THEORIES CONCERNING THE CHANGES PRODUCED IN THE EUTECTICS STRUCTURE AT THE RAPID SOLIDIFICATION

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Abstract
The paper presents the aspects concerning the thermodynamics and kinetic of the formation of supersaturated solid solutions at ultrarapid solidification.

1. THE THERMODYNAMICS AND KINETIC OF THE FORMATION OF SUPERSATURATED SOLID SOLUTIONS AT ULTRARAPID SOLIDIFICATION

For an alloy with a given composition, the maximum degree of solubility extension in solid state corresponds to the situation when the solidification is produced without the redistribution by diffusion of the soluble element between the solid and liquid solution. In this case after the solidification, the alloy is made of a homogenous solid solution with a composition $c_0$ identical with the on of the fusion out of which it was formed. Such a massive solidification without composition alteration is possible in certain kinetic and thermodynamic conditions, namely at subcooling degrees which bring the fusion to temperatures below the value $T_0$ at which the free energy of liquid solution equals the free energy of solid solution. In the same time the maintaining of a uniform composition in the solid solution, identical with the one in the liquid solution demands the providing of special conditions. Essentially it is necessary that the solidification front should flat or with a slight curve because any disturbance which leads to a cellular or dendritic solidification front is accompanied by the emergence of a subsidiary phase most often being part of an eutectic composition. A brief presentation of the thermodynamic and kinetic conditions necessary for the solubility extension in solid solutions beyond the equilibrium values is given by the literature [1].

1.1. Thermodynamic Considerations

The experimental data shows that in a series of alloys, especially those based on Al, which are interesting for the present paper, by super-rapid solidification, one can obtain solubility extensions in solid solution which exceed by far the compositions for which, in equilibrium conditions, there can be seen a subsidiary phase $\beta$ either by eutectic reaction or by peritectic reaction.

The solubility extension in solid solution $\alpha$ can be analyzed in these cases by defining some transformation temperatures in the chart of phase equilibrium according to the representation in fig.1 for an alloy of $c_0$ composition (which is biphasic in equilibrium conditions, $\alpha$ differs from $\beta$). There can be defined in figure 1a (system with peritectic reaction) and in figure 1b (system with eutectic reaction) the following phase transformation temperatures: $T_{L}^1 = \text{liquidus temperature (crystallization beginning)}$ of the subsidiary phase $\beta$; $T_P$, respectively $T_E = \text{temperature of zero-variants reaction (peritectic and eutectic)}$; $T_L = \text{liquid temperature of the solid solution } \alpha \text{ with extensive solubility}$; $T_S = \text{solid temperature (end of crystallization)}$ of the solid solution $\alpha$ with extensive solubility; $T_{N} = \text{germination temperature for the formation, by a process without diffusion, of an supersaturated solid solution } \alpha \text{ with the same composition } c_0 \text{ as the fusion}$.

Taking into consideration the data of fig.1, it can be deduced that the role of high cooling
speed, necessary when the super-rapid solidification is applied in order to obtain the maximum extension effect of solubility in solid state, is to ensure a subcooling $\Delta T$ of the fusion which will bring it suddenly at temperature $T_N$ at which the liquid solution will be transformed by a process without diffusion into an supersaturated solid solution $\alpha$ with the same composition $c_0$ as the fusion. Such a subcooling $\Delta T$ will suppress any other solidification processes which imply diffusion and redistribution by diffusion of the soluble element. This way it will be suppressed the subsidiary phase $\beta$ crystallization at subcooling under $T_L^1$; it will be suppressed the primary phase $\alpha$ crystallization with extensive solubility at subcooling under $T_L$, it will be suppressed the crystallization by peritectic or eutectic zero-variant reaction at subcooling under $T_P$ or under $T_E$.

The attentive examination of the representations of fig.1 show that the maximum effect of solubility extension in solid state achieved by solidification without redistribution by diffusion of the soluble element is easier to be achieved if the inclination of the solidus curve for the solid solution $\alpha$, whose solubility extension is targeted, is smooth. This way the systems Al-Cr, Al-Zr, Al-Hf or Al-Mn in which $T_S$ raises or decreases slowly depending on the soluble element content (the smooth inclination of solidus curve for phase $\alpha$) the solubility extension in phase $\alpha$ is easily obtained even at medium cooling speeds which are used at the casting. But in systems like Al-Mg or Al-Si in which $T_S$ is rapidly modified depending on the soluble element content the fraction of solidified material without redistribution by diffusion is small in concentrated alloys even when very high cooling speeds are used.

*Figure 1.* Temperatures of phases transformation in the phasic equilibrium charts of the allow systems with zero-variable reaction to crystallization

- a) system with peritectic reaction, b) system with eutectic reaction;
- $T_L^1 =$ liquidus temperature (at the beginning of crystallization of the second phase $\beta$);
- $T_P$, $T_E =$ temperature of the zero-variant reaction (peritectic respectively eutectic);
- $T_L =$ liquidus temperature of primary solution $\alpha$ with extensive solubility; $T_S =$ solidus temperature (of ending of crystallization) of primary solution $\alpha$ with extensive solubility;
- $T_N =$ germination temperature of the slid solution with maximum extension of the solubility made without the redistribution of the soluble element (repartition coefficient equal to unity)
Out of the data presented briefly in the previous lines we can conclude that the role of high cooling speeds at the super-rapid solidification of crystalline alloys is to furnish the necessary subcooling for the germination and growing process in such a way as other phases should become competitive instead of the equilibrium ones.

In the special case of solubility extension in primary solid solutions they become competitive suppressing the forming of subsidiary phases which in normal conditions would appear by peritectic or eutectic reaction.

The details of the kinetics involved in the germination and development processes of the crystalline phases at the super-rapid solidification will be shown based on the analysis made in literature \[1,2\], taking into consideration the conditions at solidification interface, the thermic transfer and the diffusive mass transfer.

**Kinetic and interface conditions.** The formation of an supersaturated solid solution as an effect of the solubility extension induced by ultrarapid solidification can be reduced to the problem of increasing only one crystalline phase in a pluricomponent fusion (for simplification we'll consider a fusion with 2 components A and B). The increasing of the crystalline phases is made by the displacement of the solid/liquid interface, which in the absence of convection demands the solving of the equations of diffusive mass transfer in the solid and liquid phase by observing the equilibrium equations at interface. Among the many possibilities for choosing the dependent and independent variables in paper \[1\] are the interface temperature \(T_i\) and the composition \(C^*_S\) of the solid phase at interface, both being dependent on the liquid composition at interface \(C^*_L\) on the medium curve of the interface \(K\) and on the \(v\) normal speed at interface. By solving the equations of mass and thermic transport we obtain two functions which in general form (neglecting other variables such as the crystallographic orientation and the flows density in the crystalline net) can be written:

\[
T_i = T_i - mC^*_L - T_i\Gamma K - f(v, C^*_L) \\
C^*_S = [K_e g(v, C^*_L)]C^*_L
\]

In the relations (1) and (2) the expression \(T_i - mC^*_L\) represents the lowest point when the alloy fusion begins \(T_i = \) fusion temperature of the majority component A and \(m = \) teh inclination of liquidus curve from the chart of phasis equilibrium considered for simplification as being straight); the term \(T_i\Gamma K\) represents the lowest fusion point owing to the curve \(K\) of the interface where \(\Gamma\) represents the capillarity constant usually expressed as the ratio between the superficial tension liquid/solid and the fusion enthropy; \(K_e\) represents the coefficient of diffusion in the equilibrium conditions of the minoritary element B in solid phase and in liquid phase; the expression \([K_e g(v, C^*_L)]\) represents the repartition coefficient in non-equilibrium conditions dependent on the speed \(v\) of interface displacement; this coefficient tends towards the value 1 at very high solidification speeds.

In equilibrium conditions, the repartition coefficient differs from the unity being calculable with the horizontal rule from the position of the solidus and liquidus curves in the chart of phasic equilibrium.

The extension of solubility in solid state at ultrarapid solidification is in fact based on the phenomenon of blocking the solution in the soluble element ("solute trapping" in English terminology) phenomenon which takes place when the repartition coefficient deviates from the equilibrium value \(K_e\).
1.2. The Influence of the Solidification Speed Over the Microstructure of the Biphasic Alloys

The theoretical analysis in literature [1,2], together with the experimental data of observing the microstructures resulted in different solidification conditions leads to a series of relevant conclusions for the possibilities of solubility extension in solid state induced by the ultrarapid solidification. These conclusions can be discussed in a more concise way based on the representations in figures 2,3. In all the analysed cases, it was taken into consideration a binary system of alloys with the phasic equilibrium chart presenting limited solubility of the components in solid state and eutectic reaction at crystallization.

In all the cases, it was considered that the solidification is produced with positive thermic gradient in liquid (the heat is eliminated through the solid formed by solidification). It was also taken in consideration the fact that the thermic gradient in liquid is especially important in determining the microstructure at slow solidification speeds but its influence loses its importance at high speeds of solidification. These considerations are reflected both in the theory of the area of mixed development of eutectics and in the theory of absolute stability of the flat solidification front and of the constitutional subcooling at the solidification of pluricomponent alloys [1,3].

![Figure 2](image1.png)

**Figure 2.** The influence of the solidification speed over the formation of the microstructures in an alloy containing metallic isomorphous phases with low fusion entropy.

- a) curve $T_0$ (dotted line in the phasic equilibrium chart) is continuous; 
- b) the modification of the solidification speed produces an area of associated development of the eutectic phases with symmetrical position towards the nominal eutectic composition.

![Figure 3](image2.png)

**Figure 3.** The influence of the solidification speed over the formation of the microstructures in an alloy system containing a metallic phase with low fusion entropy and a non-metallic phase or a compound with high fusion entropy.

- a) curve $T_0$ (dotted line in the phasic equilibrium chart) are intersected at a composition displaced by comparison with the eutectic composition; 
- b) the changing of the solidification speed produces an area of associated development of the eutectic phases placed asymmetrically in comparison with the nominal eutectic composition.
In the representations of fig. 2a,b, it is considered a binary system of alloys, in which the eutectic has 2 terminal solid solutions $\alpha_1$ and $\alpha_2$ isomorphous such as, for example, the system Cu-Ag. The system is typical for the eutectics which contain non-faceted phases (metallic with low fusion entropy). The curve $T_0$ is continuous and presents a relatively insignificant displacement of about 100°C under the solidus curves of equilibrium (fig.2a). For such a system the modification of the solidification speed (fig.2b) produces an area of development associated with the eutectics phases which has a symmetrical position in comparison with the nominal eutectic composition from the phasic equilibrium chart (fig.2a). The limits of the area of associated development of the eutectic (fig.2b) strongly depend on the solidification speed. At lower solidification speeds ($<10^3$ cm/s) and at little subcooling of the fusion the area of associated development is determined by the criterion of constitutional subcooling. In these conditions the area of associated development is increasing considerably and it allows the formation of microcomposite alloys with structural alignment of the phases by controlled solidification [4-6].

At intermediary solidification speeds in fig.2b, the area of associated development of the eutectic is narrowing, being bordered by areas in which the microstructure is of hypoeutectic or hypereutectic type containing primary dendrites and eutectics of the terminal solid solution $\alpha_1$, respectively $\alpha_2$. Finally, at very high solidification speed in fig.2 b, the eutectic and the dendritic solidification are replaced by the monophasic solidification in the whole domain of composition of the alloys system (fig.2b): in this situation, it takes place the formation of a continuous series of isomorphic solid solutions $\alpha$ produced by solidification without redistribution by diffusion of the soluble element, corresponding to a value of the repartition coefficient $k_{\text{ef}}=1$. This way, by ultrarapid solidification, it is obtained a maximum extension of the solubility in solid state for the entire composition domain of the system.

In the representations from fig. 3 a,b, it is considered a binary system of alloys in which the eutectic contains solid solution $\alpha$ metallic with non-faceted development and low fusion entropy next to phase $\beta$ with high fusion entropy and faceted development [1,5]. Characteristic examples for this case are represented by the system Al-Al$_3$Fe or the system Ni-Ni$_3$Nb. For such a system the curves $T_0$ for the 2 phases $\alpha$ and $\beta$ of the eutectic are intersected at a relatively high temperature and at a composition displaced in comparison with the nominal eutectic composition from the phasic equilibrium chart (fig.3a). More specifically, the intersection point of the curves $T_0$ is displaced towards the phase Al$_3$Fe (alloy also studied in our paper [7]) present in the equilibrium structure obtained at the solidification speed <0.1 mm/s, as it was to be expected primary crystals of the compound Al$_3$Fe and the eutectic Al-Al$_3$Fe. At solidification speeds between 0.1 mm/s and 0.8 mm/s the alloy presents a structure made of the compound Al$_3$Fe and of the eutectic Al-Al$_3$Fe. Between 0.8 mm/s and 7 mm/s, the structure is made only from the eutectic Al-Al$_3$Fe. Over 7 mm/s the alloys is made of primary dendrite of solid solution $\alpha$ (Al) and of the eutectic Al-Al$_3$Fe. Finally, at super-high solidification speeds this alloy presented monophasic structures made entirely of solid solution $\alpha$ (Al) supersaturated. The justification of this succession of the structures that appear at the changing of solidification speed is clearly shown in fig.3b on the vertical for the composition of a hypereutectic alloy (marked by the dotted vertical).

In conclusion, as it is shown in the typical examples of fig.2 and fig.3, the solubility extension in solid state with the enlargement of the range of compositions in which the alloys have a monophasic structure is given theoretically and practically for 2 sets of solidification conditions.

a) Low solidification speeds ($v<\frac{DG}{\Delta T_0}$), where $D$ is the coefficient of diffusion in liquid of the soluble element, $\Delta T_0$ is the interval of temperature between liquidus and solidus and the thermic gradient $G$ in liquid is sufficiently abrupt for suppressing the constitutional
subcooling in the fusion at the solidification front. These conditions define what is called "conditioned stability" of the flat solidification front against the cellular and dendritic perturbations which lead to segregation.

The attainment of the conditioned stability demands the application of controlled, undirectioned solidification and even for very diluted alloys it doesn't produce important solubility extensions in solid state.

b) High solidification speeds (> $DT_0/\Gamma_k$), where $\Gamma_k$ is constant of capillarity or the coefficient Gibbs-Thomson, represented by the ratio $\gamma/\Delta S$ between the interfaceted energy and the fusion entropy and $k_e$ is the coefficient of repartition at equilibrium for the soluble element. Such conditions define what is called "the absolute stability" against any disturbances of low range waves. These disturbances are suppressed in such conditions because of the high effect of capillarity, which it might produce. The theoretical moulding of the thermic transport shows that the advance speeds of the solidification front necessary for obtaining the absolute stability are attained by methods of laser glazing or electrons fascicle as well as in other methods of ultrarapid solidification. The theoretical considerations also show that, in conditions of absolute stability, the coefficient of repartition tends towards 1. This means that it ensures massive solidification without redistribution by diffusion of the soluble element between the solid and the liquid phase (solute trapping), so it guarantees maximum extension of solubility in an alloy with given composition $c_0$.

2. MODIFICATION OF EUTECTIC STRUCTURES AND THEIR REPLACEMENT WITH OTHER COMPETITIVE STRUCTURES AT ULTRARAPID SOLIDIFICATION

The eutectic solidification structures and their replacement with other competitive structures at ultrarapid solidification. The eutectic solidification implies an enlargement of the constitutive phases with a common front of solidification which implies a certain degree of attaching the thermic fields and the diffusion fields of the eutectic phases. A detailed analysis of the eutectic development way and of the morphology specific to the eutectic constituent of alloys is presented in literature [3]. Some alloys, such as the eutectic alloy Al-Al$_2$Cu, can maintain the associated development producing a microstructure with typical lamellar morphology:

$$\lambda = B_1R^{-1/2}$$  \hspace{1cm} (3)

$$\Delta = B_2R^{1/2}$$  \hspace{1cm} (4)

$$\lambda = B_3\Delta T$$  \hspace{1cm} (5)

where $\lambda$ is the distance between plates in eutectic, $R$ is the advance speed of the associated solidification front and $\Delta T$ is subcooling at the solidification front. The conditions from the relations (3)-(5) have typical values for alloys $B_1 \equiv 10\mu m^{1/2} s^{1/2}$, $B_2 \equiv 10Ks^{1/2}/\mu m^{1/2}$ and $B_3 \equiv 1\mu mK$. The diminishing of interplates distance $\lambda$ from the eutectics microstructure at the increase of speed $R$ (expressed by the relation (3)), respectively at the increase of the fusion subcooling degree (expressed by the relation (5)), presents importance in a practical point of view since it can help estimate the speed of ultrarapid solidification.

On the other hand, the destabilisation of the front associated development of the eutectic at the changing of solidification conditions may lead to the formation of other types of structures which get into the competition with the eutectic structure (occurrence of amorphous structure, occurrence of intermediary phases-crystalline metastable occurrence of solid supersaturated solutions with extensive solubility). The ability to maintain an associated eutectic
development in conditions of solidification characterized by high values for R and $\Delta T$, thus of maintaining the competitiveness of the eutectic structure by comparison with different other metastable structures, depends on the factors which determine the form of the associated developing area. The symmetrical (fig.2) and respectively asymmetrical (fig.3) forms of the associated developing area decide over the microstructures which will display the alloys in the vicinity of the eutectic composition at the modification of solidification conditions.

3. CONCLUSIONS

In appreciating the structural modifications induced by the increase of solidification speed, the information regarding "the associated developing area" in a certain system of alloys allows the application of the criterion called of "competitive development". Within this criterion it is considered that the composition domain $\Delta c$ of the associated development front of the eutectic biphasic solidification moves at higher speeds and at lower subcooling degrees than the individual phases. This criterion of competitive development allows us to explain the replacement, at high solidification speeds, of equilibrium eutectic (for example, the eutectic austenite-graphite in the system Fe-C or the eutectic Al-Al$\textsubscript{3}$Fe in the system Al-Fe) by a non-equilibrium eutectic in the composition of which is a metastable phase (for example the austenite eutectic - Fe$_3$C, respectively the Al-Al$\textsubscript{3}$Fe).

REFERENCES
4. PETRESCU, M., Buletinul Institutului Politehnic Bucuresti, seria Chimie-Metalurgie, tom XL, nr. 1, p. 79.
7. PETRESCU, N., CRISTEA LIDIA, Aliaje de aluminiu cu metale de tranzitie solidificate ultrarapid, Metalurgia, 40 (9), 1988, p. 448-455.