Metastable Microstructures in Rapidly Solidified Ni Rich TiNi Alloys

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The metastable microstructures in two rapidly solidified Ni rich Ti-Ni alloys are studied. A first report of the presence of a cubic phase with three times the lattice parameter of B2-TiNi in melt spun $\text{Ti}_{40}\text{Ni}_{60}$ alloy is presented. This phase has precipitated from the massively solidified B2-TiNi. We also report the formation of a faulted structure (A^9), polytypic to TiNi_3 along with TiNi_3 in melt spun $\text{Ti}_{30}\text{Ni}_{70}$ alloy. It is argued that this structure is stabilised due to a specific valence electron by atom ratio.

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I. Introduction

The Ti-Ni system shows three intermetallic compounds- Ti_2Ni , TiNi and TiNi_3 under equilibrium⁽¹⁾. Inter-metallic Ti_2Ni with a small homogeneity range (~ 0.2 at%Ni) forms by a peritectic reaction at 1257 K. However, TiNi and TiNi_3 intermetallic compounds form by congruent solidification. TiNi has a large homogeneity range (49.5 to 57 at%Ni). The TiNi_3 is generally regarded as a line compound, although recent results suggest the existence of a homogeneity range⁽²⁾. Under conditions away from the equilibrium, the Ti-Ni system is known for its glass forming ability⁽³⁾⁻⁽⁵⁾. In addition, a phase A^{21} which is a polytypic structure of TiNi_3 has been observed very close to TiNi_3 composition⁽⁶⁾. Ordering and decomposition, two extreme phenomena, are also found in the Ni rich side of the Ti-Ni system⁽⁷⁾. Although detailed investigations on the phase formation under non-equilibrium conditions in the Ti rich side exist⁽⁸⁾⁻⁽¹¹⁾, the alloys on the Ni rich side have attracted less attention. We have selected two representative nickel rich alloys for the present study with an aim to understand the structural and microstructural developments in these alloys under non equilibrium conditions.

II. Experimental Procedure

The alloys chosen are $\text{Ti}_{40}\text{Ni}_{60}$ and $\text{Ti}_{30}\text{Ni}_{70}$. Under equilibrium condition, they represent two phase mixtures of TiNi and TiNi_3 . The alloys are melt-spun under vacuum using a copper wheel. In all cases a wheel speed of 45 m/s is used. The samples are characterized by X-ray diffraction technique using a Huber Guinier diffractometer and transmission electron microscopy using a JEOL 2000 FX II microscope operating at 200 kV.

III. Results

1. $\text{Ti}_{40}\text{Ni}_{60}$ alloys

The X-ray diffraction pattern of the melt spun alloys reveals sharp B2 peaks of TiNi phase in addition to a superimposed broad peak (Fig. 1(a)). Further details of the structure and the microstructure were obtained by TEM. The microstructure of the melt spun alloy of $\text{Ti}_{40}\text{Ni}_{60}$ composition shows two different morphologies. One of them, which is more abundant, primarily contains metallic glass with ultrafine TiNi particles dispersed in the glassy matrix (Fig. 2(a)). The lack of contrast often makes it difficult to identify these particles in the bright field micrographs. However, the diffraction pattern clearly reveals the presence of these particles in the form of Debye rings (inset Fig. 2(a)). The other type of microstructure contains equiaxed grains (Fig. 2(b)). Under suitable contrast condition at higher magnification, one can also see very fine particles densely distributed in the matrix (inset in Fig. 2(b)). Diffraction patterns from the grains show two types of spots. The strong spots can be indexed in terms of B2- TiNi reflections with a lattice parameter of 0.295 nm. The weak spots can also be indexed in terms of a cubic cell (henceforth identified as γ) with a lattice parameter three times that of the B2 cell (0.885 nm) and sharing a cube on cube orientation relation. Dark field imaging establishes that the weak spots do not originate from double diffraction. The [100], [110] and $[\bar{1}11]$ zone patterns are shown in Fig. 3 together with the schematics illustrating the indexing. Figure 4 shows a bright field micrograph with insets of the central grain imaged with $(\bar{1}10)_{\text{TiNi}}$ and (001) $_{\gamma}$ reflections. Imaging with unique γ reflections (Fig. 4, right inset) lights up the fine particles in these cases.

Fig. 1 (a) X-ray diffraction pattern of $\text{Ti}_{40}\text{Ni}_{60}$ alloy showing B2-TiNi and glass (b) X-ray diffraction pattern of $\text{Ti}_{30}\text{Ni}_{70}$ alloy showing TiNi₃ and metastable A^9 structure.

2. $\text{Ti}_{30}\text{Ni}_{70}$ alloys

The X-ray diffraction pattern indicates the presence of TiNi₃ phase together with an unknown phase (Fig. 1(b)). The TEM investigations of as-solidified microstructure of $\text{Ti}_{30}\text{Ni}_{70}$ alloy show an equiaxed grain structure (Fig. 5(a)). A careful examination of these reveals that a fair number of regions shows a mixed morphology consisting of faulted regions along with fault free region (Fig. 5(b)). Figure 6(a), (b) and (c) show the electron diffraction patterns from the fault free regions. The streaks in Fig. 6(a) come from an adjoining faulted region. The patterns can be indexed in terms of equilibrium TiNi₃ phase corresponding to [010], [101] and [111] zones. The lattice parameters are found to be $a=0.5$ nm and $c=0.83$ nm.

The selected area diffraction patterns from the faulted regions reveal a hexagonal structure (A^9) with rhombohedral symmetry isotypic with BaPb_3 with $a=0.51$ nm and $c=1.88$ nm. The reflection from the unknown phase in the X-ray diffraction pattern can be indexed satisfactorily with this structure. Figure 7(a) shows an electron diffraction pattern of a [010] zone of the A^9 phase containing streaks due to faulting along c direction. The

Fig. 2 (a) Electron micrograph of melt spun $\text{Ti}_{40}\text{Ni}_{60}$ alloy showing very fine B2-TiNi dispersion in glass in most of the regions. The diffraction pattern obtained from this region is shown as inset. (b) Electron micrograph in some region showing very fine dispersion of a cubic phase in TiNi matrix in melt spun $\text{Ti}_{40}\text{Ni}_{60}$ alloys. Inset shows the presence of cubic particle in TiNi matrix.

indices are shown schematically in Fig. 7(b). Figure 7(c) shows BF microstructure of the corresponding region. The dark field images using (003) and (001) reflections are shown in Fig. 7(d) and (e).

IV. Discussion

1. Microstructure in glass forming alloys

The formation of a glass in $\text{Ti}_{40}\text{Ni}_{60}$ alloy confirms the earlier report of glass formation in this alloy by rapid solidification⁽⁴⁾⁽⁵⁾ and is consistent with the glass forming range of 34–84 at%Ti calculated by Bormann and coworkers using a subregular solution model⁽¹¹⁾. However, in our experiment, the glass coexists with TiNi. The most interesting observation of the present study is the coexistence of an equiaxed microstructure of TiNi grains containing a coherent precipitate. We also note that the formation of TiNi₃ is completely suppressed at this composition. The failure to see any B2 domain boundaries and the equiaxed morphology with no second phase at the boundaries for a composition falling in the two phase

Fig. 3 (a), (c) and (e) are the selected area diffraction patterns of $[100]$, $[110]$ and $[\bar{1}\bar{1}1]$ zones of TiNi. Very faint spots corresponding to the cubic precipitates are also seen. (b), (d) and (f) show corresponding schematic sketches. M represents matrix B-TiNi and p represents the cubic precipitate phase.

region of equilibrium diagram indicates that B2-TiNi formed directly from the melt by a massive solidification. This is further confirmed by the coherent precipitates inside the grain in the as solidified condition indicating the metastable nature of the as solidified TiNi grains that start decomposing during cooling. As discussed later, these precipitates normally appear in a slightly Ni rich TiNi alloys after prolonged aging.

It is generally believed that massive solidification of crystalline phases and glass formation cannot occur simultaneously. One of the criteria widely used for glass formation is a sloping T_0 curve such that the liquid does not cross T_0 curve before glass transition temperature⁽¹²⁾. This criterion is successful in many cases where the forma-

tion of metallic glass on rapid solidification is reported⁽¹³⁾. However, there exists no basic physical reason precluding competition between glass formation and massive solidification. The latter depends upon the solid-liquid interface velocity and the motion of the solute away from the interface. Both depend on the diffusivity of the solute in the melt. In a glass forming liquid the viscosity increases with undercooling resulting in a decrease in diffusivity. The critical trapping velocity in such a case may be small. Therefore, in a glass forming alloy, it is possible to have a window of cooling rate where nucleation followed by growth satisfying the trapping condition can compete with glass formation. An example of such a situation has already been discussed by Massalski⁽¹²⁾ for the Ti-Cu sys-

Fig. 4 Bright field image showing very fine γ particles in B2-TiNi matrix. The insets are the dark field images from $(\bar{1}10)_{\text{TiNi}}$ and $(001)_{\gamma}$.

tem. Our results suggest that in $\text{Ti}_{40}\text{Ni}_{60}$ alloy, similar situation exists and a local variation in cooling rate has resulted in two distinctively different morphologies.

Precipitation in near equiatomic Ni rich alloys has been studied earlier^{(14)–(16)}. Nishida and Wayman⁽¹⁴⁾ have reported a Ti_2Ni_3 phase in the Ti-52 at%Ni alloy which on cooling undergoes a tetragonal to an orthorhombic to a monoclinic phase transformation. None of our diffraction patterns could be indexed on the basis of these structures. Beyer and coworkers⁽¹⁵⁾ have reported a cubic precipitate ($a=0.88$ nm) during aging at 873 K in Ti-51.6 at%Ni and Ti-53.7 at%Ni alloys. The composition of the precipitate was reported to be close to Ti_5Ni_9 . Thus, the coherent precipitate observed by us in the quenched structure in $\text{Ti}_{40}\text{Ni}_{60}$ alloy may be similar or identical to that reported in the dilute alloys. Similar B2 based ordered phase with a tripling of the lattice parameter has been reported in transition metal rich aluminium alloys⁽¹⁷⁾⁽¹⁸⁾. The analysis suggests that these are γ brass type of structures based on the basic B2 type lattice. Evidence suggests that the γ brass structure can exist in different ordered states. The presently observed structure which is isotypic with the Al_4Cu_9 phase, may represent a B2 type of ordered structure of a basic bcc structure of γ brass.

2. Faulted structure in melt spun $\text{Ti}_{30}\text{Ni}_{70}$ alloys

Increasing the nickel component to 70 at% leads to the formation of the line compound TiNi_3 by rapid solidification. However, instead of the two phases, TiNi and TiNi_3 , we have observed a faulted phase which is polytypic to TiNi_3 coexisting with TiNi_3 . No evidence for the presence of the TiNi phase could be obtained in the present investigation. The intermetallic compound TiNi_3 has a hexagonal structure with close packed planes stacked in the c direction. It has a space group of $P6_3/\text{mmc}$ and is denoted by A^4 . Variation in stacking of the close-packed plane can lead to different structural variants.

One of the possibilities for the stability of the faulted

Fig. 5 (a) Electron micrograph showing equiaxed morphology of TiNi_3 phase in melt spun $\text{Ti}_{30}\text{Ni}_{70}$ alloys (b) A faulted phase (A^9) is seen along with intermetallic TiNi_3 in the melt spun $\text{Ti}_{30}\text{Ni}_{70}$ sample.

structure is the dependence of structure on the valence electron by atom ratio. By replacing 'Ni' by 'Ti' in TiNi_3 , one can obtain various types of stackings (A^4 , A^{10} , A^9 and A^{21}) like in the case of Ti-Ni-Nb and Ti-Ni-Cu systems⁽¹⁹⁾⁽²⁰⁾. The stacking symbols and lattice parameters of the various stackings of Ti-Ni-Nb are shown in Table 1. A^4 and A^9 are seen in the Ti-Ni-Cu system⁽²⁰⁾. Pfeifer and coworkers have shown that all structural variants of TiNi_3 are possible in the binary Ti-Ni system⁽²¹⁾. Bhan has reported A^{21} and A^4 structures in $\text{Ti}_{27}\text{Ni}_{73}$ alloy when quenched from 1573 K⁽⁶⁾. He has also seen A^{21} with traces of A^4 structures in the $\text{Ti}_{33}\text{Ni}_{67}$ alloy when quenched from its melt.

A^4 and A^{10} have hexagonal symmetry. However, A^9 and A^{21} have rhombohedral symmetry. 'Ni' is a transition metal with valence electron concentration zero. It is well known that 'Ni' takes the value of 0.3 at high temperatures⁽²¹⁾ and Ti has a value of 4. Hence TiNi_3 structure has electron by atom ratio of 5/4. When Ti replaces Ni in TiNi_3 , it can take different stacking variants yielding A^{10} , A^9 and A^{21} structures corresponding to electron by atom ratio of 13/10, 12/9 and 30/21 respectively.

The present work is the first transmission electron

Fig. 6 Selected area diffraction patterns of the various zones of the TiNi_3 phase. (a) [010], (b) [101], (c) [111].

microscopic evidence for the presence of a faulted structure in the Ti–Ni system. The A^9 structure is seen along with A^4 . The A^{21} reported by Bhan is not seen in the present study. The lattice parameters of A^{21} structure as reported by Bhan are $a=0.2549$ nm and $c=4.3684$ nm which is quite different from that of A^9 . The lattice parameters calculated for the A^9 structure seen in the present work are $a=0.51$ nm and $c=1.88$ nm. This is found to be very close to a similar structure seen in the Ti–Ni–Nb system⁽¹⁹⁾.

Van Vucht has discussed in detail about the size effect in the AB_3 type intermetallic compounds⁽¹⁹⁾. He has tried to explain the structures in terms of Cu_3Au and Ni_3Sn structures. Cu_3Au is having a close packed cubic structure and it forms when $r_A/r_B=1$. Ni_3Sn is having a close packed hexagonal structure with a higher r_A/r_B value where r_A and r_B are the radius of the atoms. The structure with r_A/r_B in between these two, can be explained as a

mixture of these two structures. Although he could use the concept of size satisfactorily for most of the systems, in some systems like in Ni_3Ti – Ni_3Al and Ni_3Ti – Ni_3Zr , it was not successful. In the present case, Ni_3Ti is having a stacking of ‘hchc’ with 50% hexagonality. If the Ni is replaced by Ti, the hexagonality should decrease according to the size argument. This is because, in Ni_3Ti , Ti by Ni (r_A/r_B) ratio is 1.18. If Ti replaces Ni, r_A/r_B should decrease and hence it is expected to take a more cubic structure. In the present case, the A^9 structure isotypic with BaPb_3 structure is seen which is having a stacking of (chh)³. This implies that the size effect is not valid in our case. The observed faulted structure is most likely stabilised because of composition shift since the alloy composition and the TiNi_3 intermetallic composition are different.

Fig. 7 (a) [010] zone of A⁹ phase. (b) Schematic sketch of [010] zone of A⁹ phase. (c) Zone image of A⁹ phase. (d) and (e) DF image from (003) and (001) of A⁹ phase.

Table 1 Various structural variants of TiNi₃ observed in Ti-Ni-Nb.

Composition	Notation	Type	Structure symbol	e/a ratio	Lattice parameters (nm)	Symmetry
Ni ₃ Ti	A ⁴	Ni ₃ Ti	(ch) ²	5/4	$a=0.5109$ $c=0.8299$	P6 ₃ /mmc
Ni ₃ (Ti _{0.97} , Nb _{0.03})	A ¹⁰	TaPd ₂	(chhch) ²	13/10	$a=0.5106$ $c=2.081$	P6 ₃ /mmc
Ni ₃ (Ti _{0.89} , Nb _{0.11})	A ⁹	BaPb ₃	(chh) ³	12/9	$a=0.5115$ $c=1.8809$	R $\bar{3}$ m
Ni ₃ (Ti _{0.67} , Nb _{0.33})	A ²¹	Ni ₃ Sn	(chhhhhh) ³	30/21	$a=0.513$ $c=0.4211$	R $\bar{3}$ m
Ni ₃ (Ti _{0.25} , Nb _{0.75})	—	Cu ₃ Ti	h	—	$a=0.511$ $b=0.453$ $c=0.421$	P6 ₃ /mmc
			o	—		Pmmn

V. Conclusions

(1) A glassy phase has been observed in $\text{Ti}_{40}\text{Ni}_{60}$ specimens in agreement with the glass forming range in this system.

(2) A cubic phase with a tripling of the lattice parameter of B2-TiNi has been observed in limited regions of $\text{Ti}_{40}\text{Ni}_{60}$ samples. These cubic precipitates formed by solid state precipitation during cooling. This cubic precipitate is having a structure isotypic with Al_4Cu_9 .

(3) A faulted structure (A^9), with rhombohedral symmetry, polytypic to TiNi_3 phase has been observed in melt spun $\text{Ti}_{30}\text{Ni}_{70}$ alloys. It has lattice parameters $a=0.51$ nm and $c=1.88$ nm. The faulted structure has been stabilised by specific valence electron by atom ratio.

REFERENCES

- (1) J. L. Murray: *The Ti-Ni System, Phase Diagrams of Binary Titanium Alloys*, (Binary Systems; Review), ASM International, (1987), p. 197.
- (2) C. C. Jia, K. Ishida and T. Nishizawa: *Experimental Methods of Phase Diagram Determination*, ed. by J. E. Morral, R. S. Schiffman and S. M. Merchant, The Mineral and Materials Society, Warrendale, USA, (1994), p. 31.
- (3) D. E. Polk, A. Calka and B. C. Giessen: *Acta Metall.*, **26** (1978), 1097.
- (4) K. H. J. Buschow: *J Phys. F*, **13** (1983), 563.
- (5) K. H. J. Buschow: *J. Appl. Phys.*, **56** (1984), 304.
- (6) S. Bhan: *J. Less-Common Metals*, **25** (1971), 215.
- (7) D. E. Laughlin: *Acta Metall.*, **24** (1976), 53.
- (8) S. H. Whang: *Undercooled Alloy Phases*, ed. by E. W. Colling and C. C. Koch, TMS-AMIE, Warrendale, USA, (1987), p. 163.
- (9) R. Nagarajan, K. Aoki and K. Chattopadhyay: *Metall. Mater. Trans.* (in press).
- (10) C. Seeger and P. L. Ryder: *Mater. Sci. Engg.*, **A179/A180** (1994), 641.
- (11) R. Bormann and K. Zoltzer: *Phys. Stat Sol. (a)*, **131** (1992), 691.
- (12) T. Massalski: *Proc. 5th Inter. Conf. on Rapidly Quenched Metals*, ed. by S. Steeb and H. Warlimont, Elsevier Science Publishers B.V., (1985), p. 171.
- (13) S. H. Whang: *Mater. Sci. Engg.*, **57** (1983), 87.
- (14) M. Nishida and C. M. Wayman: *Metall. Trans.*, **18A** (1987), 785.
- (15) J. Beyer, R. A. v. d. Brakel and J. R. T. Lloyd: *International Conference on Martensitic Transformation*, Japan Inst. Metals, (1986), p. 703.
- (16) J. J. Swens, P. F. Willemse and J. Beyer: *J. de Physique*, **49** (1988), c6, 359.
- (17) G. V. S. Sastry, K. K. Bariar, K. Chattopadhyay and P. R. Rao: *Z. Metallkunde*, **71** (1990), 756.
- (18) V. T. Swamy, S. Ranganathan and K. Chattopadhyay: *J. Mater. Res.*, **4** (1989), 539.
- (19) J. H. N. Van Vucht: *J. Less-Common Metals*, **11** (1966), 308.
- (20) F. J. J. Van Loo, G. F. Bastin and A. J. H. Leenen: *J. Less-Common Metals*, **31** (1978), 111.
- (21) H. U. Pfeifer, S. Bhan and K. Schubert: *J. Less-Common Metals*, **14** (1968), 291.