

# The effect of vanadium additions on the precipitation behaviour of Ni–Co–Cr–Nb alloys

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Four Ni–Co–Cr–Nb–V alloys containing varying amounts of vanadium were solution treated and then aged at 923, 1023 and 1123 K for various lengths of time. The structure of the solution treated alloys was single phase fcc. The presence of 1 wt % vanadium was adequate to promote the formation of metastable  $\gamma''$  phase with a  $DO_{22}$  type of ordered bct structure. An increase in ageing time and temperature, and a decrease in the vanadium/niobium ratio caused an increased amount of stable  $\beta$  phase, with a  $Cu_3Ti$ -type orthorhombic structure, to precipitate. The precipitation of the metastable phase  $\gamma''$  has been explained in terms of the Engel–Brewer correlation.

## 1. Introduction

Many nickel-based superalloys are strengthened by the precipitation of ordered cubic ( $L1_2$ )  $\gamma'$  phase and ordered tetragonal ( $DO_{22}$ )  $\gamma''$  phase [1–3]. These phases are  $Ni_3X$ -type compounds where X represents the solute atom, such as Ti, Al, Nb. The  $\gamma'$  phase forms coherently either as small spherical or cubic precipitates in the fcc matrix ( $\gamma$ ) such that  $\{100\}\gamma' \parallel \{100\}\gamma$ . The  $\gamma''$  phase precipitates coherently as small disc-shaped particles on  $\{100\}\gamma$  planes with  $[001]\gamma'' \parallel \langle 100 \rangle \gamma$ .

In alloys containing about 39 wt % nickel, 39 wt % cobalt, 17 wt % chromium and 3 to 8 wt % niobium, only the equilibrium phase  $\beta$ - $Ni_3Nb$  with  $Cu_3Ti$ -type orthorhombic structure has been observed [4]. None of the two metastable phases has been found. However, addition of elements aluminium and iron to these alloys causes precipitation of metastable phases  $\gamma'$  and  $\gamma''$  [5–7]. Such behaviour has generally been attributed to the electronic contribution from the alloying elements and their influence on lattice misfits [6–8]. Vanadium is a bcc element like niobium and both

belong to the same periodic group. Vanadium, therefore, appears unlikely to be effective in promoting the formation of the metastable phases,  $\gamma'$  or  $\gamma''$ . However, vanadium does form a stable compound,  $Ni_3V$ , having a  $\gamma''$ -type structure in the nickel–vanadium system [9, 10]. Also small additions of niobium to nickel–vanadium alloys modify the mechanism of formation of  $Ni_3V$  from continuous ordering to discontinuous precipitation [10]. Therefore, in this investigation the influence of the addition of various amounts of vanadium on the precipitation behaviour of Ni–Co–Cr–Nb alloys has been examined.

## 2. Material and experimental techniques

The compositions of the alloys examined in this investigation are given in Table I. These alloys were made in an induction melting furnace under an argon atmosphere using 99.99% pure alloying elements except niobium whose purity was 99.95%. The melts were cast and homogenized for three days at 1423 K in an argon atmosphere and cold swaged with frequent intermediate anneals at 1423 K. The swaged rods were cold

TABLE I Composition of alloys

	Alloy I		Alloy II		Alloy III		Alloy IV	
	(wt%)	(at%)	(wt%)	(at%)	(wt%)	(at%)	(wt%)	(at%)
Ni	38	38.4	37.2	37.5	35.9	36.0	34.9	34.9
Co	38	38.2	37.2	37.3	35.9	35.9	34.9	34.8
Cr	15	17.1	14.6	16.1	14.2	16.1	14.2	16.0
Nb	8	5.1	8.0	5.1	8.0	5.1	8.0	5.1
V	1	1.2	3.0	3.5	6.0	6.9	8.0	9.2
V/Nb	—	0.23	—	0.68	—	1.35	—	1.8

rolled to 1.0 mm and 125  $\mu\text{m}$  thick strips. The former was used for the hardness measurements whereas the latter was used for the thin foil electron microscopic examination. The foils were prepared by the electrolytic polishing technique using a 5% perchloric acid-methanol bath at 12 V and at 223 to 233 K. All heat treatments were carried out in argon-filled Vycor capsules and were terminated by rapid quenching in water.

The specimens were solution treated at 1423 K, water quenched and then aged at 923, 1023 and 1123 K for various lengths of time. The ageing kinetics were followed by hardness measurements and structural studies were conducted by transmission electron microscopy (TEM) techniques.

### 3. Results

#### 3.1. Ageing kinetics

The variation in hardness with ageing time for all the four alloys at various ageing temperatures is shown in Figs. 1a and b. At the ageing temperature of 1123 K the maximum hardness increase for alloys I, II, III and IV is seen to be 73, 81, 93 and 100% respectively. At the ageing temperature of 1023 K the ageing curve of alloy IV seems to reach a plateau after an initial hardness increase of 60% and before continuing to increase further. Such behaviour suggests the possible presence of a two-stage precipitation process. To demonstrate the influence of vanadium addition on the hardness ageing data of these alloys the ageing curve of a vanadium-free 8 wt% niobium, 38 wt% cobalt, 37 wt% nickel, 17 wt% chromium alloy, published earlier [4], is reproduced in Fig. 1c. Although the ageing was done at 973, 1073 and 1233 K, the effect of the absence of vanadium is apparent.

#### 3.2. Microstructures

The structure of the solution treated specimens of all the four alloys was single phase fcc. The lattice parameter of alloy IV was determined by X-ray diffractometry to be 0.3594 nm. Compari-

son of this value with the lattice parameters of the alloy containing 37 wt% nickel, 38 wt% cobalt, 17 wt% chromium and 8 wt% niobium ( $a = 0.3556 \text{ nm}$ ) [4] and of the  $\gamma''$  phase ( $a \approx 0.3600 \text{ nm}$ ) [7] suggests that addition of vanadium tends to increase the lattice parameter of the matrix and reduces the mismatch with  $\gamma''$ .

During the early stages of ageing of alloy IV at 923 K discrete precipitate particles were not observed but their presence was indicated by the selected area diffraction pattern (SADP). An example is shown in Fig. 2a which is the structure of a specimen aged for 1 h at 923 K. Its SADP is illustrated in Fig. 2b. The analysis of the diffraction pattern suggests that the thin foil orientation is  $[001]$ , and the superlattice reflection spots are due to the existence of a disc-shaped ordered b c t,  $\text{DO}_{22}$  phase, on the  $\{100\}$  matrix planes with the  $c$ -axis parallel to the  $\langle 100 \rangle$  matrix direction as has been observed in several other nickel-based alloys [6–8, 11]. The mottled surface observed in Fig. 2a can be attributed to the coherency strains around  $\gamma''$  precipitate particles which are too small to be resolved in the dark field. The specimen did not reveal the presence of any other type of precipitate, but stacking faults were present. These stacking faults did not have any precipitate particles associated with them.

The effect of increasing the ageing temperature was to increase the rate of precipitation appreciably as demonstrated by the microstructure of a specimen aged for 1 h at 1123 K in Fig. 3. Although discrete  $\gamma''$  precipitate particles are not observed their presence was confirmed by electron diffraction analysis. This figure shows that in addition to  $\gamma''$ , lath-shaped precipitates and stacking faults are also present in this specimen. The lath-shaped precipitates were identified with the help of diffraction patterns as equilibrium orthorhombic  $\beta$  phases which formed on the  $\{111\}$  matrix planes. No precipitate was observed in association with the stacking faults. The microstructure of the

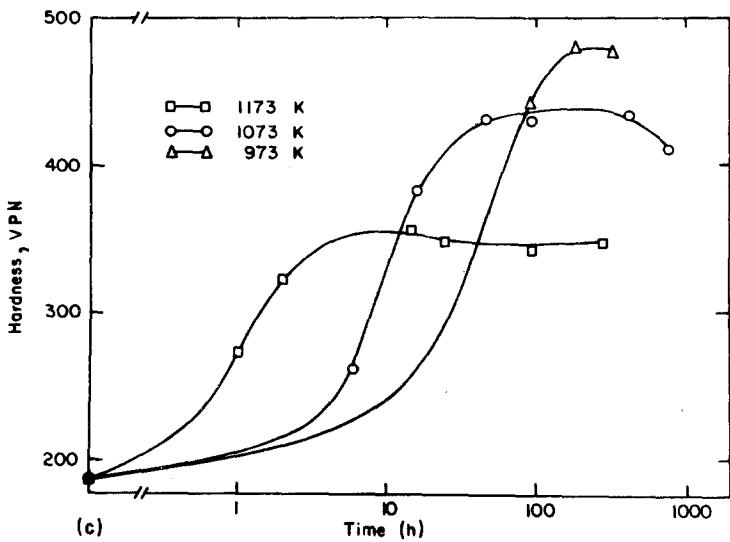
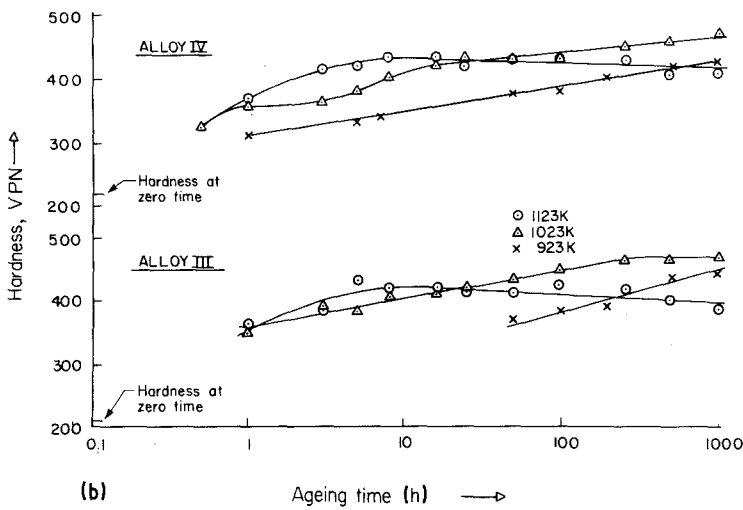
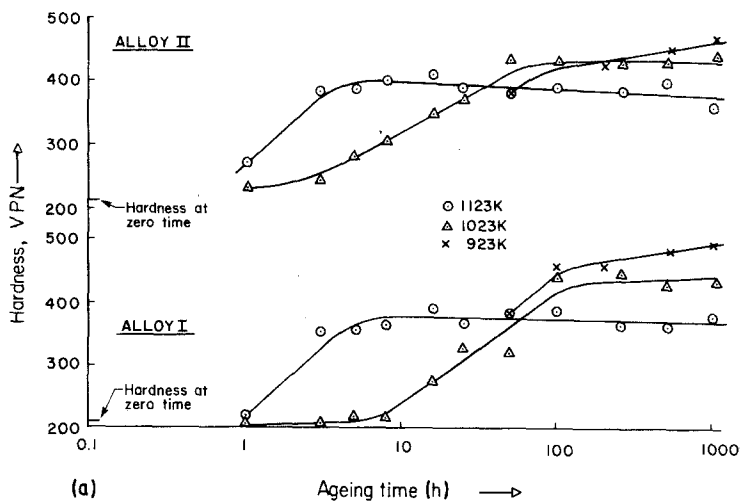


Figure 1 (a) Hardness ageing curves for alloys I and II at 923, 1023 and 1123 K. (b) Hardness ageing curves for alloys III and IV at 923, 1023 and 1123 K. (c) Hardness ageing curves of a vanadium-free 8 wt% niobium, 38 wt% cobalt, 37 wt% nickel, and 17 wt% chromium alloy [4].

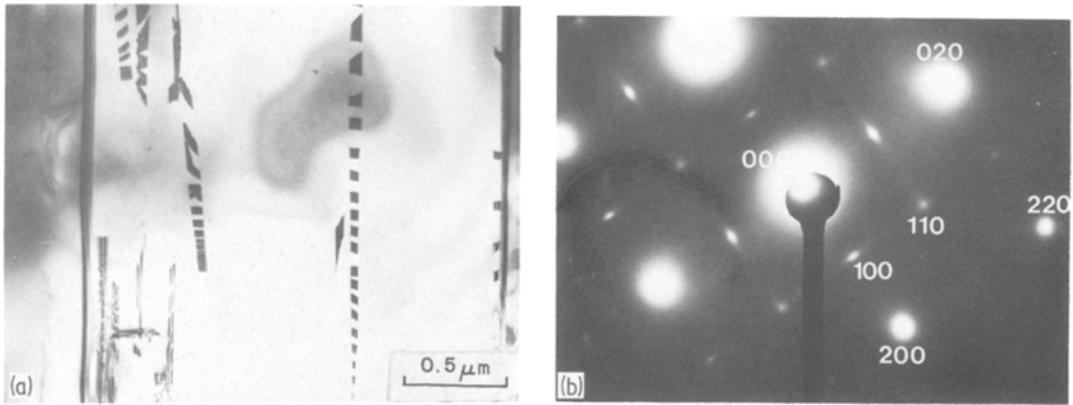


Figure 2 (a) TEM structure of alloy IV aged for 1 h at 923 K. (b) SADP of structure shown in (a). The matrix zone axis is  $[001]$  and the additional reflections are due to  $\gamma''$  precipitates.

specimen aged for 1 h at 1023 K was similar but contained fewer laths of  $\beta$ .

An increase in ageing time coarsened the  $\gamma''$  precipitates and encouraged or increased the formation of  $\beta$  precipitates. As illustrated in Fig. 4a and b the structure of a specimen of alloy IV, aged for 3 h at 1023 K consists predominantly of  $\gamma''$  phase with a few laths of  $\beta$  phase. The grain boundary precipitates are also identified as  $\beta$ . Precipitate-free zones around them and around the laths of  $\beta$  within the matrix are observed. When ageing was continued for 50 h, a significant increase in the number of laths of  $\beta$  phase occurred and  $\gamma''$  was also seen to coarsen appreciably. This is shown in Fig. 5a which is the bright-field microstructure whose crystallographic orientation is  $[001]$ , and in Figs. 5b and c which are the dark-field structures of Fig. 5a with  $(1/2\ 10)$   $\gamma''$  and  $(201)$   $\beta$  reflections, respectively. When ageing of

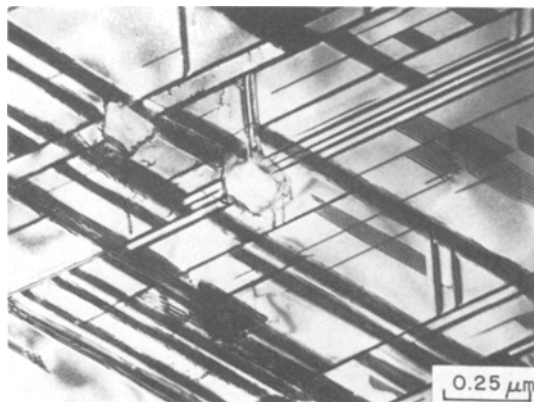


Figure 3 TEM structure of alloy IV aged for 1 h at 1123 K showing lath-shaped  $\beta$  phase precipitates and stacking faults.

alloy IV was continued to 1039 h at this temperature, only laths of orthorhombic  $\beta$  phase were present (Fig. 6). However, at 923 K a large amount of  $\gamma''$  was still present even after 1039 h of ageing.

A similar precipitation sequence was observed in alloys III, II and I. However, a decrease in the vanadium/niobium ratio was found to encourage precipitation of the  $\beta$  phase. For example, alloy III with a vanadium/niobium ratio of 1.35 contained primarily laths of  $\beta$  and some  $\gamma''$  when aged for 1 h at 1123 K. The structure with a mottled appearance of the matrix is shown in Fig. 7, which may be compared with Fig. 3 showing the structure of an identically treated specimen of alloy IV.

Stacking faults in alloy IV originated at laths of  $\beta$ , grain boundaries and undissolved particles. However, they were observed only in alloy IV having (niobium + vanadium) content of 14.3 at %, but not observed in alloys I, II and III having (niobium + vanadium) content of  $< 12$  at %. Such behaviour is expected as the stacking fault energy of nickel is reported to be reduced by solutes having an electron hole number,  $N_v$ , greater than that of nickel [12] and the value of  $N_v$  for niobium and vanadium is 5.66 while that of nickel is 0.66.

#### 4. Discussion

The results of this investigation demonstrate that the addition of vanadium to Ni–Co–Cr–Nb alloys promotes precipitation of the metastable phase  $\gamma''$ . One hour of ageing at 973 K is enough to produce precipitates of only  $\gamma''$  phase. An increase in the time and temperature of ageing and a decrease in the vanadium content of the alloy result in precipitation of the lath-shaped equilibrium phase

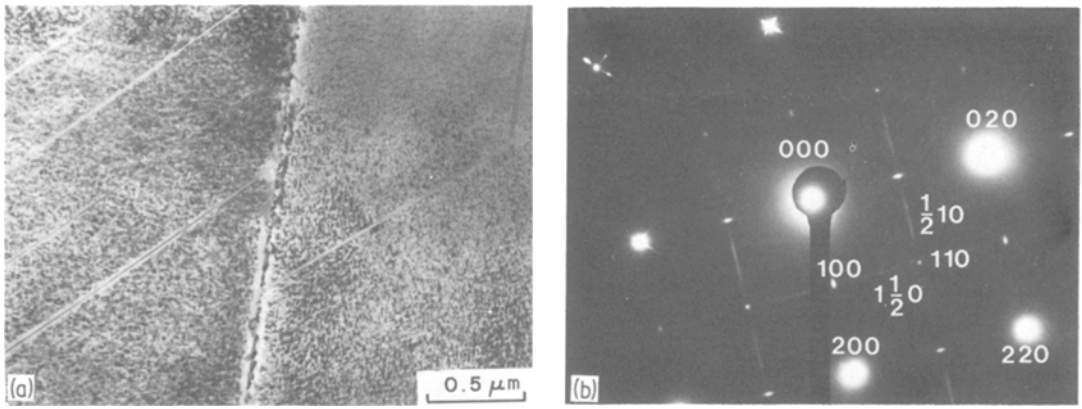


Figure 4 (a) TEM structure of alloy IV aged for 3 h at 1023 K. The  $\gamma''$  precipitate-free zones around lath-shaped  $\beta$  and grain boundary precipitates are observed. (b) SADP of the right grain of structure shown in (a).

$\beta$  and upon continued ageing up to 1039 h at 1023 K the  $\gamma''$  phase disappears completely and only  $\beta$  phase remains. The two-stage ageing behaviour suggested by the hardness ageing time curve of alloy IV at 1023 K (Fig. 1) can be attributed to the initial hardening due to precipitation of metastable  $\gamma''$  phase and subsequent hardening due to the appearance of  $\beta$ .

The metastable phase  $\gamma''$  whose precipitation

is induced by the presence of vanadium has been found in other alloys [6, 7, 13] where the lattice misfits are low. The lattice misfits in the alloys used in this investigation are also low. However, this is not a sufficient condition for the precipitation of a metastable phase. Low misfit does not promote precipitation of the  $\gamma''$  phase in Ni–12.5 at% Nb alloys [7]. But small additions of iron, which do not change misfit significantly give rise to precipitation of the  $\gamma''$  phase [7]. Thus, along with low lattice misfit, high stability of the metastable phase is necessary for its precipitation. Vanadium may alter the relative stabilities of the phases  $\beta$  and  $\gamma''$ .

Stabilities of  $A_3B$ -type compounds like  $\beta$ ,  $\gamma''$  and  $\gamma'$  do not depend significantly on the atomic size factor, but depend primarily on electron concentration [14]. If electron concentration,  $e/a$ , is taken as the ratio of total electrons

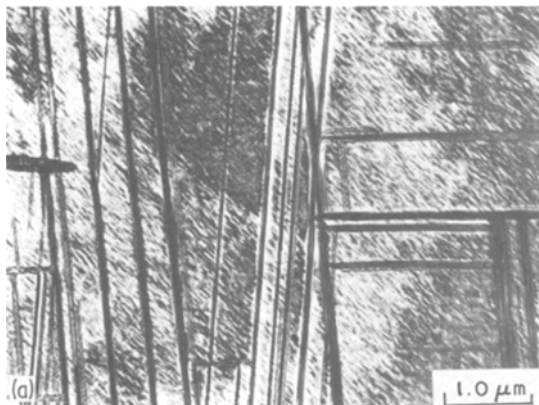
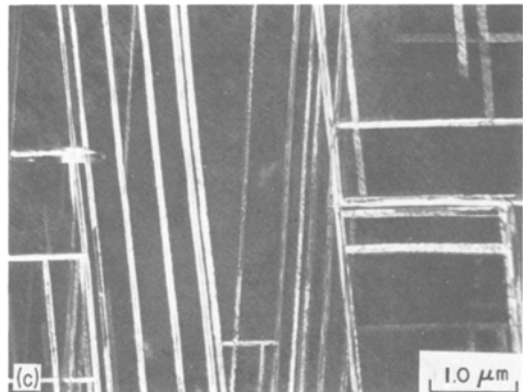
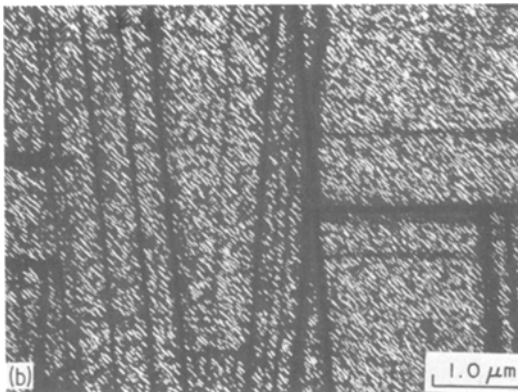


Figure 5 (a) TEM structure of alloy IV aged for 50 h at 1023 K. (b) Dark-field structure of  $\gamma''$  precipitates present in (a). (c) Dark-field structure of laths of  $\beta$  phase present in (a).



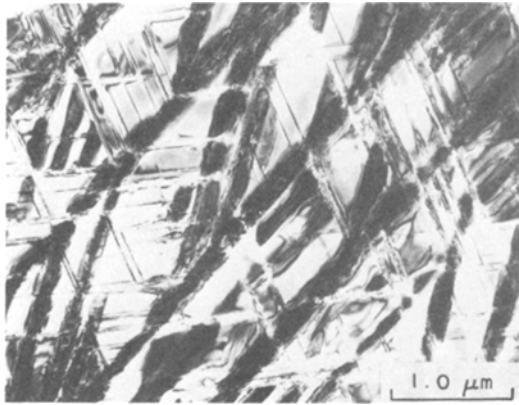


Figure 6 TEM structure of alloy IV aged for 1039 h at 1023 K. Only a lath-shaped  $\beta$  precipitate is observed.

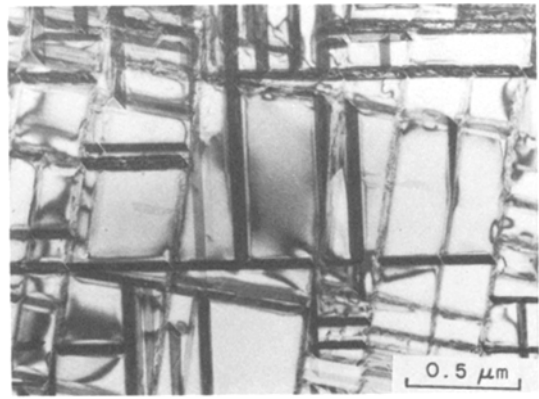


Figure 7 Structure of alloy III aged for 1 h at 1123 K. The precipitates are primarily lath-shaped  $\beta$  phase.

outside the inert gas shell to the number of atoms, an electron concentration of  $< 8.65$  promotes  $L1_2$  ( $\gamma'$ ) structures and a concentration  $> 8.65$  promotes  $DO_{22}$  ( $\gamma''$ ) structures.  $Cu_3Ti$ -type structures, such as  $\beta$ - $Ni_3Nb$ ,  $Ni_3Ta$  and  $Ni_3Mo$ , are found at  $e/a > 8.75$ . Alloying elements which substitute in  $A_3B$  for its components and decrease the electron concentration, would increase stability and promote formation of  $\gamma''$  and  $\gamma'$  precipitates. Vanadium like aluminium, titanium and tantalum is expected to substitute for niobium in  $Ni_3Nb$ , while cobalt may substitute for nickel, and chromium like iron may substitute for both niobium and nickel [15–18]. This approach has been used to explain the role of solute additions in a number of alloys [5, 19, 20]. However, vanadium and niobium have the same electron concentration. Therefore, vanadium is not expected to induce precipitation of  $\gamma''$ . This is contrary to the findings of this investigation. This model also cannot explain the role of iron and chromium in some alloys [4, 6, 7]. Thus, the free electron concentration approach appears to be unsatisfactory.

The effect of alloy substitution on stability is also predictable through the Engel–Brewer correlation. According to the Engel–Brewer model [21] each structure is characterized by a definite  $(s + p)$  electron to atom ratio. The energy of a structure is determined by the promotion energies of electrons to the appropriate  $(s + p)$  configuration and the bonding energies of all the  $(s + p)$  and unpaired  $d$  electrons. The characteristic ranges of  $(s + p)$  electron to atom ratios of  $bcc$ ,  $hcp$ ,  $DO_{22}$  ( $\gamma''$ ),  $L1_2$  ( $\gamma'$ ) and  $fcc$  structures are 1 to 1.5, 1.75 to 2.25, 2.5 to 2.62, 2.75 to 3.00 and 3 respectively [7, 21, 22]. The electron concentration, characteristic of

the  $Cu_3Ti$ -type of structure of the  $\beta$  phase, is not known. The orthorhombic structure of the  $\beta$  phase may be considered to be a slightly distorted  $hcp$  structure in which  $(001)_{hcp} \parallel (010)_{ortho}$  and  $[100]_{hcp} \parallel [100]_{ortho}$ . In an ideal close-packed arrangement lattice parameters  $a$ ,  $b$  and  $c$  of the orthorhombic structure are in the ratio  $2:(8/3)^{1/2}:3^{1/2}$ . Since the lattice parameters of  $\beta$ - $Ni_3Nb$  are [6]:  $a = 0.5110$  nm,  $b = 0.4251$  nm and  $c = 0.4541$  nm, a contraction of only 0.71% of  $c$  and an expansion of only 1.87% of  $a$  would make the ratios ideal. If the small distortions are ignored, the atomic arrangements on the  $(010)$  plane of  $\beta$  and the  $(112)$  plane of  $\gamma''$  become identical as shown in Figs. 8a and b [23]. These figures also show that ordering in the two structures results in the same rectangular arrangement of solute atoms and the difference arises primarily from the hexagonal  $AB$  type of stacking in  $\beta$  and cubic  $ABC$  type of stacking in  $\gamma''$ . Because of rectangular ordering the unit cell of  $\gamma''$  is tetragonal rather than cubic. Thus,  $\beta$  may be considered to have an  $hcp$  structure with ordering of solutes the same as that in the  $\gamma''$  phase. The electron concentration characteristics of  $\beta$ , may, therefore, be assumed to be around 2.37 which is in between those of  $\gamma''$  and  $hcp$  phases. Any substitution which increases the electron concentration in  $Ni_3Nb$  should increase the stability of  $\gamma''$ . Although vanadium and niobium have the same  $bcc$  crystal structure, the  $(s + p)$  electron concentration in niobium is 1.0, while that in vanadium is 1.5 [2]. Hence substitution of niobium by vanadium should increase the stability of the  $\gamma''$  phase.

In conclusion, vanadium increases the stability of  $\gamma''$  by substituting for niobium in  $Ni_3Nb$  and

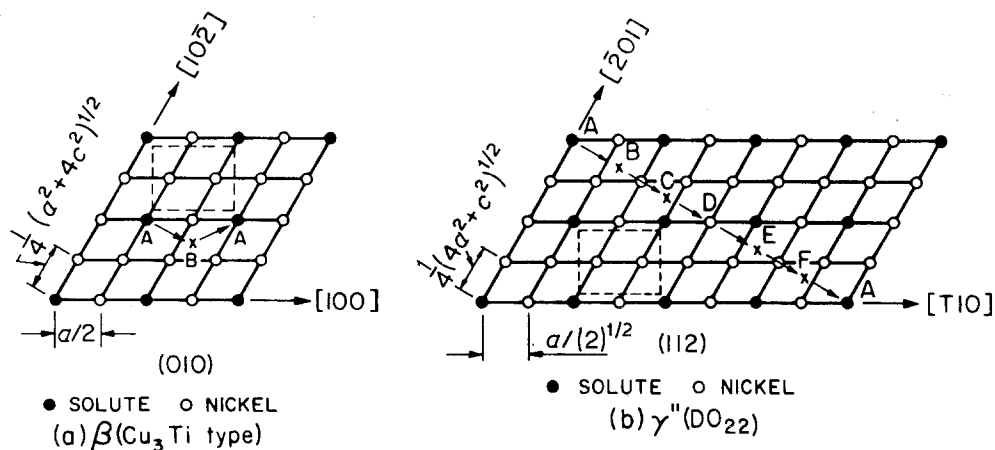


Figure 8 The ordering and stacking sequence in (a)  $\text{Cu}_3\text{Ti}$ -type orthorhombic  $\beta$  phase, (b)  $\text{DO}_{22}$ -type order bct  $\gamma''$  phase. A, B, C, D, E and F represent layers of atoms and X denotes the location of solute atom in the layers above A.

increasing its (s + p) electron concentration. Vanadium also reduces the lattice mismatch of  $\gamma''$  with the matrix by increasing the lattice parameter of the latter. Vanadium additions, therefore, are expected to induce precipitation of the metastable phase  $\gamma''$  as observed in the present investigation.

## 5. Summary and conclusions

The ageing characteristics of four Ni–Co–Cr–Nb–V alloys containing 8 wt% vanadium were investigated in the temperature range of 923 to 1123 K. One per cent vanadium was observed to be sufficient to induce precipitation of disc-shaped metastable  $\gamma''$  phase with a  $\text{DO}_{22}$ -type ordered bct structure. Precipitates of the  $\gamma''$  phase only were found in the alloy with 8 wt% vanadium after 1 h of ageing at 923 K. An increase in ageing time and temperature, and a decrease in the vanadium/nickel ratio caused precipitation of the equilibrium  $\beta$  phase with a  $\text{Cu}_3\text{Ti}$ -type of orthorhombic structure. The precipitation of the metastable phase  $\gamma''$  in these alloys has been satisfactorily explained in terms of the Engel–Brewer correlation.

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