possible to obtain a good estimation for the foil thickness. From these measurements, the number of vacancies in a known volume of the material could be calculated. Such calculations of the vacancy concentration were done for three different quenching temperatures, 1200°C , 1275°C and 1350°C . After quenching, the samples were aged at 500°C for 12 hours and this ageing was found to be sufficient for all the quenched-in vacancies to diffuse to voids. The results are plotted in Fig.24, and from the slope of this plot of the vacancy concentration (n/N) as a function of reciprocal temperature, it was possible to deduce a value of 1.45 ± 0.2 eV for the energy of formation of a pair of vacancies, one on the Ni sublattice and one on the Al sublattice. In addition to the inaccuracies in the measurements that are evident in Fig.24, the vacancy concentrations estimated here also suffer from the handicap of being made on micro-volumes of material and the value of E_f could not be determined to a greater accuracy.

In the course of the quenching experiments, some observations were also made on samples which had some impurity precipitates. Quenching followed by ageing at temperatures around 500°C in these samples shows (Fig.26) that void

Figure 24 $\ln(2n/N)$ vs. $1/T$ for NiAl samples quenched from three different temperatures (1200°C, 1275°C and 1350°C). The value of E_f can be deduced from the slope of the straight line plotted.

Figure 25 Voids in near-stoichiometric NiAl quenched from 1300°C and aged, before thinning, for 16 hours at 500°C.

Figure 26 Areas from quenched and aged NiAl samples containing impurities, showing the ease of void nucleation at impurities.

a

b

a

b

nucleation occurs much more easily at the precipitate-matrix interface. Evidently, voids first nucleated on the impurity particles and grew by absorbing all the vacancies in the vicinity. But the low ageing temperature (500°C) apparently prevents long range diffusion and a uniform distribution of voids seems to have subsequently formed. The ease of nucleation of voids on impurity particles might explain why many large voids are seen in as-prepared NiAl samples. Voids might nucleate at an early stage during the cooling and might sweep up a large number of the thermal vacancies possibly trapped in the material by an impervious oxide.

4.3 OFF-STOICHIOMETRIC COMPOSITIONS

As described in the introduction, in β -NiAl, diffusion and especially intrinsic diffusivities of Ni and Al, are profoundly composition dependent. In order to get a more complete understanding of the influence of oxidation on vacancy behavior in this phase, it was therefore necessary to investigate alloys of different compositions. It was for this purpose that two more β phase alloys were prepared with compositions on either side of the stoichiometric composition. These were not single crystal samples but were coarse-grained polycrystals, and their method of preparation and slow cooling has already been described.

4.3.1 Ni-rich Alloy

Results of annealing experiments on the Ni-rich alloys will now be described. It was found that as prepared thin foils of these samples were almost free of dislocations and no loops were seen. In order to understand vacancy behavior during annealing, it was necessary to introduce dislocations into these thin foils and then make observations of any dislocation climb that might occur. The thin foils were therefore carefully deformed with fine tweezers to introduce a fairly high density of dislocations in the thin foils.

Long irregular screw dislocations with $\vec{b}=\langle 100 \rangle$ can easily be introduced in these alloy thin foils and it has been observed that any vacancy supersaturation results, upon annealing, in spiraling and eventual loop formation from these screw dislocations.⁹

The deformed thin foils were annealed at 10^{-8} torr for 2 hours at 600°C . After this annealing treatment, many dislocation loops were found in some areas of the samples. But surprisingly, when the foils were further annealed, at 600°C and at 650°C , loop growth was not observed. Evidently, the initial loop formation and growth was due to an inherent vacancy supersaturation present in these thin foils in spite of the fact that these were annealed and slowly cooled samples. The implications of this observation will be discussed in the next chapter. Fig.27 shows the behavior of the loops from one of the above samples when annealing is further continued at 700°C . In Fig.27, at $t=0$, an area is shown from a sample already annealed for about 3 hours at 600°C and 1 hour at 650°C in UHV. The same area is then shown after a further anneal of 15 minutes at 700°C . Some loop shrinkage can be observed in this case. But when the annealing is continued at 700°C , the shrinkage trend is reversed and the loops start to grow and continue to grow rapidly with time. This is very similar to the behavior of loops in the slowly-cooled, near-stoichiometric alloy. The only difference in the two cases is that the kinetics for climb of loops are more favorable in the Ni-rich alloys - i.e., at the same temperature, climb occurs more rapidly in these alloys. Climb processes have been observed in the Ni-rich alloys at temperatures as low as 650°C if annealing is continued for a few hours whereas in the near-stoichiometric alloy, no significant climb was noticed below 700°C .

Two other important observations were also made in these annealing experiments on the Ni-rich alloys. It was found that in a particular thin foil sample, loops in thinner regions of the foil grew at a faster rate than loops

Figure 27 Annealing sequence for a Ni-rich alloy sample annealed at 700°C, at 10^{-8} torr pressure. The sample as shown in the first micrograph had already been annealed for 3 hours at 600°C and subsequently for 1 hour at 650°C. The annealing temperature was then raised to 700°C and the sequence of anneals at this temperature was started at $t=0$. The annealing times in minutes, at 700°C, are marked.

$t=0$

15

30

45

60

75

in thicker regions of the foil (Fig.28). As seen in Fig.28a, in very thin areas, loop growth is so rapid under these conditions that the square equilibrium loop shape is no longer maintained. The dependence of loop growth on the position of the loops in foil of varying thickness is better illustrated in Fig.29. Loop growth as a function of annealing time has been plotted for loops of similar size in foil areas roughly 5000 Å, 7000 Å and 10,000 Å thick. It is very clear that the rate of loop growth depends on the foil thickness in the corresponding area, higher growth rates occurring in thinner areas of the foil. These observations indicate that the source of vacancies is the foil surface. More evidence to support this came from stereo microscopy observations which showed that in any particular area, loops which lay close to one of the foil surfaces grew at a faster rate than loops which lay close to the center of the foil. Finally, it can be seen in Fig.29 that the rate of increase of loop area increases with annealing time. Since the increase in area of the loops is a direct measure of the number of additional vacancies absorbed by the loops, it is evident that vacancy diffusion to the loops is occurring at an increasing rate as annealing proceeds. This behavior is very similar to that of loops in the near-stoichiometric alloy (Fig.13), where it was shown that the rate of increase of loop area increased with annealing time for loops of all sizes.

4.3.2 Al-rich Alloy

Annealing experiments very similar to these were also performed on the Al-rich alloy. Loop growth, very similar to that observed in the near stoichiometric and Ni-rich alloys, was also seen in these Al-rich alloys. Some typical results are illustrated in Fig.30. As shown in Fig.30, pronounced loop growth occurs in thin foils of the Al-rich alloy at temperatures as low as 600°C. In this case also, it was observed that the rate of vacancy diffusion to the loops increased with time. Evidently, vacancy diffusion is fastest

Figure 28 Loops in a Ni-rich alloy sample: (a) from a thin area and (c) from a thick area. The areas in (a) and (c) are shown in (b) and (d) respectively after annealing for 75 mins. at 700°C and 10^{-8} torr pressure. One of the loops in the top left side of (a), has grown much faster than its neighbor - stereo microscopy showed that the faster growing loop is closer to the foil surface.

a

b

c

d

Figure 29 Percentage increase in loop area as a function of annealing time, for three loops, in a Ni-rich alloy sample annealed at 700°C and 10^{-8} torr pressure. The three loops examined here were all initially about 1200 Å square, but were located in 3 different areas of the sample - loops a, b and c lay in areas where the foil thicknesses were roughly 0.5μ, 0.7μ and 1μ respectively.

Figure 30 An annealing sequence from an Al-rich alloy sample, annealed at 600°C and 10^{-8} torr pressure. The annealing times in minutes are marked.

$t=0$

30

60

90

in this alloy because loop growth due to vacancy injection from the surface was seen even at temperatures below 600°C , whereas signs of vacancy injection were seen in the Ni-rich alloy and the near-stoichiometric alloy only at temperatures above 650°C and 700°C respectively. The other difference observed in the Al-rich alloys was that the vacancy dislocation loops were not as crystallographic as the loops seen in the other two alloys - they tended towards circular shapes. While this is not obvious from Fig.30, where the loops are very small, larger loops in the Al-rich alloys were found to be nearly circular in shape.

4.4. AUGER SPECTROSCOPY

In conjunction with the annealing and electron microscopy experiments, Auger Electron Spectroscopy was used in the course of these studies, to investigate the nature of the oxide formed during annealing. These studies were carried out in a PHI Scanning Auger Microprobe equipped with a cylindrical mirror analyzer. The instrument has scanning and imaging capabilities and can also be used for continuous depth profiling using ion sputtering. Thus the specimen surface can be sputtered off with a beam of Argon ions, with the beam current being variable, and the Auger peak-to-peak heights (i.e. concentrations) of six different elements can be simultaneously monitored using a multi-channel analyser. The following settings were most commonly used:

Primary electron beam voltage = 5kV

Primary electron beam current = $10\mu\text{A}$

Electron multiplier voltage = 1000V

Modulation amplitude = 2V

Time constant = 0.3

Rate = 5eV/sec.

The primary electron beam was allowed to raster over an area approximately 100 μ m. square during most of the analysis. In the 0-2keV range, both Ni and Al have two sets of peaks. However, the low energy MNN signal from Ni (with the main peak at 61 eV) and the LMM signal from Al (with the main peak at 68 eV) were too close together to be accurately resolved in this Auger system. As a result, in all the analyses, the LMM signal from Ni (with the main peak at 848 eV) and the KLL signal from Al (with the main peak at 1396 eV) were used. The sensitivity of the Auger process is much lower for Al than for Ni - i.e., the Al Auger signal is much weaker than the Ni Auger signal. A primary beam energy of 5kV was used here because it was found to enhance the KLL Al Auger signal. Since very high spatial resolution was not needed, it was possible to use a high primary beam current of 10 μ A to get an improved signal-to-noise ratio. By using a small modulation amplitude of 2V, overlapping peaks could be better resolved. In addition to recording Auger spectra, depth profiles of many specimens were recorded. To do this, as mentioned earlier, a beam of argon ions was directed onto the sample at the focal point of the spectrometer. The sputtering beam current could be measured using a Faraday cup. As layers of material were sputtered away by the argon ion beam, the relative concentrations of upto six elements could be continuously monitored. It was necessary to relate the sputtering beam current and the time of sputtering to the depth sputtered. Accurate measurement of the sputtered depth in such an analysis is far from easy. A rough value for the sputtering rate was obtained by determining the beam current and time necessary to sputter away the room-temperature oxide on NiAl, Ni and Al samples. The oxide layers formed at room temperature on most metals and alloys is estimated to be 30-50 Å thick.⁶³ By assuming the room-temperature oxide layer on NiAl to be 30 Å thick and by measuring the sputtering beam current and the average exposure time necessary to remove this assumed 30 Å of oxide,

it was possible to roughly 'calibrate' the sputtered depth to the beam current and time. This method is estimated to be accurate to within a factor of two and has previously been used by Hutchings.⁴¹ The Argon ion beam could also be rastered over the sample surface to a limited extent and this ensured that the area being sputtered was at least an order of magnitude larger than the area being analysed by the electron beam.

A large number of samples oxidized under many different conditions, were examined in the Auger Spectrometer. Typical depth profiles from electron microscope samples annealed for 2 hours at 700°C in UHV and 10^{-5} torr of oxygen are shown in Fig.31. No trace of Ni was found on the surface of the sample annealed in oxygen. The outer layers of this sample showed only oxygen and Al (and some carbon contamination). This outer layer (presumably Al_2O_3) extends to a depth of about 150 Å. At this point the relative concentrations of Al and O₂ start decreasing and at the same time, the Ni signal appears and starts increasing in magnitude. In this region of transition between the Al_2O_3 and the alloy substrate, the concentration of Ni rises monotonically from zero to its concentration in the bulk alloy whereas the oxygen concentration decreases monotonically to zero in the bulk alloy. The relative concentration of Al also eventually levels off to its value in the bulk alloy. But a small minimum is seen in the Al concentration before it reaches its equilibrium value. The sample annealed under the same conditions in UHV instead of oxygen (Fig.31b), has a very similar depth profile but with one important difference - an outer layer of pure Al_2O_3 is not seen. There are traces of Ni even at the surface and this Ni concentration starts increasing as soon as sputtering commences. This absence of an outer Al_2O_3 layer simply seems to be because of the much slower oxidation rate in UHV - samples annealed for much longer periods in UHV (5-6 hours) at this temperature did show an outer Al_2O_3 layer with almost no traces of Ni.

Figure 31 Auger concentration profiles from thin foil samples annealed for 2 hours at 700°C, with the annealing atmosphere being (a) 10^{-5} torr of oxygen, (b) UHV ($<10^{-8}$ torr).

In Fig.32, typical Auger spectra are shown at various stages during the depth profiling of a sample such as the one shown in Fig.31a. The spectra were recorded from the outer Al_2O_3 layer, the transition region and the substrate respectively. It can be clearly seen that there is no trace of Ni in the outer region which contains only Al and O. In the transition region, Ni peaks have appeared while the Al and O signals are both reduced in magnitude. Finally as shown in Fig.32c, the oxide has been completely sputtered away and only Ni and Al signals are present. An effort was made to understand the nature of the transition region which lies between the outer Al_2O_3 layer and the substrate. In order to do this, the fine structure of the LMM Ni peaks and the KLL Al peaks was closely examined at various stages during the depth profiling since it is known that the chemical nature of the atoms present can change the fine structure of the Auger peaks and also shift their energy. The Auger spectrometer used here did not have the accuracy and stability to monitor chemical shifts less than a few eV in magnitude. But it was found that there were changes in peak heights which could be readily seen. In Fig.33, the LMM Auger spectra are shown for Ni in bulk NiAl and in the transition region soon after the Ni signal starts to appear. While the major peaks at 848eV, 783eV and 716eV were very similar in the two cases, the peaks at 828eV and 760eV were much larger in the Ni signal from the transition region than in that from NiAl. This difference was consistently found in many samples. For comparison, Ni Auger spectra were also recorded from pure Ni samples and Ni samples oxidized at 1000°C in air (presumably NiO). These spectra are also shown in Fig.33 and in these cases it can be seen that there is little or no trace of the 828eV and 760eV peaks. From these observations, it appears that in the first part of the transition region (when the Ni concentration is 10-20 at.%), the Ni atoms may have formed a mixed oxide or spinel with Al and O_2 atoms. Further indications for this

Figure 32 Auger spectra recorded at various stages during the depth profiling of a sample such as that in Fig.31a: (a) from the outer oxide layer, (b) from the transition region and (c) after the oxygen has been removed (i.e., from the substrate).

Figure 33 LMM Auger spectra for Ni in (a) NiAl, (b) the transition region in the concentration profiles, (c) pure Ni and (d) Ni oxidized at 1000°C in air.

possibility came from the fact that the Ni LMM spectra from the oxide formed at room temperature on NiAl samples looked very similar to the spectra shown in Fig.33b. Since diffusion at room temperature is very slow in NiAl, the room temperature oxide might very well be a combined oxide of Ni and Al and since the Ni spectra from the first part of the transition region closely resemble the Ni spectra of the room temperature oxide, there might be a region of combined Ni and Al oxide just beneath the outer Al_2O_3 layers in these samples. In order to try and confirm this, the Al KLL spectra were also closely examined. The Al spectra from the outer layer closely resembled the spectra from Al in pure Al_2O_3 (Fig.34a) and was easily distinguishable from the Al spectra in pure NiAl (Fig.34b) and pure Al (Fig. 34c). But while differences were often seen between the above spectra and the Al spectra in the transition region, consistent results were not obtained and the information was too ambiguous to reach any conclusions.

The results described above are for oxidized TEM samples of the near-stoichiometric alloy. These were compared with Auger analysis of bulk samples oxidized in air to form thicker oxide layers and with oxidized samples of the off-stoichiometric alloys. Typical results of these observations are shown in Fig.35. While the oxide layers are much thicker, a comparison of Fig.35 and Fig.31a shows that the results are qualitatively identical. There is a definite region of transition which clearly is not due to escape depth phenomena since this would affect only layers about 50 Å or less in thickness. The oxidation behavior of the off-stoichiometric alloys (Fig.35 a and 35c) is very similar to the oxidation behavior of the near-stoichiometric alloy. From several such comparisons, it seems that as the Ni content of the alloy is raised in this composition range, the transition zone becomes narrower. The reason for this is not understood at this time but is probably related to the profound changes of diffusion rates with composition.

Figure 34 KLL Auger spectra for Al in (a) pure Al, (b) pure Al_2O_3 and (c) NiAl .

Figure 35 Concentration profiles from alloys of three different compositions, annealed for 5 hours at 700°C in air.
(a) Al-rich alloy, (b) Near-stoichiometric alloy and
(c) Ni-rich alloy.

4.5 BULK OXIDATION

The evidence from the annealing experiments overwhelmingly indicates that vacancies are generated continuously during oxidation. This could happen only if the oxide grows by the diffusion of metal atoms outward from the metal substrate, through the oxide to the oxide-oxygen interface. This seems plausible here because mainly Al_2O_3 is formed and diffusion data on Al_2O_3 indicates that Al diffuses faster than oxygen in this compound.^{52,53} In contradiction to this, work on alumina forming compounds indicates that the Al_2O_3 forms by grain-boundary diffusion of oxygen, thus growing into the substrate.^{23,24} It was therefore felt that it was necessary to perform a bulk oxidation experiment to determine if indeed Al_2O_3 grows outward in NiAl as the thin foil annealing experiments indicated. In order to do this, inert markers (0.01" thick Pt wires) were spot-welded on to the polished surface of a single crystal of NiAl and this was oxidized in a furnace open to air, for 5 days at 1300°C. It was then removed and examined in optical and scanning electron microscopes. A scale of Al_2O_3 was found on the surface which had spalled off in most areas leaving only a few patches on the sample (Fig.36). Optical and SEM micrographs (Fig.37) indicated that this scale was formed outside the original substrate surface. The substrate surface was found completely covered with ridges and craters which could possibly be voidage created during the oxide formation (Fig.38). That the Al_2O_3 scale is formed by outward diffusion of Al was confirmed by examining cross-sections of the oxidized sample (Figs.39 and 40). The Pt wires used as markers here were apparently too big for this purpose and the spot welding has caused cracking in the substrate but it can be seen that not only has a coherent scale formed over the substrate but the Pt wire is also covered by a layer of Al_2O_3 (as revealed by Auger Spectroscopy and energy-dispersive spectro-

Figure 36 Optical micrograph of a NiAl single crystal block oxidized for 5 days at 1300°C in air, showing that the outer scale has spalled off in most areas, leaving only a few patches still adhering to the substrate. The long wire running across the block is a platinum marker.

Figure 37 SEM micrograph of the scale and the substrate adjacent to a Pt wire marker.

Figure 38 Optical micrograph of the substrate surface below the outer scale.

Figure 39 Cross section of the oxidized NiAl block showing that the scale forms outside the original substrate surface. The Pt wire marker can be seen on the left and is also covered by a layer of oxide. (Secondary electron image).

Figure 40 Cross section of the oxidized NiAl block at high magnification. (Secondary electron image).

a

b

scopy in the SEM). This is very strong evidence that the formation and growth of Al_2O_3 in these alloys does occur by cation diffusion. As can be seen, only a single oxide layer was found - if a spinel layer exists it is too thin to be detected here.

5. DISCUSSION

The implications of the results from the various experiments remain to be examined. The relevance of the various theories on the effects of oxidation on the behavior of vacancies will now be discussed in the light of the present results. While this project is aimed at better understanding vacancy behavior as a consequence of oxidation in β -NiAl alloys, any general implications which might possibly be extended to other systems will also be considered.

The first important result which emerged from these studies was that the results of the previous study of this kind by Fraser et al,⁹ do not necessarily prove that oxidation injects vacancies into β -NiAl. The single crystals of NiAl used by Fraser et al in their observations of loop and void growth during annealing, were zone-melted and allowed to cool in place. The cooling rate is not known but is estimated to be quite rapid, and it is possible that supersaturation of defects may develop. The implication of this retained supersaturation is that the energy of migration of vacancies is high, so that vacancy motion is not sufficient to allow annihilation at sinks. However, the experiments involving dislocation climb in previous investigations and in the present work strongly indicate a relatively mobile defect. An alternative explanation involves the nature of the surface, where the oxide which inevitably forms during cooling, is impervious to vacancies, so that the surfaces no longer act as sinks. This possibility has been discussed by Harris,²⁰ and as he points out, if a material does indeed form an oxide impervious to vacancies, thermal vacancies would be retained. A large number of vacancies would be annihilated at internal sinks, but a significant concentration would remain in the material if the cooling rate is fairly high. Even if the cooling rate is very slow, in relatively

perfect materials, all the vacancies might not be annihilated because of the low density of available sinks. Indeed, signs of a retained vacancy supersaturation were found in the present experiments, even in the slowly cooled alloys, and in accordance with the above explanation, a larger number of vacancies was found to have been retained in the slowly cooled Ni-rich and Al-rich alloys, which had much lower dislocation densities than the slowly cooled near-stoichiometric alloy. Since more defects were present in the latter, more sinks were available for vacancies to be annihilated during the slow cooling, resulting in lower retained vacancy concentrations. Thus, in deliberately deformed thin foils of the slowly cooled material, especially from the off-stoichiometric alloys, screw dislocation spiraling and resulting loop formation, was found to commence immediately after the annealing treatment was started. The rate of loop growth decreased with time and loop growth eventually stopped, clearly indicating that the vacancy supersaturation had been eliminated. Since these samples were very slowly cooled, there seems little possibility of a quenched-in supersaturation. However, it is conceivable that upon slow cooling and in the absence, as in these cases, of a reasonable number of active sinks, the vacancies would form a large number of small clusters, for example, associated with an impurity atom. Upon the introduction of a number of real sinks (dislocations) and reheating, the clusters would then dissolve and the vacancies would be annihilated at the sinks, with a corresponding decrease in energy of the crystal. This explanation is more plausible in these cases than that of Harris, who has used a different argument to justify thermal vacancy retention in slowly cooled materials. According to him, a limited number of the vacancies trapped by the impervious oxide would be annihilated at internal sinks. Such annihilation would produce dimensional changes in the material. But a strongly adherent oxide would provide a mechanical restraint

to prevent the substrate from changing dimensions. As a result, many vacancies, Harris implies, would be left in solution. But in the present case, the annealing and slow cooling of the alloy blocks was carried out at very low oxygen partial pressures and the oxide layers found on the surfaces were very thin. It is very unlikely that such thin oxide layers can prevent the deformation of a block of material more than 3/8" thick. Instead, vacancy supersaturations in the slow cooled alloys can be better explained on the basis of difficulty of annihilation due to low densities of vacancy sinks such as dislocations.

It is, therefore, reasonable to assume that dislocation climb in the fast cooled, near-stoichiometric alloys can only be explained on the basis of a retained vacancy supersaturation. This is the only explanation which is consistent with the observations on these samples that oxygen partial pressure had no effect on loop growth and that loops near the thin foil surfaces grew slower than loops in the interior. In the experiments on the fast cooled NiAl, the results of Fraser et al, on loops in the very same material, were essentially reproduced. It is felt therefore, that the results of Fraser et al can also best be explained on the basis of a retained vacancy supersaturation, and do not necessarily prove that vacancies are injected by surface oxidation. Further, Fraser et al had concluded that vacancy defects found by previous investigators in as-grown specimens of NiAl⁷ and those defects produced by quenching and ageing discs of NiAl⁶ were likely to be due to vacancy injection by surface oxidation and not due to low vacancy formation energy. This conclusion of Fraser et al also seems inadequate since the present work shows that thermal vacancies can easily be retained in this compound - to prove that vacancy injection is due to surface oxidation, it must first be confirmed that excess thermal vacancies are not present. As will be shown later, the conclusion of Fraser et al, that oxidation

injects vacancies into NiAl, was inadvertently correct, in that the dislocation climb observed in their experiments was probably due in large part to a retained vacancy supersaturation as described above. Large concentrations of thermal vacancies can be generated because, as confirmed by measurements on voidage in quenched and aged samples of NiAl, the vacancy formation energy is quite low in this compound - it was determined in the present work to be 1.45 ± 0.2 eV to form a pair of vacancies. This means that the vacancy concentration at the melting point ($\approx 1640^\circ\text{C}$), could be as high as about 2%. (It is important to note that the ageing of the quenched samples was carried out at 500°C , a temperature at which, the annealing experiments showed, there is little or no vacancy injection by oxidation.) As will be shown, in the β -phase alloys, vacancies can also be injected into the sample by surface oxidation. But it will also be shown that this is significant only at higher temperatures. In addition, while growth of existing vacancy defects was frequently observed during oxidation, nucleation of internal defects was never seen. When all these factors are considered, it seems very likely that vacancy defects, especially voids, found in as-prepared samples and in samples of NiAl quenched and aged at low temperatures (where oxidation is insignificant), are formed by agglomeration of thermal vacancies rather than by vacancy injection during oxidation.

The earlier work of Fraser et al,⁹ is the only investigation which deals with the possibility of vacancy injection during oxidation of NiAl, and there are no reports of such vacancy injection in other intermetallic compounds. It has been shown here that their results do not necessarily prove that vacancies are injected by oxidation of the thin foil surfaces because a supersaturation of thermal vacancies seems to have pre-existed in the thin foils. It now has to be considered if indeed oxidation does inject vacancies. Since this is investigated by observations on loops and voids, it is

imperative to start with samples which are not supersaturated with thermal vacancies. To do this, in the case of the near-stoichiometric alloy, the single crystals were annealed at 900°C for 1 day and slowly cooled at 5°C/hour. These slow cooled single crystals were then deformed about 1% in compression along [001] at 650°C at very low strain rates. Discs were then cut for electron microscopy, chemically cleaned and annealed in air for 1 hour at 600-700°C to reduce the dislocation density. This procedure was followed in order to obtain a high density of loops with a low density of other line defects. It was found that this procedure also resulted in thin foil samples with little or no thermal vacancy supersaturation - as later results on the off-stoichiometric alloys showed, slow cooling alone seems inadequate to eliminate all thermal vacancies in solution and in the above case of the near-stoichiometric alloy, the deformation and annealing treatments seem to have eliminated the thermal vacancy supersaturation still left after the slow cooling. This was confirmed by the annealing experiments because no loop growth was observed whatsoever at temperatures below 650°C, whereas in the fast cooled samples, even at annealing temperatures as low as 550°C, loops were found to grow right from the beginning.

Since samples could thus be prepared without a supersaturation of thermal vacancies, annealing experiments on these samples could be used to investigate the effects of oxidation on vacancy defects in thin foils. The initial experiments showed, as mentioned earlier that no noticeable loop growth occurred at temperatures as high as 650°C at oxygen pressures as high as 10^{-4} torr. But in samples annealed at 700°C, climb of dislocation loops became apparent. The general features of annealing experiments at 700°C and 750°C have been outlined in section 4.2.1. In general, it was found that loops decreased in size during the initial periods of the anneal but this trend is reversed when the annealing is continued and the loops continuously

increase in size with time. This is clearly illustrated in Fig.11, which is an annealing sequence at 750°C in UHV. In Fig.12, the variation of loop size with annealing time is shown for 700°C and 750°C and at each temperature, for samples annealed in UHV and in 10^{-5} torr oxygen. In plotting this data, several loops of approximately the same initial size (≈ 1000 Å) were considered in each of the four samples. This had to be done because the percentage change in loop size was strongly dependent on loop size - smaller loops exhibited a much higher rate of growth or shrinkage. There are evidently two reasons for this - when the surface acts as a vacancy sink, the driving force for loop shrinkage (due to dislocation line tension), is greater for the smaller loops than for larger loops. Under these conditions, the smaller loops therefore shrink faster. On the other hand, if the surface injects vacancies, equal vacancy fluxes from the surface would cause a higher percentage growth in the smaller loops. Smaller loops therefore also grow faster than larger loops, in spite of the fact that line tension favors just the opposite. In addition, it was observed that the rate of change of loop size was also affected by general loop and dislocation density in the area - all the loops and other dislocations in a particular area act as sinks for vacancies and therefore for a given vacancy flux, loop sizes were more affected in an area of lower dislocation density than in an area with a higher dislocation density. Other factors which were found to affect the rate of change of loop size were the foil thickness and the depth of the loop below the foil surface - the significance of these observations will be discussed later. The rates of loop growth or shrinkage therefore depend on a variety of factors. To compare loop size changes at different temperatures or pressures accurately and quantitatively, it is necessary to compare loops of the same size lying in areas of identical foil thickness and at identical distances from the foil surfaces and in addition having an iden-

tical distribution of other loops and dislocations in the vicinity. Such pre-conditions were found to be impossible to achieve and quantitative studies or comparisons could not be done. Only in a few cases were samples found in which the above mentioned conditions were comparable and reasonable comparisons could be made. These are the four samples used in the comparisons of Fig.12 but it must be understood that while the general trends in these samples are accurately depicted and real differences were seen in loop size change between these samples, the data itself is not statistically accurate. The effects of annealing and the resulting oxidation on vacancy defects can, nevertheless, be seen from these experiments. The results in Fig.12 can be consistently explained only on the basis of vacancies injected by surface oxidation. Initially, the surface is clean. Depending on the temperature and pressure, annealing for a certain minimum time is necessary before a continuous oxide layer is formed which prevents the surface from acting as a vacancy sink. For a vacancy dislocation loop in a thin foil, Smallman and Dobson⁶⁴ have expressed the rate of change of loop radius r with time as

$$dr/dt = AD_s[(C_s/C_0)-(C_l/C_0)]$$

where A is a geometrical factor depending on the diffusion geometry and the Burger's vector, D_s is the co-efficient of self diffusion, C_0 is the equilibrium vacancy concentration and C_s and C_l are the vacancy concentrations in equilibrium with the foil surface and the loop respectively. C_l is given by $C_l = C_0 \exp(\Delta F/kT)$ where $\Delta F(=dE/dn)$ is the change in the loop energy per vacancy emitted. For a vacancy loop ΔF is positive and $C_l > C_0$. If the surface acts as a perfect vacancy sink, then $C_s \approx C_0$. Therefore dr/dt will be negative and the loop will shrink when annealed at temperatures where diffusion can occur. In the present case, this seems to occur in the initial annealing periods when general loop shrinkage is observed. Evidently, before the formation of a continuous oxide layer, the surface does act as

an efficient vacancy sink. After the initial period of general loop shrinkage, an intermediate stage was generally observed in which some loops continued to shrink while the rest of the remaining loops reverse the trend and start to grow. In a case like this, where some loops are growing and others shrinking, it might be expected that due to the line tension forces, the smaller loops would still be shrinking while the larger loops had started to grow. But this was not the case - it was often found that smaller loops in some areas had started to grow even as larger loops in nearby areas were still shrinking. This behavior can be better explained on the basis of a discontinuous oxide rather than on the basis of differences in loop size. Apparently the impervious oxide has formed in some areas leading to loop growth in these areas. But it seems a continuous oxide layer has not yet formed and the shrinking loops might lie beneath discontinuities in the oxide. Eventually the oxide covers the whole surface and no more loop shrinkage is seen - all the remaining loops monotonically grow with annealing time. These features are illustrated for the 750°C annealing sequence in Fig.11, but similar behavior was found for all annealing temperatures in the 700-800°C range. It is clear from Fig.12 that at 750°C, loop growth occurs much more rapidly than at 700°C. It is also clear that at a given temperature, loop growth occurs more rapidly when the annealing is carried out in 10^{-5} torr of oxygen than in UHV. These observations are consistent with vacancy injection due to surface oxidation. The fact that loop growth is so strongly temperature dependent indicates that oxidation involves diffusion of atoms toward the surface with a corresponding diffusion of vacancies inward from the surface. The exact nature of the diffusion will be considered later. But it seems clear here that loop growth is being caused by oxidation, particularly since increasing the oxidation rates (by annealing in the presence of oxygen) increases the loop growth rates. Fig.13 further confirms

that the vacancies involved in loop growth originate at the surface. The area enclosed by typical loops of three different sizes is plotted as a function of time. In each case it can be seen that the rate of loop growth increases with time. This is very similar to the observations of Dobson et al.⁴² who in similar experiments found that the rate of loop growth increased with annealing time in an Al-0.65% Mg alloy. It was suggested by them that the reason for that observation was that diffusion of Mg to the surface to form MgO was rate controlling. As oxidation proceeded, according to Dobson et al, vacancies are injected into the sample. The increased vacancy concentration in the sample leads to increased diffusion of Mg and increased rates of formation of MgO. This further results in increased vacancy injection rates which would explain increasing rates of loop growth. A very similar process could be occurring in the present case during oxidation of NiAl samples. As can be seen in Fig.13, the flux of vacancies into the sample increases with length of the anneal. The above observations on the slowly cooled near-stoichiometric NiAl clearly indicate that surface oxidation is injecting vacancies into this compound.

The evidence from the experiments on near-stoichiometric NiAl was strongly supported by observations on the off-stoichiometric alloys. As has been shown earlier, in both the Ni-rich and Al-rich alloys, vacancies are injected into these alloys by surface oxidation during annealing. The effect on loops in the Ni-rich alloy when it is annealed at 10^{-8} torr and 700°C (Fig.27) are very similar to the effects seen in the near-stoichiometric alloy (Fig.11) at 750°C. The only difference in the two cases is that the diffusion of vacancies responsible for loop growth occurs faster in the Ni-rich alloy. Results on the Al-rich alloy also show loop growth due to vacancies originating from the surface, and vacancy diffusion rates at this composition are even faster. The fact that vacancies originate

from the surface is particularly well demonstrated in Figs.28 and 29. It has been very clearly shown there that loops lying in thin regions of the foil grow much faster than those lying in thicker regions. A typical case has also been shown in Fig.28, where if two loops lie very close to each other, the one nearer the foil surface absorbs most of the vacancies being injected and as a result, grows much more rapidly than its neighbor. Finally, another typical result is demonstrated in Fig.29 where it can be seen that the loop growth rate increases with time in a similar manner to that in the near-stoichiometric alloy (Fig.13). This increasing loop growth rate was found to be generally true for all the three alloy compositions. In all three cases therefore, it is clear that the vacancies causing loop growth are not retained thermal vacancies, but originate from the surfaces of the thin foils. Surface oxidation is injecting vacancies into β -NiAl in the 600-900°C range. (At above 800°C, as seen before, loops cannot be used to demonstrate vacancy injection but internal voids, which are more stable than loops at these temperatures, also grow by absorbing injected vacancies as shown in Figs.18 and 19.)

To demonstrate vacancy injection into thin foils, experiments similar to those used in this project have been used by some previous investigators. In particular, as discussed earlier, loop growth has been seen in thin foils of the hexagonal metals Zn, Mg and Cd and in dilute Al-Mg alloys. But since Harris²⁰ has recently argued that such experiments cannot be used to demonstrate vacancy injection, the present results have to be considered in the light of his arguments. Firstly, according to Harris, in materials where the oxide acts as a barrier to vacancy diffusion, a significant fraction of the thermal vacancies could be retained during cooling and the diffusion of these vacancies to loops could be the major reason for loop growth in thin foils. Since retention of a large vacancy supersaturation would be

difficult in the very thin electron-transparent areas of these samples, he implies that these areas are replenished by long range diffusion of vacancies from thick areas of the samples. This argument clearly does not hold in the present case of loop growth in NiAl. Firstly, it has been shown that while retention of thermal vacancies seems to be relatively easy in these alloys, most of the loop growth observations cannot be explained on this basis. As reported earlier, some loop growth has been observed which could be attributed to retained thermal vacancies - for instance in all the fast cooled NiAl samples and even in slow cooled samples of the off-stoichiometric alloys. In such cases, the loop growth rates slow down with time and eventually there is no more growth - this would be consistent with a supersaturation of thermal vacancies which is reduced to the equilibrium value as the annealing proceeds. But loop growth of a different kind has been found in the above samples after the initial loop growth has stopped and also in samples which had little or no retained thermal vacancies to start with. In these cases, as described earlier, loop growth is not due to quenched-in vacancies because the loop growth rates increase with time. Furthermore, the loops do not grow by vacancy replenishment from thicker areas of the sample because loops in thinnest regions of the samples (farthest away from the bulk areas) are the fastest growing loops. The thin area shown in Fig.28a for example lies farther away from the bulk regions of the sample than the thicker area shown in Fig.28c. The faster growth rates in thinner areas clearly implies that the rates are determined by proximity to the surface - direct evidence is also available from stereo images that loops closer to the surface grow faster. In addition, increasing the oxidation rates has been shown to increase loop growth rates. This above argument of Harris is therefore not applicable in the present case. The second argument of Harris pertaining to loop growth is that stresses induced by oxidation can sig-

nificantly affect loop growth rates. He proposes, for example, that the changes in the rate of vacancy loop growth in thin foils of Zn and Mg upon changing the annealing atmosphere is due to changes in the levels of the induced stresses. As pointed out earlier, these stresses are generated mainly because the Pilling-Bedworth ratio is usually different from unity. But again, the present results are not consistent with Harris's model. In proposing the stress model, Harris has considered the effect of a compressive stress induced by oxidation on loops normal to the plane of a thin foil. Clearly, as shown by him, such a compressive stress normal to the loop plane would encourage vacancy loop growth. But if loops were also present in this foil in orientations parallel to the foil plane, the same compressive stress system would have the opposite effect on these loops. Thus loops in different orientations would be affected differently. On the other hand, in the NiAl samples studied here, usually loops were found on all three {100} planes and during annealing no systematic differences were observed in the behavior of loops in the different orientations. Loops parallel to the foil plane were found to behave similarly to loops lying perpendicular to the foil plane. These observations rule out the possibility that stresses induced by oxidation are the determining force behind loop growth. Furthermore, Harris claims that when the annealing atmosphere is changed from vacuum to air, loop growth rates in Mg are increased because the Pilling-Bedworth ratio is less than unity whereas the opposite effect is seen in Zn because the ratio is greater than unity. In the present case of NiAl, Al_2O_3 is the oxide formed and the Pilling-Bedworth ratio is known to be greater than unity. Therefore, according to the model of Harris, an effect similar to that in Zn should be seen - i.e., increasing the oxygen partial pressure should decrease loop growth rates. But the effect observed was in fact the opposite (Fig.12). It must be concluded that the evidence for vacancy injection

obtained in this system is indeed valid.

Of course it must be conceded that Harris discussed these possibilities only in pure metals. He does say that vacancy injection is quite likely to occur during oxidation of alloys but he attributes that to selective oxidation of one constituent. This possibility now has to be considered in developing a mechanism for vacancy injection in NiAl. It is clear from the Auger experiments that the primary oxide formed is Al_2O_3 . There were some indications that some spinel (NiAl_2O_4) might be present as a thin intermediate layer by studying the fine structure on the LMM Auger spectra of Ni. But this could not be confirmed because the depth profile did not show the existence of a definite intermediate layer. (In this connection, it must be mentioned that in the course of similar experiments, Hutchings⁴¹ did find what seemed to be a definite intermediate layer during an Auger depth profile analysis. This intermediate layer seemed to have a composition close to that of the spinel NiAl_2O_4 . It is not understood why such a clear intermediate layer was seen by Hutchings but was not seen in the present work. It could very well be, that the continuous variation in composition seen in the intermediate region merely indicates the presence of a non-stoichiometric spinel with a range of compositions.) The bulk oxidation experiments also showed that a scale of Al_2O_3 is formed on these alloys and this scale seems to form by cation diffusion - i.e., the oxide grows by outward diffusion of Al ions. This is the major phenomenon that leads to the possibility of vacancy injection because diffusion of cations toward the oxide-oxygen interface means that a counter flow of vacancies will diffuse towards the metal-oxide interface. If vacancy injection were to take place, these vacancies in the oxide would appear in the substrate as metal vacancies.

The above evidence indeed indicates that this happens in oxidized NiAl

thin foils. However, it is necessary to determine whether the injection is due to selective oxidation of Al. A counterflow of vacancies due to selective oxidation of one element in an alloy is a well established phenomenon related to the Kirkendall effect, as pointed out by Harris.²⁰

In other words, initial formation of Al_2O_3 could deplete the surface regions of Al, and continued growth of Al_2O_3 would require the diffusion of Al atoms to the surface, which is most likely to happen by corresponding vacancy diffusion into the sample from the surface. These vacancies could then be a reason for loop growth.

On the other hand, vacancy injection may simply be due to the fact that injection due to oxidation might have caused a build-up of vacancies near the surface. A vacancy concentration gradient would therefore be set up and vacancies would start diffusing inward down this gradient causing growth of internal vacancy defects. This would be a more general mechanism for vacancy injection, not related to selective diffusion and oxidation of Al, and thus applicable to pure metals as well. It will now be shown that there are inconsistencies for both the above possible mechanisms for vacancy injection when comparing with experimental data.

Firstly, the more general possibility will be considered, that of injection being due to the development of a vacancy concentration gradient. Any proposed mechanism must be capable of explaining the acceleration of loop growth rates with time. It could be argued that as oxidation continues, more and more vacancies are formed at the substrate surface. (This could occur only if vacancy generation rates at the surface are higher than the rates of vacancy diffusion away from the surface. Such an assumption seems reasonable since the oxide layers in these initial stages are very thin.) As a result, the vacancy concentration gradient between the surface and the interior would increase with time, leading to increasing vacancy diffusion

rates and accelerating loop growth rates. The difficulty with this model is that it requires the retention of relatively high vacancy concentrations in solution in the surface regions of the alloy. If other vacancy sinks are present in these regions, any vacancies generated would quickly diffuse into these sinks and it would be very difficult to build up a high concentration of vacancies in solution. Indeed it is found in all the samples that interfacial voids are formed at the alloy surface at a very early stage. As seen earlier, the surfaces of the thin foils are covered by a uniform distribution of faceted voids which continue to grow (Figs.20-23). Douglass and his co-workers^{22,23} have suggested that the formation of such voids in alumina forming compounds, is related to the fact that the diffusivity of Ni is much higher than that of Al in their alloys. As a result, when a concentration gradient is set up by the selective oxidation of Al, Ni would diffuse into the sample and Al would diffuse towards the surface. Since Ni diffusion rates are much faster, the difference would be made up by diffusion of vacancies along with the Al atoms toward the surface. These vacancies, according to Douglass et al agglomerate at the interface to form voids. A problem with this model is that it requires large concentrations of vacancies to be initially present in the interior of these samples. Besides, it does not apply in the present case because internal vacancy defects have been found to grow at the same time as the interfacial voids grow (Fig.10). The vacancies involved in interfacial void growth therefore must be generated by oxidation. Since these voids are present at the surface of the alloy, they would act as excellent sinks for vacancies being generated and would prevent the development of a high vacancy supersaturation in the surface regions. Since vacancy sinks are present right at the surface, it is very unlikely that internal loop growth is due to the development of a vacancy concentration gradient and subsequent injection into the sample. The

possibility arises therefore that loop and internal void growth could be due to selective diffusion and oxidation of Al. But the growth of voids on the alloy surface cannot be due to selective diffusion of Al. It clearly seems to be associated with vacancies generated by the growth of the oxide by cation diffusion outward. The evidence indicates that Al ions diffuse through the oxide to the oxide-gas interface. A counter flow of vacancies occurs and leads to the formation of vacancies on the Al sublattice. However, from a knowledge of the defect structure of NiAl, it is clear that such a situation would be unstable. There would be a movement of Ni atoms on to the Al sublattice until the number of vacancies on both sublattices is equal. Equal numbers of Ni and Al vacancies would then be freed and these would form the interfacial voids. Harris²⁰ has defined vacancy injection as the reappearance of cation vacancies across the interface as metal vacancies. This is clearly happening in NiAl and if such a definition is followed, then vacancy injection indeed occurs in β -NiAl.

It remains to be understood why vacancies are injected into the interior of these alloys. The fact that growth of internal defects occurs due to a flux of vacancies from the surface shows that a counter-flow is set up between the central regions of a thin foil and its surfaces. If vacancies diffuse in, then metal atoms must diffuse out. It has been shown that as annealing is continued, vacancy diffusion rates into the sample are increased. It has also been shown that there is likely to be very little build-up of vacancies near the surface. The accelerating rates of loop growth can therefore only be explained on the basis of selective diffusion and oxidation of Al. The formation of Al_2O_3 could deplete Al in the surface layers. (Here again, it has to be assumed that diffusion in the alloy is slower than diffusion in the oxide layer - a plausible assumption if, as in this case, the oxide layer is only $\approx 100 \text{ \AA}$ thick.) Continued depletion of Al could

reach a stage where oxides of Ni start to form even at Al concentrations as high as 42 at.%⁴⁰ - this is presumably due to the fact that the activity of Al decreases by several orders of magnitude when the Al concentration is decreased by just a few percent in this composition range.⁶⁵ Therefore, in order for continued formation of Al_2O_3 , the surface depletion of Al has to be minimized by diffusion from the bulk. If Al atoms diffuse to the surface from the interior, a counter-flow of vacancies develops and leads to growth of internal vacancy defects. As this process continues, the vacancy concentration of the sample is gradually raised and it is very reasonable to assume that this would increase the diffusion rates of Al. The increasing rate of loop growth with time could then be attributed to the increasing diffusion rates in the alloy. This then implies that the growth of internal defects is due to the selective diffusion and oxidation of Al. The only problem here is that similar phenomena are observed in alloys of all three compositions tested here, whereas diffusion data available in the literature predict otherwise. According to the recent and fairly comprehensive work of Shankar and Seigle,²⁵ in Ni-rich compositions, the intrinsic diffusivity of Ni is about 3 times higher than that of Al, whereas Al diffuses faster than Ni in Al-rich alloys. This would imply that when concentration gradients are present, in Ni-rich alloys, Ni should be the dominant diffusing species whereas in Al-rich alloys, mainly Al should be diffusing. On the other hand, in the mechanism proposed above, it is suggested that internal vacancy defect growth in both Ni-rich and Al-rich alloys is due to the fact that Al alone is diffusing. There seems, therefore, to be a conflict between the mechanism proposed here and the diffusion data in the literature. It must be pointed out that the previous diffusion work was done on bulk specimens which did not have large defect concentrations present. On the other hand, the present experiments have been carried out using thin foil samples in which vacancies

are present in large numbers. It is conceivable that under these conditions, the diffusion characteristics are quite different from the bulk values. In other words, the tendency of oxidation to inject vacancies into the thin foils in large numbers might indeed enhance Al counter-diffusion to the extent that selective diffusion of Al could occur in all three alloy compositions studied here. In any case, a better understanding of these processes can only be obtained after studying alloys in a much wider composition range.

Before summarizing the various processes taking place during oxidation in these alloys, it remains to be explained why no vacancy injection occurs when the thin foils of the near-stoichiometric alloy are annealed in UHV at temperatures $>850^{\circ}\text{C}$ (Figs.16 and 17). In addition to the fact that internal defects continued to shrink as the annealing was continued, it was also found that interfacial voids were not formed in these thin foils. It seems clear from these observations, that the mechanism causing vacancy injection in all the other cases, is no longer operative at $T>850^{\circ}\text{C}$ in UHV. Auger analysis showed that the oxide layers on these samples were very similar to those formed on samples annealed in UHV at lower temperatures (Fig.31b) where vacancy injection does occur. It seems that there are no differences in compositions of the oxide formed. The explanation for the above observations therefore seems to be related to the oxidation mechanism itself. From all the other experiments, it is clear that an oxide forming by cation diffusion outwards through the oxide, injects large numbers of vacancies into the substrate. The fact that internal voids continuously shrink and that interfacial voids are not formed at all during annealing in UHV at $T>850^{\circ}\text{C}$, strongly implies that the oxide is forming by anion diffusion inward through the oxide. If the oxide were to form by diffusion of oxygen ions inward, all the oxide would be formed within the initial envelope of oxide formed. This would lead to compressive stresses being generated since the Pilling-Bedworth ratio

is greater than unity. These stresses could be relieved by vacancy flow into the oxide. Under such conditions, the oxide would therefore act as a sink rather than a source for vacancies thus explaining the above experimental observations. In order to test this hypothesis, an additional experiment was carried out (Fig.41). A sample from the slowly cooled near-stoichiometric alloy containing voids was first annealed for 4 hours in 10^{-5} torr oxygen at 700°C . As can be seen in Fig.41a, a large number of interfacial voids were formed as a result of this treatment. A continuous oxide layer has evidently formed on the surface by cation diffusion. This same sample was then annealed at 950°C in UHV. If under these conditions the system reverts to oxide formation by anion diffusion (as proposed above), then, in spite of the fact that a continuous oxide layer is already present, both internal and interfacial voids should shrink. It is clear from Fig.41 that this is precisely what happens. These observations can only be explained in terms of an oxide forming by anion diffusion. Evidently, a change in oxidation mechanism does take place when the temperature is raised beyond about 850°C and the pressure in the annealing chamber is $<10^{-8}$ torr. The reason for this mechanism change is not clear at this time, but is probably related to the fact that vacancy defects in these samples become very unstable at these high temperatures, especially because of the high diffusion rates. As a result, there is a very strong driving force for vacancy diffusion out of the samples. At the same time, since the oxygen partial pressure is extremely low, the driving force for oxidation would be quite low. Under these conditions, a strong tendency for vacancy movement outward would encourage a counter-flow of oxygen ions inward, even if oxygen ion diffusion is slower than Al ion diffusion in the oxide. The oxide would therefore form by anion diffusion. This would also explain why at these temperatures, the system reverts to cation diffusion when the oxygen pressure is raised (Fig.19) - in this case, the

Figure 41 Shrinkage of internal and interfacial voids in a sample from the near-stoichiometric alloy, when the sample was annealed at 950°C in UHV ($<10^{-8}$ torr). The annealing time in minutes are marked. The sample as shown in the first micrograph (at $t=0$), was previously annealed for 4 hours in 10^{-5} torr of oxygen, to introduce the large number of interfacial voids.

t=0

15m

40m

driving force for oxidation would be much larger and cation diffusion would be favored if, as seems to be the case, cation diffusion is faster in this oxide than anion diffusion.⁵³

The model proposed above to explain the various experimental observations made in the course of this work, can now be summarized. The processes taking place when thin foils of β -NiAl alloys containing vacancy defects, are annealed (at temperatures above about 600°C and oxygen partial pressures less than about 10^{-4} torr), can be listed as follows:

1. Initially, before a continuous oxide layer is formed, the surfaces act as vacancy sinks and vacancies diffuse from the interior to the surfaces.
2. As soon as a continuous oxide layer is formed, it prevents the surface from acting as a vacancy sink. The oxide forming is predominantly Al_2O_3 with a possible thin intermediate layer of the spinel and it grows by diffusion of metal ions, specifically Al ions, outward through the oxide, to react with the oxygen in the environment.
3. A counter flow of vacancies occurs from the oxide/gas interface towards the metal/oxide interface. These vacancies are injected into the substrate as metal vacancies.
4. Interfacial voids are formed at an early stage by agglomeration of these vacancies injected at the interface. They continue to grow as a result of the oxidation.
5. As oxidation proceeds, the surface is depleted of Al. Diffusion of Al from the interior to the surface occurs, to replenish the surface layers with Al. This outward diffusion of Al occurs by vacancy diffusion so that some of the vacancies in the surface regions are injected into the sample and cause loop and void growth.
6. Under certain conditions, namely during annealing in UHV at $T > 850^\circ\text{C}$, the mechanism of oxidation changes. Instead of forming by cation diffusion,

the oxide starts forming by anion diffusion. As a result, the oxide acts as a sink rather than a source for vacancies, and vacancy defects in the substrate continuously shrink as the oxidation continues.

The experiments in the present work have firmly established that vacancies are injected by oxidation into β -NiAl under conditions where the oxide grows by cation diffusion. Interfacial voids are formed from vacancies generated by outward flow of cations through the oxide. Internal vacancy defects also grow as a result of vacancy injection due to selective diffusion and oxidation of Al. It is not surprising that vacancies are generated during the growth of an oxide by cation diffusion. The interesting question is how these vacancies subsequently behave. As pointed out by Gibbs and Hales,⁶⁶ the question is of commercial importance because these vacancies could affect the system in a variety of ways. They could remain in supersaturated solid solution and influence the kinetics of oxidation. They could precipitate out as voids at the interface which could then affect the morphology and growth rate of the protective scale. Voidage at the interface could also lead to scale separation and loss of corrosion protection. But if void nucleation is difficult and the vacancies are forced to diffuse to internal defects, second phase particles or precipitates, it might be possible to maintain scale adhesion and protection for a longer period. At the same time, dislocations and grain boundaries might not be desirable sinks because if large numbers of vacancies are annihilated at these sites, the substrate would shrink in volume and might eventually pull away from the oxide, especially if the oxide is strong and brittle. Internal voids, and voids formed at second phase particles are better vacancy sinks since there would be very little dimensional change in the substrate if vacancies are annihilated at these sites. At any rate, it would be useful to know under what conditions injected vacancies can be made to diffuse to the more desirable sinks. Hutchings and Loretto,⁴⁰

have shown that NiAl samples with abraded surfaces exhibit better scale adherence than those with electropolished surfaces. This is presumably because the dislocations and other defects introduced by abrading the surface provide sinks for vacancies which might otherwise form interfacial voids. In accordance with this, they also found that the substrate below the spalled-off oxide in the electropolished samples, had an extensive network of voids. In the present work it has been found that the injected vacancies mostly agglomerate to form interfacial voids. It has been shown that internal voids nucleate with ease at impurity particles (Fig.26) and it is possible that the interfacial voids also nucleate very easily due to impurities present on the surfaces. Indeed, the Auger analysis of the thin foil samples (Fig.31) shows that the surfaces of these samples are contaminated with carbon during exposure to the electron beam during electron microscope observations. It is possible that interfacial voids are formed at a very early stage by vacancies agglomerating at these impurities on the thin foil surfaces. But even in oxidized bulk samples (not exposed to any electron beam), the entire substrate surface was found to be covered with voids (Fig. 38). Since these voids are formed so easily, it has not been possible to investigate whether existing internal defects are good sinks for vacancies. Internal vacancy defects have been found to grow but this seems to be due to selective diffusion and oxidation of Al. It is very likely that in alloys, this problem will always arise during oxidation. In the ultimate analysis, to determine whether injected vacancies diffuse deep into the sample in the absence of any selective oxidation of one component, detailed experiments similar to those carried out here, would have to be carried out on pure metals.

6. CONCLUSIONS

The present work has been aimed at investigating possible defect generation during surface oxidation of β -NiAl alloys. It has been shown that the results of a previous investigation, which were used to demonstrate vacancy injection due to oxidation, do not necessarily prove so, and in fact can be better explained on the basis of retention of thermal vacancies. At the same time, through experiments on samples with little or no supersaturation of thermal vacancies, it has been shown that oxidation (even during high vacuum annealing) does inject vacancies into the three Ni-Al alloys (in the 47.5 - 52.5 at.% Al range) studied here. This process occurs at temperatures above roughly 600°C, 650°C and 700°C for the Al-rich, Ni-rich and near-stoichiometric alloys respectively. The vacancies seem to be generated as a counter flow to cations diffusing outward during the growth of the oxide. The oxide formed is predominantly Al_2O_3 with a possible thin layer of a spinel being present between the metal and the Al_2O_3 . Contrary to previous studies on alumina forming compounds where the alumina was found to grow into the substrate by oxygen diffusion, the alumina formed on these alloys, under most conditions seems to grow outward, presumably by diffusion of Al ions. (This was evident from the bulk oxidation experiments.) The outward diffusion of cations leads to a diffusion of cation vacancies inward from the oxide-gas interface. These cation vacancies in the oxide appear on the other side of the interface as metal vacancies. As a result of this vacancy injection, faceted voids are formed at the surface of the alloy substrate and grow as the annealing is continued. At the same time internal vacancy dislocation loops and voids are also found to grow during the oxidation of thin foils. Higher rates of loop growth were observed for loops closer to the foil surfaces and also for samples annealed in higher partial

pressures of oxygen. Loop growth rates were found to increase with time. It has thus been confirmed that both interfacial voids and internal vacancy defects grow as a result of oxidation. A large number of the vacancies generated, diffuse to the interfacial voids nearby, but some of the vacancies diffuse to the internal loops and voids, presumably to provide a counter-flow for Al atoms diffusing outward. It is suggested that this Al diffusion from the interior to the surfaces, occurs in order to replenish the Al content of surface layers which have been depleted of Al by the formation of the Al-rich oxide.

The vacancy injection process takes place in near-stoichiometric NiAl at all temperatures above about 700°C when the annealing is carried out in the presence of some oxygen. But in the samples annealed in UHV ($<10^{-8}$ torr), vacancy injection takes place only at temperatures below about 800°C. At $T > 850^{\circ}\text{C}$ in UHV, it is proposed that the oxide formation mechanism changes from cation diffusion to anion diffusion. Internal vacancy defects and even interfacial voids continuously shrink, rather than grow, in samples annealed under these conditions.

During the course of this work, it was also noticed that thermal vacancies can easily be retained in large numbers in these alloys. From quenching and ageing experiments and using electron microscopy, a value of 1.45 ± 0.2 eV has been obtained for the energy of formation of a pair of vacancies - one on each sublattice. While only an approximate value could be obtained for the vacancy formation energy, it is felt that this still is a better estimation than those of previous investigators. Thus, as previously proposed, the vacancy formation energy is indeed fairly low and large numbers of thermal vacancies (upto about 2%) can be retained during cooling since the oxide is impervious to vacancies. In fact, as shown in this work, the oxide not only acts as a barrier for vacancies diffusing to the surface, but itself acts as another source of vacancies.

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