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STRUCTURAL PHASE TRANSITIONS IN METALLIC GLASSES: CRYSTALLIZATION OF METALLIC GLASS INTO ORTHO-RHOMBIC PHASE

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The possiblity of describing the polymorphous crystallization of the metallic glass $Fe_{75}B_{25}$ into the ortho-rhombic crystalline phase Fe_3B is discussed within the framework of the phenomenological theory of metallic glasses [1]. The Landau thermodynamic potential expansion for the case of ortho-rhombic symmetry of crystals is considered to the fourth and the sixth order in the order parameter. The phase diagrams in the plane of the expansion coefficients are analysed. The obtained results are compared for the crystallization of the metallic glass Fe_3B.

СТРУКТУРНЫЕ ФАЗОВЫЕ ПЕРЕХОДЫ В МЕТАЛЛИЧЕСКИХ СТЕКЛАХ: КРИСТАЛЛИЗАЦИЯ МЕТАЛЛИЧЕСКОГО СТЕКЛА В РОМБИЧЕСКУЮ ФАЗУ

В работе в рамках феноменологической теории металлических стекол [1] обсуждается возможность описания полиморфной кристаллизации металлического стекла $Fe_{75}B_{25}$ в ромбическую кристаллическию фазу Fe_3B. Рассматривается разложение Ландау по параметру упорядочения вплоть до четвертого и шестого порядков для термодинамического потенциала в случае ромбической симметрии кристаллов. Проведен анализ фазовых диаграмм в плоскости коэффициентов теплового расширения. Полученные результаты сравниваются с результатами по кристаллизации металлического стекла Fe_3B.

I. INTRODUCTION

During a crystallization process stable and metastable crystalline phase may appear in metallic glasses [2, 3, 4, 5, 6]. A theoretical description of these processes is still unsatisfactory.

The aim of this paper is to discuss the possibility of determining crystalline phases which may appear by polomorphous crystallization of the metallic glasses

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for which the coupling of the primary order parameter to the magnetization vector may be neglected (within the framework of the phenomenological theory of metallic glasses [1]).

Our description of metallic glass crystallization processes includes ortho-rhombic, tetragonal, trigonal, and hexagonal classes of symmetry of crystals but does not include cubical, triclinic and monoclinic classes of symmetry.

We analyse the Landau thermodynamic potential expansion for the case of the ortho-rhombic symmetry of crystals introduced but not investigated further in [1].

The Landau thermodynamic potential expansion was restricted to the fourth order of the order parameter in [1]. Here we show that for the full thermodynamic analysis of the related phase transition it is necessary to include also terms of higher order in the Landau thermodynamic potential expansion (up to the sixth order). Therefore the thermodynamic potential expansion to the sixth order in the order parameter is considered and the phase diagram in the plane of the expansion coefficients is analysed. The obtained results are then discussed and compared for the material mentioned above.

II. THE LANDAU THERMODYNAMIC POTENTIAL EXPANSION

II.1. The Landau thermodynamic potential expansion to the fourth order of the order parameter

The Landau expansion of the thermodynamic potential for the case of ortho-rhombic symmetry of a crystal has the form [1]:

$$\Phi = \Phi_0 + A(Q_1^2 + Q_1 Q_2 + Q_2^2) + BQ_1 Q_2 (Q_1 + Q_2) + C[Q_1^4 + Q_2^4 + 3Q_1^2 Q_2^2 + 2Q_1 Q_2 (Q_1^2 + Q_2^2)] . \tag{1}$$

The expansion coefficients A, B, C are temperature and pressure dependent and we assume that the coefficient C is positive, $C>0$.

Here the primary order parameter introduced in [1] is the symmetric tensor of the second order with zero trace:

$$Q_{ij} = \frac{1}{3} \mathrm{Diag}\,(Q_1, Q_2, -Q_1 - Q_2) . \tag{2}$$

The order parametr (2) is introduced in paper [1] as the order parameter for triclinic, monoclinic and ortho-rhombic classes of crystal symmetry. But the order parameter (2) is an invariant tensor, for example, for the symmetry class 222 and therefore it cannot describe a phase of symmetry lower than the ortho-rhombic symmetry.

II.2. The Landau thermodynamic potential expansion to the sixth order of the order parameter

Nonvanishing invariants of the fifth and the sixth order which may be constructed from the order parameter matrix (2) are as follows:

$$\mathrm{Tr} Q_{ij}^5 = -\frac{5}{3^5}(Q_1^4 Q_2 + 2Q_1^3 Q_2^2 + 2Q_1^2 Q_2^3 + Q_1 Q_2^4) \tag{3}$$

$$\mathrm{Tr} Q_{ij}^3 \, \mathrm{Tr} Q_{ij}^2 = -\frac{6}{3^5}(Q_1^4 Q_2 + 2Q_1^3 Q_2^2 + 2Q_1^2 Q_2^3 + Q_1 Q_2^4)$$

and

$$\mathrm{Tr} Q_{ij}^6 = \frac{1}{3^6}[2(Q_1^2 + Q_1 Q_2 + Q_2^2)^3 + 3Q_1^2 Q_2^2 (Q_1 + Q_2)^2]$$

$$(\mathrm{Tr} Q_{ij}^3)^2 = \frac{9}{3^6} Q_1^2 Q_2^2 (Q_1 + Q_2)^2$$

$$(\mathrm{Tr} Q_{ij}^2)^3 = \mathrm{Tr} Q_{ij}^4 \, \mathrm{Tr} Q_{ij}^2 = \frac{8}{3^6}(Q_1^2 + Q_1 Q_2 + Q_2^2)^3 .$$

The Landau thermodynamic potential expansion to the sixth order by the order parameter has the form:

$$\Phi = \Phi_0 + A(\eta_1^2 + \eta_2^2) + B(\eta_1^3 - 3\eta_1 \eta_2^2) + C(\eta_1^2 + \eta_2^2)^2 + D(\eta_1^2 + \eta_2^2)(\eta_1^3 - 3\eta_1 \eta_2^2) + E(\eta_1^2 + \eta_2^2)^3 + F(\eta_1^3 - 3\eta_1 \eta_2^2)^2 \tag{4}$$

where $\eta_1 = \frac{\sqrt{3}}{2}(Q_1 + Q_2)$ and $\eta_2 = Q_1 - Q_2$.

The expansion coefficients A, B, C, D, E, F are temperature and pressure dependent. The stability condition requires: $E>0$ and $F+E>0$.

The thermodynamic potential of the form (4) has already been analysed by Izjumov and Siromjatnikov [7] in connection with the description of structural phase transitions in compounds of the type of Nb_3Sn with a cubical symmetry of crystals.

II. RESULTS AND DISCUSSION

The analysis of the Landau thermodynamic potential expansion to the fourth order by the order parameter (1) gives the phase diagram shown in Fig. 1. in the plane of the expansion coefficients A, B. It does not qualitatively differ from that which was obtained in [1] by the analysis of the thermodynamic potential expansion by a one-component order parameter for the case of the tetragonal (trigonal or hexagonal) symmetry of crystals. The liquid — crystal phase transition line is given by the line $A = B^2/(27C)$.

The liquid phase is characterized by the state

$$Q_{ij} = \mathrm{Diag}\,(0,0,0),\ \Phi = \Phi_0. \tag{5}$$

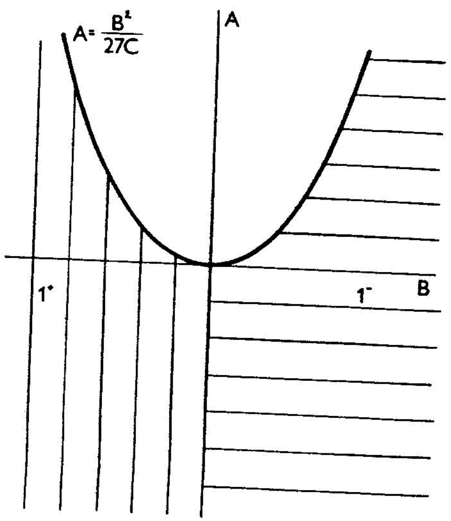

Fig. 1. Phase diagram in the plane of expansion coefficients *A, B* for the Landau thermodynamic potential expansion to the fourth order by order parameter.

A crystalline phase which corresponds to a minimum of the thermodynamic potential (1) is found to be given by the state $(Q_1 = Q_2)$

$$Q_{ij} = \mathrm{Diag}\,(Q, Q, -2Q) \tag{6}$$

where

$$Q = \frac{-B + \sqrt{B^2 - 24AC}}{12C}$$

$$\Phi = \Phi_0 + \left(\frac{B + \sqrt{B^2 - 24AC}}{12C}\right)^3 \left[B - \frac{3}{4}(B + \sqrt{B^2 - 24AC})\right], \text{ for } B > 0.$$

The liquid phase is a metastable phase for those values of the expansion coefficients A and B which lie between the lines $A = 0$ and $A = B^2/(27C)$. As in [1] we suppose that crystallization of the metallic glass is a transition of the system from a metastable state of the undercooled liquid into a crystalline state with a lower value of the thermodynamic potential. The thermodynamic potential expansion (1)

describes only one crystalline phase which may appear by the crystallization of the metallic glass. It is the tetragonal (trigonal or hexagonal) phase. The expansion (1) does not describe the expected crystallization into the ortho-rhombic phase.

No we show how the phase diagram changes if the terms of the fifth and the sixth order by the order parameter are added to the Landau thermodynamic potential expansion.

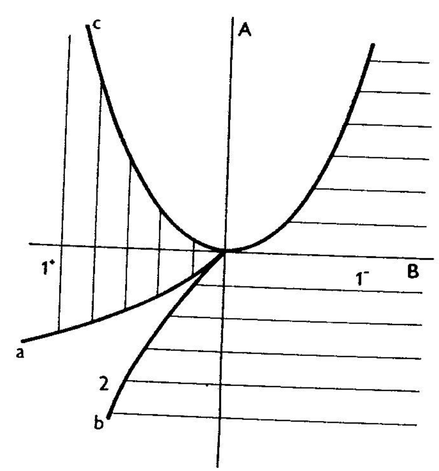

Fig. 2a. Phase diagram in the plane of expansion coefficients *A, B* for the Landau thermodynamic potential expansion to the sixth order by order parameter for $\Delta = 4CF - D^2 > 0$.

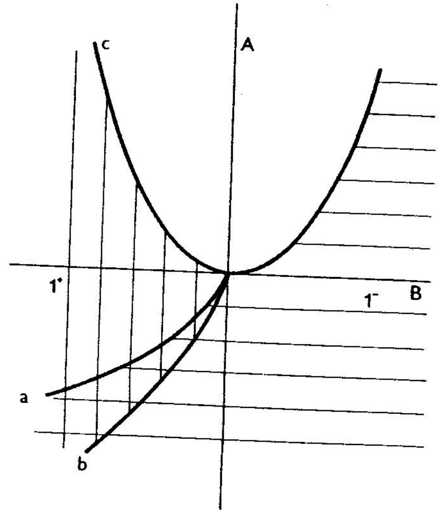

Fig. 2b. Phase diagram in the plane of expansion coefficients *A, B* for the Landau thermodynamic potential expansion to the sixth order by order parameter for $\Delta = 4CF - D^2 < 0$.

The phase diagram in the plane of expansion coefficients A, B for the thermodynamic potential of type (4) (analysed in paper [7]) is schematically shown in Fig. 2. The phase diagram for $\Delta = 4CF - D^2 > 0$ is shown in Fig. 2a. The phase denoted by 1^+ and 1^- are tetragonal (trigonal or hexagonal), phases. The phase denoted by 2 has the symmetry which belongs to the case of the ortho-rhombic symmetry of crystals. The lines a and b are the second phase transition lines while the line c is the first order phase transition line.

In Fig. 2b the phase diagram for $\Delta < 0$ is shown. In this case the phase 2 is not stable at all. Between the lines a, b the phases $1^-$and 1^+ may coexist. The liquid phase is metastable for those values of the expansion coefficients A and B which lie between the lines $A = 0$ and c.

If we suppose that the metallic glass corresponds to this metastable state of undercooled liquid, then the previous results may be interpreted in the following way: The thermodynamic potential expansion (4) predicts polymorphous crystallization of the amorphous metastable state only to the tetragonal (trigonal or hexagonal) crystalline phase. Suppose, however, that the state of a metallic glass is under thermodynamic conditions in the area between the lines a and b (Fig. 2a); here the state of a metallic glass is neither the stable nor the metastable state of the undercooled liquid. Hence this glass crystallizes directly to the orthorhombic crystalline phase. In papers [2, 3, 4] the polymorphous crystallization of the magnetic metallic glass Fe_3B is described. The observed crystalline phases are different because of different conditions of crystallization.

Paper [2] describes the appearance of the ortho-rhombic Fe_3B phase by the crystallization of amorphous Fe-B alloys annealed at 615 K. Paper [4] describes the crystallization of amorphous Fe-B alloys and a tetragonal Fe_3B phase is observed, which appears by heating from 670 to 740 K. Paper [3] refers to the appearance of a tetragonal Fe_3B phase and a small extent of an ortho-rhombic Fe_3B phase by heating amorphous Fe-B alloys from 790 K to 810 K.

The theory of crystallization of metallic glasses developed in [1] and here and applied to the material mentioned above is consistent with this experimental observation if we assume that almost all the volume of the amorphous samples at higher temperatures [3] ($A>0$) corresponds to a metastable undercooled liquid state (this state crystallizes to the tetragonal phase Fe_3B). The small extent of the observed ortho-rhombic Fe_3B phase may be explained within our theory by assuming the presence of a small extent of an amorphous phase which does not correspond to a metastable undercooled liquid but some kind of nonequilibrium amorphous state. Intuitively one should expect the appearance of the ortho-rhombic phase Fe_3B as a result of the crystallization process.

The tetragonal phase Fe_3B has a higher symmetry than the ortho-rhombic one. According to our theory it is expected for smaller temperatures (for which $A<0$) that the amorphous state will crystallize directly to the ortho-rhombic phase — as described in [2]. Such kind of experiments, i.e. crystallization of amorphous samples at various values of temperature and the observation of different resulting crystalline phase for $A>0$ and $A<0$ ($T>T_0$ and $T<T_0$) should give information about the temperature T_0 and about the character of the amorphous state (metastable for $A>0$ and nonequilibrium for $A<0$).

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