Homogeneity Range and the Martensitic Transformation in TiNi

R. J. WASILEWSKI, S. R. BUTLER, J. E. HANLON, AND D. WORDEN

It is shown that the structure homogeneity range of the B2 TiNi compound is very restricted below 500°C. A new phase, containing 58 at. pct Ni and structurally related to Ni_3Ti, forms peritectoidally at 625° ± 20°C. The precipitation in nickel-rich TiNi is very slow, and a metastable, supersaturated B2 structure can be readily retained. At equilibrium the martensitic transformation takes place at ~60°C, independent of the overall composition. Quenching from 600°C and above raises the transition temperature in titanium-rich, and lowers it markedly in nickel-rich compositions. The resulting martensite structure in the latter is also believed to change with increasing the prior anneal temperature. The observations reported previously on the transformation behavior must be considered as obtained on nonequilibrium, metastable materials, which may account for the discrepancies in the observed property variation. Close control of the processing variables is necessary to ensure reproducibility, particularly if nonequilibrium transformation behavior is desired.

THE remarkable behavior of the intermetallic compound TiNi was first reported by Buehler and Wiley.[1,2] They found it to be ductile and impact resistant; to exhibit unique damping properties; and to be quench-hardenable at some compositions. The "mechanical memory" effect was reported by Buehler,[3] who observed that specimens deformed at room temperature tend partially to recover their original shape on first heating to moderate (~100°C) temperatures. All these anomalies were initially rationalized in terms of the decomposition of TiNi to Ti_2Ni and $TiNi_3$, in agreement with the equilibrium diagrams proposed earlier.[4,5] X-ray diffraction data interpreted as confirming this view were presented.[6] Furthermore, the decomposition of the "metastable" TiNi structure at approximately 50°C was stated to be stress-sensitive, one *or* the other of of the above compounds being predominantly formed depending on whether the applied stress was tensile or compressive.[3]

The existence of a diffusionless transformation in TiNi was first suggested by Purdy and Parr.[7] Subsequent investigations[8-18] have now established beyond doubt that the structure transition occurring in the vicinity of room temperature is martensitic and cannot involve diffusion. A wide disagreement, however, exists between the observations reported by different investigators on the transformation behavior. This is illustrated by the different effects of the composition on transformation temperature reported, Fig. 1. It is obvious, therefore, that factors other than composition must also be significant in affecting the transformation behavior, and presumably also the related properties of the compound.

Inasmuch as the utilization of TiNi is likely to depend largely on reliable property reproducibility, it is essential that the factors affecting the properties be suitably controlled. It is reasonable to assume that most of the properties of interest—and in particular the memory behavior—are directly related to the martensitic transformation. The study of the factors affecting this transformation is, therefore, of both basic and applied interest.

We shall discuss here the effects of the composition and of the prior heat treatment on the martensitic transformation behavior. It will be shown that in nickel-rich compositions the equilibrium conditions are difficult to attain. The usual preparation of TiNi specimens results in nonequilibrium material, with consequent property variation. At equilibrium the structure homogeneity range of TiNi below 550°C is very narrow and its martensitic transition temperature essentially independent of composition. It is possible that both the transformation temperature and its range may be varied within quite wide limits by controlling the extent of

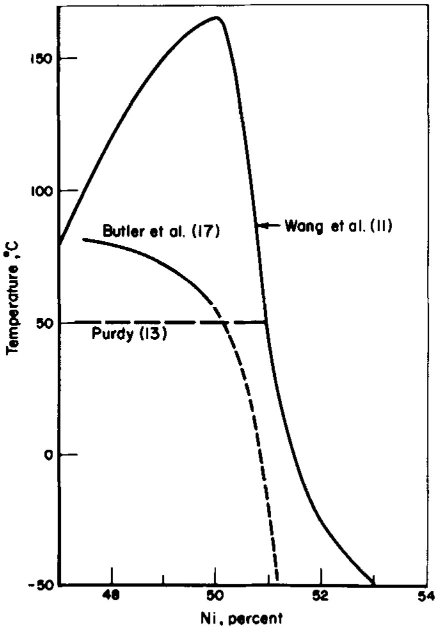

Fig. 1—The variation of the martensitic transformation temperature with composition reported for TiNi, Refs. 11, 13, and 17.

R. J. WASILEWSKI is Senior Technical Advisor, Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio. S. R. BUTLER is Associate Professor, Lehigh University, Bethlehem, Pa. J. E. HANLON is Research Physicist, Central Research Department, E. I. du Pont de Nemours & Co., Wilmington, Del. D. WORDEN is Senior Technologist, Composite Sciences, Inc., Newport, Del.

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the deviation from equilibrium conditions in these materials.

EXPERIMENTAL MATERIALS

Some twenty compositions between 47 and 53 pct Ni* and three high-nickel (55.0, 57.0, and 60 pct) compositions were prepared by multiple nonconsumable arc melting of iodide titanium, and of Inco 270 nickel rod which had been premelted in hydrogen. The compositions containing 48 to 52 pct Ni were subsequently forged and rolled at 750° to 800°C to a $\frac{1}{8}$-in.-thick strip. The remaining compositions were used in "as-cast" condition.

All the compositions were determined by a check of the materials balance, and are accurate to ±0.1 pct. Most of the specimens were annealed for 72 hr at 1000°C and water quenched, to ensure homogenization prior to further heat treatments. Spot-check analyses after the homogenization anneals showed the interstitial content as <200 ppm (oxygen and nitrogen combined). Semiquantitative spectrometry showed no metallic impurities at >100 ppm, major impurities being cobalt and tungsten, each at approximately 80 ppm.

The heat treatments were carried out in evacuated (10^{-6} torr) silica ampoules with the specimens wrapped in tantalum foil. Except when otherwise noted, the heat-treated specimens were quenched by breaking the ampoules under water on the completion of the anneal.

EXPERIMENTAL METHODS

Metallographic, hardness, and X-ray diffraction observations were carried out, usually on a section of the heat-treated specimens. In a number of cases, X-ray diffraction patterns and thermal expansion were investigated above and below room temperature. A number of electron-microprobe analyses were carried out, and replica electron microscopy was used to resolve some fine transformation structures. In addition, some transport properties, in particular the thermoelectric power, were frequently measured.

TiNi is very difficult to prepare in powder form, unless the starting material contains a large amount (>500 ppm) of interstitial contamination. Essentially all of the data presented here were obtained on flat, bulk specimens, some 25 by 20 by 1.5 mm^3, prepared by machining the hot-rolled or cast material. In most cases the surfaces were prepared for metallographic examination prior to the diffraction patterns being taken. Significant preferred orientation was present in all the specimens investigated. The presence of textures and the frequently observed poorly defined diffraction patterns were taken into account in the interpretation of the experimental results.

The texture problem was minimized by simultaneously processing several (typically 6 to 8) compositions under identical conditions of temperature and deformation. All the "as-prepared" compositions exhibited the β structure at 150° to 200°C, and the β (bcc) textures were checked for every batch of specimens. Without exception, the textures in every batch were found essentially identical, as judged by the relative intensities of the (110) and (200) reflections. In comparing the diffraction patterns of specimens from any given batch we can, therefore, assume that any *strong* lines obtained at some compositions indicate the presence of a new structure. The presence of *weak* new lines, however, could possibly be due to minor texture differences.

It was also found that significant changes in both the line intensities and, particularly, in resolution, can take place on aging at ambient temperatures. Such changes are especially marked when temperature fluctuates. To minimize spurious effects, therefore, all the diffraction patterns of any given batch of heat-treated specimens were taken at the same time, usually within 72 hr of the quench.

EXPERIMENTAL RESULTS

1) X-Ray Diffraction

A) CUBIC B2 STRUCTURE

When quenched from 700°C or above *all* the compositions between 47 and 55 pct Ni showed predominantly the body-centered structure. The presence in most of the patterns, regardless of the texture, of a well-resolved (321) reflection permitted a reasonably accurate determination of the lattice parameter. The variation of the parameter with composition, as shown for quenching temperature of 850°C in Fig. 2, is in agreement with the early data.[19] For the lower quenching temperature of 650°C, however, the effect of composition on the lattice parameter is reversed, the lattice parameter *increasing* with increasing nickel content. While the cause of this reversal is not clear, it is evident that some change occurs at (or near) 650°C. Specimens quenched from 600°C and below, regardless of composition, did not exhibit a β pattern sharp enough to permit accurate parameter measurement.

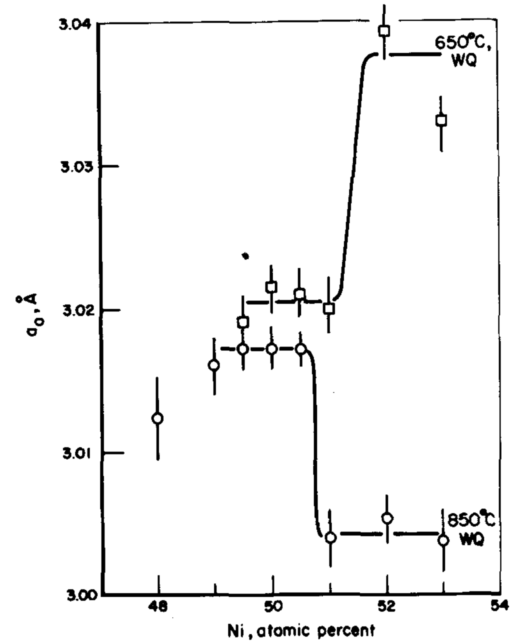

Fig. 2—The variation of the B2 structure lattice parameter (at 25°C) with composition for two quenching temperatures. Error bars indicate the estimated error in a_0, as derived from $d(321)$ measurements. (Cu$K\alpha_1$ = 1.54050Å).

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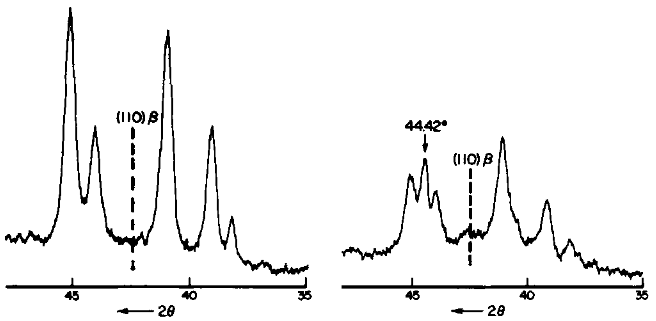
*At. pct Ni used throughout.

The presence of an ordered B2 structure was unambiguously confirmed from MoK_α patterns of slowly cooled (100) texture specimens. Strong (100) reflections were present, with the intensity ratio $I(200)/I(100)$ of the order of 10 for all compositions from 47.9 to 52.4 pct Ni. The (100) superlattice reflections were also usually observed in the (110) texture specimens containing ≥50.5 pct Ni and quenched from 650°C; it is therefore believed that these were also ordered. The occasionally observed absence of the superlattice reflection in a number of the (110) texture specimens cannot be taken as indicative of a disordered structure, since the texture in those was very strong, and no (200) reflection was present.

B) MARTENSITIC STRUCTURE PATTERNS

As reported previously[8] the best patterns of the martensite structure were obtained on slowly cooled specimens. Even the best patterns, however, were characterized by the presence of only a few well-defined (but broad) lines, over a small angular range spanning the strong (110) β reflection. The remainder of the pattern consisted of very diffuse lines, merging into the background, in all the specimens. A typical martensite part-pattern in TiNi slowly cooled after a long anneal at 500°C is shown in Fig. 3(*a*). Such patterns were observed in all of the specimens containing 47 to 53 pct Ni annealed at or below 600°C, although the lines become broader with decreasing, and weaker with increasing, nickel content. A very broad (110) β line was observed after this anneal only at ≥52 pct Ni, Fig. 3(*b*). Contrary to the previous observations,[18] obtained on specimens slowly cooled after a short-time anneal at 650° to 700°C, the nickel-rich compositions *do* transform above 25°C when equilibrated at 500° to 600°C. Furthermore, the martensite pattern obtained after such anneal suggests no structure variation with composition reported earlier by Wasilewski *et al.*,[18] but not by Dautovich and Purdy.[12]

The effects of higher anneal temperatures were reinvestigated on the (100) texture specimens, slowly cooled from 650°C. These showed broad martensite lines in the vicinity of (110) β reflection. In addition, however, they also showed two (for ≤50.2 pct Ni), or three (≥50.8 pct Ni) strong lines close to the (200) β reflection. The transition temperatures for so heat-treated compositions containing >51 pct Ni are below room temperature, as shown in Fig. 4. A large number of patterns now obtained supports the earlier contention[18] that two different martensite structures are formed in TiNi furnace cooled from ≥650°C, one forming at ≤50.2 and the other at ≥50.8 pct Ni. The former is the structure observed, regardless of composition, in compositions subjected to a long-time anneal at ≤600°C, Fig. 3. Therefore, the lower transformation temperature, and the different martensite structure in nickel-rich compositions annealed at ≥650°C must be ascribed to nonequilibrium conditions, presumably due to incomplete precipitation of excess nickel.



(*a*) (*b*)

Fig. 3—The major lines of the martensite pattern, as affected by composition, in Ti-Ni slowly cooled after a long-time anneal at 500°C. CuK_α radiation. The position of (110) B2 line shown by dashed line. (*a*) 49.5 pct Ni, 1344 hr/500°C/AC; (*b*) 51 pct Ni, 1344 hr/500°C/AC.

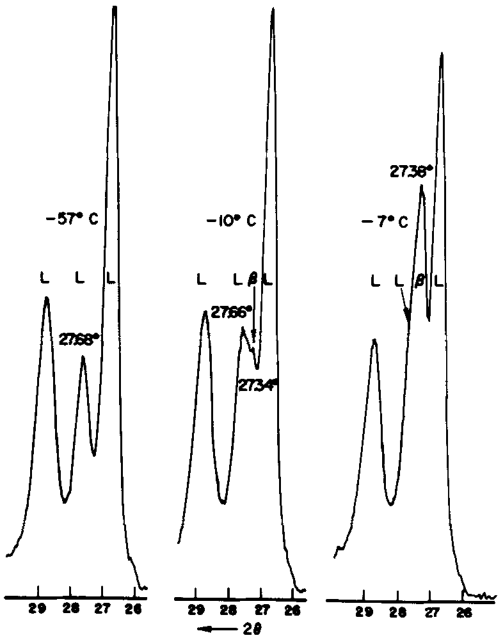
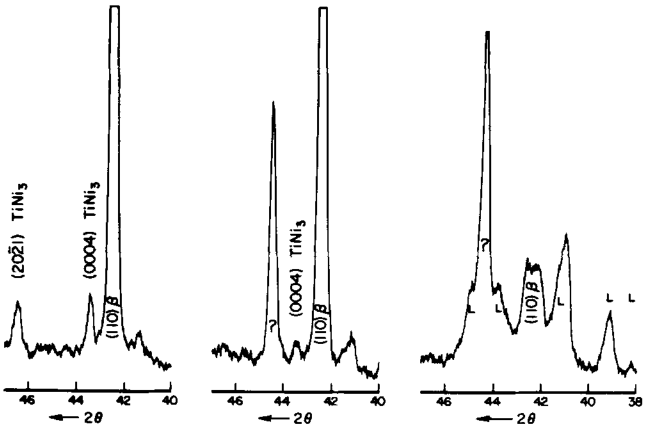


Fig. 4—The discontinuous transition of the martensite structure on heating nonequilibrated Ti-50.8 at. pct Ni from −57° to −7°C. The transition is not complete, but the (200) B2 line is seen to appear at −10°C and grow in intensity without a simultaneous shift and broadening of the low-temperature structure lines (*L*). MoK_α radiation.



(*a*) (*b*) (*c*)

Fig. 5—Part patterns of Ti-52 pct Ni as affected by prior heat treatment. All specimens initially homogenized at 1000°C. CuK_α radiation. (*a*) 168 hr at 650°C, quenched. B2 + $TiNi_3$. (*b*) 336 hr at 600°C, quenched. B2 + Ti_2Ni_3. (*c*) 1330 hr at 500°C, quenched. Martensite (*L*), + Ti_2Ni_3 + residual B2.

The discrepancy between the earlier observations reported by Dautovich and Purdy[12] and by the present authors[18] must have arisen from the different final heat treatment used, *i.e.*, 500°C[12] and 650°C,[18] respectively. The former would lead to the early stages of formation of equilibrium TiNi composition, while the latter must have resulted in TiNi supersaturated with nickel at room temperature. The different martensite structure must, therefore, be due to the nonequilibrium condition of the nickel-rich material.

The discontinuous character of the martensitic transition at 50.2 pct Ni was shown previously.[18] The similarly discontinuous appearance of the (200) β line on heating the nonequilibrium 50.8 pct Ni martensite is evident in Fig. 4. Thus the martensite transformation in both the equilibrium and the metastable TiNi composition is discontinuous. The transition cannot, therefore, take place by a progressive distortion of the parent β lattice, as proposed by Wang *et al.*[8,9,11] In such case a progressive shift and, possibly, a broadening of the β lines in the vicinity of the transition would have to be present.

C) PRECIPITATE STRUCTURES

For quenching temperatures of 650°C and above, the presence of $TiNi_3$ was readily confirmed by the appearance of (0004) and (20$\bar{2}$1) lines of the hexagonal $TiNi_3$ structure, at (CuK_α) 2θ of 43.2 and 46.46 deg, respectively, Fig. 5(*a*). These were particularly marked in the (110) texture specimens, suggesting a crystallographic precipitation habit of the $TiNi_3$ in the B2 matrix. In titanium-rich compositions no unambiguous identification of the presence of Ti_2Ni was usually possible, though the strong (511/333) line was occasionally observed. Invariably, however, the martensitic structure was also present, though with broad and ill-defined reflections.

For the lower quenching temperature of 600°C the $TiNi_3$ lines were no longer seen, and a strong, new line at (CuK_α) 2θ = 44.44 deg appeared instead in the patterns, Fig. 5(*b*), of nickel-rich compositions. On further lowering the prequenching temperature to 500°C, the B2 structure can no longer be retained by quenching, and the martensite structure is formed above 25°C even at 53 pct Ni; the 44.44 deg line, however, is strong and well defined, Fig. 5(*c*). Furthermore, although the martensite lines are broad, they correspond to those shown in Fig. 3(*a*) and it is presumed that both these patterns are due to the same martensite structure.

The appearance of this new line has been investigated in the composition range of 51 to 57.5 pct Ni. Of particular interest here are the observations on the latter composition. When homogenized for 72 hr at 1000°C and quenched, it shows the presence of $TiNi_3$, Fig. 6(*a*). Similar patterns were observed on specimens quenched from temperatures down to 650°C, Fig. 6(*b*). On subsequent annealing at 600°C, however, the new lines appears in addition to the existing lines of B2 and $TiNi_3$ structures, Fig. 6(*c*), and increases in intensity with increasing anneal time.

An interesting effect also observed is illustrated in the patterns of Fig. 7. It can be seen that the result of very slight working of the surface, by abrading it on 400 silicon carbide paper, causes a marked change in the diffraction pattern. The new structure line and the (0004) $TiNi_3$ reflection are both almost completely removed. The original pattern of Fig. 7(*a*) can be restored by a subsequent anneal for 20 min at 600°C. This suggests that the precipitate can be readily disordered to a distorted β structure by a minor amount of work.

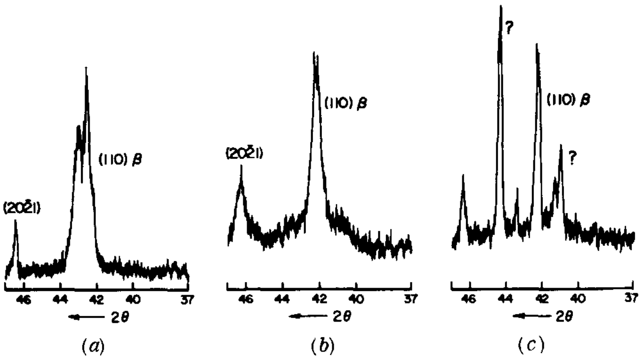


Fig. 6—Part-patterns of Ti-57.5 pct Ni as affected by prior heat treatment. CuK_α radiation. (*a*) 72 hr at 1000°C, quenched. B2 + $TiNi_3$. (*b*) +168 hr at 650°C, quenched. B2 + $TiNi_3$. (*c*) +336 hr at 600°C, quenched. B2 + Ti_2Ni_3 (+ $TiNi_3$).

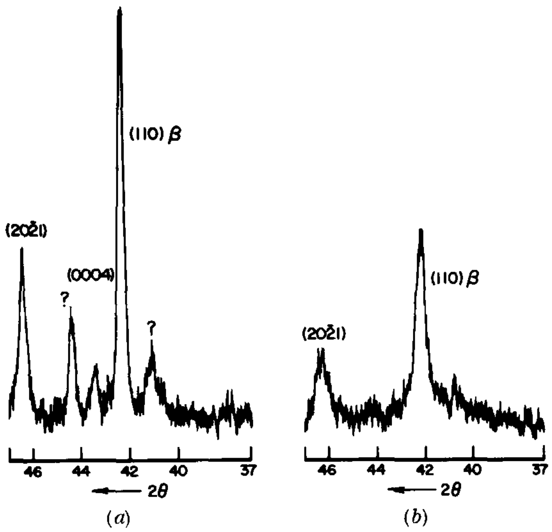


Fig. 7—Part-pattern of Ti-57.5 pct Ni, CuK_α radiation. (*a*) As annealed 168 hr at 650°C, quenched. B2 + Ti_2Ni_3 + $TiNi_3$. (*b*) The same surface as abraded on 400 emery. Note the disappearance of the new structure.

Neither the strong line observed, nor several much weaker lines seen in some of the patterns, correspond to any of the known structures in the TiNi system. These lines, however, correspond very closely to a stacking variant of the $TiNi_3$ structure observed by Pfeifer *et al.*[20] apparently stabilized by a deficiency of nickel and the consequent increase in the concentration of the conduction electrons.

2) Metallography

The microstructures typically observed in TiNi prepared and processed by the usual laboratory or commercial methods are not single phase,[6,7,18,21] generally containing the precipitate of $Ti_4Ni_2O_x$ in the transformed matrix, even in the nickel-rich compositions. The formation of a nickel-rich phase, intermediate between TiNi and $TiNi_3$ has been previously suggested to take place at approximately 650°C.[18] Extensive metallographic examination was, therefore, carried out on all the X-ray diffraction specimens.

No significant variation of the amount of second phase with prior heat treatment was observed in all the compositions containing ≤50 pct Ni. A typical structure shows transformed martensitic matrix containing the Ti_2Ni precipitate, Fig. 8. There is no significant variation in the amount and the distribution of the minor phase with the anneal temperature up to 1000°C, indicating an essentially vertical phase boundary. Incipient melting was observed at 1050°C, and the Ti_2Ni peritectic decomposition temperature is taken in agreement with that reported by Margolin *et al.*[22] as 1025° ± 20°C. Lower incipient melting temperatures were observed in several high-oxygen (500 to 800 ppm) alloys prepared earlier, and it is concluded that the low peritectic temperature reported by Pool and Hume-Rothery[5] must have been due to oxygen contamination.

The size of the martensite plates varied with the anneal temperature, cooling rate, and composition. The intermediate compositions, containing 50 to 51 pct Ni, exhibited generally featureless microstructures, the appearance varying widely depending on the metallographic preparation and the etchant used. A typical example is shown in Fig. 9.

The anneal-temperature effect on the structure of higher nickel compositions is much more marked, as illustrated in Fig. 10 for Ti-52 pct Ni. The precipitate formed at 750° and 650°C has been unambiguously identified as $TiNi_3$ by electron microprobe analysis. That formed at 600° and 500°C, however, was similarly analyzed and found to contain 58 ± 2 pct Ni only.

The precipitate analysis findings are further supported by the variation in the morphology of the nickel-rich precipitates with the precipitation temperature. $TiNi_3$ forms as an equiaxed phase at higher temperatures, but changes to a crystallographic habit at 650°C, Figs. 10(*b*) and (*c*). The comparison of Figs. 10(*c*) and (*d*) indicates that in the 52 pct Ni TiNi, the Widmanstätten precipitate of $TiNi_3$ present after the 650°C anneal has been replaced by another Widmanstätten structure and a platy precipitate after an additional 500 hrs at 500°C. As shown in Fig. 11, both of these are the same phase, and are surrounded by a transformed matrix. A much more regular growth of the new phase is observed at higher nickel contents, with the matrix

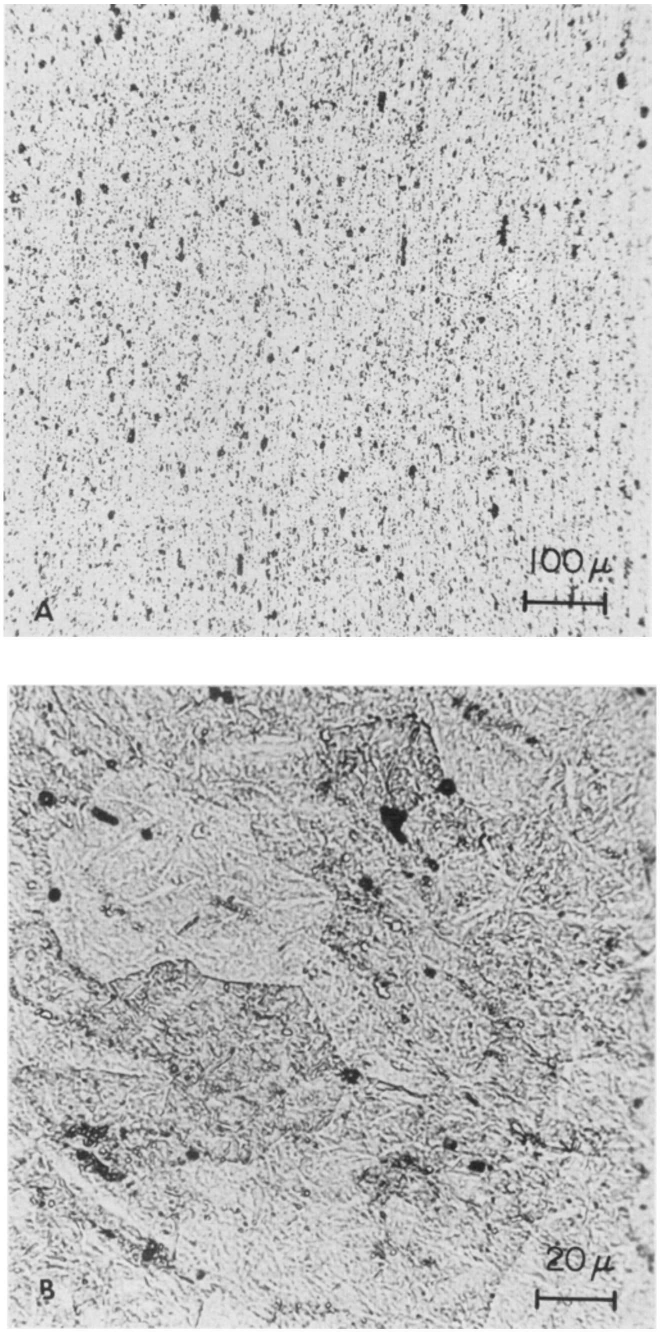


Fig. 8—Ti-50 pct Ni: Typical structure of a conventionally process material (swaged rod), air cooled after normalizing anneal, 30 min at 650°C. (*a*) Longitudinal and (*b*) transverse section. Martensitic matrix with (mainly etched out) Ti_2Ni precipitate.

Fig. 9—Ti-50 pct Ni, showing the effect of prior homogenizing anneal at 650°C. Final anneal: 1000 hr at 650°C, quenched. Note the traces of the B2 boundary, coarser martensite areas, and much finer second-phase precipitate.

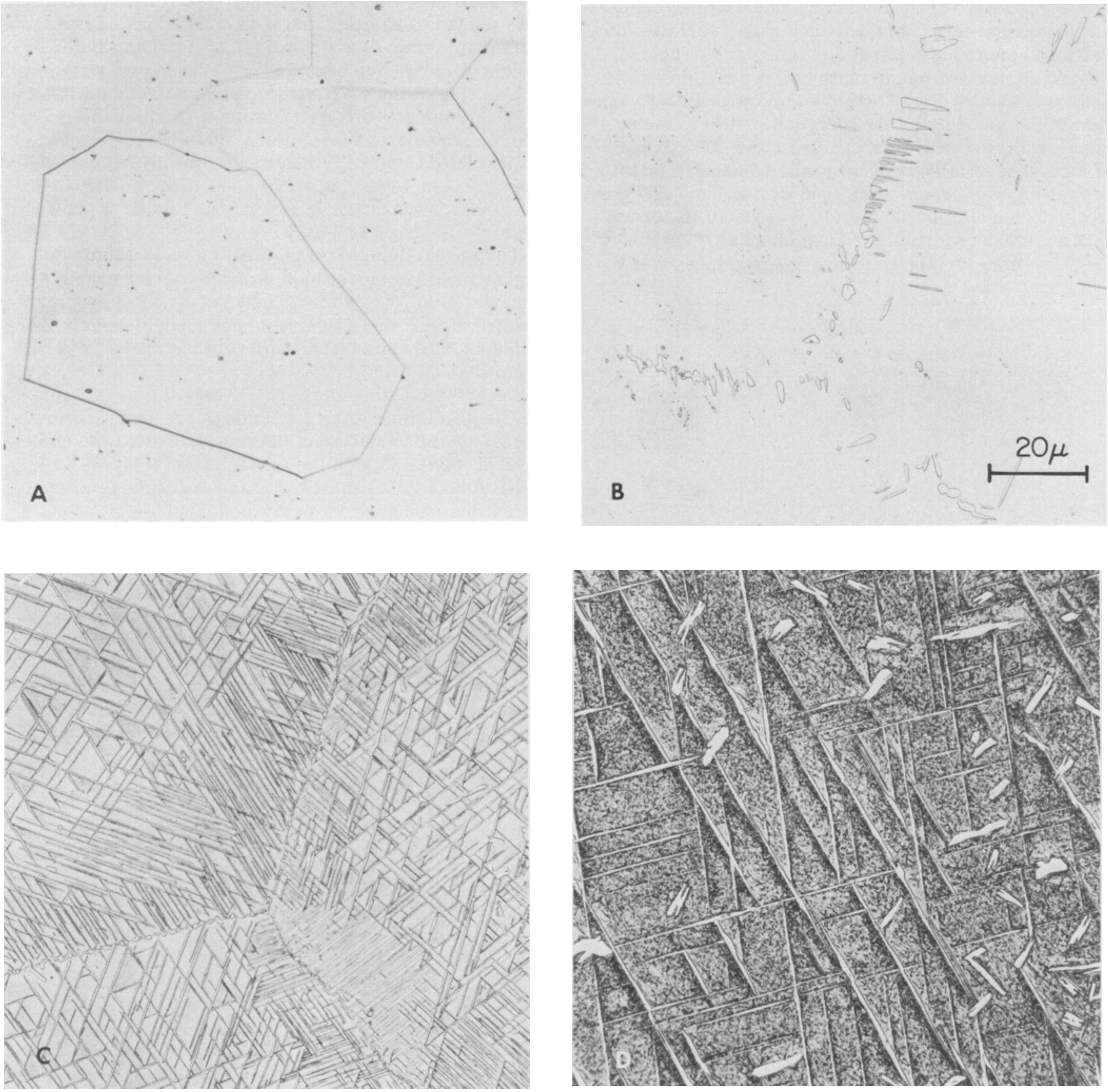


Fig. 10—The effect of prior anneal temperature on the structure of Ti-52 pct Ni. (*a*) 24 hr at 1000°C, quenched. B2 structure. (*b*) 1000°C + 72 hr at 750°C, quenched. B2 + predominantly equiaxed, grain boundary, $TiNi_3$. (*c*) 1000°C + 168 hr at 650°C, quenched. B2 matrix + grain boundaries and Widmänstatten $TiNi_3$. (*d*) Specimen (*c*) plus 500 hr at 500°C, quenched. A new, platy precipitate has replaced the Widmänstatten $TiNi_3$, and a general precipitation took place in the matrix.

apparently transformed even at 55 pct Ni, Fig. 12.

It is concluded that a new structure is formed in the binary system between TiNi and $TiNi_3$, stable below 625° ± 20°C and of approximate composition $Ti_{42}Ni_{58}$ (which we shall for convenience refer to as Ti_2Ni_3). Furthermore, the structure homogeneity range of TiNi at 500°C and below must be very narrow, since Ti_2Ni is present at 49.5 pct Ni, and the new phase at 51 pct Ni.

3) Thermal Expansion

The transformation behavior of a number of compositions was checked on the X-ray diffraction and metallographic specimens over the range of −40° to 150°C. Micromeasurement strain gages were cemented on to the polished specimen surfaces and monitored continuously during heating and cooling at 1°C per min.

Although no reliable data can be obtained on the thermal-expansion coefficients, this method provides a convenient means of determining the temperature at which the contraction (due to the martensite → B2 transformation) occurs. Typical contractions observed on compositions quenched after 672 hr at 600°C are shown in Fig. 13. The midpoint temperatures of transition (on heating) fall within the range of 57° ± 12°C for compositions from 49.5 to 52 pct Ni. The sharpest

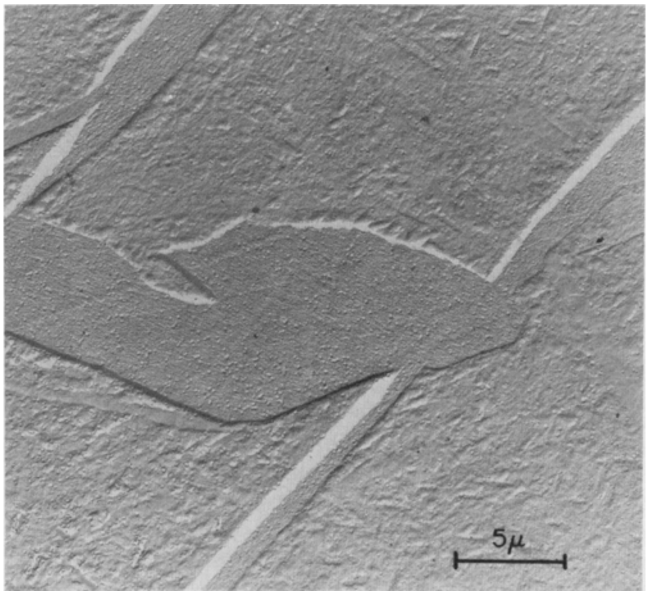


Fig. 11—The structure of Ti-52 pct Ni of Fig. 10(*d*), as seen in replica under higher magnification. The mottled matrix is transformed, and the same phase forms the platy and the crystallographic precipitate.

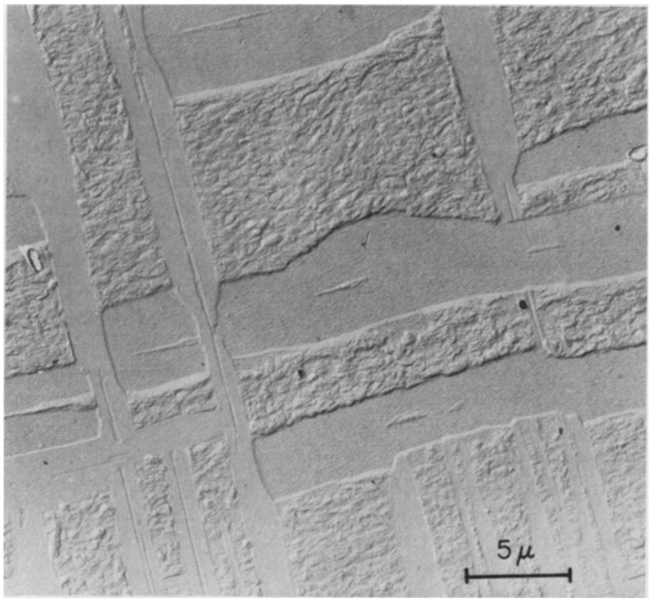


Fig. 12—The structure of Ti-52 pct Ni, homogenized at 1000°C, annealed for 1000 hr at 600°C and quenched. The matrix is again transformed at room temperature, in spite of the high nickel content.

transitions were observed at 50.0 and 50.5 pct Ni. In all cases, however, the transition contraction amounted to 3 to 5×10^{-4}, as contrasted with the previously reported value of 18×10^{-4} on "normalized" stoichiometric compound.[18]

Dilatometric measurements on a 51.0 pct Ni rod similarly annealed showed a transition temperature of 59°C (range 54° to 65°C), and a contraction on heating of 3.2×10^{4}. The same rod reannealed for 72 hr at 650°C and quenched showed a transition temperature of −4°C (range −16° to +5°C), and a contraction of 19×10^{-4} on heating. This again demonstrates the importance of nonequilibrium conditions.

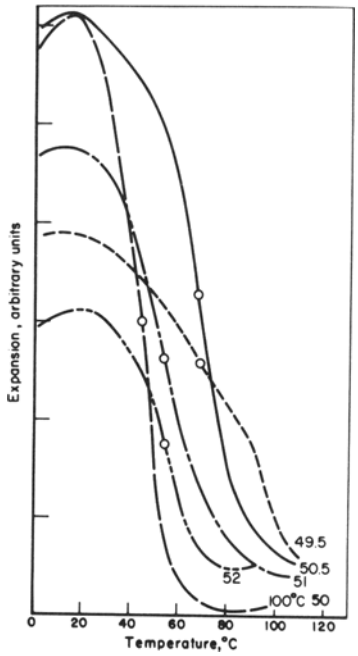


Fig. 13—The midpoint temperatures of martensitic transformation on heating, as determined by strain-gage techniques for TiNi compositions containing 49.5-52 pct Ni equilibrated at 600°C. No significant variation with composition is present.

4) Ti-Ni Equilibrium Diagram

The experimental observations are summarized in the part-diagram shown in Fig. 14. The following points have been established.

a) The maximum melting point lies at 50.6 ± 0.2 pct Ni, rather than at the stoichiometric 1:1 composition.

b) On the titanium-rich side, the TiNi phase boundary descends steeply to the Ti_2Ni peritectic horizontal at 1025° ± 20°C and 50.0 ± 0.25 pct Ni. The boundary then continues vertically, with no measurable solubility of excess titanium in the B2 structure.

c) On the nickel-rich side, the boundary has been determined to 1050°C, and is characterized by a rapidly increasing solubility of excess nickel in the B2 structure at higher temperatures.

d) A new structure formed peritectoidally in nickel-rich compositions at temperatures below 625° ± 20°C. Its composition is close to Ti_2Ni_3, and the structure related to that of $TiNi_3$.

e) The homogeneity range of TiNi at 500°C and below is narrow, and probably significantly less than 0.5 pct Ni.

DISCUSSION

1) Homogeneity Range of TiNi

The large solubility of nickel in the TiNi structure at 750°C and above and the sluggish precipitation below 650°C make it easy to retain a metastable, nickel-rich TiNi composition. This is of special significance in materials containing 51 pct Ni, which have been considered particularly suitable for investigation because of their reported convenient transformation temperature range.[1] It is obvious, however, that an equilibrating anneal at 500°C results in a major change in the transformation behavior. Since this change is revers-

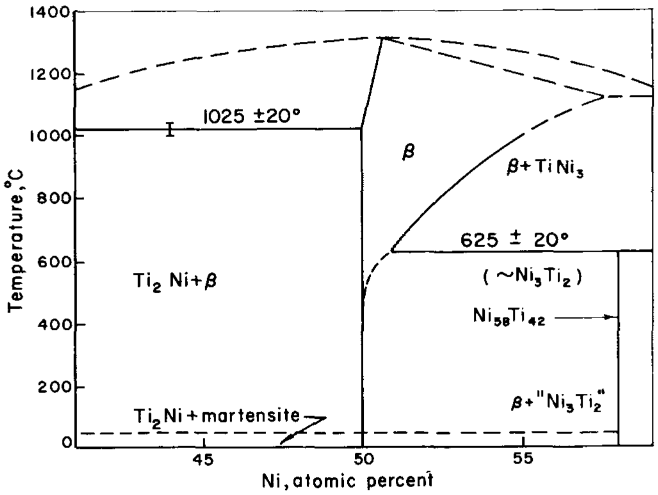


Fig. 14—Proposed equilibrium diagram of the Ti-Ni binary system in the vicinity of the equiatomic composition. (The liquidus temperatures, and the solidus of nickel-rich composition, were taken from Refs. 5 and 21.)

ible by annealing at 650°C, it is reasonable to suggest that the latter anneal results in a nonequilibrium structure being retained at room temperature. We note that even at 50.3 pct Ni diffraction-pattern anomalies, interpreted as a periodic variation in the composition within the lattice, have been reported in a furnace-cooled material by Starke and Lee.[23] Such periodic variation may well indicate a preprecipitation stage in a supersaturated solution. The striped contrast observed in transmission electron microscopy[12, 23] may be interpreted as due to such crystallographic segregation.

It is concluded that the equilibrium homogeneity range of the TiNi structure is very narrow at 500°C and below, and may even be limited to a fixed composition. Attaining conditions close to equilibrium is difficult in compositions containing 50 to 51 pct Ni, as long-time anneals at temperatures of the order of 500°C and below are required.

There are indications that some changes do take place in supersaturated, metastable nickel-rich compositions even at room temperature. These consist of the reported observations of structure,[23] electrical resistivity,[17] and the heat of transformation[24] variation in aging. This is particularly well illustrated in the measurements of Bernan *et al.*,[24] who determined the heat of transformation in three successive heating and cooling runs as 495, 457, and 402 cal per g-atom, respectively. It is obvious that their measurements indicate initially nonequilibrium conditions, and a decrease on cycling through the transformation range to the lower (equilibrium) value of 370 ± 20,[18] or 310[13] cal per g-atom. (Incidentally – although the composition of the specimen used is stated to be equiatomic by Bernan *et al.*,[24] the observed transition temperature and range indicate it must have been nickel-rich, probably containing ~50.5 pct Ni).

2) Peritectoid Reaction

The formation of a new structure reported here is not in accord with the recent findings of Marcinkowski *et al*. These authors conclude, predominantly on the basis of transmission electron microscopy of two compositions, that two martensite structures exist;[25, 26] that the formation of a complex transition structure precedes that of $TiNi_3$;[28] and that a eutectoid decomposition of TiNi into Ti_2Ni_2 and $TiNi_3$ takes place at 640°C, with the eutectoid composition tentatively set at ~51.5 pct Ni.[28]

We have already suggested a number of reasons why this interpretation of the thin-film observations may be erroneous.[29] The most obvious argument against the existence of the eutectoid, however, lies in the martensitic transformation behavior. For optimum and sharp transformation, an anneal of cold-worked TiNi at 500° to 600°C is stated to be required.[30] Under these conditions, the proposed eutectoid decomposition would be rapidly initiated, and the amount of the B2 structure present decreased due to formation of Ti_2Ni and $TiNi_3$. The latter two compounds, however, *do not* undergo a structural transition, hence their formation can hardly serve to optimize the transformation behavior. Accelerating the peritectoid reaction, by the same processing sequence, should lead to rapid precipitation of excess nickel from the supersaturated B2 phase, thus leading to a sharp transformation of the "near-equilibrium" B2 structure.

3) Ni_3Ti_2 Structure

In the work of Pfeifer *et al.*[20] the existence of stacking variants of the $TiNi_3$ structure has been reported. The hexagonal $TiNi_3$ has the DO_{24} structure, characterized by a close-packed sequence of 4 planes in the *c*-axis direction, and designated by Pfeifer *et al.*, as A4. They observed stacking variants of 10, 9, and 21 similarly close-packed sequences in quenched compositions with decreasing nickel contents.

The comparison of the diffraction patterns observed here with those kindly supplied by Professor Schubert for these stacking variants permitted the identification of the phase present as A10. In view of the uncertainty involved in the microprobe analysis the formula Ti_2Ni_3, rather than $Ti_{42}Ni_{58}$, is suggested. The A10 variant, however, was observed at much higher nickel contents in the "as-cast", nonequilibrium compositions investigated by Pfeifer *et al.*[20]

4) Transformation Behavior

a) Nickel-rich compositions show a major variation in transformation behavior with the prior heat treatment. This is ascribed to the incomplete precipitation of nickel, and the consequent supersaturation of the retained β structure. The effect is particularly significant at lower nickel contents (<51 pct Ni), in which the precipitation of nickel to the equilibrium solute content occurs below 600°C and requires long anneal times. Since in the past work such compositions have been predominantly used, the variation in the observed transformation behavior must have been due to the varying extent of supersaturation with nickel.

From the crystal-structure data reported here it is concluded that excess nickel in TiNi causes a marked lowering in the martensitic transformation temperature, as well as the formation of a martensite of a different structure. According to Dautovich and Purdy,[12] excess nickel is present as a substitutional defect.

When subjected to low-temperature anneals to ensure the precipitation of excess nickel to the equilibrium solubility limit, these compositions all transform at the same temperature (~60°C), independent of the overall composition. The transition is sharpest at 50 to 50.5 pct Ni, and the martensite product structure is also independent of composition. Therefore, the equilibrium homogeneity range of the TiNi structure at room temperature range must be quite narrow.

b) Titanium-rich compositions show relatively minor variations in transformation behavior, consistent with the very limited tolerance of the TiNi structure for excess titanium.

The only effect observed in these compositions quenched from $\geq 650°C$ was an increase of the transition temperature to approximately 100°C, and a broadening of the transformation-temperature range. The reasons for that are not clear. It is possible that, with excess titanium, vacancy defects on the nickel sublattice in the B2 lattice may be energetically favored, and that at higher temperature thermal vacancy formation will also be more marked. The accommodation of the transformation strains may, in turn, be facilitated by the presence of large vacancy concentrations, hence lower "supercooling" past the theoretical M_s temperature needed before the martensite forms. Conversely, the retention of substitutional excess nickel atoms on the titanium sublattice in the metastable nickel-rich compositions depresses the transition, possibly because of a lower tolerance of the martensite structure for this type of defect.

It is of interest here to compare the effects of the structure defects on the martensitic transformation temperature in TiNi with the corresponding behavior in other comparable materials. The substitutional defects present lower the transformation temperature, and result in a different martensite structure. This seems comparable to the behavior of Au-47.5Cd, in which also low-temperature anneals cause significant changes in transformation behavior.[31] Perhaps the variation in M_s temperature with composition in AuZn and in CuZn are also defect-related. It would appear that vacancy defects are less effective than the substitutional atoms in affecting the transformation.

c) Transformation shear may be qualitatively estimated from the character of the martensite diffraction pattern, in which only a few lines in the vicinity of (110) B2 are usually reasonably well resolved. This suggests that the maximum shear required may be close to $\langle 110 \rangle$ B2 direction, so that relatively large and strain-free martensite domains can form in specimens with (110) texture on the surface. The very poor resolution of other lines in (110) texture specimens suggests either a very small martensite domain size or high residual strains for shear directions other than that of the normal to the surface. This, if correct, further suggests that anisotropic and sharp transformation behavior may be attained in highly textured materials, processed to develop a strong axial $\langle 110 \rangle$ B2 texture by, *e.g.*, drawing above the peritectoid (but below the recrystallization) temperature.

CONCLUSIONS

1) It is concluded that the equilibrium TiNi structure has a very narrow homogeneity range below 500°C, and that a structure related to $TiNi_3$ but of the approximate composition Ti_2Ni_3 forms peritectoidally at 640°C. At equilibrium the B2 structure TiNi transforms martensitically to a complex structure at 57° ± 12°C, regardless of the overall composition of the two-phase material. The earlier observations of the composition-dependent transformation temperature were obtained on nonequilibrium, metastable materials, whose transformation behavior can vary depending on the prior work and heat-treatment history.

2) Assuming that the anomalous behavior, notably the "mechanical memory", of TiNi is directly related to the transformation, it follows that any properties observed to date (particularly on nickel-rich composition) are characteristic only of the specific nonequilibrium conditions of the experimental materials. This applies equally to the fundamental characteristics (as the martensite structure and the M_s temperature), and to the mechanical- or physical-property variation necessary for engineering design. An excellent example of the mechanical-property variation is obtained from the comparison of tensile properties reported by Rozner and Wasilewski[14] and by Buehler and Cross[30] for differently processed materials.

3) The transformation behavior is only slightly affected by prior processing in titanium-rich, but very significantly so in nickel-rich compositions. This is suggested as due to the different types of structure imperfections formed on each side of the equiatomic composition. The major defect in the nickel-rich TiNi is believed to be substitutional nickel atom. Equilibrium conditions can be attained by prolonged heat treatment at 500°C and below.

4) If nonequilibrium transformation behavior is to be utilized, the means of controlling the extent of departure from equilibrium, and of the defects present, will have to be developed to ensure reproducibility.

5) Extreme caution should be applied in interpretation of observations on materials of this type derived on ill-characterized specimens, on one or two compositions only, or not confirmed by the use of other experimental techniques. A difference of 1 at. pct in composition, or of 100°C in the anneal temperature, can cause drastic variation in the behavior of the material.

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