Short communication

On the phase separation in nanoscale particle systems: the role of external environment (exemplified on W-Cr pseudo-alloy)

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Abstract: Due to their unique combination of physicochemical properties, heavy tungsten-based pseudo-alloys with an ultrafine-grained structure produced from nanoparticles by advanced powder metallurgy techniques have become a subject of considerable research interest. In this work, within the framework of a thermodynamic approach, we simulate the features of the phase composition in *core-shell* nanoparticles formed from a phase-separating solid solution, using the heavy *W-Cr* pseudo-alloy as a model system. For a binary system with limited solid-state solubility, a specific effect is demonstrated: in contrast to macroscopic systems, the equilibrium composition and volume fraction of the coexisting nanophases vary significantly depending on the chemical nature of the external environment. The environment dictates the surface energy of the outer interface. The set of considered modellin dispersion media includes argon (a common sintering atmosphere), hydrogen (an annealing atmosphere), and several others. For two distinct heterogeneous states of the *core-shell* structure, temperature dependences of the equilibrium phase composition in each state were obtained. A thermodynamic interpretation of the observed regularities is provided, based on three possible mechanisms for reducing the free energy of the system.

Keywords: nanoparticles, solution decomposition, chemical thermodynamics, solubility, core-shell structure, tungsten, chromium.

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О твердофазном расслаивании в наночастицах бинарных сплавов: роль внешней среды (на примере псевдосплава W-Cr)

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Аннотация: Благодаря уникальному набору физико-химических свойств тяжелые вольфрамовые псевдосплавы с ультрамелкозернистой структурой, полученные из наночастиц современными методами порошковой металлургии, стали объектом повышенного интереса исследователей. В данной работе в рамках термодинамического подхода смоделированы особенности фазового состава наночастиц со структурой ядро-оболочка расслаивающегося твердого раствора на примере тяжелого псевдосплава W-Cr. Для системы двух компонентов, ограниченно растворимых в твердом состоянии, продемонстрирован специфический эффект, заключающийся в том, что в отличие от систем в макроскопическом состоянии, равновесный состав и объемная доля сосуществующих нанофаз существенно варьируются в зависимости от химического состава внешней по отношению к системе среды, задающей поверхностную энергию внешней межфазной границы. Набор рассмотренных модельных дисперсионных сред включает аргон (распространенная среда для спекания), водород (среда для отжига после

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спекания) и ряд других. Для двух различных гетерогенных состояний структуры ядро-оболочка получены области температурные зависимости равновесного фазового состава системы в каждом из состояний. Описана термодинамическая интерпретация полученных закономерностей на основе трех возможных механизмов понижения свободной энергии системы.
Ключевые слова: наночастицы, распад раствора, химическая термодинамика, растворимость, структура ядро-оболочка, вольфрам, хром.

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Heavy pseudo-alloys based on W (characterized by limited mutual solubility of the components and synthesized by methods alternative to direct alloying) are of significant scientific and practical interest due to a combination of unique physicochemical properties realized in an ultrafine-grained state. Pseudo-alloys of the $W-Cr$ system are characterized by high corrosion and ablation resistance at elevated temperatures [1, 2], the ability to self-passivate in oxidizing environments [1], and significant fracture resistance under dynamic loading conditions [3]. The combination of these and other special properties [4, 5] determines a wide range of their structural and functional applications. In particular, the $W-Cr$ system is considered a highly promising material for fusion energy [6], including for first-wall and divertor components in ITER and DEMO reactors; in this context, the self-passivation phenomenon upon oxidation significantly reduces material volatility compared to pure W in a loss-of-vacuum accident (LoVA) scenario, where hot (~ 1000°C and above) tungsten oxidizes intensely to form volatile WO_3, which can lead to significant erosion and radioactive contamination. When used as a core material for high-rate impacts [3], the $W-Cr$ system demonstrates a range of advantages, including lack of pyrophoricity, relatively low carcinogenicity, and enhanced ductility, reducing the risk of brittle fracture. These materials are also effective against multilayer barriers, exhibit a tendency toward localized adiabatic shear banding, and enable high density to be achieved upon consolidation of nanopowders [7].

Materials of this class are predominantly synthesized using modern additive powder metallurgy methods [1-5], such as selective laser melting (SLM), selective laser sintering (SLS), and, in particular, spark plasma sintering (SPS) [1, 2]. The SPS method is based on high-rate heating of a nanopowder charge material placed in an electrically conductive (usually graphite) die by passing short (tens of milliseconds) high-power current pulses through it. The process is carried out in a vacuum or a controlled inert gas atmosphere (most

commonly argon) while simultaneously applying uniaxial pressure. This regime ensures the formation of an ultrafine-grained structure in the consolidated material and inhibits grain growth due to extremely high heating rates (up to 2000-2500°C/min). An important feature of the SPS technology is the ability to directly control the key parameters of the formed nanostructure by adjusting the applied pressure, the temperature–time sintering regime, the cooling rate, and other variables directly during the process. The process is often completed by hydrogen annealing of the obtained samples.

In the macroscopic state, $W-Cr$ system alloys do not form a continuous series of solid solutions, exhibiting a miscibility gap with an upper critical solution temperature of 1906 K without the formation of intermetallic phases [1, 8, 9]. When using additive powder metallurgy technologies, the main ways to control the physicochemical properties of such materials are the formation of supersaturated solid solutions [1, 10] as well as grain boundary segregations with an enhanced content of the dissolved component [4]. At the same time, when analyzing phase equilibria in small-volume systems, it is necessary to take into account a number of characteristic features. These features manifest themselves in a significant dependence of the mutual solubility of the components and the equilibrium volume fractions of coexisting phases on volume [8, 9, 11-18], nanoparticle shape [9, 12, 15], and a number of other factors [13, 16, 18]. An increase in the relative energy contribution of interfaces leads to a shift in equilibrium positions depending on the morphology and thermodynamic characteristics of the interfaces; consequently, the equilibrium phase composition of small-volume structures differs significantly from the phase composition of the same systems in the macroscopic state. These features can be modeled using equilibrium chemical thermodynamics and a number of other methods [18] (the applicability of thermodynamic methods to the analysis of phase equilibria in small-volume systems, as well as the limits of their applicability, are discussed in [19]).

The present work is a continuation of a series [8, 9, 11, 14, 16,17] on phase equilibria in heavy pseudo-alloys based on W and is devoted to an effect specific to small-volume structures, associated with the influence of the external environment on phase equilibria, which sets the thermodynamic characteristics of the external interface. A change in the external interface energy in different environments leads to an additional shift in the free energy minima, accompanied by a change in the equilibrium composition of all phases constituting the system, including even those that do not share a common interface with the external environment. Within a somewhat simplified approach, this effect was first mentioned using another system as an example in [20].

The object of modeling in the present work is spherical particles of the

$W-Cr$ system with a diameter of 40 nm of equivalent composition. In the temperature range below the upper critical solution temperature, it is assumed that upon decomposition of the solid solution in the particle, a core-shell structure forms (a single spherical inclusion of one solid solution surrounded by a layer of a solid solution of a different composition). The basic equations of the model describing phase equilibria in small-volume structures in the case of systems with solid-phase miscibility gaps are given in [12, 14] (and specifically for the $W-Cr$ system in [8, 9]). The criterion for the equilibrium phase composition of the system is the minimum of the Gibbs free energy, taking into account the energy contribution of all interfaces. The Gibbs free energy of the $W-Cr$ system obtained within the framework of the Redlich–Kister polynomial model is given in [8, 9], where the influence of the external environment was not considered. The following model external environments are considered: argon (one of the most common atmospheres for sintering; no chemical interaction; van der Waals-type adsorption is very weak; the surface tension of pure substances is practically indistinguishable from values in vacuum) and hydrogen (widely used as an annealing atmosphere, effectively reducing oxide films and preventing their formation; actively adsorbs on clean surfaces; adsorption is sufficiently strong to noticeably lower the surface tension, but neither W nor Cr form stable hydrides at atmospheric pressure). Additionally, propane (both physical adsorption of propane at the interface and propane pyrolysis at elevated temperatures on the particle surface with the formation of pyrocarbon and hydrogen, as well as the process of carbon chemisorption by the surface) and CO in the pressure range of 10^{-4}–10^{-2} atm (in this pressure range, CO dissociation and intense adsorption on the surface occur, with no catastrophic mass loss due to oxidation) are considered.

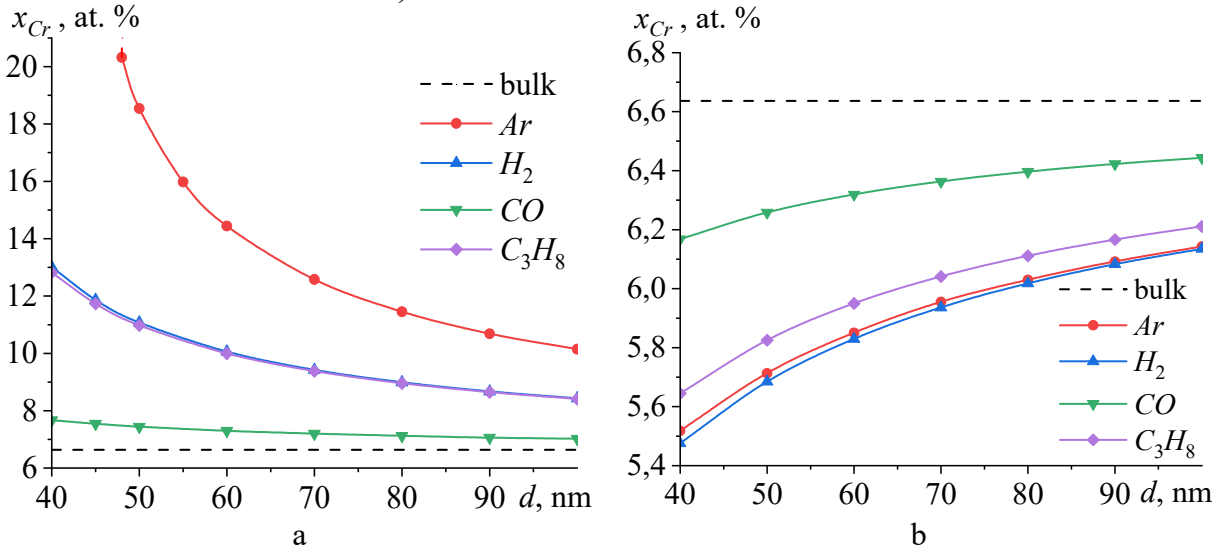

Fig. 1. Dependences of the solubility limits of Cr in W on the diameter d for a particle of an equiatomic composition in states 1 (a) and 2 (b). The dashed line corresponds to the composition of macroscopic phases.

As shown previously, in core-shell structures, two stable heterogeneous states are possible, differing in the mutual arrangement of the coexisting solid solutions. In the case of macroscale phases, where the energy contribution of interfaces is small, the free energy of both states is the same, and the equilibrium phase composition in both cases corresponds to reference data. In small-volume structures, the energy contribution of interfaces becomes significant, which leads to a noticeable shift in the minima of the Gibbs free energy (see Fig. 1 in [8]); consequently, the equilibrium compositions and volume fractions of coexisting phases in the two heterogeneous states differ from the reference values, differ from each other, and depend on the volume of nanoparticles, the energy characteristics of interfaces, and a number of other factors. Below, for brevity, the state with a *Cr*-based core phase is referred to as «state 1». «State 2» corresponds to a core-shell structure with a *W* - based core phase. The free energy of state 1 is higher.

Fig. 1 shows the dependences of the equilibrium fractions (solubility limits) of *Cr* in the *W*-based phases in states 1 and 2 at $T = 1200$ K on the particle diameter. In an argon atmosphere (where the external interface energy is highest among all considered environments, surface tensions of pure *W* and *Cr* are $\sigma_W \approx 3{,}150$ J/m^2, $\sigma_{Cr} \approx 1{,}850$ J/m^2) a decrease in particle diameter in state 1 from 100 to 48 nm is accompanied by an increase in the solubility limit of *Cr* in *W* from ~10,2 to ~20,3 at. %, while the solubility limit of *W* in *Cr* decreases, and the equilibrium volume fraction of the core phase noticeably drops from ~ 40,5 vol.% at $d = 100$ nm down to ~35 vol.% at $d = 50$ nm. In state 2, the trends are partially opposite: the solubility of *Cr* in *W* decreases from ~ 6,1 at.% at $d = 100$ nm down to ~ 5,5 at.% at $d = 40$ nm while the solubility limit of *W* in *Cr* and the volume fraction of the core phase also decrease slightly. In hydrogen ($\sigma_W \approx 2{,}200$ J/m^2, $\sigma_{Cr} \approx 1{,}600$ J/m^2) and propane ($\sigma_W \approx 2{,}050$ J/m^2, $\sigma_{Cr} \approx 1{,}400$ J/m^2) atmospheres, similar tendencies are observed in state 1: for example, for a hydrogen atmosphere, a decrease in particle size from $d = 100$ nm down to $d = 40$ nm leads to an increase in the solubility limit of *Cr* in *W* from ~ 8,4 to ~ 13 at. %, the solubility limit of *W* in *Cr* decreases, and the volume fraction of the internal phase decreases from ~ 41,6 to ~ 38,5 vol.%. In state 2, the solubility of *Cr* in *W* decreases to ~ 5,48 at.% at $d = 40$ nm from ~ 6,1 at.% at $d = 100$ nm, the solubility limit of *W* in *Cr* increases slightly, and the volume fraction of the core phase also decreases slightly. In a propane atmosphere in state 1, the solubility limit of *Cr* in *W* increases from ~ 8,4 at.% at $d = 100$ nm up to ~ 12,8 at.% at $d = 40$ nm, the volume fraction of the core phase decreases from ~ 41,6 to ~ 38,7 vol.%; in state 2, the solubility of *Cr* in *W* decreases from ~ 6,2 at.% to ~ 5,64 at.%. In a *CO* atmosphere, these trends are least pronounced, but the analogous tendencies are fully preserved.

Note that the considered size range corresponds to relatively «large»

particles in which the formation of a surface layer enriched due to physical adsorption or chemisorption does not affect the vast majority of atoms in the bulk (the fraction of surface atoms increases from ~ 1% at d = 100 nm to ~ 2,4% at d = 40 nm). Some reduction in the amount of substance forming the considered «solid solution» phases corresponds to a slight leftward shift along the curves in Fig. 1 while preserving the configuration of the curves themselves. The obtained trends can be interpreted thermodynamically as a consequence of the realization of three possible mechanisms for reducing the free energy in a core-shell structure: (1) transfer of matter from the internal (core) phase to the external (shell) phase, accompanied by a reduction in the extent of the internal interface; (2) preferential enrichment of the shell phase with the component having a lower surface tension at the interface with the external environment; (3) retention of a homogeneous state without the formation of an internal interface («volume-controlled segregation», «surface energy-controlled segregation», and «suppression», respectively, in the terminology of [9]).

Upon realization of any of the mechanisms, the energy «gain» associated with a decrease in the interface energy exceeds the «loss» associated with the formation of supersaturated solutions compared to the values for the macrophase. In the system under consideration, *W* has both a larger molar volume and a larger surface tension at the interface with the external environment than *Cr* [9, 16, 17]. For example, for nanoparticles in any of the considered external environments in state 1, a decrease in the particle volume leads to the simultaneous realization of mechanisms 1 and 2 and to an increase in the fraction of *Cr* in the shell phase, accompanied by a decrease in the volume fraction of the core. For particles in state 2 in argon and propane atmospheres, mechanism 2 dominates (the fraction of *W* in the shell phase decreases somewhat, accompanied by some decrease in the volume fraction of the core phase), while in a hydrogen atmosphere, mechanism 1 dominates (a noticeable decrease in the volume fraction of the core phase compensates for some increase in the fraction of *W* in the shell). The break in the curve for argon in Fig. 1 on the left indicates the particle diameter at which the minimum of the Gibbs free energy corresponding to the considered heterogeneous state 1 disappears, transitioning to a position corresponding to a homogeneous state without solution decomposition (suppression in the terminology of [9]). These mechanisms are described in detail in [9, 12], which also consider a possible case of their competition, leading to qualitatively different dependences of mutual solubilities on volume and temperature for different compositions of the system.

The obtained estimates of the influence of the initial composition of nanoparticles on their equilibrium phase composition in the heterogeneous state can be supplemented by taking into account the influence of nanoparticle

morphology and a number of other specific factors [9, 12, 16], which, together with methods for accounting for a wide range of real geometric features of nanoparticles [9, 18], including fractal ones [12, 14, 21], methods for calculating equilibrium size and shape distributions of nanoparticles [22], and algorithms for determining the fractal dimension of nanoparticles from electron microscopy data [21], provide a complete set of tools for controlling the phase composition and properties of functional nanostructured materials.

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