Ni₈X Phases in the Systems Ni-V, Ni-V-Nb, and Ni-V-Ta

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In nickel-base alloys at the composition Ni_8X, where "X" may be combinations of V, Nb, and Ta, the ordering reactions have been investigated by employing electrical resistivity and electron diffraction techniques. The critical temperature for the order-disorder reaction is estimated to be 405°C for Ni_8V and is shown to decrease linearly with increasing vanadium content across the pseudo-binary sections Ni_8Nb-Ni_8V and Ni_8Ta-Ni_8V, in agreement with calculations based upon the Bragg-Williams model. A secondary ordering reaction between V and Nb atoms has been observed in nickel-base alloys at the composition $Ni_8(V_{0.5}Nb_{0.5})$.

1. Introduction

Recent investigations of phase-transformations in alloys of nickel with two of the elements in group V of the periodic table have led to the discovery of the ordered phases Ni_8Nb [1] and Ni_8Ta [2]. The frequent similarities observed in the phase-diagrams between elements of the same periodic group suggest that the ordered phase, Ni_8V, may exist when vanadium is alloyed with nickel. The Ni-rich portion of the binary phase diagrams for Ni with Ta, Nb, and V, as presented by Pearson [3], exhibit several similarities. The solid solubility, as reported in the absence of the Ni_8X phases, extends to several at. % and at 25 at. % solute each of these systems forms an ordered Ni_3X phase. The solid solubility range and the melting points of the Ni_3X phases correlate with the atomic size factors, as shown by Pearson and Hume-Rothery [4]. These correlations between the respective phase-diagrams provide a basis for predicting the existence of the Ni_8V phase.

Rudman [5] has considered the effects of the atomic size factor upon the existence of ordered phases. His arguments show that in alloys containing atomic species of different size it is not possible to account for the existence of ordered phases on the basis of size effects alone; furthermore, a negative enthalpy of mixing is required if the ordered phases are to exist. The atomic size factor will determine the "visibility" of the phase, so that systems with large atom size differences are expected to exhibit ordered phases that are stable up to high temperatures and extend over a wide range of composition. When these arguments are applied to the Ni-V system, an ordered phase such as Ni_8V may form, but it is deduced that the "visibility" of such a phase should be low.

It has been shown [1, 2] that electron diffraction and electrical resistivity measurements are sensitive techniques for the study of the Ni_8X phases. The present investigation has employed these techniques to determine whether or not the Ni_8V phase exists. The atomic diameters of V, Ta, and Nb are markedly different from that of Ni, but these elements exhibit similar alloying behaviour when combined with nickel [3]. Under these conditions an order-disorder reaction might occur in ternary nickel-base alloys of the type Ni_8X where X is a combination of V with either Nb or Ta.

2. Experimental Procedure and Results

Several alloys of the Ni_8X composition were prepared by levitation-melting, using 99.7% purity vanadium, niobium and tantalum of 99.99+ % purity, and nickel 270 tubing which has a purity of 99.97%. The charges were 6 to 8 g total weight, and the amount of each constituent was weighed to 0.001 g. In order to melt each by levitation, the lump vanadium and pieces of Nb or Ta sheet were enclosed in capsules fabricated from the nickel tubing. The alloy charges were then levitation-melted in a purified He atmosphere without contamination or weight

loss. The levitated alloys were chill-cast into buttons and subsequently cold rolled to sheet about 0.5 mm thick. Specimens cut from this sheet were then solution heat-treated under purified helium at 1300°C for $\frac{1}{2}$ h and quenched in 10% NaOH.

The lattice parameters of the various alloys were determined by diffractometry, using CuKα radiation. The value of the lattice parameter computed from each peak was plotted as a function of the Nelson and Riley parameter [6]. The final value of the lattice parameter for each alloy was determined by extrapolating a least-squares fit of these data to $2\theta = 180°$. Fig. 1 presents the lattice parameter for these alloys plotted as a function of alloy composition and shows the values predicted according to the method of Moreen *et al* [7]. The close correlations between the predicted lattice parameter values and the corresponding value determined by experiment, indicate that the alloy compositions used in this study were accurate to within 0.1 at. % of the original verified composition.
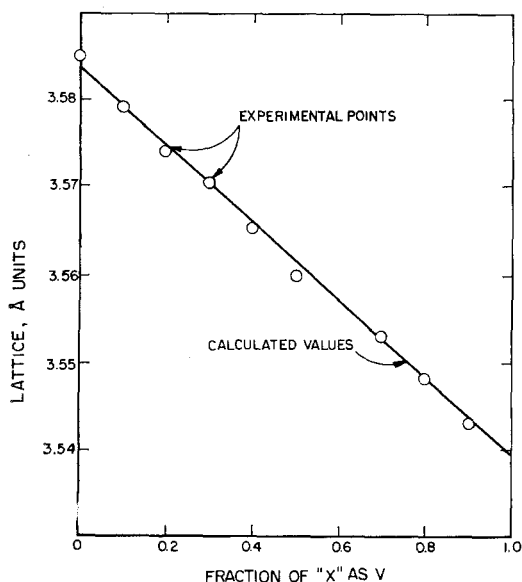

Figure 1 Lattice parameters of ternary Ni$_8$X alloys.

The specimens used for electron microscopy and electrical resistivity were aged in molten salt at temperatures ranging from 250 to 400°C for times ranging from 66 h at 400°C to 1100 h at 250°C. The aged alloys were examined by electron diffraction in a JEM-7 electron microscope equipped with a 7° tilt-360° rotation stage.

The electron diffraction patterns of a number of specimens contained numerous superlattice spots as shown in fig. 2. The specimens which did not exhibit superlattice spots corresponded to the alloys with vanadium contents greater than that in the Ni$_8$(Nb$_{0.4}$V$_{0.6}$) composition for Ni-V-Nb alloys or the Ni$_8$(Ta$_{0.5}$V$_{0.5}$) composition for the Ni-V-Ta alloys. The Ni$_8$(Nb$_{0.5}$V$_{0.5}$) composition after ageing at 300°C for 250 h plus 350°C for 525 h exhibited additional superlattice reflections, as shown in fig. 3. Dark field microscopy on the superlattice reflections could not resolve the individual ordered domains, indicating that the size of the domains is less than 50Å.

Elevated temperature electrical resistivity measurements were also performed on the aged alloys to determine the existence of ordering and to determine the order-disorder temperature [8]. The temperature and the potential drop across each specimen were recorded alternately every 30 sec while the resistivity specimens were heated *in vacuo* over the temperature range 250 to 650°C at a rate of 20°C/h. An example of the data obtained in this manner is shown in fig. 4. The potential drop was measured during the heating of specimens which had been aged and were thus expected to be partially ordered. After the disordered condition had been established by heating, the potential drop was again measured during the cooling cycle. (The cooling was too fast to allow order to be re-established.) A resistivity ratio was determined for specific temperatures by dividing the potential drop on heating by the corresponding potential drop obtained during cooling. The resistivity ratio data from the aged Ni-Nb-V alloys are presented in fig. 5, and the data from the Ni-Ta-V alloys are presented in fig. 6.

Elevated temperature electrical resistivity ratio values have also been measured in the same manner for several of the ternary Ni-Nb-V alloys in which the resistivity specimens were gas-cooled from 1300 to 600°C in 10 to 15 sec and then quenched to room temperature. These alloys were aged at 300°C for periods ranging from 66 to 300 h after quenching and prior to the resistivity measurements. The alloys which received this delayed quench exhibited a linear temperature dependence of resistivity, and no abrupt change of slope such as that shown in fig. 4.

The progress of the ordering reaction in several Ni-Nb-V alloys has been studied by measuring the electrical resistance at liquid nitrogen
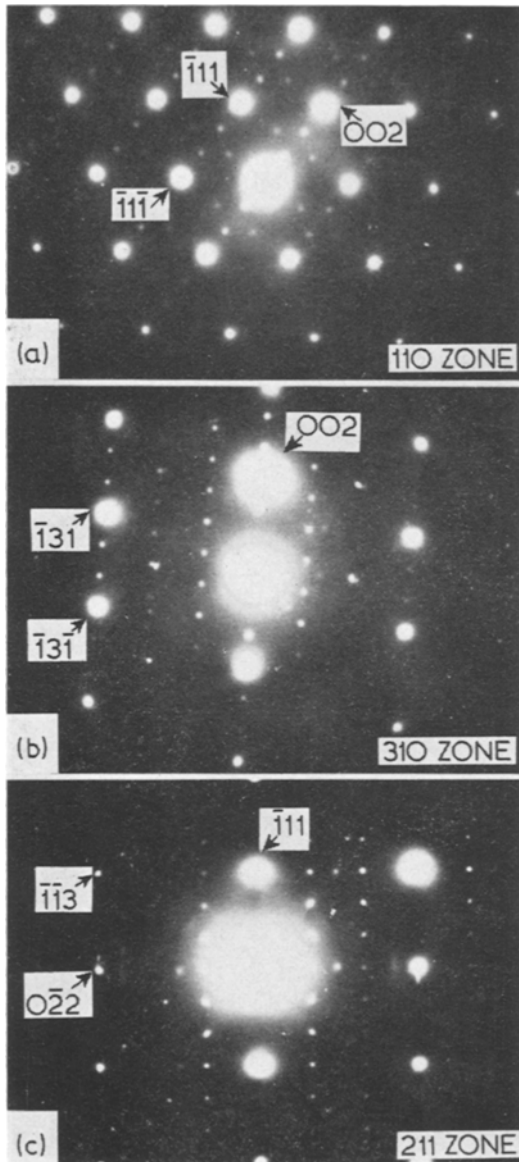
Figure 2 Electron diffraction patterns of aged Ni₈V alloys.

Figure 3 Electron diffraction patterns of Ni₈(Nb₀.₅V₀.₅) alloy aged 250 h at 300°C and 525 h at 350°C.

temperature after ageing for successive increments of time at 300°C. The ratio of the resistivity of an aged specimen to that of an as-quenched specimen is plotted in fig. 7 for several ternary compositions ranging from Ni₈Nb to Ni₈V. At any given time, the decrease in the resistivity ratio increased in magnitude with an increase in the niobium content of the alloy. The only exception to this behaviour was the alloy with the composition Ni₈(Nb₀.₅V₀.₅) in which the decrease of resistivity was somewhat more rapid than that in the Ni₈(Nb₀.₆V₀.₄) alloy.

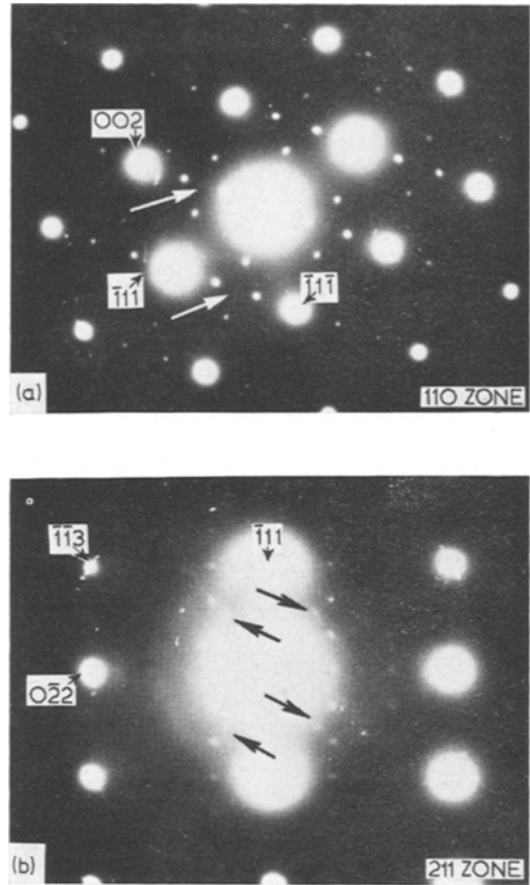## 3. Discussion of the Results

3.1. The Order-Disorder Reaction

The elevated temperature electrical resistivity results shown in figs. 5 and 6 are characteristic of the behaviour expected when an order-disorder reaction occurs. The existence of an ordered structure in aged Ni-Nb-V alloys is confirmed by the superlattice spots in the electron diffraction patterns of fig. 2. These electron diffraction patterns are identical to those reported for ordered phases of the type Ni₈X in the Ni-Nb and Ni-Ta systems [1, 2]. The unit cell of the Ni₈X structure can be described as fct comprising three multiples of the fcc lattice in the a dimension and one unit cell in the c direction. Three variants of the ordered phase form in the fcc matrix, with the following crystallographic relationship:
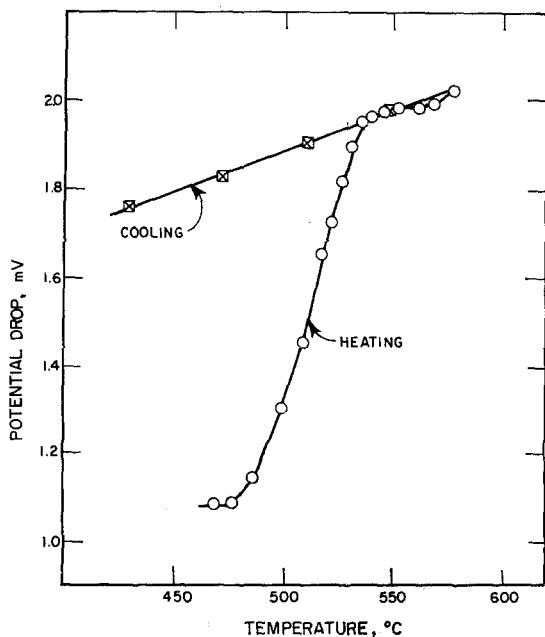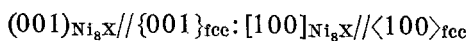
Figure 4 High temperature electrical resistivity data from Ni$_8$Nb alloy.

Figure 5 Electrical resistivity ratio data of aged Ni-Nb-V alloys. Arrows indicate temperature of deviation from a ratio of 1.00.

$(001)_{Ni_8X}//\{001\}_{fcc}: [100]_{Ni_8X}//\langle100\rangle_{fcc}$

In the ternary alloys of composition Ni$_8$X with vanadium contents greater than that of the Ni$_8$(Nb$_{0.6}$V$_{0.4}$) composition, the electron diffraction results did not show the existence of the fc tetragonal ordered structure. This apparent anomaly is attributed to two separate causes. First, because of the close proximity of Ni and V in the periodic table, the atomic scattering factors of Ni and V are quite similar, and a very weak intensity is expected for the superlattice reflections under the most favourable diffraction conditions. In addition, the degree of order which has been attained in vanadium-rich alloys appears to be quite low, as evidenced by the relatively small change in the resistivity ratio shown in figs. 5 and 6 at the critical temperature. The reasons for this low degree of order will be considered in more detail below. The combined effect of these two factors is to reduce the intensity of any superlattice reflections from the ordered phase below the limits of detection in ternary alloys rich in vanadium.

It was not possible to resolve a domain structure in the aged alloys by means of dark field electron microscopy, indicating that the actual domain size is smaller than the limit of resolution of the electron microscope, which is
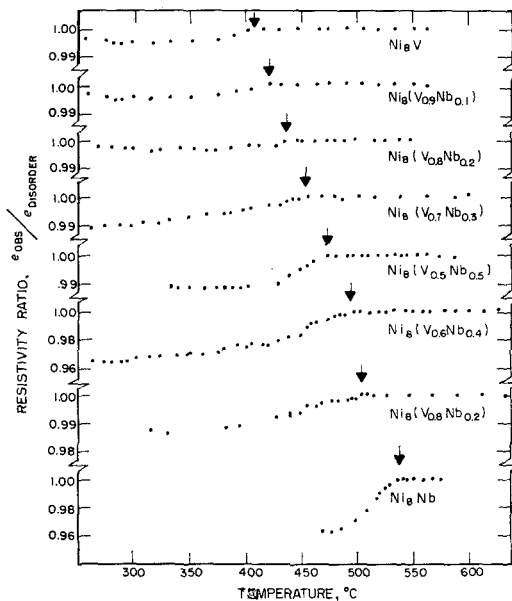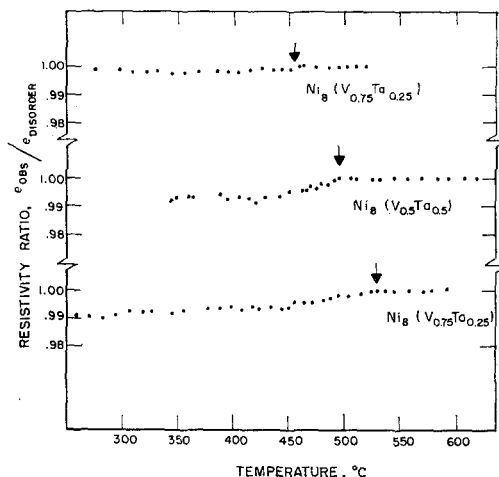

Figure 6 Electrical resistivity ratio data of aged Ni-Ta-V alloys. Arrows indicate temperature of deviation from a ratio of 1.00.

about 50Å. In ternary alloys, which have been aged at 300°C, a domain size of less than 50Å is comparable to the domain size reported for Ni$_8$Ta alloys after a similar treatment [2].

The curves shown in figs. 5 and 6 indicate that the discontinuity corresponding to the breakdown of long-range order is less resolvable as the vanadium content of a ternary alloy is increased. This observation is consistent with the expecta-

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tion that a lower degree of order is present in the vanadium rich alloys, as evidenced by the absence of superlattice reflections in the electron diffraction patterns. Fig. 7 shows that the rate of ordering, as indicated by the relative decrease in resistivity as a function of time, is very slow at the binary Ni_8V composition and increases with increasing niobium content in ternary alloys. On
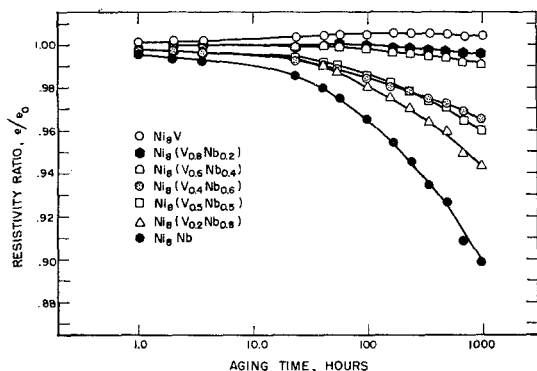

Figure 7 Electrical resistivity change in Ni-Nb-V alloys aged isothermally at 300° C.

the basis of these observations it is impossible to attain more than a very limited degree of order in the binary composition Ni_8V. This kinetic effect can be explained by considering the major factors affecting ordering at the composition Ni_8V. First, it is evident from figs. 5 and 6 that the critical temperature for ordering in the composition Ni_8V is lower than that of the other Ni_8X phases, and therefore at a given ageing temperature the amount of supercooling below the critical temperature will be less as the vanadium content in the ternary alloy is increased. An attempt to increase the extent of supercooling by lowering the ageing temperature is self-defeating because of the inherent reduction in atomic mobility. Secondly, the ordering energy for the Ni_8V composition is expected to be lower than that of either the Ni_8Nb or Ni_8Ta compositions because of the smaller size differences between the Ni and V atoms, only 0.09Å, compared to a difference of 0.18Å between Ni and either Nb or Ta. Thus, the volume free energy difference or driving force characteristic of a specific amount of undercooling will be reduced for the Ni_8V composition.

The elevated temperature resistance measurements on the specimens which received the interrupted quench show that no measurable

ordering has occurred in these specimens. It has been shown [2, 9] that the formation of Ni_8Nb and Ni_8Ta is sensitive to the quench-rate and that a rapid quench in 10% NaOH is essential for measurable rates of ordering in these alloys. It is evident that the ternary compositions also require a "hard" quench if they are to exhibit measurable reaction rates.

3.2. Composition-Dependence of the Critical Temperature

The dependence of the critical temperature for the ordering reaction on the alloy composition is shown in fig. 8 for Ni-Nb-V and Ni-Ta-V ternary alloys. Both the Ni_8V-Ni_8Nb and Ni_8V-Ni_8Ta pseudo-binary reactions exhibit a linear dependence of the critical temperature with vanadium content. On the basis of the high temperature electrical resistivity results shown in curve A of fig. 5, and by extrapolation of the linear composition dependence of the critical temperature in fig. 8, the critical temperature of the Ni_8V composition is estimated as 405°C.
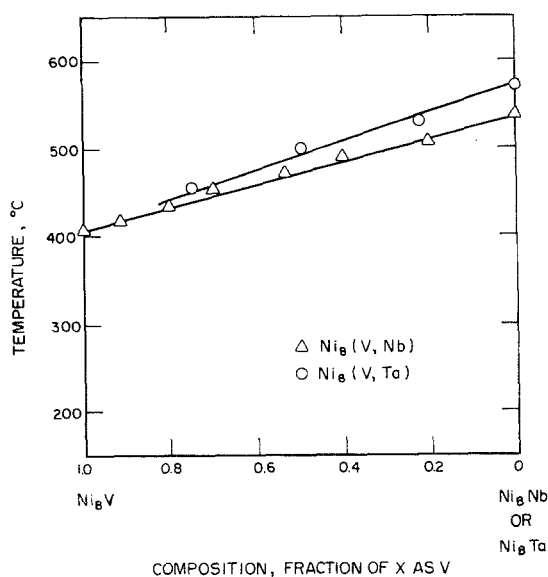

Figure 8 Composition dependence of the order-disorder critical temperature for Ni_8X phases.

The critical temperature for the ordering reaction in ternary alloys has been calculated from a development of the Bragg-Williams analysis [10] as detailed in the appendix. The dependence of the critical temperature, θ on the

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alloy composition is given by equation 8 of the appendix,

$$\theta = \frac{N}{2}\frac{Z}{k}\sum_i\sum_j\sum_k c_i\,c_j\,V_{ijk}[1 - f_{ij}\,g_{ijk}]$$

The f_{ij} and g_{ijk} factors in equation (8) can be derived from a knowledge of the stoichiometry and the structure of the Ni_8X phase. The coordination numbers for the various shells are also readily obtained from the structure. Unfortunately, the pair-wise interaction energy terms, V_{ijk}, cannot be evaluated. However, for each of these factors it is basic to the pair-wise interaction model that these terms depend only upon the identity of the two atoms of the pair and are independent of the surroundings [11]. Since all of the alloys used in the present study are of the general composition Ni_8X, c_{Ni} is constant, and $c_V = 1/9 - c_{Nb}$. Accordingly, equation (8) is linear with respect to the concentration of vanadium. This concentration dependence agrees with the experimental relationship shown in fig. 8, and substantiates a linear extrapolation to determine the critical temperature of the Ni_8V composition.

Rudman [5] has argued that consideration of only the atomic size factor is insufficient to account for the existence of ordered phases. An examination of the effects on ordering of differences in the atomic sizes of Ni, Nb, Ta, and V shows that Rudman's analysis is consistent with the conditions accompanying the formation of Ni_8X phases. The atomic radii of the atoms as given by Pearson [3] are: Ni = 1.24Å, V = 1.33 Å, Nb and Ta = 1.42 Å. These values lead to a misfit of V in a Ni matrix of 0.09Å and of Nb or Ta in Ni of 0.18Å. As shown by the Bragg-Williams analysis and by fig. 8, the composition-dependence of the critical temperature is linear and decreases to 405°C at the Ni_8V composition. A consideration of the atom size values together with the results of the present investigation point to the fact that differing size factors are not the only parameters determining the stability of Ni_8X ordered phases. By adding vanadium to reduce the atomic misfit by one-half, the critical temperature is lowered less than 200°C, suggesting that electronic factors must also assume an important role in the reaction. The differences in the critical temperatures of Ni_8Nb and Ni_8Ta must also be attributed to chemical interactions since both solute species have identical atomic sizes.

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3.3. Ordering at the $Ni_8(Nb_{0.5}V_{0.5})$ Composition

The extra set of superlattice spots in fig. 3 has been identified with a secondary ordering effect involving only the vanadium and niobium atoms. The unit cell of the resulting structure is shown in fig. 9, together with the unit cell of the Ni_8Nb structure which has been included for comparison purposes. The new structure can be formed from the Ni_8Nb type structure if secondary ordering of the Nb and V atoms occurs along the direction of their closest approach.
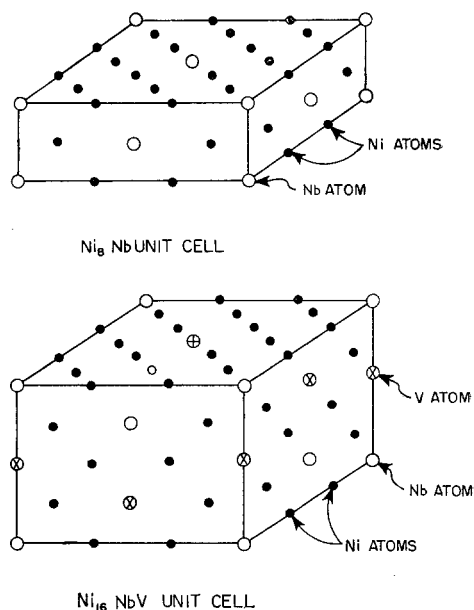

Ni_8 Nb UNIT CELL

Ni_{16} NbV UNIT CELL

Figure 9 Proposed unit cell for the $Ni_{16}NbV$ crystal structure.

The low intensity of the new superlattice spots is attributed to the difficulty in achieving a perfectly ordered arrangement of the V and Nb atoms with respect to one another and with respect to the nickel atoms. Since the atomic scattering factors of Ni and V are quite similar, it can be argued that the intensity of these new spots, which is proportional to $(f_{Nb} - f_V)$, should be comparable with the intensity of the Ni_8X superlattice spots, which is proportional to $(f_{Nb} - f_{Ni})$. However, if the perfection in the degree of order between Ni sites and the "X" sites is considerably greater than that for the distribution of the Nb and V atoms between the alternate X sites, then the observed disparity in intensities is to be expected. The relatively

sluggish kinetics for the secondary ordering reaction can be explained in terms of the structure of the ordered phase and the atomic size differences of the species involved. The formation of the Ni$_8$X structure must be considered as an intermediate step in a ternary alloy where X represents both V and Nb. In this case the size difference between Ni and the X atoms is significantly larger than that between V and Nb. The driving force for the ordering of Nb and V cannot include pair-wise bond energies for nearest neighbour positions, since the ordered arrangement of nickel is unchanged by the secondary reaction; therefore, only second, fifth, or higher order neighbours can be involved [12]. In view of these considerations, the driving force for this secondary ordering should be quite low, leading to sluggish reaction rates. Accordingly, the isothermal resistivity data plotted in fig. 7 show only a slight increase in the rate of ordering of the Ni$_8$(Nb$_{0.5}$V$_{0.5}$) composition in comparison with that of the Ni$_8$(Nb$_{0.4}$V$_{0.6}$) and Ni$_8$(Nb$_{0.6}$V$_{0.4}$) compositions.

No secondary ordering was observed at the composition Ni$_8$(Ta$_{0.5}$V$_{0.5}$). It has been shown [2] that the kinetics of Ni$_8$Ta formation are slower than for Ni$_8$Nb, an observation that accounts for the apparent absence of secondary ordering of the Ta and V atoms even after prolonged ageing. At the composition Ni$_8$(Ta$_{0.5}$Nb$_{0.5}$) there is little reason to expect that secondary ordering should occur in view of the identical sizes of Ta and Nb.

4. Conclusions

1. Ordered phases with a structure similar to the prototype Ni$_8$Nb have been identified in ternary alloys with a variety of compositions of the types Ni$_8$(Nb, V) and Ni$_8$(Ta, V).
2. The ternary Ni$_8$X phases show a linear dependence of the order-disorder critical temperature on composition, and this is in agreement with calculations based upon the Bragg-Williams analysis.
3. A secondary ordering reaction has been detected in alloys at the composition Ni$_8$(V$_{0.5}$Nb$_{0.5}$).

Acknowledgement

Appendix
The Composition-Dependence of the Order-Disorder Critical Temperature

The Bragg-Williams analysis [10] has been applied to ternary alloys in order to evaluate the composition dependence of the order-disorder critical temperature. According to Bragg and Williams, the critical temerature, θ, is

$$\theta = ZV/k \qquad (1)$$

where Z is the co-ordination number, V is the energy of ordering, and k is the Boltzmann constant. If a multicomponent system is considered where the concentration of the component is c_i, and the average bond energy about the ith atom is V_i^{ave}, the energy of the system is

$$V^s = \sum \tfrac{1}{2} N c_i \, V_i^{ave} \qquad (2)$$

where N is the number of atoms. Assuming the usual pair-wise bond energy, i.e., that the bond energy between two atoms depends upon the identity of the atoms and is independent of all other atoms in the neighbourhood,

$$V_i^{ave} = \sum_j \sum_k P_{jk} \, V_{ijk} \qquad (3)$$

where P_{jk} is the probability of encountering an atom of the j species in the kth nearest neighbour shell, and V_{ijk} is the bond energy between the i atom and a j atom in the kth shell. Substituting (3) into (2)

$$V = \frac{N}{2} \sum_i \sum_j \sum_k c_i \, P_{jk} \, V_{ijk} \qquad (4)$$

Then

$$V = \frac{N}{2} \sum_i \sum_j \sum_k c_i \, V_{ijk} \, [P_{jk}^r - P_{jk}^o] \qquad (5)$$

where the superscripts r and o refer to the randomly disordered state and the ordered state respectively. Combining (5) with (1)

$$\theta = \frac{N}{2} \frac{Z}{k} \sum_i \sum_j \sum_k c_i \, V_{ijk} \, [P_{jk}^r - P_{jk}^o]$$

$$\dots \dots (6)$$

Now for a randomly disordered alloy, the probability of locating a given type of atom at any lattice site is equal to the atomic concentration of that species, $P_{jk}^r = c_j$. In a fully ordered alloy this probability is given by

$$P_{jk}^o = g_{ijk} f_{ij} c_j \qquad (7)$$

where g_{ijk} is a geometric factor relating the

probability of finding a j atom in the kth shell about an i atom, and f_{ij} relates the concentration in the stoichiometric ordered phase. Substituting and rearranging

$$\theta = \frac{N}{2} \frac{Z}{k} \sum_i \sum_j \sum_k c_i \, c_j \, V_{ijk} \, [1 - f_{ij} \, g_{ijk}]$$

$$\ldots \ldots (8)$$

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