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COMMENTS ON "THE EARLY STAGES OF THE TRANSFORMATION IN DILUTE ALLOYS OF TITANIUM IN NICKEL."

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In describing the decomposition of supersaturated Ni-12 at.% Ti, Watts and Ralph [1], hereafter designated W-R,

(i) give an incorrect and misleading description of the early-stage transformation microstructure observed by conventional transmission electron microscopy (CTEM), and

(ii) propose subsequently that ordering precedes compositional segregation, whereas previously it has been found that these processes are either concurrent [2] or that the reverse is true [3].

The purpose of this note is to clarify the terms appropriate for describing either tweed or modulated structures and to reconfirm the ideas related to the decomposition sequence in nickel-titanium alloys.

W-R [1] state that the fine-scale striated microstructure they observe "....is essentially the same as the 'tweed contrast' observed by Tanner in Ni_2V and other systems...." A re-reading of the references cited [4,5] and others [6,7] will clarify that tweed, a term originally coined by Armitage [8], is meant to describe only those linear variations in contrast which lie roughly parallel to the traces of {110} planes of a transforming parent cubic solid solution (see Fig. 1). This, as will be seen below, is distinctly and significantly different from the {100} striated structures observed in Ni-Ti [1,3] and other spinodal alloys [9,10].

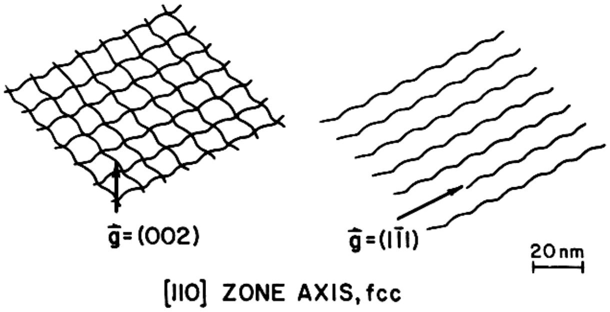

Fig. 1. Schematic of <110> tweed microstructure. Note that the striations lie along traces of {110} planes and that one set of striations is out of contrast for $\vec{g}$ = (111).

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The {110} tweed was first observed in low-temperature aged Cu-2 wt.% Be alloys [6,8]; later it was found during long-range ordering at large undercoolings in stoichiometric CuAu, CoPt, Ni_3V, Ni_2V, Ni_4Mo, etc. [4], and most recently, during the aging of off-stoichiometric Ni-rich Ni-Mo [11] and Ni-V alloys [7]. In each and every instance, these transformations involve the formation of a phase with tetragonal symmetry from, and coherent with, its cubic parent matrix [4]. Qualitatively, this type of microstructure has been most satisfactorily explained in terms of a net-matrix strain contrast arising from the strain field interactions of a large number-density of regularly arranged, closely spaced "point centers" of tetragonal distortion (particles) [12-16]. The tetragonal and cubic cells are mutually parallel and the three tetragonal orientation variants are mutually perpendicular.

The striations in the CTEM image are uniquely related to diffuse strain "rel-rods" at fundamental reflections in diffraction patterns. The real space striations and the "rel-rods" in reciprocal space follow precise strain-derived conditions for visibility which have been illustrated in detail by Tanner [6] for Cu-2 wt.% Be and by Okamoto and Thomas [5] for Ni_4Mo (cf. Fig. 1 and 2). It is these unique properties in morphology and diffraction effects that have been suggested as a method for distinguishing between modes of continuous transformation (whether spinodal ordering or spinodal clustering) [7] where the ordered second phase is tetragonal, e.g., Cu-Ti [10] and Ni-Mo [11].

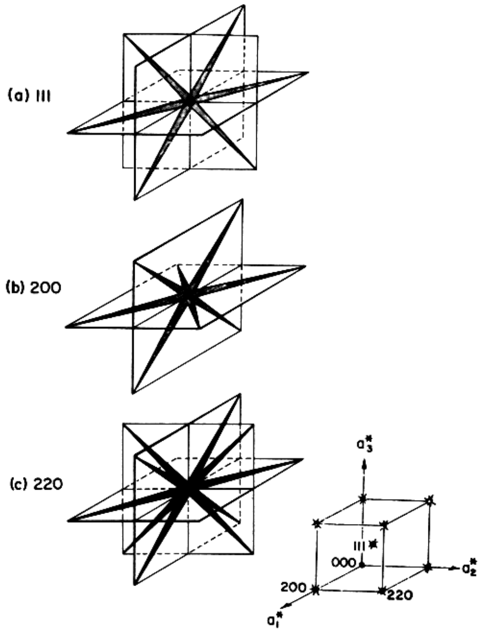

Fig. 2. Schematic representation of the <110>* "rel-rods" observed in specimens which contain {110} tweed from Ref. 6. Notice how the number of "rel-rods" varies with $\{hk\ell\}$.

For Ni-Ti the ordered phase is cubic like its parent matrix. Hence, the discussion of tweed in the manner used by W-R is inappropriate and confusing. The striations in this system lie along the traces of {100} planes in real space (see Ref. 3 , Figs. 4 and 5; cf. Ref. 1, Fig. 1). These striations obey the following visibility conditions; those parallel to an operating $\vec{g}$ reflection are absent; see Fig. 3, which is a schematic representation of the microstructure described in Ref. 3.

The striations in this type of microstructure have been correlated unambiguously with modulations in the local composition [17] which evidences itself by concomitant strain modulations. These strain modulations give rise to satellite reflections in the reciprocal lattice which flank the fundamental reflections in the<100>* directions, as shown in Fig. 4. From the figure it can be seen that the satellites are absent if the vector joining the satellite to its fundamental reflection is perpendicular to the reciprocal lattice vector. (n.b. Satellites arising from structure factor modulations are usually much weaker in intensity than those arising from strain modulations. We therefore have not included them in Fig. 4.)

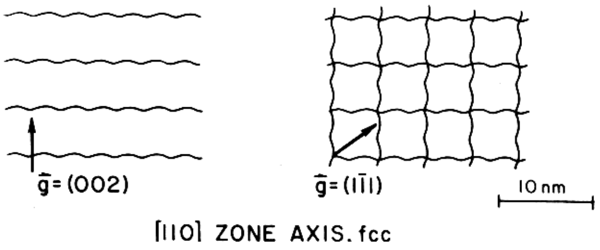

Fig. 3. Schematic of the {100} spinodal microstructure observed before distinct particles can be imaged in BF. The striations are parallel to traces of {100} planes and the microstructure observed with $\vec{g}$ = {111} operating contains two sets of striations (cf. Fig. 1).

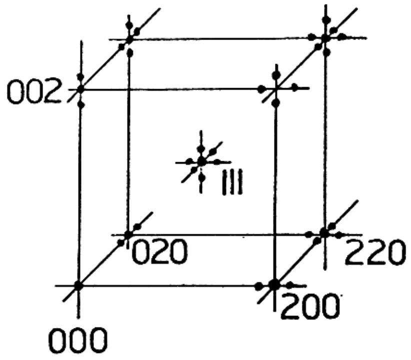

Fig. 4 The distribution of satellites in reciprocal space arising from strain modulations in real space for spinodal clustering along <100>.

The satellites have spacings inversely proportional to the wave length of the real space modulation, independent of $\vec{g}$. These characteristics are quite different, and easily distinguishable, from those of a tweed microstructure.

It should be emphasized that the experimental findings of W-R do not conflict with those of Laughlin [3]; but that the description and succeeding discussion do. Unfortunately Figure 1 of W-R does not include any crystallographic data. However, the facts that the operating $\vec{g}$ is given as $(\bar{1}\bar{1}1)$ and that two sets of striations are present rule out the existence of {110} tweed in the microstructure (cf. Ref. 1, Figs. 1(b) and 3(b)). The microstructure is entirely consistent with a {100} spinodal clustering decomposition, as indeed are the satellite positions. The importance of this to the decomposition sequence of supersaturated nickel-titanium is that W-R propose that ordering precedes compositional segregation, whereas previously,it has been found that these processes are either concurrent [2] or that the reverse occurs [3]. It seems unlikely to us that ordering is the first reaction, and the evidence put forward by W-R is not convincing in this respect.

Firstly, ordering does indeed occur from the start of the transformation in Ni-14% Ti, but is clearly confined to discrete regions which have higher average composition than that fo the surrounding disordered matrix [2]. It is interesting to note that the composition modulation amplitude associated with these regions is 6% Ti [2], the same as that found in quenched Ni-12% Ti by W-R [1]. This implies that clustering had already occurred.

Secondly, the lattice parameter difference commensurate with a composition excursion of 6% Ti is 2 x 10^{-1}nm or 0.6% (the variation of lattice parameter being 0.1% per % Ti in this system [18]). This is considerably greater than the contraction due to ordering, estimated as 1.23% by W-R [1] or as 0.13% from the measured [2] average lattice contraction on aging Ni-14% Ti multiplied by the volume fraction of the ordered phase. Thus,the lattice parameter modulations due to composition fluctuations would give rise to more marked satellite reflection than those due to the ordering contraction. That these modulations are also present in the quenched alloy of W-R [1] indicates that clustering, not ordering, is primarily responsible for the presence of satellites.

Our results and interpretation have recently been substantiated by Wood, Mills, Bingham and Bee [19]. They report that in a Nimonic 80A alloy ordering is subsequent to spinodal decomposition. Fig. 7(b) of their paper shows one set of {100} striations. These were present before any superlattice reflections could be observed. Unfortunately they, like W-R, term the {100} contrast "tweed". Nevertheless the *mechanism* and *sequence* of phase separation proposed by Wood,et al. is identical to ours.

In summary, W-R's description of the decomposition process in Ni-Ti is not consistent with experimental results which show quite clearly that the alloy decomposes along <100> directions. The ordering occurs either concomitant with, or subsequent to, the initial decomposition. The observed satellites arise from the fluctuation in the lattice parameter that exists because of the development of composition modulations.

Acknowledgments

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References

1. A.J. Watts and B. Ralph, Acta Met. 25, 1013 (1977).
2. R. Sinclair, J.A. Leake and B. Ralph, Phys. Stat. Sol.(a) 26, 285 (1974).
3. D.E. Laughlin, Acta Met. 24, 53 (1976).
4. L.E. Tanner and H.J. Leamy, *Order-Disorder Transformations in Alloys*, H. Warlimont, Ed. p. 180. Springer-Verlag, Berlin (1974).
5. G. Thomas, *Modern Diffraction and Imaging Techniques in Materials Science*, S. Amelinckx, R. Gevers, G. Remaut and J. Van Landuyt, Eds., p. 131. North-Holland,Amsterdam (1970).
6. L.E. Tanner, Phil. Mag. 14, 111 (1966).
7. L.E. Tanner and D.E. Laughlin, Scripta Met. 9, 373 (1975).
8. W.K. Armitage, PhD Thesis, University of Leeds (1963); see also,W.K. Armitage, P.M. Kelly and J. Nutting, Proc. 5th Int. Cong. Elect. Micr., K4 (1962).
9. E.P. Butler and G. Thomas, Acta Met. 18, 347 (1970).
10. D.E. Laughlin and J.W. Cahn, Acta Met. 14, 1295 (1975).
11. L. Nesbit and D.E. Laughlin, Acta Met. 26, 815 (1978).
12. P.J. Fillingham, PhD Thesis, Stevens Institute of Technology, Hoboken,NJ (1973).
13. P.J. Fillingham, H.J. Leamy and L.E. Tanner, *Electron Microscopy and Structure of Materials*, G. Thomas, R.M. Fulrath and R.M. Fisher, Eds., p.163. Univ. of Calif. Press, Berkeley, CA (1972).
14. Ph. Eurin, J.M. Penisson and A. Bourret, Acta Met. 21, 559 (1973).
15. V.A. Phillips and L.E. Tanner, Acta Met. 21, 441 (1973).
16. Yu. D. Tyapkin, *Ann. Rev. Mat. Sci.*, Vol. 7, R.A. Huggins, Ed.,p.209. Annual Reviews Inc., Palo Alto, CA (1977).
17. R. Sinclair, R. Gronsky and G. Thomas, Acta Met. 24, 789 (1976).
18. R. Sinclair, PhD Thesis, Cambridge University, (1972).
19. J.V. Wood, P.F. Mills, J.K. Bingham and J.V. Bee, Met. Trans. 10A, 525 (1979).