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MECHANISM OF POROUS STRUCTURE FORMATION IN INTERMETALLIC SYNTHESIS

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The specific features of diffusional mixing of metals in synthesis of intermetallides, with one component being in the liquid state, are considered, and the nature of stresses in the diffusion zone is discussed. A model of a porous powder body is proposed to predict the behavior of mixtures in intermetallic synthesis in a thermal explosion regime. Analytical equations describing the sign and magnitude of volume changes of powder bodies in synthesis are obtained and experimentally checked. Examples are presented to illustrate the synthesis of highly porous materials.

The goal of the present work is to bring to the attention of investigators interested in the scientific principles of self-propagating high-temperature synthesis (SHS) of intermetallides some new ideas developed in this field of research. New approaches are concerned with the diffusion interaction of solid and liquid phases, substance flow in a diffusion zone, a model of a two-component powder body, a mechanism of porous structure formation in intermetallic synthesis, and a quantitative description of the porosity of intermetallides synthesized under thermal explosion conditions.

For reasons of space, only fundamental principles of the new trend will be discussed. They are treated in detail in [1], where the authors also consider the distinctive features of a liquid phase in intermetallic systems and the method of low-temperature activation of the exothermal effect in powder mixtures by using small quantities of dopants. The high effectiveness of the new approaches, including their use for an analytical description of the volume changes in powder bodies due to intermetallic synthesis in a thermal explosion regime, is indicated with the use of dilatometry in a great deal of experimental material.

Synthesis of Intermetallides in Contact with a Liquid Phase. In intermetallic SHS, including that under thermal explosion conditions, a liquid phase is involved in the general case. Therefore to understand the processes participating in synthesis, of fundamental importance is a knowledge of the mechanism of diffusional mixing or interaction of solid and liquid phases. Although no rigorous theory exists, it is commonly supposed that dissolution of a solid-state body in a liquid phase is accomplished through transfer of atoms from the solid surface to the liquid phase and then diffusion of them from the phase boundary into a melt [2]. In keeping with this, it is generally agreed that on interaction of a solid metal with a liquid one the intermetallides may be formed either by crystallization from the liquid phase or through a chemical reaction of the components at the phase boundary followed by a growth of an intermetallic layer due to diffusion [3]. In the latter case, it is assumed that on contact of the both metals a chemical reaction proceeds to form an intermetallide just at the interface of the reacting metals but the reaction itself is not directly associated with dissolution. The compound layer may grow due to diffusion of the solid component through the layer to the melt boundary [4].

An alternative supposition is that intermetallides at the metal-melt interface are formed through diffusion of atoms from a liquid to a solid phase up to the concentration at which the solid phase in the surface layer is no longer stable and undergoes a phase transition [5]. Such a supposition is a consequence of the more general principle of diffusional interaction of solid and liquid components, according to which dissolution of the first in the second component proceeds by diffusion of solvent atoms from the liquid to the solid phase up to formation of solid solutions in the surface layer whose concentration enables them to transfer into the liquid through melting [6]. In this case, the solid solutions formed at the phase boundary are based on an intermetallide that, according to the

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phase diagram, is in equilibrium with the liquid phase. The new approach provides not only an adequate explanation of the processes at the interface but also permits their control. Therefore we employ precisely this approach to estimate the volume changes in powder bodies due to intermetallic synthesis in a thermal explosion regime as well as to analyze other experimental results given below.

Substance Flow in a Diffusion Zone. Since in intermetallic synthesis one-way diffusion of atoms from a liquid to a solid phase takes place, it is important to know what stresses develop in the diffusion zone of the solid phase and how substance flow, known as the Kirkendall effect, is accomplished. The majority of investigations of this effect in the diffusion zone deal with diffusion vapors, i.e., two samples of unlike metals that possess a common boundary through which atoms are exchanged by diffusion. In any diffusional pair in the diffusion zone and the regions adjacent to it stresses develop that cause dislocations and, consequently, material flow [7]. One should distinguish the diffusion zone pertaining to component A from that based on component B since the stresses and deformations developed in them differ considerably in their nature, magnitude, and sign.

There are two basic stresses in the diffusion zone that differ in their nature, namely, concentrational and diffusional [8]. Because of insufficient attention to the nature of stresses their quantitative estimation is often based on an account of concentrational stresses [9]. In [8, 10], the authors mistakenly think that the stresses in a diffusion zone in intermetallic synthesis are due to different specific volumes of the new phase and the components in a diffusion pair. But in reality, diffusion stresses and the related Kirkendall effect are responsible for the considerable stresses and strains observed on formation of intermetallides [11].

To compare concentrational and diffusional lattice deformations by magnitude and sign, we have estimated them quantitatively for some alloys under unipolar diffusion conditions provided that the concentration in the diffusion zone amounts to 1 at.%. As it has turned out, the concentrational dilatation of a lattice may be of any sign, depending on whether a metal is a solvent or a diffusant. On the contrary, the sign of the diffusional deformation of the lattice, to which a one-way flow of atoms is directed, is always positive, which corresponds to a volume increase. But in magnitude, the diffusional dilatation of the lattice markedly exceeds the concentrational one. As a result, the total local deformation of the diffusion zone is also positive. In forming an intermetallide at a melt boundary this will cause an increase in particle size in the solid phase that is proportional, in magnitude, to the number of atoms transferred into the lattice.

Model of a Two-Component Powder Body. A model must, on the one hand, reflect an actual structure of compacted mixtures and, on the other hand, be sufficiently simple for mathematical manipulations. A drawback of the well-known two-particle Frenkel model [12], widely used in the literature to describe the kinetics of sintering, is the neglect of the nature of the surrounding particles, the presence of pores between the particles, and the so-called arch effect caused by the skeleton structure of a powder body. The multiparticle model of a two-component powder body [13] is free of the above shortcoming. Since in a wide concentration range of the components of a binary powder mixture the particles of one of the components are mainly surrounded by those of the other component, an elementary volume of the powder body may be considered as a group of arbitrary, in form and size, particles that are in contact or adjacent, to a some extent, to each other. Of those, the central particle is the additive component, while a monolayer of particles around it is the basic component of the powder body, and free gaps between the particles are interparticle pores. In real powder bodies, obtained by compacting mixtures, the particles of the basic component form a relatively rigid skeleton of the compacted powder owing to their rather tight packing due to compaction. Friction and adhesion forces make the particles stick together, thus causing the so-called arch effect. This implies that large pores forming for some reason in a powder body, whose sizes are comparable to or much in excess of those of the surrounding particles, cannot collapse because freely moving particles occupy the pores and form an "arched ceiling" around them. The multiparticle model may take into account this property of real powder bodies under the assumption that particles do not change their relative position in it after diffusional interaction of the components. This assumption is identical to the supposition that rearrangement of particles with "long-range order", which could result in occupation of pores during synthesis or sintering, is impossible.

In intermetallic synthesis, particles of one of the components must pass into the liquid state. The main difference between interaction of the components with participation of a liquid phase and solid-phase interaction is not a change, due to the appearance of a melt, in the capillary forces at the contact of particles of the solid phase but rather a considerable increase of the surface of the interacting particles due to wetting of particles with the melt and its spreading. Just this circumstance strongly enhances the formation of intermetallides, thus causing immediate manifestation of the related thermal and volume effects. A second distinctive feature of the interaction of components when one of them is in the liquid state is that diffusional mass transfer at the interface, on intermetallide formation, is directed toward the solid phase if the melting point of this intermetallide is lower than that of the more refractory component. An increase of the volume of the solid-phase particles due to diffusion of atoms out of the melt makes their geometric centers, as a consequence of the arch effect, move apart, thus increasing the dimensions of the entire powder body. Particles of the second component absorbed by the solid phase leave behind pores, that copy the configuration and size of these particles in a raw powder molding, as has been anticipated in the model.

Powder Body Porosity Produced by Intermetallic Synthesis. The growth of particles with diffusion of atoms from a liquid phase to them is a direct consequence of an increase in the mass of the particles when virtually no transfer of atoms occurs in the opposite direction, i.e., from the solid to the liquid phase. An additional increase in the lattice volume upon intermetallide formation may take place due to an increase in the lattice parameter because of a new type of rearrangement. However, this increase is much less than in the case of generation of new sites occupied by diffusate atoms of the second component. Moreover, intermetallide formation may also be accompanied by contraction of the lattice. Nevertheless, as a result of unipolar diffusion additional sites for foreign atoms are generated in the lattice with any sign of its dilatation, thus increasing the volume of the solvent overall. Since the magnitude of the increment in the solvent volume due to diffusion is determined by the number of new sites in the lattice, it depends on the total amount of the component passed into the solvent and is independent of the character of the concentration distribution in it.

If we assume that the melt completely wets particles of the solid phase and that atoms from the liquid phase diffuse uniformly over their entire surface, including the spots of mutual contacts, then this is identical to the supposition that the particles preserve their initial form in intermetallic synthesis. Geometric similarity of the particles of the solid phase before and after synthesis is indicative of an increase of the volume of interparticle pores as well as of the space occupied at first by the second component in the same proportion as that of the volume of the solid phase. This circumstance allows us to solve quite rigorously the problem on the degree of porosity of a synthesized intermetallide. Such an analytical dependence of the final porosity of a two-component powder body η on its initial porosity and the concentration of the second component c_s, absorbed by the first component in synthesis, is obtained in [11]:

$$\eta = \eta_0 + c_s(1 - \eta_0). \tag{1}$$

An experimental check of Eq. (1) showed that it describes fairly well the basic porosity of synthesized intermetallides. However, because of evolution of high temperatures due to heat release and regrouping of particles due to formation of a considerable amount of liquid phase the growth of the powder body in synthesis is affected, as a rule, by shrinkage caused by sintering. Taking account of the shrinkage, we may write Eq. (1) in the form [14]

$$\eta = kc_s + \eta_0(1 - c_s), \tag{2}$$

where the empirical coefficient $k \leq 1$.

The validity of relation (2) was verified by German with coworkers [15, 16]. Statistical analysis of the experimental results for the Fe-Al [15] and Fe-Ti [16] systems confirmed its validity with a high degree of reliability.

Volume Growth in Intermetallic Synthesis as a Means of Obtaining Highly Porous Materials. The technology of obtaining porous materials by sintering loose or compacted powders suffers from their shrinkage during sintering. As a result, the sintered materials have insufficiently high porosity. To increase the porosity by preventing shrinkage and forming new pores, a porogene is added to the initial powder, where it decomposes or evaporates on sintering, thus leaving voids in its place. But since the porogene contaminates the material, it worsens its sinterability, strength, and anticorrosion properties.

The developed concepts about the physical nature of the growth of powder bodies in intermetallic synthesis show promise that the material porosity may be increased by adding a porogene that does not require its removal. This is achieved by absorption of the porogene, which incorporates it, as a dopant, into the composition of the material to be sintered.

Relations (1) and (2) show that in intermetallic synthesis the porosity levels off throughout the volume of the material since the denser regions increase their porosity to a greater extent than the looser regions.

Ti-Al alloys may serve as an example of producing highly porous materials by intermetallic synthesis. The porosity of these alloys is 60-70%. They are used for manufacture of anodes of volume-porous electrolytic capacitors and preparation of supports of catalysts of high-temperature reactions.

NOTATION

η, final porosity of two-component powder body; η_0, initial porosity; c_s, concentration of the second component; k, empirical coefficient.

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