

EXPERIMENTAL OBSERVATIONS OF CONTINUOUS TRANSFORMATIONS IN BINARY ALLOYS

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Theoretical analyses of continuous transformations in crystalline solid solutions, *viz.*, clustering, ordering and their combinations, have been approached from various viewpoints and most recently, deFontaine (1,2) has attempted to formulate a unified treatment for these processes. Experimental studies utilizing X-ray diffraction (XRD), selected area electron diffraction (SAD), transmission electron microscopy (TEM) and field-ion microscopy (FIM) have become increasingly effective in correlating direct observation of the transitions with theory. However, there is often some degree of controversy regarding the interpretation of experimental observations in this field. Such is the case in the work to be discussed here which deals with variations in transformation mode from one alloy system to another where the final assembly is comprised of two phases: one disordered and the other ordered.

The earliest theories of continuous transformations were primarily concerned with the clustering of like atoms, namely spinodal decomposition (3), or *spinodal-clustering* according to deFontaine's terminology (1,2). Here, when the disordered parent phase is rapidly quenched to low temperatures, it can become unstable to large-scale (30-100Å) concentration fluctuations and then proceed to separate into two disordered phases of differing composition, but usually identical crystal structure. A variety of clustering systems have been examined and the results have shown both the kinetics and microstructure to agree excellently with theoretical predictions (3-6).

Subsequent theoretical analyses applied to long-range ordering (7-10) have indicated that a disordered solid solution of specific stoichiometry may, upon substantial undercooling below its critical ordering temperature, become unstable to ordering fluctuations (concentration fluctuations of interatomic dimensions). In this case, the parent phase spontaneously orders, *i.e.*,

undergoes *spinodal-ordering* (1,2).* TEM and SAD observations of the reactions in certain stoichiometric alloys have been interpreted as evidence of this mode of transformation (9,11,12).

In the latest continuous transformation theory, Richards and Cahn (13,14) considered the behavior of alloys whose equilibrium two-phase state at low temperatures is comprised of a disordered terminal solid solution and a stoichiometric ordered phase. Their treatment indicates that the decomposition of the high-temperature parent can proceed by various modes, with intermediate paths being possible at any stage of the reaction. Restricting ourselves to the simplest and most probable view, the prominent processes may be expected to be: (a) nucleation of the equilibrium phase within the disordered phase, (b) continuous mode I - metastable spinodal-clustering and the ordering of the solute-rich phase either consecutively or concurrently, or (c) continuous mode II - metastable spinodal-ordering of the quenched solid solution. Evidence for continuous modes I and II have been found in recent studies of Ni-Ti (15-17), Cu-Ti (18,19), Ni-V (20-22) and Ni-Mo (20,23,24) alloys.

In alloys of Ni with 8-14 at.% Ti, TEM shows the development of $\langle 100 \rangle$ clustering modulations and SAD reveals associated satellites at the f.c.c. reflections during the initial stages of decomposition after quenching and aging (17). These effects are very closely followed by the appearance of superlattice reflections of the metastable *cubic* $L1_2$ (Cu_3Au type) ordered structure originating from the Ti-rich regions. FIM studies of an alloy of higher Ti content found the phase separation and ordering processes to be virtually concurrent (16).

A similar sequence with identical initial microstructural and diffraction effects results during the aging of Cu-Ti alloys (17-19). In this case, however, the metastable Ti-rich regions subsequently order into the *tetragonal* $D1_a$ (Ni_4Mo type) structure. It is to be noted that the initial phase separation stage in both these systems proceeds in the manner well documented for spinodal-clustering in the classic Cu-Ni-Fe system (5). The observed morphology of the f.c.c. clustering modulations is consistent with the expected effect of elastic anisotropy according to theory (3). That is, the $\langle 100 \rangle$ directionality (as shown for example in Fig. 1) follows for an anisotropy factor $A > 1$,** where A for each alloy has been considered comparable to that for the solvent elements (25), *viz.*, $A_{\text{Ni}} = 2.5$ and $A_{\text{Cu}} = 3.2$.

In marked contrast, the decomposition of Ni-V (20-22) and Ni-Mo (20,23,24) alloys exhibit rather different morphology. The initial microstructure is one of fine-scale striations lying parallel to traces of $\{110\}$ planes (see Fig. 2).

*Richards (13) used "continuous ordering" to describe this process, but deFontaine (2) has chosen to reserve this term for a special variation of spinodal-ordering.

** $A = 2c_{44}/(c_{11} - c_{22})$, where c_{ij} are the elastic constants of the material.

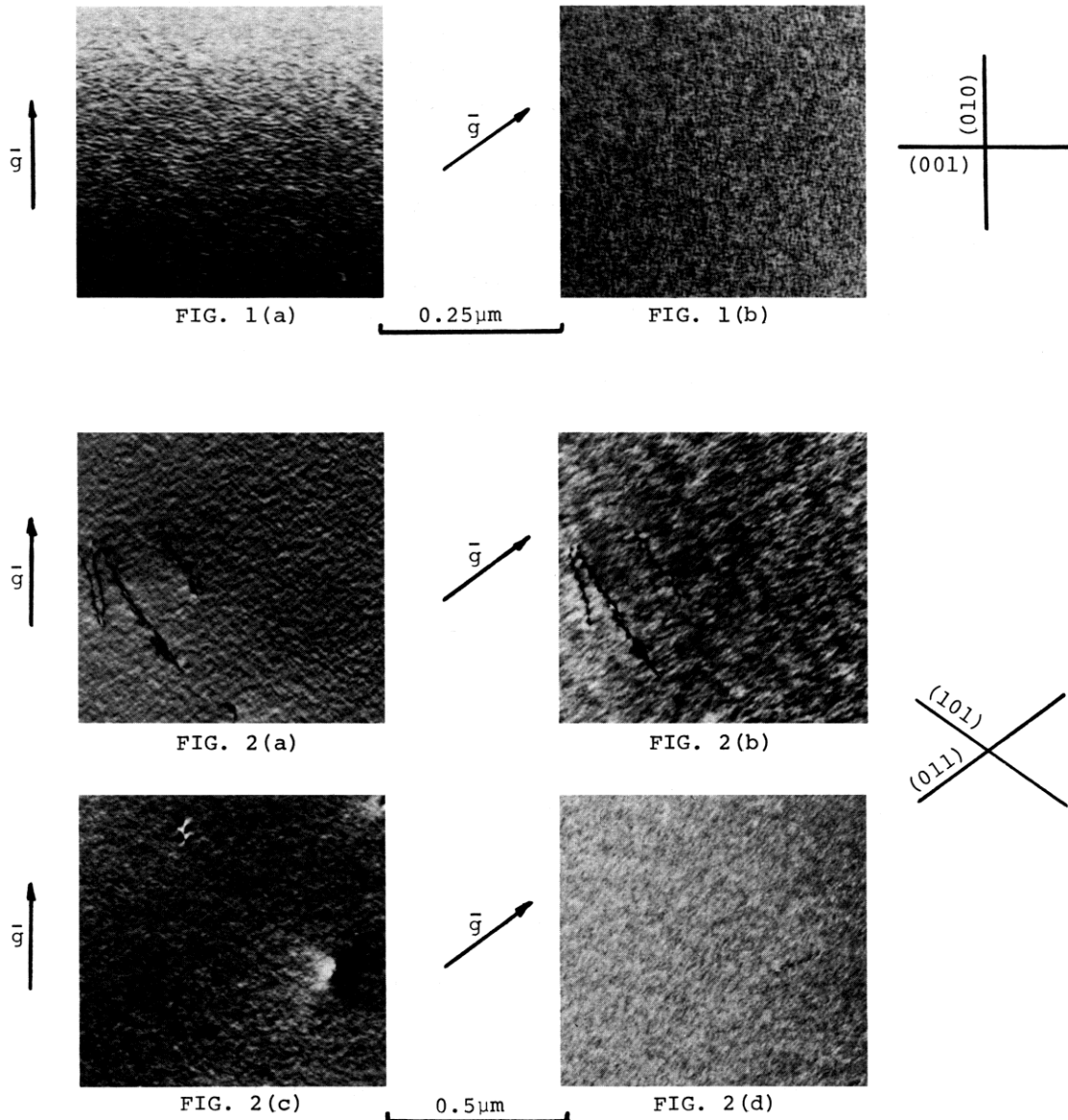


FIG. 1 Cu-6.8 at.% Ti, iced brine quenched from 900°C, aged 1 min. 400°C. Bright field two beam electron images, foil near [110]. (a) $\bar{g} = 002$, composition modulations along (001) traces. (b) $\bar{g} = 1\bar{1}1$, composition modulations along (001) and (010) traces. Diffraction patterns show satellites along $\langle 100 \rangle$. For a more detailed description of these effects see Laughlin & Cahn (19).

FIG. 2. Bright field two beam electron images, foil near [110]. (a) & (b) Ni-18 at.% V, iced brine quenched from 1000°C, aged 10 min. 600°C. (a) $\bar{g} = 002$, tweed striations along (011) and (101) traces. (b) $\bar{g} = 1\bar{1}1$, tweed striations only along (011) traces. (c) & (d) Ni-16.7 at.% Mo, iced brine quenched from 900°C, aged 18 hrs. 600°C. (c) $\bar{g} = 002$, tweed striations along (011) and (101) traces. (d) $\bar{g} = 1\bar{1}1$, tweed striations only along (011) traces. Diffraction patterns show $\langle 110 \rangle$ strain rellods. Tanner (35) gives detailed description of these effects as seen in a Cu-Be alloy; also see review by Thomas (36).

In addition, there is no evidence of satellites flanking the fundamental reflections in diffraction patterns. Superlattice reflections for the tetragonal ordered phases [$\text{Ni}_3\text{V}(\text{DO}_{22})$ in Ni-V alloys and $\text{Ni}_4\text{Mo}(\text{Dl}_a)$ in Ni-Mo alloys] appear as aging proceeds and ultimately, quasi-periodic two-phase assemblies develop in both systems. Moreen, *et al.* (22) interpret the Ni-V behavior as characteristic of spinodal-clustering followed by ordering (mode I), where the initial composition modulations are along $\langle 111 \rangle$ directions in the f.c.c. parent. The $\{110\}$ morphology is said to result from the interaction of certain $\{111\}$ modulations according to a model proposed by Cahn (26). This interpretation requires that $A < 1$ for these alloys (3); however, the authors make no attempt to justify their implication that V alters the elastic properties of the solvent Ni in this direction, and there is no data in the literature to support this assumption. Furthermore, and perhaps of more importance, Moreen, *et al.* (22) ignore the absence of $\langle 111 \rangle$ directed satellites which would be expected to form during the initial spinodal-clustering process (3).

An alternative interpretation is that the Ni-V and Ni-Mo transformations proceed by means of spinodal-ordering (mode II). This view is based on a different identification of the microstructure which follows from observations of long-range ordering transitions (12). The $\{110\}$ striated microstructures described above are identical to the "tweed" strain contrast associated with spinodal-ordering in stoichiometric Ni_3V (27) and Ni_4Mo (9), as well as Ni_2V (11), Ni_2Cr (28), CuAu (29), CoPt (30), *etc.* In all these systems the parent-to-product shape-change is the same, *viz.* cubic \rightarrow tetragonal. It has been suggested (11,12) that when the parent f.c.c. phase in each system becomes unstable to its particular ordering fluctuations, the initial atomic rearrangements give rise to correlated regions of tetragonal distortion within the cubic matrix. The resultant "net matrix strain" produces the characteristic $\{110\}$ tweed. The nature and extent of the correlation have yet to be established unambiguously. However, calculations where the strain has been represented by dense arrays of infinitesimal prismatic dislocation loops (point sources of tetragonal strain) show that: (a) randomly arranged strain centers are insufficiently correlated to produce such a regular contrast and (b) only certain two-dimensional arrays can successfully simulate the observed tweed (31,32). In addition, these particular arrays prove to be the most favorable in terms of elastic interaction energies (32-34).

According to the foregoing arguments, we contend that TEM and SAD have the potential for distinguishing between continuous transformation modes in alloys where a shape-change is involved. This is particularly striking when comparing the mode I behavior of Cu-Ti (Fig. 1) and the mode II behavior of Ni-Mo (Fig. 2), where both systems possess identical parent and product crystal structures. The details of mode I transformations are sufficiently well understood (16-19) so that reliable quantitative structural and kinetic analyses can be made with the techniques being utilized up to the present (though improvements should be possible with the use of high resolution TEM which allows for direct lattice

imaging). On the other hand, less is known about mode II transformations as was pointed out in a previous paper (12), so that further study of the early stages of spinodal-ordering reactions is required. Such work is in progress for both the Ni-V and Ni-Mo systems (20).

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