Development of domain structure associated with the diffusionless cubic-to-tetragonal transition in ZrO_2-Y_2O_3 alloys

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Microstructural change associated with the diffusionless cubic-to-tetragonal (c–t) transition was examined in arc-melted ZrO_2-Y_2O_3 alloys with yttria content 3 to 5 mol %. It was found that a two-step microstructural change occurred during the transition. A domain structure with antiphase domain boundary-like contrast is formed initially and plate-like or lenticular features later. The domain size decreases with increasing yttria content of the alloy. The change of domain size seems to be related to the change in T_0 temperature with composition. The nature of the c–t transition is discussed in this paper.

1. Introduction

It has been clarified that the cubic-to-tetragonal (c–t) transition in yttria-containing partially stabilized zirconia (Y-PSZ) has a unique nature. Cohen and Schaner [1] have first suggested from careful optical microscopy examinations that the c–t transition of zirconia is a martensitic transformation. Andersson and Gupta [2] have inferred from the ZrO_2-Y_2O_3 phase diagram that the c–t transition can be induced by a martensitic transformation in Y-PSZ. Andersson *et al.* [3] have reported that the c–t martensitic transformation occurs when a sintered Y-PSZ containing less than about 7 mol % Y_2O_3 is quenched from the cubic phase region through the M_s temperature. The c–t transformation takes place by plate growth in a similar manner with the tetragonal-to-monoclinic martensitic transformation [3] which is responsible for the transformation toughening of PSZ. The plate-like or lenticular t'-ZrO_2^* with various sizes has commonly been found in Y-PSZ prepared by the melting technique [5–7] as well as conventionally sintering materials [3]. The t'-ZrO_2 has almost the same yttria content as the matrix [5, 6], being different from t-ZrO_2 with a lower yttria content which is formed by precipitation during ageing in the cubic/tetragonal two-phase region. It was found that some of the t'-ZrO_2 had a size of more than a few micrometres and could easily be found by optical microscopy. If the plate-like or lenticular t'-ZrO_2 exists in the c-ZrO_2 matrix as first interpreted [3, 5], the c–t transition is regarded as a martensitic transformation and the microstructure is the partially-transformed structure, which is a common structural feature of metallic materials in the temperature range between M_s and M_f [8].

It has, however, recently been pointed out that the diffusionless c–t transition is not such a simple transition. Lanteri *et al.* [9] have shown that forbidden reflections for the cubic fluorite structure always appear in the entire region of quenched alloys containing about 3.4 to 7 mol % Y_2O_3, i.e. in both matrix and plate-like or lenticular features. The domain structure appears in dark-field images taken by a 1 1 2 forbidden reflection. They have insisted that t'-ZrO_2 formed by the diffusionless c–t transition is characterized by a domain structure and that the plate-like or lenticular features are twins of t'-ZrO_2 induced for mechanical accommodation. If this is the case, the c–t transition always goes to completion during cooling.

The nature of the diffusionless c–t transition is very complicated and has not fully been understood yet. In the present study, the domain structure was examined in Y-PSZ with various yttria contents, and the nature of the transition is discussed.

2. Experimental procedure

Zirconia and yttria powders with nominal purity 99.9% supplied by Rare Metallic Co. Ltd (Tokyo) were used for starting materials. ZrO_2-Y_2O_3 alloys containing 3 to 5 mol % Y_2O_3 were prepared by arc-melting. Details of the preparation of melted alloys have been reported in an earlier paper [5]. Button-shaped samples with a weight of 1 to 2 g were obtained. They were cooled from the melting temperature to 1000° C in about 10 sec on a water-cooled copper hearth after melting. The local compositional change in the sample was within about 10% of the average composition of each alloy. Microstructural examinations were made of the arc-melted alloys without any heat treatment. Thin foils for electron microscopy were prepared by conventional methods. They were examined in a JEM 200B electron microscope operated at 200 kV.

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*The non-transformable tetragonal phase with high yttria content is termed t'-ZrO_2 in this paper, following an earlier proposal [4].
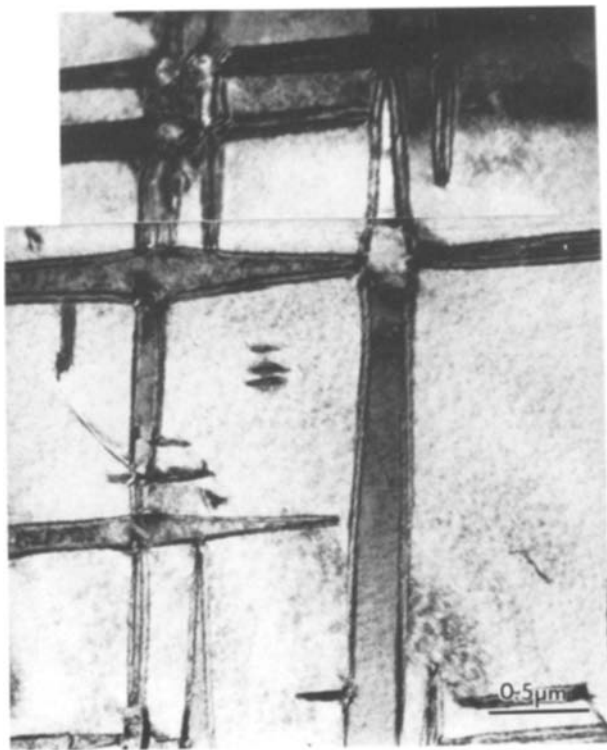
Figure 1 Bright-field image of ZrO_2–4 mol % Y_2O_3 alloy.

3. Results

Fig. 1 shows the microstructure of ZrO_2–4 mol % Y_2O_3 alloy, in which lenticular features are seen in the matrix. This type of microstructure has commonly been found in melted alloys [5–7]. No special features are seen in the matrix and lenticular phase in the bright-field image, but the characteristic domain structure appears in the dark-field image taken by a 1 1 2 forbidden reflection of the fluorite structure.

Fig. 2 is an example of the domain structure in ZrO_2–4 mol % Y_2O_3 alloy. The domains are separated by curved interfaces with antiphase domain boundary-

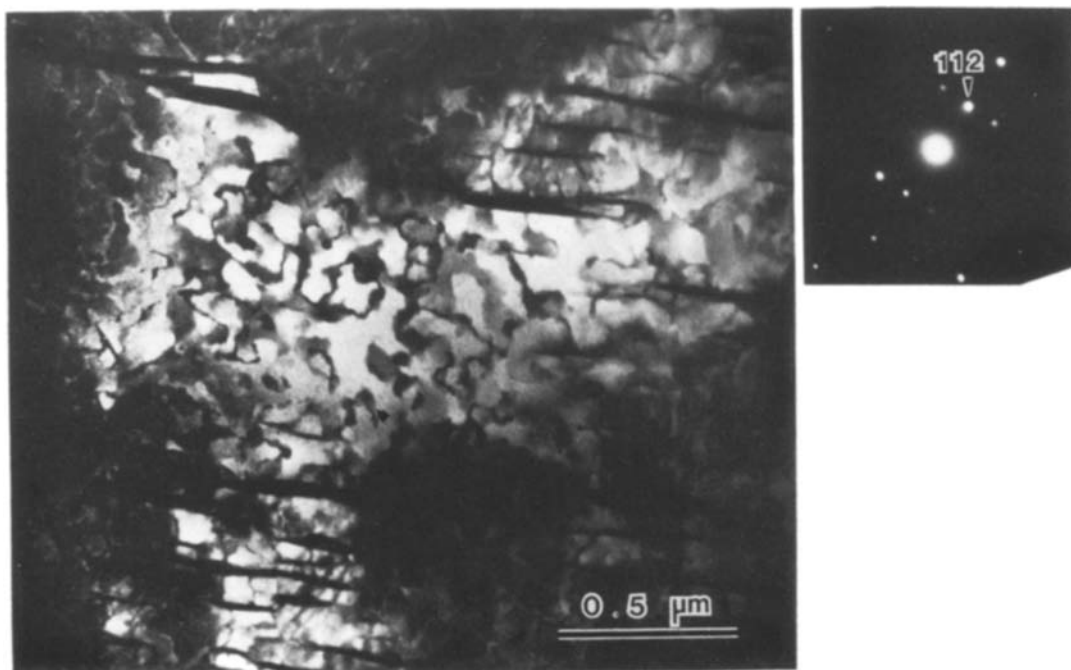like contrast. It was found that the domain structure was developed throughout the sample in all alloys examined in the present study.

Fig. 3 shows the domain structure in a twinned area in ZrO_2–3.5 mol % Y_2O_3 alloy. This type of microstructure is called thin-plate t'-ZrO_2 by other workers [10]. Alternate regions appear bright in the dark-field image, showing that these regions have the same crystallographic orientation, i.e. a single variant of t'-ZrO_2. It is noted that some domain boundaries shown by bold arrows look continuous across the twins. This was also found in lenticular t'-ZrO_2. The fact seems to indicate that the domains were formed first and twins or lenticular t'-ZrO_2 later during cooling from the high-temperature cubic phase region.

Fig. 4 shows another example of the domain structures in a twinned area of ZrO_2–3.5 mol % Y_2O_3 alloy. Figs 4a to c are the same region taken by 1 1 2 reflections from three different variants. The direction of the 1 1 2 diffracting vector is shown by an arrow in each micrograph. The twinned area consists of three variants of t'-ZrO_2 and the domain structure is developed in every variant.

Fig. 5 is a double-exposed print of Figs 4b and c. Two variants of t'-ZrO_2 are brightly imaged in Fig. 5. The domain boundaries in adjacent variants are not continuous across the interface. The continuity of the domain boundaries may be lost by the generation of a twinned structure, because the twinned structure is considered to be formed after the generation of domains with continuous boundaries as mentioned before.

It was found that the domain size decreases with increasing yttria content. Fig. 6 shows the domain structure in three alloys with different yttria contents. In ZrO_2–3 mol % Y_2O_3 alloy (Fig. 6a), fairly large domains and twins are formed. In this micrograph, the continuity of domain boundaries is seen in alternate
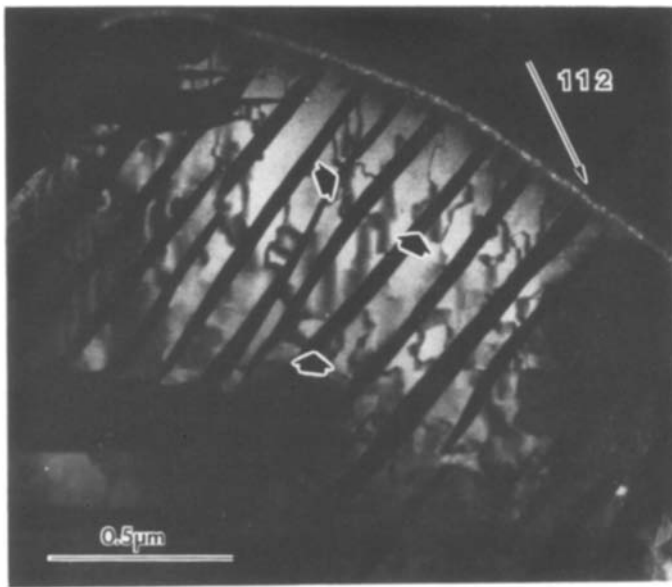

Figure 2 The domain structure in ZrO_2–4 mol % Y_2O_3 alloy. The foil was slightly tilted from the $\langle 1\,1\,1 \rangle$ orientation and the image was taken by a 1 1 2 forbidden reflection as indicated in the figure.

Figure 3 The domain structure in a twinned area of ZrO_2-3.5 mol % Y_2O_3 alloy. The arrow shows the direction of a 1 1 2 reflection used for taking the dark-field image.

bright regions as well as in Fig. 3. On the other hand, very fine domains are developed in ZrO_2-5 mol % Y_2O_3 alloy (Fig. 6c). Fine twins were often seen in the alloy, which were not clearly observed in bright-field images. The domain size in ZrO_2-4 mol % Y_2O_3 alloy (Fig. 6b) is intermediate between the two alloys containing 3 and 5 mol % Y_2O_3.

Fig. 7 is a plot of domain size against yttria content of the alloy. The domain size decreases almost linearly with yttria content in the composition range.

4. Discussion
The present work has shown that a domain structure is developed throughout a sample rapidly cooled from the single cubic-phase region in ZrO_2-Y_2O_3 alloys with yttria content 3 to 5 mol %. The domain structure is formed not only in melted alloys, but also in conventionally sintered materials [9, 10]. It seems that a domain structure is always developed during the diffusionless c–t transition. It should be noted that a change in crystal structure accompanying the domain structure, which may be a phase transition, has the nature of a second-order phase transition, because the domain structure always appears in the entire region a sample.* Lanteri *et al.* [9] have insisted that the domain structure itself is t'-ZrO_2 as it is imaged by 1 1 2 forbidden reflections. According to their interpretation [9], the diffusionless c–t transition always goes
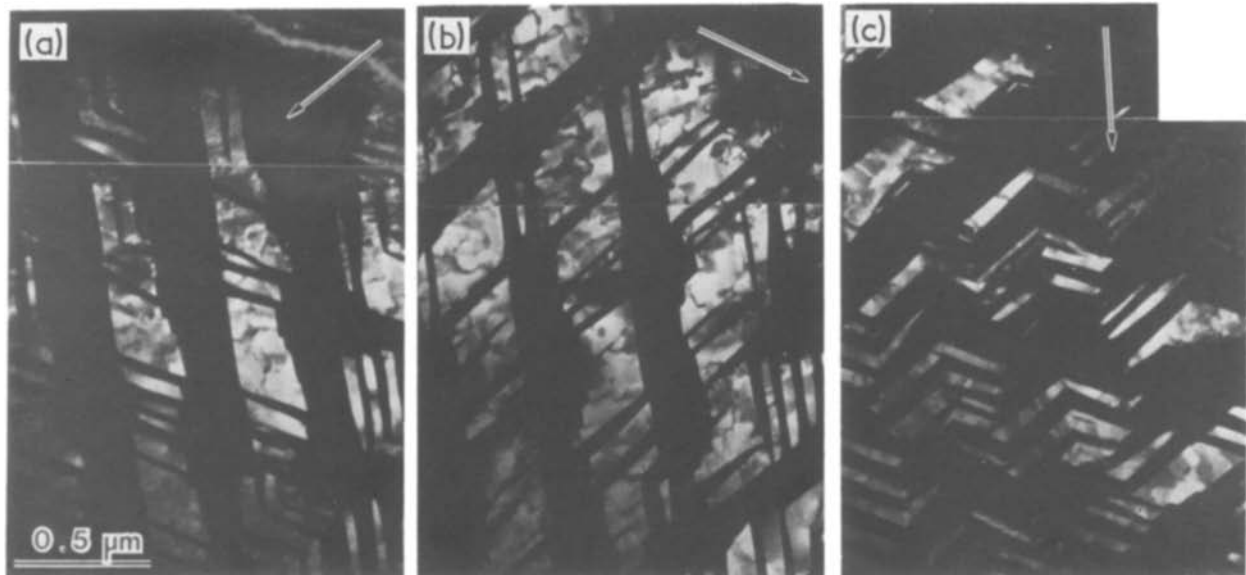

Figure 4 (a–c) The domain structure in a heavily-twinned area of ZrO_2-3.5 mol % Y_2O_3 alloy. The micrographs are the same region taken by different 1 1 2 reflections. Each 1 1 2 reflection is indicated by an arrow in the micrograph.

*The terms first and second order used in this paper refer to the thermodynamic order of a phase transition. The first-order transition is defined as the transition whose first partial derivative of free energy G with respect to temperature or pressure is discontinuous at the transition temperature T_c. The first partial derivative of G is continuous but the second derivative is discontinuous at T_c in the second-order transition. The thermodynamic parameters of enthalpy, entropy and volume, which are first derivatives of G, are discontinuous at T_c in the first-order transition, but continuous in the second-order transition [11]. A discontinuity appears in parameters such as specific heat and compressibility in the second-order transition [11]. The definition is mathematically clear. However, it is not so easy to decide the thermodynamic order of a particular phase transition. Careful examinations of the change in various parameters around the T_0 temperature of the c–t transition in ZrO_2-Y_2O_3 must be made to clarify the nature of the transition.

Figure 5 Double-exposed print of the micrographs in Figs 4b and c. Two variants of t'-ZrO$_2$ are brightly imaged. The domain structure is not continuous in two adjacent variants.

to completion; c-ZrO$_2$ and t'-ZrO$_2$ never coexist in rapidly cooled alloys. The plate-like or lenticular features such as Fig. 1 should be regarded as twins in t'-ZrO$_2$ which were introduced for mechanical accommodation during the diffusionless c–t transition [9]. Their results include very important information on the nature of the c–t transition. However, its nature is not fully understood in their interpretation as discussed below.

Fig. 8 shows four types of binary phase diagram with various phase transitions. Figs 8a and b are systems with an order–disorder phase transition. The two-phase region exists in Fig. 8a but not in Fig. 8b. The order–disorder transitions in systems of the type of Figs 8a and b are believed to occur by first- and second-order phase transitions, respectively [12]. Fig. 8c is the phase diagram with a miscibility gap. In this system, the phase separation is induced by diffusional processes. Fig. 8d is the system with two-phase region, in which the α and β phases have

different crystal structures, and the diffusionless $\alpha–\beta$ phase transition is expected to occur by a first-order transition.

Among the four systems, only Fig. 8b does not have a two-phase region. Assuming that metastable phases do not participate in phase transitions, only the transition of the system in Fig. 8b always goes to completion by a diffusionless mechanism. The c–t equilibrium in ZrO$_2$–Y$_2$O$_3$, however, has generally been accepted to be the type of Fig. 8d [13]*. The two-phase structure composed of c- and t-ZrO$_2$ has commonly been found in heat-treated ZrO$_2$–Y$_2$O$_3$ alloys [15, 16]. Such a microstructure is possibly developed in the systems of Figs 8a, c, and d, but not in Fig. 8b. That is, the accepted c–t equilibrium in the ZrO$_2$–Y$_2$O$_3$ system is not consistent with the proposal that the diffusionless c–t transition is always completed during cooling [9]. It may be insisted that t'-ZrO$_2$ is different from equilibrium t-ZrO$_2$. However, t-ZrO$_2$ and t'-ZrO$_2$ are the same phase and only differ in composition.

Another explanation is that the domain structure is associated with a metastable transitional phase or pre-martensitic phase. Such a transitional phase does not appear in the equilibrium phase diagram. Sugiyama et al. [10] have reported that the forbidden reflections have already appeared in electron diffraction patterns from annealed ZrO$_2$–5.8 mol % Y$_2$O$_3$ alloy, when 4 0 0 reflections from c-ZrO$_2$ are found in the X-ray diffraction profile. The generation of thin plates corresponds to a splitting of the 4 0 0 reflections in X-ray diffraction, which is characteristic of t'-ZrO$_2$ [10]. They have insisted that oxygen ions can be displaced without losing cubic symmetry in the fluorite structure, and the martensitic c–t transformation is preceded by such a displacement. The explanation is in accordance with the present observation that the domain structure is formed prior to the generation of twins or lenticular features. The actual displacement of oxygen ions, however, has not been clarified yet, because very limited information on the arrangement
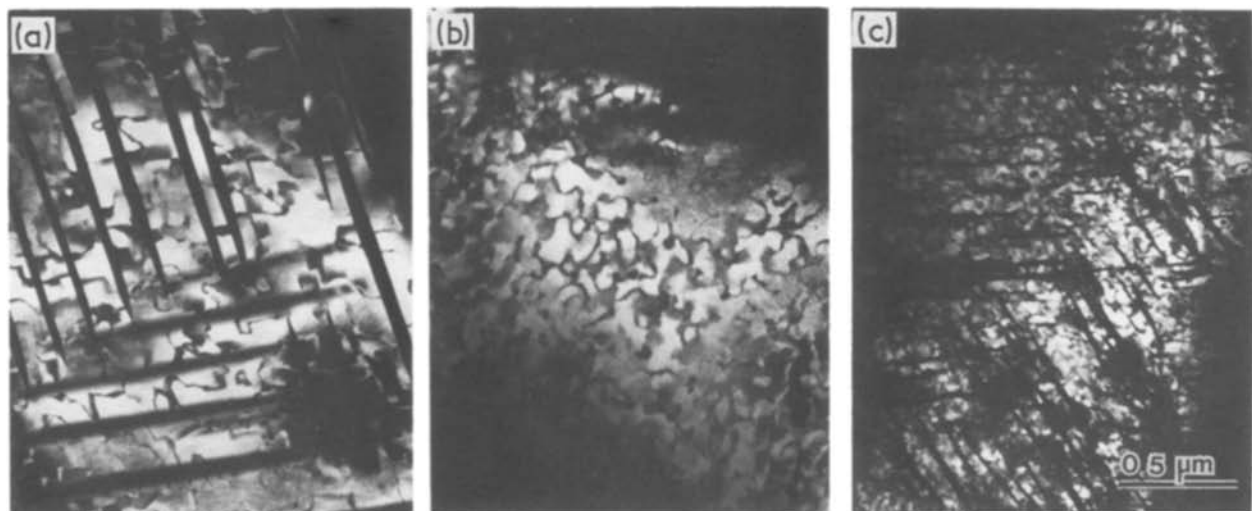

Figure 6 The domain structure in three ZrO$_2$–Y$_2$O$_3$ alloys with yttria content (a) 3 mol %, (b) 4 mol % and (c) 5 mol %. Note that the domain size decreases with increasing yttria content.

*It has recently been reported [14] that the c–t two-phase region is narrower than that reported by Scott [13] at high temperatures, and the phase boundaries have a characteristic shape. This fact may indicate that the c–t equilibrium is not a simple two-phase equilibrium as in Fig. 8d. The unique nature of the diffusionless c–t transition may also be reconsidered from a knowledge of the c–t equilibrium.

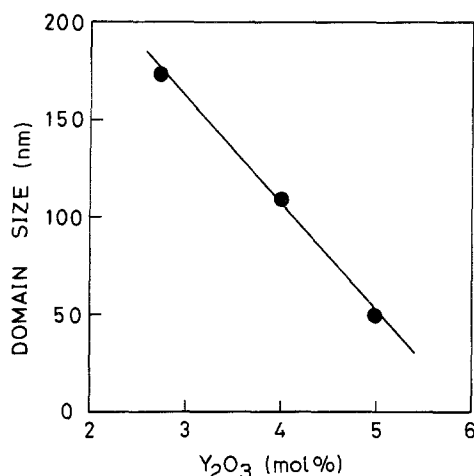*Figure 7* A plot of domain size as a function of yttria content of the alloy.

region of samples in dark-field images taken by a 1 1 2 forbidden reflection for the cubic fluorite structure.

3. The diffusionless c–t transition is characterized by a two-step microstructural change; the initial development of the domain structure is followed by the generation of plate-like or lenticular features.

4. The domain size decreases with increasing yttria content of the alloy. This fact may be related to the decrease in T_0 temperature with increasing yttria content.

The diffusionless c–t transition has quite a unique nature. Further detailed study is necessary to make clear the nature of the transition.

of oxygen ions is obtained from X-ray or electron diffraction. Such an oxygen displacement has to be confirmed experimentally in future studies for verifying the presence of a transitional phase in the diffusionless c–t transition.

Finally, the change in domain size with yttria content will be discussed. It is expected that the T_0 temperature of the c–t equilibrium decreases with increasing yttria content of the alloy [2]. It seems, therefore, reasonable that the diffusionless c–t transition starts at higher temperatures in alloys with a lower yttria content. The domains formed at high temperature may grow during cooling. The author has found such domain growth during isothermal holding at high temperatures, and this will be reported in a separate paper. The domains in alloys with lower yttria content are probably formed at higher temperatures and have much time to grow during cooling to room temperature, i.e. a larger domain size in lower-yttria alloys is likely to be due to domain growth. The change in domain size with yttria content seems to be related to the composition dependence of the T_0 temperature.

5. Conclusions

Microstructures associated with the diffusionless c–t transition were examined in ZrO_2–Y_2O_3 alloys with 3 to 5 mol % Y_2O_3. The results obtained are as follows.

1. Plate-like or lenticular t′-ZrO_2 is seen in the matrix in bright-field images of all the alloys examined.

2. A characteristic domain structure with antiphase domain boundary-like contrast appears in the entire

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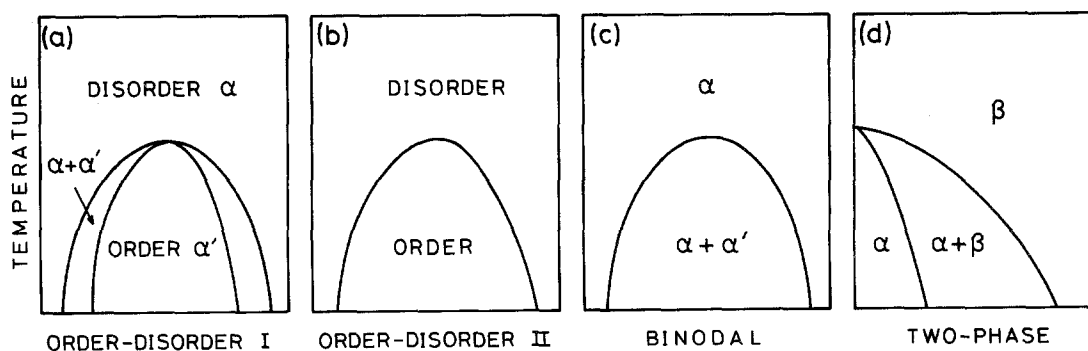11. P. G. SHEWMON, "Transformations in Metals" (McGraw-Hill, New York, 1969) p. 261.

Figure 8 Four types of binary phase diagram (see text).

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