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PHASE COMPOSITION OF MULTICOMPONENT ALUMINUM BRONZES CRITERIA-BASED EVALUATION (PART 1. SUPERSATURATED COPPER A-MATRIX AND PHASE COMPOSITION OF CU–AL–X SYSTEM MULTICOMPONENT BRONZES STABILITY CRITERIA)

Purpose. To establish structurally reliable and thermodynamically justified criteria for assessing alloys supersaturated copper α-matrix stability and predicting the phase composition of multicomponent bronzes formed under crystallization and subsequent cooling non-equilibrium conditions.

Methodology. Methodology is based on thermodynamic analysis, structural-parametric approach and experimental data generalization combination. Copper matrix condition was estimated by parameter Δ (theoretically required and actual Cu content ratio). Thermodynamic analysis was performed within Gibbs energy minimization framework, taking into account small deviations and components with Δ activities connection. Structural and mechanical properties were evaluated using K_R criterion.

Findings. To assess in multicomponent bronzes single-phase state fixing or losing conditions, concentration parameter Δ has been proposed, which characterizes the conditions for solid solution non-equilibrium stability loss under casting conditions. It has been shown that at $\Delta \gtrsim 1$ conditions for secondary phase's formation arise. K_R criterion has been proposed to assess structural and mechanical properties. It has been proven that Δ and K_R joint using provides "composition-stability-structure-properties" relationship for multicomponent aluminum bronzes comprehensive description.

Originality. For the first time, quantitatively consistent system has been established of correlations between supersaturation parameter Δ, compositional criterion K_R and structural parameter φ – Cu–Al–Si–Mn–Sn system bronzes secondary phases volume fraction, which are formed under non-equilibrium conditions of solidification and in solid state subsequent cooling and are inherent in castings manufactured using foundry sand and metal molds.

Practical value. Using indicator (Δ) and criterion (K_R), proposed in the work, will allow increasing Cu–Al–Si–Mn–Sn system bronzes phase composition and properties predicting accuracy when changing their alloying elements concentrations. to reduce the time spent and resources during new alloys development or known bronze grades composition optimization by building regression and predictive models for managing their phase composition and properties. A parameter and criterion have been developed, along with an approach to creating new alloys and improving the existing alloys, their analysis, etc.

Keywords: *bronze, structure, parameter, criterion, thermodynamics, solubility, aluminum, tin, phase composition*

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Introduction. In context of cast parts requirements for reliability, durability, and functional stability increasing, traditional approaches to improving their properties by alloys microalloying [1], chemical composition optimizing [2], modifying [3], and modifying with pressure treatment or melt during crystallization vibration combining [4, 5] do not ensure for cast parts operational properties required set stable achievement. This is due not only to the fact that these approaches are mostly aimed at structure empirical control without sufficiently formalized description of relationship between its formation conditions, alloy phase composition, and cast material final characteristics, but also to their features and reliable technical implementation significant limitations in industrial conditions.

Therefore, today, one of the most effective and efficient ways for casting alloys structure and properties control remains their alloying. In particular, Fe, Mn, and Ni invasion into aluminum bronzes allows for significant changes in their phase composition, structural components morphology and, as a consequence, mechanical, corrosion, and tribological properties level. Adding Sn to silicon and aluminum bronzes allowed to

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material wear resistance and plasticity significantly (in times) increasing due to solid solution condition and secondary phases formation nature changes. Structure compositional control similar ideology is also implemented in new generation multicomponent alloys, in particular in high-entropy systems (HES), which are characterized by the tendency to form stabilized multicomponent supersaturated solid solutions [6, 7]. However, despite experimental data significant amount, structure formation in multicomponent systems (MCS) universal quantitative regularities remain poorly defined.

From this point of view, key role in preferential properties desired complex required levels forming of multicomponent, in particular, copper alloys is played by solid solution state (α-Cu), which acts as matrix in which secondary phases form and evolve. That the ratio between supersaturated solid solution amount and secondary phases, their morphology and reticular difference determine cast alloy mechanical and functional properties complex. At the same time, casting alloys structure formation occurs, as a rule, under non-equilibrium crystallization conditions, which limits the classical equilibrium phase diagrams and thermodynamic models [8, 9] applicability.

As a result, correlations established to date between multicomponent alloys microstructure and properties are predominantly qualitative or empirical in nature, which, in generalized parameter absence that would integrate structure formation thermodynamic and kinetic factors, in particular solid solution supersaturation degree and its conditions stability and/or decomposition, does not allow for their phase composition reliable quantitative prediction [10, 11].

Thus, parameters and criteria elaboration that allow quantitatively assessing multicomponent copper alloys structural state formed under non-equilibrium conditions and establishing relationship between matrix solid solution supersaturation degree, its stability conditions, and secondary phases formation is modern and relevant scientific and applied problem in materials science.

Literature review. Phase composition predicting of multicomponent metal alloys, in particular bronzes, which structure is formed under real casting conditions, remains complex scientific problem that does not have universal solution.

In early stages of metals science development, alloy compositions have been selected by resource- and time-consuming trial and error method. Approaches further development has been associated with classical thermodynamics formation, in particular J. W. Gibbs works, which laid the basement for fundamental ideas about systems phase equilibrium and minimum free energy. On this basis, experimental methods for phase diagrams constructing have been developed, allowing determining lines and regions of phases' equilibrium existence in binary and multicomponent systems.

In multicomponent alloys developing practice, binary phase diagrams analysis is traditionally used, which allows, in a first approximation, to estimate alloying elements solubility limits, homogeneous solid solutions formation tendency or its phase decomposition, as well as other phases, in addition to α-solid solution, and/or secondary phases forming possibility. Additionally, crystallochemical solubility criteria (W. Hume–Rothery rules) have been used, which allow a qualitative assessment of solid solutions formation conditions based on atomic size factor, solute and solvent crystal lattice structure, valences similarity, electronegativity difference and have been formulated in following provisions form [12, 13]:

- components relative difference in atomic radii (δ) should not exceed approximately 15 %, since significant mismatch leads to free energy elastic component increasing;
- solute and solvent crystal structures similarity reduces energy consumption for common lattice formation;
- valence and electron concentration (VEC) proximity favors the solid solutions formation [14, 15];
- components small difference in electronegativities (Δχ) reduces mixing enthalpy chemical component and, accordingly, promotes mutual solubility [16, 17].

However, these approaches have a limited application scope, since they do not fully take into account component interactions enthalpic effects, short-range order, and multicomponent systems peculiarities, where the energy state is determined by multiparticle interactions set [15, 18]. In this regard, binary diagrams should be considered as useful but insufficient tool for multicomponent bronzes phase composition predicting.

Theoretical approaches further development is associated with solid solutions stability thermodynamic analysis using. Within classical thermodynamics framework, homogeneous solution is stable under composition Gibbs free energy dependence positive curvature condition, while its negative curvature corresponds to local stability losing and system transition to phase separation. In this case, global equilibrium regions (binodal) and local instability (spinodal) boundaries, which determine solid solution decomposition mechanisms, are distinguished.

However, classical thermodynamics describes only system stability conditions and does not take into account the structure formation kinetics. For this purpose, Cahn–Hilliard theory [19, 20] has been used, which allows to take into account spatiotemporal evolution of concentration inhomogeneity and relationship between diffusion kinetics and structure morphology. At the same time, semi-empirical models, in particular Miedema's model [21], have been developed, allowing mixing thermal effects estimation.

Materials science development current stage is characterized by computational thermodynamics (CALPHAD) methods [22] widespread using, which allow multicomponent systems phase composition equilibrium predicting based on thermodynamic databases and are based on binary and ternary components interactions parameterization [23]. In parallel, approaches based on high-entropy alloys concept, i.e. parameters such as ΔH_{mix}, ΔS_{mix}, Ω, δ, *VEC*, as well as machine learning methods, ICME, and first-principles calculations, are being developed.

Thus, phase transformations in solid solutions modern theories are based on system thermodynamic stability analysis, which is determined by the nature of Gibbs free energy dependence on composition [24, 25]. Within classical thermodynamics framework, homogeneous solid solution is stable under Gibbs function positive curvature condition, that is, when the second free ener-

gy derivative with respect to composition ($\partial^2 G/\partial x^2$) is positive. In opposite case, when the second derivative is negative, system loses local thermodynamic stability and enters spinodal instability region, where small composition fluctuations lead to free energy decreasing. That is, condition $\partial^2 G/\partial x^2 = 0$ defines the spinodal limit as the limit of local stability losing, while the binodal is determined by the chemical potentials equality condition and corresponds to the system free energy global minimum. At the same time, phase stability complete picture is determined not only by local conditions, but also by the system free energy global minimum as a whole. In this context, binodal boundary defines phases equilibrium coexistence region and is given by components in coexisting phases chemical potentials equality conditions (common derivative to the Gibbs energy curve condition) [26].

In structure formation theory, as mentioned above, together with binodal boundary, there is spinodal boundary, between which there is non-equilibrium state region, in which homogeneous solution is thermodynamically disadvantageous in global sense, but retains local stability with respect to small fluctuations. In this region, phase decomposition is implemented by nucleation and growth mechanism, which requires overcoming the energy barrier associated with interfacial surface formation [27].

In contrast, within the spinodal region, homogeneous state loses local stability, and decomposition occurs spontaneously without interphase boundary energy barrier formation. Therefore, the binodal limit defines global equilibrium conditions, while the spinodal limit characterizes local thermodynamic instability and the stimulus for phase disintegration.

But classical thermodynamics only determines system stability or instability conditions and does not describe structure formation kinetics. To account for concentration inhomogeneity spatiotemporal evolution, the Kahn–Hillard theory is used, in which free energy is considered as functional that depends on both local composition and its spatial gradients. This allows taking into account interfacial boundaries energy and describing concentration fields over time development.

According to this theory, diffusion processes driving force is chemical potential gradient, which makes diffusion possible within concentration gradient in spinodal region. Phase decomposition in this case occurs through small compositional fluctuations growth without new phase nuclei formation, which leads to periodic concentration clusters with characteristic spatial scale formation [28, 29].

However, binodal and spinodal limits describe, respectively, system global and local stability conditions, while Kahn–Hillard theory provides their kinetic and spatial generalization, establishing correlation between thermodynamics, diffusion kinetics, and structural morphology.

CALPHAD methods allow determining equilibrium phase composition and estimate system evolution direction. But they are based on thermodynamic equilibrium assumption and do not fully take into account kinetic restriction and/or, conversely, driving forces. In this regard, to describe real multicomponent alloys, it is necessary to distinguish between different single-phase states types that occur in both equilibrium and non-equilibrium conditions.

Separate direction in structure formation theory modern development is concept of high-entropy alloys (HEA) [30], which is based on idea of mixing configurational entropy stabilizing role, which can contribute to single-phase solid solutions formation in multicomponent systems.

For HEA concept using in new alloys elaboration, following parameters have been used [31, 32]:

- mixing configurational entropy (ΔS_{mix});
- mixing enthalpy (ΔH_{mix});
- thermodynamic stability parameter (Ω);
- size parameter, or atomic size mismatch parameter (δ);
- electronegativity difference parameter ($\Delta\chi$);
- electron concentration parameter (VEC – valence electron concentration).

According to widely cited empirical criteria, most significant in HEA development are Ω and δ, since values of $\Omega \geq 1.0–1.1$ and $\delta \leq 6.6$ % are most favorable factors for solid single-phase solution in HEA formation. Parameter Ω reflects balance between entropic stabilizing contribution and enthalpic destabilizing factors.

Despite parameter Ω statistical usefulness, modern studies significant number indicate that empirical criteria of this type do not provide multicomponent alloys phase composition reliable quantitative prediction [33]. In particular, integral parameters (δ, ΔH_{mix}, Ω, VEC) using allows tendency to form solid solution only qualitative or semi-quantitative assessment, while the phase composition accurate determination requires taking into account the thermodynamic and kinetic factors complex interaction [34].

This is especially evident under non-equilibrium crystallization conditions, when limited diffusion mobility, microsegregations and high cooling rates lead to non-equilibrium phase states formation that do not correspond to equilibrium predictions [8, 9]. This is due to the fact that limited mass transfer, temperature gradients and microsegregations presence lead to system not reaching free energy global minimum, and its evolution is determined by diffusion processes kinetic limitations, which, in turn, makes it possible to realize non-equilibrium states.

As noted above, in multicomponent alloys single-phase state stability analyzing, along with thermodynamic equilibrium global criteria, divergence between homogeneous solid solution global and local stability plays an important role (Voorhees P. W., (2004), Porter D. A., et al. (2009)). Solid solution global homogeneity is understood as its state that corresponds to system Gibbs free energy global minimum for given thermodynamic parameters and, accordingly, is thermodynamically equilibrium (Porter, et al. (2009)). In this case, any phase separation leads to system free energy increasing, therefore, to thermodynamically disadvantageous. Local homogeneity is understood as homogeneous solid solution non-equilibrium state, which corresponds to Gibbs function local minimum and remains stable only to relatively small fluctuations in composition (Cahn J. W. (1961), Porter D. A., et al. (2009)).

In this state, system can remain single-phase for long time, but in sufficiently large fluctuations or external influences (temperature changes, defects, concentration

inhomogeneity, external energy invasions, including pressure) presence, transition to more stable multiphase state is possible (Cahn J. W. (1961)). Thus, global homogeneity corresponds to system absolute thermodynamic stability, while local homogeneity is evidence of its non-equilibrium state stabilized by kinetical limitation. In multicomponent alloys that crystallize under non-equilibrium conditions, it is local homogeneity that is typical structural state at room temperature [35].

In real casting conditions, not free energy global minimum is realized, but one of the functional G local minima, accessible to system during limited diffusion relaxation time. Thus, cast alloys phase composition and structural components morphology are determined not only by thermodynamic equilibrium conditions, but also by characteristic diffusion and cooling times ratio, which limits equilibrium phase diagrams applicability for structure direct prediction.

It should be noted that in modern materials science, number of alternative approaches to new alloys development have been formed, aimed at predicting their phase composition and properties accuracy increasing. These include approaches based on machine learning methods and databases large number analysis using, which allow taking into account complex nonlinear interactions between system components [36, 37], concept of Integrated Computational Materials Engineering (ICME), which combines thermodynamic, kinetic and mechanical models [38], high-performance combinatorial experimental methods [39], as well as quantum-mechanical approaches to first-principles calculations (ab initio) [40]. At the same time, even these approaches do not allow for cast alloys structure formation full description under non-equilibrium crystallization conditions, which determine experimental "trial and error" approach important role preservation [41]. In this regard, approaches that take into account kinetic limitations, phase genesis, and percolation effects become exclusively important.

Despite significant potential of new alloys development alternative approaches, their direct use for structure predicting, in particular, cast bronzes used in foundries, is methodologically limited. This is due to the fact that castings structure formation occurs under temperature field spatiotemporal heterogeneity conditions, castings structural microsegregations, dendritic crystallization, limited diffusion and mechanical limitations associated with shrinkage and interaction with casting mold.

Machine learning (ML) methods depend on training data completeness and representativeness and, as a rule, do not reveal structure formation physical mechanism. ICME approach is conceptually most complete, but requires all interconnected sub-processes consistent and reliable description, which is extremely difficult for multi-component cast bronzes.

Combinatorial methods provide chemical compositions rapid screening, which are usually implemented under conditions not equivalent to shaped castings actual solidification.

First-principles calculations provide fundamental information about phase energetics and interatomic interactions, but do not directly describe cast microstructure formation kinetics on real casting scale.

Thus, these approaches are important auxiliary analysis tools, but do not provide direct and sufficiently reliable prediction of cast bronzes in real casting molds structure.

Despite significant progress, these approaches have fundamental limitations. CALPHAD methods are based on equilibrium assumption. HEA integral parameters are mainly empirical. Machine learning methods depend on data completeness and do not reveal the physical mechanisms. And quantum mechanical ab-initio calculations based on electronic structure analysis and do not describe microstructure formation kinetics on real castings scale. These limitations are particularly evident in casting conditions, where structure is formed by non-equilibrium crystallization in temperature gradients presence, structural microsegregations, dendritic growth and limited diffusion. Under such conditions, not free energy global minimum is realized, but one of the local minima accessible to the system for diffusion relaxation limited time, which leads to non-equilibrium phase states formation.

Therefore, existing approaches allow determining potentially possible phase composition, but do not provide cast bronzes real microstructure reliable quantitative prediction, which is formed under thermodynamic, kinetic and technological factors complex interaction conditions.

In this regard, relevant scientific task is to develop generalized parameter or system of criteria that allow quantitatively assessing matrix solid solution supersaturation degree, its stability state and secondary phases under non-equilibrium crystallization conditions formation intensity. Solving this problem opens up possibility for multicomponent cast bronzes structure and properties scientifically based prediction.

Purpose. To establish structurally reliable and thermodynamically justified criteria for alloys supersaturated copper α-matrix stability assessing and multicomponent bronzes formed under crystallization and subsequent cooling non-equilibrium conditions phase composition predicting.

Methodology. Research methodology is based on combination of thermodynamic analysis, structural-parametric approach and experimental and literature data generalization.

To quantitatively assess copper matrix state in multicomponent bronzes, matrix overload with solvent integral parameter Δ has been introduced. It has been defined as ratio of theoretically required copper content, sufficient to ensure alloying elements non-equilibrium solubility, to its actual content in alloy.

Copper mass content required to ensure alloying elements non-equilibrium solubility limit (Cu^{V}) has been determined based on alloying elements in copper matrix solubility experimental data generalization, taking into account their total influence under non-equilibrium crystallization conditions. In this case, Δ criterion has been considered as generalized concentration parameter that quantitatively characterizes the system provision degree with matrix solvent.

System state thermodynamic analysis has been performed within classical approach framework based on Gibbs free energy minimization at fixed temperature and pressure.

For phenomenological description of non-equilibrium state from equilibrium state deviation, relationship existence between component activities and parameter Δ ratio assumption has been used.

Bronzes structural and mechanical state assessment has been carried out using empirical criterion K_R, which takes into account chemical composition, alloying elements influence on matrix structural state and empirically determined mechanical properties characteristics.

Therefore, proposed methodology allows for multicomponent bronzes, formed under non-equilibrium crystallization conditions, relationship "composition – thermodynamic stability – structure – properties" comprehensive analysis.

Findings. As noted above, currently known rules and parameters for single-phase state stability assessing have limited applicability for multicomponent alloys (MCA) phase composition analyzing, for example bronzes.

In particular, parameter Ω, which is widely used to assess HEA single-phase state stability, is methodologically incorrect for MCA phase state analyzing, since in MCA:

- mixing configurational entropy is significantly lower than that of high-entropy alloys and cannot be considered as phase stabilization dominant factor;
- alloying elements interact mainly with matrix solvent atoms, rather than with each other, which determines enthalpy contribution fundamentally different nature;
- phase composition is largely determined by system components interaction features, which is reflected in multicomponent phase diagrams, and not only by alloying elements limited solubility and homogeneous solid solution Gibbs energy minimization, as in HEA.

That is, from literary sources analysis it follows – solid solutions supersaturation degree is one of the main factors that determines their phase decomposition thermodynamic driving force, new phases formation probability and secondary structural components releasing intensity [42, 43]. That is why, to describe in studied bronzes conditions for single-phase or multiphase state formation, it is advisable to use criterion that would be directly related to alloying elements in matrix solvent non-equilibrium solubility limit with its subsequent para-equilibrium stable existence in alloy final (at room temperature) microstructure.

Based on this, in the present work hypothesis has been tested that in multicomponent alloys single-phase state is realized only in case when matrix solvent amount in alloy is sufficient to ensure required limit for non-equilibrium solubility of all its alloying elements. Failure to reach this limit leads to secondary phases inevitable releasing in alloy structure. That is, such alloy multiphase nature may be due to matrix solvent deficiency (α-Cu in bronzes) in addition to multiphase structure formation cases during primary crystals direct crystallization (for copper alloys, mostly chemical compounds) or eutectic type or others phases reactions products.

Parameter Δ has been introduced in order to determine this hypothesis using possibility in concentration limits of solid solution single-phase structure stable existence and beyond their circumferences, to quantitatively assess concentration borders that provide bronzes in non-equilibrium state with single- or multiphase structure at room temperature. As to bronzes, parameter Δ is copper theoretical mass required to ensure for all alloying elements non-equilibrium solubility limit in matrix to its actual mass in real bronze ratio. That is, parameter Δ reflects system provision degree with matrix solvent (for bronzes, copper) and quantitatively characterizes condition fulfillment for non-equilibrium solubility limit achieving during multicomponent alloying.

At values $\Delta < 1$, alloy matrix (α-Cu for bronzes) has sufficient atomic solvating capacity to retain alloying elements in solid solution lattice. In this case, system single-phase state is determined mainly by solid solution stability thermodynamic factors.

At values $\Delta \gtrsim 1$, concentration loading on matrix solvent exceeds its non-equilibrium solvating capacity, which leads to single-phase state stability losing and to secondary phase formation.

Proposed parameter Δ is, in fact, concentration indicator that describes multicomponent alloys conditions for existence or losing single-phase state with several alloying elements participation. Unlike parameter Ω, which is used for HEA, parameter Δ is directly related to quantitative solubility limitations and characterizes balance between matrix solvent actual content and total necessity for matrix solvent to accommodate alloying components in it.

Parameter Δ physical meaning is that each alloying element in multicomponent alloy requires certain positions, i.e., matrix solvent portions for stable existence in solid solution. In complex alloying case, total concentration loading on matrix lattice increases, which leads to its non-equilibrium solvation capacity decreasing. Thus, criterion Δ reflects matrix lattice overloading with alloying elements degree.

It should be noted that Δ definition is first-order working approximation adopted to construct an engineering criterion and does not claim to complex multicomponent thermodynamic interactions accurate describing. From physical point of view, parameter Δ is appropriate to consider as generalized supersaturation parameter, reflecting changings in energetic feasibility of alloying elements presence in copper α-solid solution composition under limited diffusion and non-equilibrium crystallization conditions.

With bronzes alloying degree increasing to values $\Delta \approx 1$, alloying elements are mainly contained in α-phase, which corresponds to energetically favorable state of their presence in copper matrix compared to alternative crystallochemical states (secondary phases or intermetallics). As Δ approaches value one, non-equilibrium single-phase structure loss and system alternative ways to reduce free energy implementing probability increases sharply, in particular, dissolved component clustering without solvent initial crystal lattice syngonia changing or second phase excretion [44, 45].

Further Δ growth means that total concentration load on matrix lattice exceeds its non-equilibrium solvation capacity. In this case, alloying elements in α-Cu composition presence energetic feasibility decreases and system reduces its free energy by secondary phases forming.

That is, parameter Δ is not phase equilibrium classical thermodynamic criterion. It should be considered as engineering parameter reflecting the moment of non-equilibrium single-phase solid solution loss in real multicomponent alloys formed under non-equilibrium casting conditions.

In this case

$$\Delta = Cu^V/Cu,$$

where Cu is actual copper mass content in bronze; Cu^V is a copper mass content required to ensure equilibrium

solubility limit simultaneously for all alloying elements in bronze.

Based on this, transition from single-phase to multiphase state is expected under condition – $\Delta \gtrsim 1$, and its conditionally physical meaning can be interpreted as follows:

$\Delta < 1$ – matrix solvent ensures alloying elements solubility;

$\Delta \gtrsim 1$ – supersaturated solid solution;

$\Delta \gg 1$ – single-phase state significant thermodynamic instability.

From thermodynamic point of view, supersaturated solid solution decomposition driving force is determined by components chemical potentials difference in system non-equilibrium and equilibrium states, which is consistent with general approaches to describing supersaturation as driving force for phase transformations [46].

Thermodynamic stability conditions and system equilibrium at fixed temperature T and pressure P (based on fact that under equilibrium thermodynamic conditions system state is determined by corresponding thermodynamic potential minimum) are as follows: at T, V = const – Helmholtz free energy, and at T, P = const – Gibbs free energy [46].

In Callen (1985) and DeHoff (2006) works it has been shown that under isothermal-isobaric state conditions, multicomponent system equilibrium is determined by Gibbs free energy minimum, which can be represented as function of temperature, pressure and system state internal parameters, characterizing its composition and structure

$$G = G(T, P, x_1, x_2, ..., x_n),$$

where x_i is system internal parameters that can characterize its composition and structure.

Such parameters may include component concentrations, phases transformation degree, order parameters (η), which characterize structural or chemical ordering degree (for example, long-range order degree or new phase fraction), as well as generalized state coordinates (ξ_i), which describe system microstructural characteristics (phases volume fractions, grain size, defects density, etc.) [47].

To analyze the system equilibrium conditions small deviation from arbitrary state, described by variations in internal parameters, change in Gibbs energy can be represented in form of expansion to second order, which allows investigating both stationarity conditions and equilibrium state stability nature.

According to thermodynamics classical provisions, necessary condition for equilibrium is Gibbs function stationarity with respect to all internal parameters, which corresponds to thermodynamic driving forces absence in system. At the same time, even this execution condition does not guarantee system stability state.

Equilibrium stability is determined by Gibbs energy surface curvature nature. To maintain steady state, it is necessary that any small deviation be accompanied by system energy increasing, which mathematically corresponds to second-order quadratic form positive definiteness. In multidimensional case, this is equivalent to positive definiteness of matrix Gibbs energy second derivatives.

Based on this, it follows that, according to minimal thermodynamic potential principle, system equilibrium state at fixed T and P corresponds to function G minimum.

System small deviation from arbitrary state

$$x_i \to x_i + \delta x_i,$$

where δx_i is small variations in internal parameters.

Change in Gibbs energy with such deviation can be expanded into Taylor series in this state neighborhood within L.D. Landau, E.M. Lifshitz (1980) phase transitions theory framework

$$G(x_i + \delta x_i) = G(x_i) + \sum_i \left(\frac{\partial G}{\partial x_i}\right)_{T,P} \delta x_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 G}{\partial x_i \partial x_j}\right)_{T,P} \delta x_i \delta x_j + ... \quad (1)$$

From expression (1) analysis it follows that expansion first term corresponds to energy value in initial state, second – to linear change in energy, and third characterizes quadratic corrections. Using expression (1) allows determining thermodynamic equilibrium condition. In this case, necessary equilibrium condition is determined by vanishing linear term expansion to zero. This, according to DeHoff (2006) and Gibbs J.W. (original works), leads to function G stationarity condition with respect to all internal variables, i.e.

$$\left(\frac{\partial G}{\partial x_i}\right)_{T,P} = 0, \quad i = 1...n. \quad (2)$$

Condition (2) means that with infinitesimal change in Gibbs energy internal parameters change in first approximation equal zero. In differential form, Gibbs stationarity condition (2) has form

$$dG = 0.$$

Physically, it means thermodynamic forces absence that tends to change system state.

For study completeness, stationary point type should be considered. In this case, function stationary point can correspond to different types of extrema – minimum, maximum or saddle point. So, condition fulfilling

$$\left(\frac{\partial G}{\partial x_i}\right)_{T,P} = 0,$$

is necessary but not sufficient to equilibrium state stability ensure.

For stable equilibrium, it is necessary Gibbs energy increasing for any small system deviation from equilibrium state. In this case, requirement for thermodynamic stability will be equivalent to second-order quadratic form positivity

$$\delta^2 G > 0,$$

where

$$\delta^2 G = \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 G}{\partial x_i \partial x_j}\right) T, P^{\delta x} i^{\delta x} j.$$

Therefore, equilibrium stability is determined by Gibbs energy second derivatives sign. And this, in turn, means that for any small deviation, energy increases. Obtained relations allow analyzing single-parameter case and multicomponent systems. As for single-parameter case, here the system will be characterized by one

internal variable x. And this means that Gibbs energy is one variable function

$$G = G(x).$$

In this case, equilibrium and stability conditions can be written. Thus, equilibrium condition has the form

$$\frac{\partial G}{\partial x} = 0.$$

Stability condition

$$\frac{\partial^2 G}{\partial x^2} > 0.$$

In this case, stability condition means that function $G(x)$ stationary point is minimal.

For multicomponent systems, situation will be different, since in several internal variables case, stability analysis requires Gibbs energy second derivatives matrix consideration, which is called Hessian matrix [46]

$$H_{ij} = \left(\frac{\partial^2 G}{\partial x_i \partial x_j} \right)_{T,P}.$$

Multicomponent systems equilibrium state stability condition is that this matrix must be positive definite. This means that inequality

$$\delta x^T H \delta x > 0.$$

for any nonzero variation vector δ_x.

In fact, this means

$$\frac{\partial^2 G}{\partial x_1^2} > 0; \qquad (3)$$

$$\begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G}{\partial x_2 \partial x_1} & \frac{\partial^2 G}{\partial x_2^2} \end{vmatrix} > 0,$$

etc. for all principal Hessian matrix minors.

On other hand, derived inequality leads to requirement that Hessian matrix all principal minors be positive.

Regarding multicomponent system stability conditions physical interpretation – if condition (3) is satisfied, then any small deviation increases system energy. As a result, system tends to return to its initial equilibrium state.

If condition (3) is not met, then deviation leads to Gibbs energy decreasing. In this case, initial state is unstable, and system naturally and spontaneously evolves to another state, which may appear itself, for example, as phase decomposition or phase transformation by multiphase reaction.

To substantiate further research, relationship between Gibbs energy and chemical potentials should be considered. For multicomponent system, Gibbs energy can be expressed in components chemical potentials terms by expression [48]

$$G = \sum_i n_i \mu_i, \qquad (4)$$

where n_i is the i^{th} component discrete units number; μ_i – i^{th} component chemical potential.

This expression gives rise to fundamental thermodynamic relation

$$\frac{\partial G}{\partial n_i} = \mu_i,$$

and Gibbs energy differential has form

$$dG = \sum_i \mu_i dn_i,$$

where G is system Gibbs free energy, J; n_i is substance i^{th} component amount, mol; μ_i is i^{th} component chemical potential, J/mol; i is an alloy component.

Therefore, equilibrium condition for permissible composition variations has form

$$dG = 0,$$

and equilibrium stability requires positive curvature of Gibbs energy dependence on system composition variables.

Therefore, multicomponent system thermodynamic equilibrium and stability conditions at fixed temperature and pressure are formulated in this way:

- necessary condition for equilibrium is Gibbs energy stationarity in internal variables terms

$$\delta G = 0,$$

which corresponds to function $G(T, P, x_i)$ extremum reaching;

- sufficient stability condition is determined by Gibbs energy matrix second derivatives (Hessian) positive definiteness

$$\delta^2 G > 0,$$

this ensures minimum Gibbs energy realization, or

$$\left(\frac{\partial^2 G}{\partial x_i^2} \right)_{T,P} > 0,$$

which is equivalent to Gibbs energy matrix second derivatives positive definiteness.

In opposite case ($\delta^2 G < 0$) stationary point corresponds to maximum or saddle point and is thermodynamically unstable.

These conditions provide thermodynamic potential minimum and determine system equilibrium state stability.

Unlike classical approach, in which internal variables are considered abstractly as generalized state coordinates, in this work they are interpreted through cast bronzes, formed under non-equilibrium crystallization conditions, structural characteristics, in particular:

- solid solution supersaturation degree;
- secondary phases volume fraction;
- structural compositions of different genesis presence.

This approach allows moving from formal thermodynamic description to structure formation processes quantitative analysis.

Taking this into account, in present work generalized criterion has been introduced that links supersaturated matrix decomposition thermodynamic conditions with kinetic and structural factors and allows describing phase transformation implementation in real (non-equilibrium) casting conditions. That is, structural-parametric description proposed in the work is adapted to minimum Gibbs energy classical conditions. This provides its practical application possibility to Cu–Al–Si–Mn–Sn system cast bronzes structures analysis.

In particular, if multicomponent system (Cu–Al–Si–Mn–Sn) based on copper is at fixed temperature T and pressure P, then system thermodynamic state is determined by isobaric-isothermal Gibbs potential value (4).

System chemical potential is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\dot{O}, \dot{D}, n_{j\neq i}}.$$

Single-phase solid solution thermodynamic stability condition is function G at given T, P, and n_i minimum. Non-equilibrium stability losing is possible if there is composition variation Δn_i, at which

$$\Delta G < 0.$$

Thus, non-equilibrium stability losing is possible if there is variation in composition Δn_i, at which, also, system free energy decreases. For further analysis, ΔG will be understood as free energy changing associated with supersaturated solid solution relaxation, i.e.

$$\Delta G_{relax} = G_{multiphase} - G_{single\text{-}phase} < 0,$$

where ΔG_{relax} is Gibbs free energy changing, which characterizes supersaturated solid solution relaxation.

Single-phase stability limit is determined by components in matrix chemical potentials and corresponding secondary phase equality condition

$$\mu_i^{\alpha} = \mu_i^{\beta}.$$

This condition sets solid single-phase solution limiting (equilibrium) composition. If copper mole fraction denoted by x_{Cu}^{eq}, which minimal required to accommodate all alloying elements in solid equilibrium solution at given temperature, and real quenched or rapidly cooled alloy copper mole fraction denoted composition is x_{Cu}^{real}, then parameter has been used to characterize matrix supersaturation

$$\Delta = \frac{x_{\mathrm{Cu}}^{eq}}{x_{\mathrm{Cu}}^{real}}. \quad (5)$$

Thus, parameter Δ quantitatively characterizes degree to which alloying elements solubility concentration limit in matrix is exceeded.

From thermodynamic point of view, solid solution stability is determined by components chemical potentials values. Component j chemical potential in solid solution is determined by expression [49]

$$\mu_j = \mu_j^0 + RT \ln \alpha_j,$$

where μ_j is standard chemical potential; R is universal gas constant, 8,314 J/mol; T is absolute temperature, K; a_j is thermodynamic component j activity.

As solvent (Cu) proportion decreases, elements with which it is doped chemical activity increases. Close to limiting composition, alloying component in non-equilibrium and equilibrium states activity ratio is expected to correlate with matrix supersaturation degree.

In first approximation, let to be assumed that non-equilibrium solid solution composition deviation degree from equilibrium state can be characterized by generalized supersaturation parameter Δ. For this case (in first approximation), components in non-equilibrium and equilibrium states activities ratio can be approximated by this parameter

$$\frac{\alpha_j^{real}}{\alpha_j^{eq}} \sim \Delta,$$

where α_j^{real} is component j activity in real alloy; α_j^{eq} is activity in equilibrium single-phase state.

Substituting this ratio into previous expression, obtaining

$$\mu_i^{real} - \mu_i^{eq} \approx RT \ln \Delta. \quad (6)$$

Then system free energy change during supersaturated solid solution relaxation can be represented as

$$\Delta G \approx -RT \ln \Delta \sum_i n_i.$$

System substance participating in thermodynamic relaxation process effective amount let to be introduced

$$n_{eff} = \sum_i n_i,$$

where n_{eff} is considered as effective substance amount proportional to copper matrix deviation from limiting single-phase state, since it is copper matrix that determines the volume in which phase decomposition is realized.

In this case

$$\Delta G \cong -RTn_{eff} \ln \Delta.$$

Value n_{eff} can be associated with copper matrix composition change during transition from non-equilibrium to equilibrium state. Since supersaturated solid solution relaxation is accompanied by alloying elements redistribution relative to copper matrix, it is advisable to express substance participating in this process effective amount in copper concentration deviation from equilibrium value terms.

Based on formula (5), difference in copper mole fractions is equal to

$$\ddot{A}x_{\mathrm{Cu}} = x_{\mathrm{Cu}}^{eq} - x_{\mathrm{Cu}}^{real} = x_{\mathrm{Cu}}^{eq}\left(1 - \frac{1}{\Delta}\right).$$

Substance amount that must be redistributed to reach equilibrium can be estimated

$$n_{eff}\ n_{\mathrm{Cu}}\left(1 - \frac{1}{\Delta}\right),$$

where n_{Cu} is copper total amount in the system (mol).

Thus, supersaturated solid solution substance participating in relaxation effective amount is determined by copper matrix composition deviation from equilibrium single-phase state degree.

Substituting resulting expression for n_{eff} into formula for free energy changes, obtaining

$$\Delta G - RTn_{\mathrm{Cu}}\left(1 - \frac{1}{\Delta}\right)\ln \Delta, \quad (7)$$

where ΔG is change in system free energy during supersaturated solid solution relaxation, J; Δ is a matrix supersaturation criterion; n_{Cu} is a copper total amount in system, mol; R is universal gas constant, J/(mol · K); T is absolute temperature, K.

This expression is not state strict thermodynamic equation, but is used as estimated phenomenological

dependence to characterize supersaturated copper matrix energetic susceptibility to phase decomposition.

Regarding expression (7) structure, it should be noted that, unlike classical thermodynamic relations, in which free energy change is given per unit volume or substance amount, in this case value n_{Cu} performs scale parameter function that characterizes matrix metal total amount involved in supersaturated solid solution relaxation process. This means that change in system free energy is proportional to copper matrix amount in which alloying components redistribution and secondary phases' formation occurs. In this case, expression (7) describes system effective copper-matrix constituent, which determines tendency to exude secondary phases in considered composition interval. That is, in essence, calculations using expression (7) determine changes in supersaturated copper matrix free energy, and parameter Δ serves as an engineering measure of solid solution supersaturation degree, which is directly related to structural transformations thermodynamic driving force through dependence type $RT \times \ln\Delta$.

In order to compare this value with classical nucleation barrier, where specific free energy is usually used, for example, J/mol, for further kinetic constructions, it should proceed to one of expression (7) forms

$$\frac{\Delta G}{n_{Cu}} = -RT\left(1-\frac{1}{\Delta}\right)\ln\Delta \quad \text{or} \quad \Delta g = -RT\left(1-\frac{1}{\Delta}\right)\ln\Delta, \quad (8)$$

as to process molar driving force where: Δg is free energy change per copper matrix mole (J/mol).

Expression (8) margins condition and physical meaning are defined as follows: at $\Delta \to 1$ will be $\ln\Delta \to 0$ and, accordingly, $\Delta G \to 0$, which corresponds to solid solution equilibrium single-phase state. When $\Delta > 1$, inequality $\Delta G < 0$ is realized, which indicates thermodynamic driving force presence for supersaturated solid solution phase decomposition. In this case, non-equilibrium single-phase state free energy exceeds equilibrium multiphase state free energy, which determines secondary phases' precipitation energetic feasibility and system transitioning to more stable state.

Thus, expression (8) allows to quantitatively estimating supersaturated copper matrix relaxation driving force and can be used as basic conditional thermodynamic characteristic in further analysis of phase formation kinetics and alloy microstructure transformation.

With Δ increasing, value $|\Delta G|$ in expression (8) acquires character close to logarithmic, which is presented by dependences in Figure and corresponds to phase transformation in multicomponent solid solutions thermodynamic potential increasing limited nature.

Presented dependencies analysis shows that with temperature increasing, system change free energy modulus increases. In particular, at temperature 873 K $|\Delta G|$ values at the same supersaturation degree are larger than at 573 K. This directly follows from temperature multiplier RT presence in expressions (7 and 8), as a result of which, as temperature increases, thermodynamic driving force for supersaturated solid solution relaxation increases. It corresponds to system effective chemical supersaturation relatively to equilibrium state. Most intensive modulus $|\Delta G|$ growth is observed in values $\Delta \approx 1.5$–2.0 (Figure) range, after which dependence alters to slower growth mode. This change nature is due to fact that with supersaturation degree further increasing, factor $(1-1/\Delta)$ gradually approaches value one, and main contribution to free energy changing measure begins to be determined by logarithmic term $\ln\Delta$.

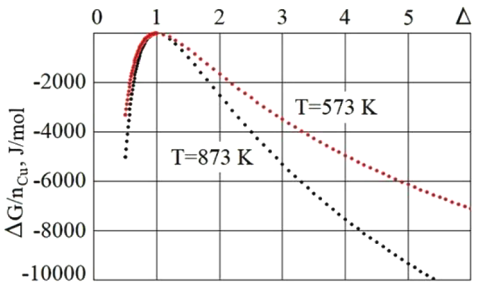

Fig. Dependences $\frac{\Delta G}{n_{Cu}} = f(\Delta)$ *at temperature 573 and 873 K*

It should be noted that for $\Delta < 1$, ΔG value in expression (7) also acquires negative sign. This is due to the fact that in this case logarithmic term $\ln\Delta$ becomes negative, while factor $(1-1/\Delta)$ also has negative value, and their product remains positive, which together with negative sign in front of expression again gives $\Delta G < 0$. However, this case physical meaning is different from supersaturation situation. If at $\Delta > 1 \Delta G$ negative value corresponds to supersaturated solid solution relaxation by secondary phases releasing, then at $\Delta < 1$ it reflects tendency of the system to reverse process – excide phases dissolution and matrix equilibrium composition restoring.

That is, value ΔG sign in expression (7) in both cases characterizes system tendency to decrease its free energy. But this process physical content is different: at $\Delta > 1$ supersaturated solid solution decomposition realizing, while at $\Delta < 1$ system composition is equalized due to secondary phases' dissolution. Point $\Delta = 1$, in fact, separates regions of system structure evolution two opposite directions.

Relation (7) analysis shows that it correctly reflects supersaturated solid solution main thermodynamic properties. In particular, at $\Delta = 1$ (Figure), which corresponds to equilibrium or non-equilibrium margin matrix state, logarithmic magnifier $\ln\Delta$ is zero, resulting in $\Delta G = 0$. This means disintegration thermodynamic driving force absence, which is fully consistent with system stable state classical thermodynamic concepts.

In matrix supersaturation case, when $\Delta > 1$, both factors $(1-1/\Delta)$ and $\ln\Delta$ acquire positive values, and naturally entire value ΔG becomes negative. This means that during supersaturated solid solution relaxation, system free energy decreases. That is, system passes to more thermodynamically favorable state. Therefore, dependence sign and general form correspond to thermodynamic stabilization fundamental principle through Gibbs potential decreasing.

It is also important to note that change in free energy on supersaturation range dependence has nonlinear appearance. It is determined by two dimensionless magnifiers output – logarithmic term $\ln\Delta$, which reflects thermodynamic contribution of components activities ratio, and factor $(1-1/\Delta)$, which characterizes matrix fraction that is actually in supersaturated state.

For small deviations from equilibrium, when $\Delta = 1 + \varepsilon$ and $\varepsilon \ll 1$, expanding these factors into series shows that

$$\ln\Delta \approx \varepsilon; \quad 1-1/\Delta \approx \varepsilon.$$

In this case, free energy change is approximately determined by relationship

$$\Delta G \approx -RT \cdot n_{Cu} \cdot \varepsilon_2.$$

This means that closed to equilibrium state ($\Delta \gtrsim 1$), driving force for disintegration increases quadratically with supersaturation increasing, which is compatible with thermodynamics general ideas about smooth change in system potential near the free energy minimum.

At matrix supersaturation parameter significant values ($\Delta \gg 1$), logarithmic term $\ln\Delta$ begins to be dominant in expression for free energy changing. In this case ΔG on Δ dependence takes character close to logarithmic trend. But such change in function nature does not lead to discontinuities or step changes appearance, since thermodynamic driving force remains supersaturation continuous function. Instead, this may exhibit itself in dependencies curvature changing which characterizing phase transformation.

Nevertheless, as already noted above, it should be emphasized that obtained expressions (7) or (8) are not multicomponent solutions thermodynamics strict general equation. It is supersaturated copper matrix energy relaxation model description, in which components chemical potentials complex system is replaced by generalized supersaturation parameter – the Δ parameter. In this context, n_{Cu} value serves as defining parameter characterizing matrix solvent total amount, through which solid solution supersaturation portion is quantitatively expressed.

That is, given ratio can be interpreted as supersaturated copper matrix free energy decreasing effective estimator during its relaxation. Its important advantage is that relation (7) directly relates parameter Δ to phase disintegration thermodynamic driving force. This allows considering Δ not only as structural or empirical supersaturation parameter, but also as system thermodynamic state relative reflection, which determines energetic tendency to create secondary phases.

From above it follows that parameter Δ does not change or modify thermodynamics classical relations. It is only used as parameter characterizing non-equilibrium solid solution composition deviation degree from equilibrium state. Thus, Δ acts as system generalized supersaturation parameter, which allows set down difference in chemical potentials in compact form.

It should be noted, as mentioned above, that idea concerning solid solutions supersaturation as their phase decomposition thermodynamic driving force is well known in physical metallurgy. However, in known works, authors usually consider this phenomenon in relation to binary systems or describe it through individual components chemical potentials difference.

In multicomponent casting alloys, this approach (parameter Δ) transpires to be difficult due to necessity to simultaneously take into account several alloying elements and structure formation in non-equilibrium conditions. Unlike traditional thermodynamic parameters, this parameter is determined on the basis of experimentally established solubility limits in non-equilibrium crystallization conditions and allows directly linking alloy chemical composition with microstructure type, being formed, secondary phases' relative volume fraction and structural components of another genesis.

In conducted studies course, it was found that Cu–Al–Si–Mn–Sn system cast bronzes mechanical properties correlate primarily with other, than α-Cu solid solution, structural components relative volume fraction [50]. However, their chemical composition, size and specific locations influence is much less obvious. Such regularity is consistent with physical metallurgy modern conceptions about heterogeneous alloys strengthening mechanisms, according to which alloy structural state genesis and, as a consequence, barriers spatial concentration and morphology play decisive role in long-distance fracture dislocations movement limiting.

In dispersion and separation strengthening classical models of alloys with single-phase structure, material strength is determined by dislocations with secondary phases' particles interaction. At invincible barrier encountering event, dislocation bypasses it using Orowan strengthening mechanism, in which required stress is determined by distance between particles. This distance, according to Gladman (1999), Courtney (2000), Cui, et al. (2024), in turn, depends on their size and volume fraction in matrix. Therefore, it is these parameters that determine alloy strengthening level.

With random particles distribution, characteristic distance between them (L) can be estimated as

$$L \sim d \cdot \varphi^{-1/3},$$

where d is a characteristic particle size; φ is secondary releases relative volume fraction.

In this case, stress required to bypass particles by dislocations (Orowan mechanism) is determined by relationship

$$\sigma \sim Gb/L,$$

where G is shear modulus; b is Burgers vector.

That is, material strength is largely determined by dispersed phases volume fraction, since increase in j leads to distance between obstacles to dislocations movement decreasing and, accordingly, to plastic deformation resistance increasing.

Similar patterns have been repeatedly observed in various alloy systems. Thus, in Liu Q., et al. (2024) work, authors studied Al–Cu–Mg–Ag system aluminum alloys. It has been established that dispersed precipitates contribution to yield strength can be directly related to their volume fraction. When precipitates fraction increases, it leads to almost proportional increasing in material strength. To quantify contribution to strength, dispersion strengthening models have been used, based on distance between particles and their bypass by dislocations corresponding stress calculation [51].

Similar conclusions have been formulated in Sun X., et al. (2020) work, devoted to Cu–Cr–Co–Si system copper alloys study. Authors found that key factors determining alloy yield strength and ultimate strength are intermetallic phase precipitates size and volume fraction. As their volume fraction increases, average distance between particles decreases, which significantly complicates dislocations movement and leads to mate-

rial strength characteristics increasing. To interpret obtained results, authors used dispersion strengthening models that take into account matrix particle distribution geometric parameters [52].

More general theoretical approach to describing secondary phases' volume fraction influence on mechanical properties has been developed in Wang X., Poole W., and Embury J. works, who studied AA6111 series (Al-Mg-Si system with the addition of Cu) aluminum alloys dispersion strengthening. Authors showed that material strength can be expressed in microstructural parameters terms, including particle size and volume fraction. Within proposed model framework, distance between particles has been determined from their spatial distribution and strength increasing has been explained by free dislocations path meaning between obstacles decreasing.

It should be noted that in cast alloys, structural components, other than α-solid solution, volume fraction influence may be enhanced due to dendritic structure formation peculiarities. In such systems, these structural components are often isolated mainly in interdendritic regions, where alloying elements concentration increases due to temperature gradient and, as a result, liquation processes. As a result, other than α-Cu structural components spatial network, in addition to the α-solid solution, is formed, including secondary phases, which connectivity increases with their volume fraction increasing. Such phases' spatial organization can lead to so-called percolation transition emergence, in which secondary phase isolated particles begin to form continuous three-dimensional network. According to percolation theory, when system components certain critical volume fraction is reached, sharp change in its macroscopic properties occurs. Such transitions classic description is presented in Kirkpatrick (1973) work, where it is shown that phases connected network formation leads to jump-wise in material physical characteristics changing.

Secondary phases spatially connected networks in cast alloys presence has been confirmed by experimental studies. Thus, Kumar S., et al., regarding Al–Mg–Si system DC-cast aluminum alloys structure, showed that intermetallic phases in as-cast state form strongly interconnected three-dimensional network formed mainly in interdendritic regions. Authors used microstructural three-dimensional reconstruction methods and showed that such network significantly affects alloy mechanical properties [53].

Similar results have been obtained by Asghar Z., Requena G., and Boller E., who investigated cast aluminum alloys for engine pistons products. Using X-ray tomography, it has been shown that increased hardness intermetallic phases form spatially connected three-dimensional network, which provides material increased strength, especially at elevated temperatures. In this work has been found that such network formation is key factor in improving mechanical properties, while individual phases chemical composition plays secondary role [54].

Additional data on secondary phases spatial connectivity influence on materials mechanical behavior has been provided in Bugelnig K., et al. work. It has been shown that change in phases with increased hardness local connectivity in cast aluminum alloys significantly affects plastic deformation processes and damage development. Authors showed that even with phases close total volume fraction, differences in their spatial connectivity can lead to noticeable changes in mechanical properties [55].

Similar patterns have been established for number of dispersion-strengthened copper alloys. Thus, in Cu–Ni–Si, Cu–Cr, and Cu–Cr–Zr systems, it has been shown that yield strength is determined primarily by distance between secondary phases particles, which, in turn, depends on their size and volume fraction (Lockyer, Noble; Hornbogen; Zhang, et al.). In these works [56, 57], strength increasing has been explained by dispersed precipitates dislocations bypassing mechanism according to Orowan regularity.

Similar results have been obtained for aluminum bronzes, where it has been shown that intermetallic ϰ-phases formation in α-matrix leads to increase in mechanical strength due to dislocation motion obstruction. Thus, if these phases number increases, resistance to plastic deformation and, accordingly, alloy hardness increase (Berlanga-Labari, et al. (2025), Nwaeju, et al., 2021).

That is, conducted studies results are in good agreement with modern conceptions about secondary and other, than α-solid solution, phases' spatial organization influence on metallic materials mechanical properties.

In particular, studied bronzes mechanical properties correlation with structural components other, than α-solid solution, relative volume fraction, observed in [50], can be explained by the fact that with their content increasing, including in interdendritic regions, gradual transition occurs from isolated particles distribution to spatially connected network formation. It is exactly this transition that leads to significant change in plastic deformation conditions and, as a result, to alloy sharp changing in mechanical properties.

As shown earlier, criterion Δ through copper content reflects dissolved elements actual concentration from their solubility limit deviation under cast structure non-equilibrium conditions formation. At Δ value increasing solid supersaturated solution decomposition thermodynamic driving force increases, which can be expressed as difference in chemical potentials terms according to equation (6).

Value Δ increasing leads to secondary phases precipitation thermodynamic driving force increasing and, as a consequence, their volume fraction in alloy structure increasing. Within nucleation classical theory, secondary phase nuclei formation rate is determined by exponential dependence on nucleation free energy

$$I \sim \exp(-\Delta G^*/kT),$$

where ΔG^* is a nucleation energy barrier.

When supersaturation increases, ΔG^* value decreases, which leads to nucleation rate increasing and formed secondary phase particles number increasing.

Thus, parameter Δ actually acts as generalized supersaturation parameter, which determines matrix supersaturation degree and, therefore, in case of alloy structure formation with α-solid solution primary formation, secondary phases, that have been released, volume fraction. Taking into account the fact that alloy mechanical properties, as shown above, are largely determined by these phases relative volume fraction, following cause-and-effect chain can be established

$$\Delta \rightarrow \varphi \rightarrow \sigma,$$

where φ is secondary phases volume fraction; σ is a material mechanical properties level.

Therefore, proposed parameter Δ can be considered as parameter that indirectly determines cast bronzes mechanical properties by secondary phases and structural components, other than the α-Cu solid solution, number controlling and their spatial connectivity in alloy structure degree. Such interpretation allows combining solid solution supersaturation thermodynamic description with material structural and mechanical characteristics and, thereby, explaining studied bronzes experimentally established properties dependence on criterion value.

Obtained result theoretical significance is that obtained expression (8) establishes functional dependence between:

- alloy chemical composition (through x_{Cu}^{real});
- limiting single-phase solubility (through x_{Cu}^{eq});
- thermodynamically unstable matrix volume fraction;
- phase disintegration driving force value.

Thus, parameter Δ acts as copper matrix state generalized characteristic, linking composition, thermodynamic stability and tendency to secondary phases forming in single phenomenological-thermodynamic model.

Obtained dependence can be used for multicomponent bronzes structural evolution quantitative prediction during non-equilibrium crystallization and subsequent heat treatment. Parameter Δ can be considered as generalized indicator of α-matrix supersaturation degree, which quantitatively scales supersaturated solid solution decomposition driving force. That is, parameter Δ is MCA phase stability independent criterion (marker), which creates basis for MCA single-phase and multiphase states conditions formation comprehensive description, in particular, in bronzes with different alloying levels, and, in fact, is generalized parameter of copper matrix chemical state deviation degree from equilibrium and can be used to assess:

- single-phase structure ultimate stability;
- tendency to disintegration;
- non-stability degree;
- different structural compositions comparative stability.

Comparing parameter Δ with parameter Ω, which is widely used to assess single-phase state stability in high-entropy alloys, it should be noted these criteria fundamental difference in physical content. Parameter Ω is based on assumption of mixing configurational entropy dominant role for single-phase solid solution in high-entropy systems stabilization. In such alloys, all elements are present in close concentrations, and no one of them plays dominant role in solvent matrix.

In multicomponent bronzes, situation is fundamentally different. This system alloys structure formation occurs with two- and even three-phase reactions realization. After that, they contain an obvious matrix solvent – α-Cu, in which alloying elements dissolve in relatively small concentrations. In this case, system phase composition is determined primarily by alloying elements solubility limits in copper matrix, and not by mixing configurational entropy value.

In this regard, it is more adequate to use concentration parameter Δ for such systems phase state describing, which characterizes alloy real composition deviation from single-phase α-solid solution thermodynamic stability region.

At the same time, parameter Δ significantly reflects two- and multicomponent alloys final microstructure genesis, which crystallization finalizes at single-phase solid solution structure formation stage. In case when alloy composition in liquid state corresponds to multiphase equilibrium existence region, structure formation genesis is more complex solidification mechanism subject with eutectic, peritectic or other reaction with subsequent solid-phase primary, secondary phases transformations and/or phases producing from multiphase reactions, which are inherent, respectively, to equilibrium, non-equilibrium or metastable phase composition diagrams.

In this work, in addition to Δ criterion, for Cu–Al–Si–Mn–Sn system alloys structural and mechanical properties assessing, empirical K_R criterion has been also used, which allows assessing bronzes for casting or deformation processing suitability. K_R criterion has been calculated by formula [50]

$$K_R = \left(1 - 0.01 \cdot nn\right) \cdot \frac{\mathrm{Al{-}Si{-}Mn}}{\left(1 + \mathrm{Sn}\right)^2},$$

where *nn* is undesirable impurities total mass content in bronze, Al, Si, Mn; Sn is corresponding alloying element mass content, %.

Criterion K_R has following structural and physico-chemical justification:

***Numerator* (Al–Si–Mn).** Aluminum (Al): Atomic radius 1,43 Å, FCC- structure similar to Cu (1,28 Å). Replacing Cu atoms, Al causes moderate alloys crystal lattice local stretching, which increases bronzes strength, hardness, and wear resistance, while slightly reducing its ductility relative to pure copper.

Silicon (Si): Atomic radius 1.32 Å, crystal lattice different from Cu. In small amounts, Si forms solid solutions, increasing bronzes fluidity and hardness, but excessive Si increasing reduces its ductility and increases hot cracks in castings probability.

Manganese (Mn): Atomic radius 1.37 Å, complex α-Mn lattice. Mn addition improves structural uniformity, reduces tendency to liquation, and increases bronze machinability. But high Mn concentrations can reduce its ductility. In aluminum presence in bronze, create intermetallics with magnetic properties.

Thus, numerator reflects alloying elements certain contribution to Cu crystal lattice stabilization and strengthening, which contributes to achieving optimal machinability and bronzes mechanical properties high levels.

Correction magnifier $(1–0.01 \cdot nn)$ takes into account undesirable impurities total mass content. Since undesirable impurities contribution in real industrial purity bronzes is small, this factor acts moderately, slightly reducing K_R, but making criterion dimensionless and more universal for practical application.

***Denominator*: $(1 + \mathrm{Sn})^2$.** Tin (Sn): atomic radius 1.62 Å, tetragonal β-Sn crystal lattice, which is significantly different from FCC in Cu. High Sn content increases hardness and reduces bronze ductility, complicating its machining modes.

Using square (2^{nd} degree) in denominator amplifies Sn effect nonlinearly, accordingly to experimental observations.

Additional digit one ensures criterion mathematical correctness for small Sn values, preventing K_R infinite values.

K_R criterion scientific essence is that it integrates chemical composition, alloying elements atomic characteristics, which influence is reflected through experimental data on mechanical properties.

It means, numerator takes into account Al, Si, and Mn positive contribution to Cu lattice stabilization and strengthening. And denominator reflects negative Sn influence due to atomic and crystalline incompatibility with Cu.

Thus, K_R is scientifically based criterion that combines bronzes mechanical characteristics empirical assessment with reticular structure physicochemical state and reflects bronzes mechanical properties values changes and mechanical and technological suitability. It integrates chemical composition, solid solution lattice saturation characteristics and mechanical properties experimental observations. That is, K_R combines empirical physical assessment with alloying elements atomic-crystallographic influence nature.

Supersaturated copper matrix obtained expression for free energy changing (7) analysis shows, that with matrix supersaturation criterion Δ increasing, system negative changing in free energy modulus should increase. This means that copper matrix supersaturation degree increasing accompanied by an increase in its relaxation thermodynamic driving force. And therefore – structural transformations intensification associated with supersaturated solid solution phase disintegration and subsequent possible two- and three-phase system transformations.

At the same time, K_R criterion reflects empirically established alloy components concentrations rational ratio, which ensures their properties optimal level [50]. It characterizes not system potential thermodynamic tendency to phase transformation, but matrix construction actual structural and spatial state, which is formed during crystallization process and alloy subsequent structural evolution.

Since both indicators (Δ and K_R) characterize same process different aspects, certain functional relationship can be expected between them. Criteria physical content suggests that with copper matrix overload degree increasing, which is reflected by increase in Δ, system structural state should change in such way that K_R indicator will change in opposite direction.

This conclusion logically follows from the fact, that parameter Δ directly enters expression for supersaturated solid solution relaxation thermodynamic driving force, while K_R criterion reflects system structural-spatial response to driving force of this realization. In other words, parameter Δ characterizes supersaturated matrix potential thermodynamic instability, while K_R is directly related to alloy current structural state.

In other words, parameter Δ describes supersaturated solid solution system deviation from non-equilibrium state degree, while criterion K_R characterizes degree of matrix construction structural integrity preservation or loss. Therefore, first parameter increasing must be accompanied by corresponding, but oppositely directed, changing in second.

Therefore, parameter Δ and criterion K_R can be considered as bronzes structural state conjunct parameters: growth in first should be accompanied by opposite change in second. In graphical presentation, this gives reason to expect corresponding dependencies of mirror-inverse nature.

Thus, as noted above, each of indicators, proposed in this work, in fact, characterizes studied systems from different points of view. Their joint use gives Cu–Al–Si–Mn-Sn system comprehensive characteristic, since:

- parameter Δ, in fact, reflects matrix supersaturation degree, determines alloying elements non-equilibrium solubility level limit, which ensures its structure transition from single-phase to two- or multi-phase state, and can be used to determine secondary phases and other, than α-Cu solid solution, structural components in alloy, relative volume fraction;.

- K_R – mechanical and technological applicability criterion that determines alloy doping crystallochemical attempting at reticular level to achieve mechanical and operational required level properties and can also be used to determine relative volume fraction of secondary phases and other, than α-Cu solid solution, structural components in material, especially for alloy components concentration combinations cases, which are characterized by phase transformations with multiphase reactions.

Conclusions.

1. Concentration parameter Δ has been proposed for single-phase state in multicomponent bronzes preserving or losing conditions assessing. It is determined by ratio between actual copper content in alloy and its amount necessary to ensure alloying elements non-equilibrium solubility limit. Parameter Δ is not phase equilibrium classical thermodynamic criterion and is considered as an engineering parameter reflecting single-phase solid solution non-equilibrium stability losing moment under real casting conditions.

2. It has been shown that parameter Δ is generalized indicator of copper matrix supersaturation degree and reflects crystal lattice overloading with alloying elements. At values $\Delta \gtrsim 1$, conditions have been formed for single-phase solid solution non-equilibrium stability losing and for secondary phases' appearance.

3. It has been found that with parameter Δ increasing, thermodynamic driving force for supersaturated solid solution relaxation increases, which is accompanied by tendency to multiply secondary phases in bronzes structure volume fraction.

4. It has been shown that parameter Δ, proposed in the work, significantly reflects two- and multicomponent alloys final microstructure genesis, which crystallization ceases with solid solution single-phase structure formation stage with its subsequent possible solid-phase transformations.

5. For Cu–Al–Si–Mn–Sn system alloys structural and mechanical properties assessing an empirical crystallochemical criterion K_R has been proposed. It characterizes their mechanical and technological applicability, in particular, for casting and/or pressure processing.

6. It has been established that parameter Δ characterizes system thermodynamic tendency to phase disintegration, while criterion K_R reflects its structure-dependent mechanical characteristics. It has been proven that combined Δ and K_R indicators using allows to bronzes structural state and its influence on properties comprehensive describing.

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Критеріальне оцінювання фазового складу багатокомпонентних алюмінієвих бронз. (Частина 1. Критерії стійкості пересиченої мідної α-матриці й фазового складу багатокомпонентних бронз системи Cu–Al–X)

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Мета. Встановити термодинамічно обґрунтовані критерії оцінювання стійкості пересиченої мідної α-матриці сплавів і прогнозування фазового складу багатокомпонентних бронз, що формуються в нерівноважних умовах кристалізації й охолодження.

Методика. Методика базується на поєднанні термодинамічного аналізу, структурно-параметричного підходу й узагальнення експериментальних даних. Стан мідної матриці оцінено за параметром Δ (відношення теоретично необхідного та фактичного вмісту Cu), термодинамічний аналіз виконано в рамках мінімізації енергії Гіббса з урахуванням малих відхилень і зв'язку активностей компонентів із Δ. Структурно-механічні властивості оцінені за критерієм K_R.

Результати. Для оцінки умов збереження або втрати однофазного стану в багатокомпонентних бронзах запропоновано концентраційний параметр Δ, що характеризує умови втрати нерівноважної стійкості твердого розчину в умовах лиття. Показано, що при $\Delta \gtrsim 1$ виникають умови для утворення вторинних фаз. Для оцінки структурно-механічних властивостей запропоновано критерій K_R. Показано, що спільне використання Δ й K_R забезпечує комплексний опис взаємозв'язку «склад – стабільність – структура – властивості» багатокомпонентних алюмінієвих бронз.

Наукова новизна. Уперше встановлена кількісно узгоджена система кореляційних взаємозв'язків між параметром пересичення Δ, композиційним критерієм K_R і структурним параметром (φ) – об'ємною часткою вторинних фаз у бронзах системи Cu–Al–Si–Mn–Sn, що утворюються в нерівноважних умовах затвердіння й подальшого охолодження у твердому стані та притаманні виливкам, що виготовляють із використанням ливарних піщаних і металевих форм.

Практична значимість. Використання запропонованих у роботі показника (Δ) і критерію (K_R) дозволить підвищити точність прогнозування фазового складу та властивостей бронз системи Cu–Al–Si–Mn–Sn при зміні концентрацій їх легуючих елементів. Це дасть змогу знизити витрати часу й ресурсів при розробці нових сплавів або оптимізації складу відомих марок бронз шляхом побудови регресійних і прогностичних моделей керування їх фазовим складом і властивостями. Розроблений параметр і критерій, підхід до створення нових сплавів та удосконалення існуючих сплавів, їх аналізу і т. ін.

Ключові слова: *бронза, структура, параметр, критерій, термодинаміка, розчинність, алюміній, олово, фазовий склад*