

This Week's Citation Classic

Ardell A J & Nicholson R B. On the modulated structure of aged Ni-Al alloys. *Acta Metall.* **14**:1295-309, 1966. [Dept. Metallurgy and Cavendish Lab., Univ. Cambridge, Cambridge, England]

The modulated microstructure of aged Ni-Al alloys evolves from an initially random spatial distribution of precipitates. The kinetics of precipitate growth are consistent with an Ostwald ripening process. The modulated structure is not a consequence of spinodal decomposition, but results from elastic interactions between the precipitates. [The *SCI*[®] indicates that this paper has been cited over 145 times since 1966.]

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October 22, 1980

"In the 1950s there was a flurry of interest in the metallurgical community in 'modulated' microstructures, i.e., precipitates which are not randomly distributed throughout the matrix solid-solution, but which tend to line up along certain, easily identifiable, crystallographic directions. In 1962, Cahn¹ published one of his classic papers on spinodal decomposition, a process whereby decomposition of the thermodynamically unstable matrix proceeds by the growth of selected composition fluctuations. These are predicted to occur along specific crystallographic directions in a more-or-less periodic manner, resulting ultimately in a modulated microstructure. Physical metallurgists were quick to recognize the importance of Cahn's theory, and it became nearly gospel that all modulated microstructures were a consequence of spinodal decomposition.

"In 1961, Lifshitz and Slyozov,² and Wagner³ (LSW) published their theories of Ostwald ripening, a process whereby precipitates of greater than average size grow at the expense of small precipitates in order to reduce the precipitate-matrix interfacial energy.

"When I arrived at the University of

Cambridge as an NSF postdoctoral fellow in August 1964, I knew virtually nothing about spinodal decomposition, and had not even heard of Ostwald ripening. After having done my graduate work at Stanford on creep, I wanted a complete change of research area, and the emerging field of transmission electron microscopy (TEM) seemed like an appropriate choice, especially since most of the exciting theoretical and experimental work on crystalline materials was being conducted in Cambridge at that time.

"Robin Nicholson of the department of metallurgy suggested that I study the precipitation process in nickel-aluminum alloys. The precipitate that forms in these alloys is shaped like a cube with rounded corners and edges, has a crystal structure closely related to that of nickel, but has a slightly larger unit cell which causes some strain in the matrix. The microstructure of these alloys evolves to a modulated microstructure.

"Using TEM to measure the sizes of the precipitates, it was obvious that during the initial stages of aging the microstructure was clearly not modulated; the precipitates were randomly distributed throughout the matrix. Only as aging proceeded did the microstructure evolve toward the modulated variety. This was not the sequence of events predicted by Cahn's theory. Furthermore, measurements of the growth kinetics were consistent with the behavior predicted by the LSW theory; the microstructure indisputably became modulated during the process of Ostwald ripening. I felt that the elastic strains in the matrix might account for the tendency towards modulation, but couldn't prove it. J. D. Eshelby, who was then in the Cavendish Laboratory, turned out to be interested in applying his considerable prowess as a theoretical elastician to the problem of elastic interactions between the precipitates in this alloy. It was he who ultimately produced the theoretical calculations proving that the precipitates became aligned to lower their elastic energy. Eshelby's contribution was published as a separate appendix to the paper.

"I believe that the paper has been highly cited because it convincingly dispelled the notion that all modulated microstructures are a consequence of spinodal decomposition, and presented an alternate plausible explanation. Also, the measurements of the precipitate growth kinetics provided the first, albeit semiquantitative, evidence that the LSW theory was correct."

1. **Cahn J W.** On spinodal decomposition in cubic crystals. *Acta Metall* **10**:179-83, 1962.
2. **Lifshitz I M & Slyozov V V.** The kinetics of precipitation from supersaturated solid solutions. *J. Phys. Chem. Solids* **19**:35-50, 1961.
3. **Wagner C.** Theorie der Alterung von Niederschlagen durch Umlosen (Ostwald-Reifung). *Z. Elektrochem.* **65**:581-91, 1961.