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Martensitic Transformations in Ferrous and Non-Ferrous
Systems -- Some Heuristic Comparisons**

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Synopsis

Phase transformations in non-ferrous systems exhibit similarities as well as some striking differences when compared with those in iron base alloys and steels. The study of these is not only of considerable theoretical and practical interest per se (because, for example, the product phase may be ferroelectric, ferroelastic, or superconducting) but such comparisons frequently shed light on the nature of the corresponding transitions and phenomena in ferrous systems. In particular, studies of the crystal geometry, morphology, and kinetics in non-ferrous systems have contributed (and are contributing) to our understanding of the behavior in steels. Three examples are described briefly to illustrate and support this thesis: (1) the Wechsler-Lieberman-Read phenomenological theory, which was developed to describe the transitions in InTl and AuCd and which was applied with such remarkable success to the (259) martensite transformation in Fe-Ni-C; (2) the apparent difference in habit plane orientation between insulating and semiconducting BaTiO_3 and KTN and the reason that the latter is rather precisely described by the W-L-R theory while the former does not seem to be. This will hopefully lead us to

introduce more physics into attempts to understand the shift in habit from (259) to (225) in steels rather than arbitrary adjustable dilatations, complex and contrived shear systems, and mathematical manipulations; (3) the "eigenthal" transformation in AuCd, which suggests that the terms "isothermal" or "athermal" applied to transformations in steels may, in some cases at least, really only describe the particular conditions under which the transition was observed and not the true nature of the transformation.

The meaning of the word "martensite" has been considerably expanded in the last 75 years and the history of its development recounted.^(1,2,3) It was first proposed by Osmond in 1895 in honor of the German metallurgist Martens to designate the hard, ferromagnetic, plate-like constituent in steel shown in Fig. 1. The martensite transformation was observed to be heterogeneous and accompanied by the formation of new interfaces with a shear-like shape change. It is, in general, not thermally activated (since it can occur very rapidly at liquid helium temperatures) and the interface between the parent (austenite) and product moves rather easily, i.e., is glissile. About 35 years ago Kurdjumov and co-workers⁽⁵⁾, and Greninger and colleagues⁽⁶⁾, began to report similar morphologies in phase transitions in non-ferrous systems, particularly those of Cu with Al, Zn, and Sn. At about the same time Ölander⁽⁷⁾ (and later Benedicks⁽⁸⁾) pointed out some of the unusual mechanical properties of the product phase resulting from a similar transformation in AuCd. Thus within a half century, the word "martensite" had been generalized to designate the product of any shear-like displacive transformation which results in surface relief effects or upheavals indicating an inhomogeneous shape

deformation even though there is little or no resemblance of the product phase to that in steels, and the phrase "martensite (or martensitic) transformation" is used to describe this special type of polymorphic phase transition characterized by certain geometric or crystallographic features even when observed in non-ferrous and even non-metallic systems.

Such transformations from one crystal structure to another--usually with a change of symmetry--have been observed primarily under conditions of continuous cooling. In addition to (1) the shape deformation which results in surface upheavals, they exhibit (2) an irrational undistorted habit plane separating parent and product whose normal is characteristic of the material, (3) a rather precise orientation relationship between principal directions and planes in the two phases and lattice correspondence, and (4) frequently a fine inhomogeneous structure, such as twins, which is usually observed in the product. In general, atoms move less than interatomic distance, nearest neighbors are maintained as far as possible, and the degree of order in the parent phase persists in the product; departures from the last mentioned feature have been discussed and a simple

scheme for classification of martensitic and martensitic-like transformations has been proposed.

The number of metallic and non-metallic systems which satisfy the geometric criteria delineated above is large (and will not be reviewed here) and it is generally accepted that most of the transitions can be described as "martensitic" and the products "martensite", although this was not always the case.⁽⁹⁾ Some materials transform to a sequence of structures of decreasing symmetry as the temperature is decreased. Thus U , BaTiO_3 , NbRu ⁽¹⁰⁾, KTN , Np , and TaRu ⁽¹¹⁾ exhibit a cubic to tetragonal to orthorhombic transformation as the temperature is lowered. Frequently, some important and useful property is associated with the product phase, such as the high hardness and ferromagnetism in iron base alloys; ferroelectricity in the titanites; order, anti-ferromagnetism or ferroelasticity in some intermetallic compounds; and a change from semiconductor to metallic conductor in some oxides. The study of phase transitions in non-ferrous systems is thus not only of considerable theoretical and practical interest per se, but an examination of the similarities--and some striking differences--exhibited when compared with the behavior of iron base

alloys frequently sheds light on the nature of the transformation in the ferrous systems. In particular, it will be shown how studies of the crystal geometry, morphology, and kinetics in non-ferrous systems contribute to our understanding of transitions and concomitant property changes in iron base alloys.

The phenomenological theory of martensite formation is a striking example of this. The crystallographic theory developed by Wechsler, the late Professor Read, and myself⁽¹²⁾ (and simultaneously by Bowles and Mackenzie⁽¹³⁾) has recently been reviewed in detail⁽¹⁴⁾ and will not be repeated here. Although the W-L-R formulation of the theory was developed to describe the transitions in InTl⁽¹⁵⁾ and AuCd⁽¹⁶⁾, it was applied with remarkable success to the '259' transformation in Fe-Ni-C.⁽¹²⁾ The first two systems can easily be observed to transform by the movement of a single interface which clearly divides the specimen into parent and product regions with the simplest geometric matching conditions across this interface. This is shown in Fig. 2 for the cubic to orthorhombic martensitic transformation in AuCd. The transformation goes to completion by the motion of the interface.

The martensite plates in steels, such as shown in Fig. 1, are geometrically much more complex. They are imbedded in the austenite and involve substantial volume and shear restraints during transformation since the transformation strains in going from f.c.c. to b.c.t. in iron base alloys are $\sim 20\%$, while for AuCd they are $\sim 2\%$. Further, the pattern of inhomogeneity or lattice invariant shear part of the total transformation distortion, while easily determined experimentally for AuCd to be the (111) twin plane shown in Fig. 2, was not observed in Fe base alloys until many years after we predicted the habit plane orientation assuming the lattice invariant shear to be (112) twins in the martensite. The rather impressive agreement between theory and experiment shown in Fig. 3 from that 1953 paper thus preceded by several years high resolution micrographs such as Fig. 1 (optical) and Fig. 4 (electron) which confirmed that this indeed was the pattern of inhomogeneity. Thus the agreement in the InTl and AuCd systems, where complete observations could be made, gave workers confidence to apply the theory to Fe base alloys which at that time presented formidable experiment difficulties, and the results suggested that even in this very complicated system, minimization of the strain energy at the interface

is the critical factor in determining the mode of transformation, the interface orientation, and the other features.

Unfortunately, as far as I know, there is no completely satisfactory theoretical description (such as exists for the 259 type) for the (225) habit in low carbon steels. In their original pronouncement of the theory, Bowles and Mackenzie introduced an adjustable parameter, δ , representing a uniform dilatation in the interface which could be varied arbitrarily so that the calculated quantities agreed better with the experimental observations for certain alloys. They found that a strain of almost 2% (i.e., a δ of 1.02) was required to obtain a theoretical habit plane near the observed (225). However, this approach predicted the wrong orientation relationship. The subsequent suggestion that the dilatation may be anisotropic and some of the attempts using different patterns of inhomogeneity and/or rather complicated combinations of shears have been discussed;⁽¹⁴⁾ none of these approaches did much more than generate publications. Indeed the experimental evidence for the conclusion that δ differs from unity has been far from convincing. Finally, Krauklis and Bowles⁽¹⁷⁾ have demonstrated that δ is not measurably different from unity

and hopefully papers belaboring it should soon cease to appear.

I have suggested another approach.^(3,14) The phenomenological theory generally ignores considerations other than minimizing interfacial strain energy. Successful application to the (259)_A habit in iron base alloys suggests that at least in the initial stages of growth in this material, other effects such as volume and shear restraints, magnetic interaction, are secondary, as pointed out by Wechsler, et al.⁽¹⁸⁾ That other forces are probably operative in determining the mode of a transformation can sometimes be inferred from the discrepancy between the crystallographic features expected on the basis of the simple theory and those observed; something about the physics and mechanism of transformations can be learned from this.

The transformation from the high temperature paraelectric (cubic) phase to the ferroelastic (tetragonal) phase in semiconducting BaTiO_3 and $\text{KTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$ (KTN) is a good example of the interrelationship among physical properties, crystal geometry, and mechanism. It has been mentioned elsewhere⁽¹⁴⁾, but is briefly included here as

an illustration of a transformation in a non-metallic system which can perhaps help us in understanding and analyzing some transformation in steels. The habit plane normal in KTN predicted by the W-L-R theory was found⁽¹⁹⁾ to be irrational and in excellent agreement with that observed-- within a few tenths of a degree; agreement is reported to be equally good for semiconducting BaTiO_3 . In insulating BaTiO_3 , preliminary observations indicate a habit plane close to $(110)_c$, approximately 5° from the irrational habit plane exhibited when the crystal is semiconducting. This significant difference is associated with the fact that in semiconducting crystals, the free charges present can neutralize the bound polarization charge inside the crystal, whereas in highly insulating crystals, the absence of free charges imposes restrictions on the paraelectric-ferroelectric boundary and the ferroelectric domain configuration. Thus the minimization of the strain energy at the interface and matching consideration can be the critical factor determining the nature of the transformation and interface boundary in semiconducting crystals, but in insulating crystals electrostatic and electrostrictive terms must be considered in the free

energy and in the theory. Perhaps we should look for some more physical reasons for the shift from (259) to (225).

The considerable shear and volume constraints and consequent large strain energy involved in the transformation from austenite to martensite in steels apparently inhibit the growth of plates once they form so that transformation proceeds by the formation of new plates and is nucleation controlled. In many non-ferrous systems such as the AuCd alloys mentioned above, the transformation goes to completion by the growth of only a few large domains of the product, or even sometimes by the movement of a single interface, as shown in Fig. 2. The large difference in hysteresis widths-- $\sim 500^\circ\text{C}$ for FeNi and 15° for AuCd-- is associated with the order of magnitude difference in strains. Further, in the iron base alloys, each plate may form very rapidly, in a microsecond, while in non-ferrous systems minutes or hours may be required for transformation. The growth in the latter may only be slow on a macroscopic scale--the interface appears to move through a small distance rapidly but then must stop to allow relaxation before it can move again.⁽²⁰⁾ The range of morphologies and rates observed is so large and

varied that the type of kinetics is not a good criterion for categorizing transformations. This is not to say, of course, that kinetics are not important in martensitic transformations. Indeed they certainly are, as in other phenomena, but the geometric or crystallographic features in a sense define transformations as martensitic since they are found in all of them.

The study of kinetics in non-ferrous systems may however contribute to our understanding of ferrous kinetics. AuCd specimens of near equiatomic composition exhibit both modes of transformation--nucleation controlled or growth controlled--depending on the thermal treatment. Furthermore, the transformation can be observed under both continuous cooling and isothermal conditions. Fig. 4 shows the transformations in a 49 pct Cd alloy single crystal for various cooling rates from unpublished work of Mullendore and myself.⁽²¹⁾ Note that the curve is invariant for all rates slower than some critical rate. Further, specimens which are quenched from temperatures just above M_s to temperatures below M_f and held transform isothermally, with the rate of transformation increasing with decreasing holding temperature. The product phase

crystal structure and microstructure are the same as when specimens are continuously cooled. Below M_f , the transformation goes to completion. At temperatures between M_s and M_f , the transition is not complete, but the final fractions of the product when the transformation ceases lie on the curve in Fig. 4, as shown by the . Since this curve is independent of the conditions under which the transformation is observed, i.e., whether under continuous cooling or isothermal conditions, I propose to call it an "eigenthern"--characteristic of the system or material, and not dependent on the particular experiment; the transformation is thus called "an eigenthal thermal transformation".

The data generating the points on this curve are shown on Fig. 5 for several transformations between M_s and M_f . Note that the here are at the termini of the rather rapid linear part of the transformation. It is these points of fraction transformed at the various temperatures which are on Fig. 4, and they are seen to fall on the curve for continuous cooling. Hence the terms "eigenthern" and "eigenthal thermal".

This concept may be applicable to transformations in steels; recent unpublished work of Entwisle⁽²²⁾ and Ragavan and Cohen⁽²³⁾ lead me to believe it may well be. Figures from their work are not yet available, but Fig. 6 from an earlier work of Entwisle⁽²⁴⁾ is similar. Although this is for a transformation to many plates rather than growth controlled, it appears sufficiently like Fig. 4 for AuCd to suggest plotting the fraction transformed in the initial more rapid isothermal part vs. temperature to see if the points fall on the curve obtained under continuous cooling conditions. If so, the transformation would be "eigen-thermal". In any event, the literature describing so-called athermal and isothermal transformations should be read with caution. Perhaps some reports should have stated "certain transformations were observed to occur under isothermal (or athermal) conditions" rather than that the "transformations are isothermal (or athermal)". Conclusions about the fundamental nature of the transformations from the usually limited and incomplete measurements are not unequivocal.

Several cases where the study of martensitic transformations in non-ferrous systems have lead (or hopefully

will lead) to a better understanding of the corresponding behavior in steels have been delineated. I suspect there are many more. Just as our understanding of the crystal geometry of martensite formation in steels came out of a theory developed for transition in non-ferrous systems, understanding and exploitation of other phenomena in iron base alloys may well spring from studies of the corresponding phenomena and property changes in non-ferrous systems.

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Fig. 1 Optical micrograph (oblique illumination) of an Fe-33.2%Ni alloy showing essentially complete $\{112\}$ internal twinning in the martensite plates. (4)

Fig. 2 Partially transformed AuCd specimen with single interface separating parent cubic (left) from twinned product orthorhombic (right). Upper-2X; lower, courtesy of B. S. Subramanya, -300X. (14)

Fig. 3 Stereographic plot of habit planes in iron nickel martensite. Grid - predicted by W-L-R theory; dots - experimental. (12)

Fig. 4 The parallel markings in this transmission electron micrograph of a martensite plate in Fe-29.7%Ni-0.42%C are $\{112\}$ transformation twins as first postulated by W-L-R many years earlier. Courtesy of Dr. I. Tamura.

Fig. 5 Transformations in single crystals of $\text{Au}_{1.02}\text{Cd}_{0.98}$ for various cooling rates. The $\blacklozenge$ are from the isothermal runs in Fig. 6 as discussed in the text; $\boxtimes$ is a self consistent point on Figs. 5 and 6. (21)

Fig. 6 Isothermal transformations between M_s and M_f . The $\blacklozenge$ indicate the fraction transformed during the rapid growth of large_s domains and are also so indicated on Fig. 4; $\blacklozenge$ is a self consistent point on Figs. 5 and 6. (21)

Fig. 7 Isothermal transformation curves for Fe-22.59%Ni-3.33%Mn. (24)