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ZrC surface segregation from a dilute $(\text{ZrC})_{1-x}(\text{NbC})_x$ solid solutions

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ABSTRACT

The spontaneous surface segregation of ZrC grains from dilute solid solutions $(\text{ZrC})_{1-x}(\text{NbC})_x$ with $(1-x) \leq 0.02$ is revealed for the first time. It is shown that the ZrC precipitation is associated with the decomposition of the homogeneous carbide solid solutions $(\text{ZrC})_{1-x}(\text{NbC})_x$. The experimental and theoretical estimates obtained for the segregation energy of ZrC are equal to -50 and -31 kJ/mol⁻¹, respectively. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

According to^[1-3], zirconium and niobium carbides with a cubic B1-type structure form a continuous series of solid solutions in the Zr-Nb-C system at temperature $T > 1273\text{K}$. Experimental data on the phase equilibria in the Zr-Nb-C or $\text{ZrC}_y - \text{NbC}_y$ systems at temperatures below 1273K are not available in the literature. However, theoretical estimates^[4] indicate that an extended region of a decomposition can be observed in the ZrC-NbC system at $T < 800\text{K}$.

EXPERIMENTAL

We studied the $(\text{ZrC})_{1-x}(\text{NbC})_x$ solid solutions in the range $0.001 \leq (1-x) \leq 0.05$. The solid solutions were synthesized by solid-phase vacuum sintering from NbC and ZrC carbides or from Nb, Zr, and C at a maximum sintering temperature of 2473K.

All synthesized samples contained only one homogeneous phase with a cubic B1-type structure and the lattice constant $a_{\text{B1}} = 0.44670\text{nm}$. The samples of the solid solutions synthesized were annealed at a tempera-

ture of 2300K under vacuum of 10^{-3}Pa for 1h. After annealing, the samples were cooled to 1300K with a rate of $200\text{K}/\text{min}^{-1}$ and then were cooled slowly to 600K. The total time of cooling was 3h. The x-ray diffraction patterns were recorded on a Siemens D-500 diffractometer. The x-ray diffraction patterns taken from the surface of annealed samples $(\text{ZrC})_{1-x}(\text{NbC})_x$ with $(1-x) \leq 0.02$ prepared from NbC and ZrC carbides demonstrate that, apart from the reflections assigned to the carbide solid solution with the lattice constant $a_{\text{B1}} = 0.44655\text{nm}$, there appear intense reflections attributed to another phase. This phase has a B1 cubic structure with the lattice constant $a_{\text{B1}} = 0.4698\text{nm}$ which is very close to the lattice parameter of $\text{ZrC}_{0.93-0.98}$ carbide^[4]. Judging from the change in the lattice parameter of solid solution after annealing and the lattice parameter of the new phase, the annealed solid solution contains ~99 mol.% NbC and ~1 mol.% ZrC. As can be clearly seen in the cross sections of the annealed samples, a very dense layer 0.1-0.2 mm thick is formed on the free surface. This layer is brighter than the bulk of the sample. The x-ray diffraction patterns of the surface regions of the annealed samples, which were syn-

thesized from Nb, Zr, and C, exhibit only the reflections of a phase with the lattice constant $a_{B1} = 0.46986$ nm, whereas the diffraction reflections from the carbide solid solution are absent.

The electron microscopic examination of the annealed samples of the $(ZrC)_{1-x}(NbC)_x$ solid solutions synthesized from NbC and ZrC revealed the presence of well-faceted precipitates (covering as much as 50% of the surface area) of the second phase on the surface of the samples. The size of precipitated grains is 5–15 μm , and the size of the main-phase grains is equal to $\sim 1 \mu\text{m}$. The precipitated grains have the form of trihedra or hexahedra which is typical of the (111) section of cubic crystals. The surface of the annealed samples prepared from Zr, Nb, and C is completely covered with grains of the precipitated phase.

The chemical composition of the precipitated phase

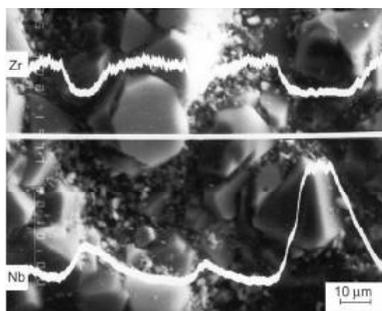


Figure 1: Distributions of the intensity of Zr and Nb characteristic x-ray radiation upon scanning of the surface of the annealed dilute $(ZrC)_{0.02}(NbC)_{0.98}$ solid solution along the white horizontal line. Maxima of the intensity of Zr and Nb characteristic x-ray radiation correspond to precipitated ZrC carbide grains and the matrix solid solution $(ZrC)_{0.02}(NbC)_{0.98}$, respectively

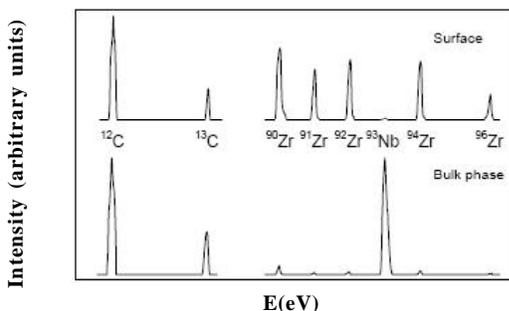


Figure 2: Distributions mass spectra of the precipitated surface phase and the bulk phase of the annealed $(ZrC)_{0.02}(NbC)_{0.98}$ solid solution. The intensity I_i is proportional to $\sim \log c_i$, where c_i is the concentration of the i -th element (isotope) in at. %.

was determined using a JEOL-SuperProbe 733 x-ray microanalyzer and an EMAL-2 laser energy-mass analyzer. The image of the surface was obtained in back-reflected electrons. The scanning over the surface with recording of the characteristic radiation revealed that the sample matrix contains niobium, whereas the precipitated grains of the new phase contain zirconium and are almost free of niobium (Figure 1).

Figure 2 displays the mass spectra of the surface and bulk regions of the annealed $(ZrC)_{1-x}(NbC)_x$ samples synthesized from Zr, Nb, and C. The mass analysis of the bulk region of the samples confirmed that it contains niobium, carbon, and a small amount of zirconium. At the same time, zirconium and carbon are the basic components evaporated from the surface completely covered with grains of the precipitated phase. The niobium content on the surface is no more than 0.5 at. %.

The results of x-ray microanalysis, laser mass analysis, electron microscopy, and x-ray diffraction unambiguously indicate that ZrC grains precipitate on the surface of the dilute $(ZrC)_{1-x}(NbC)_x$ solid solutions with $(1-x) \leq 0.02$. This phenomenon was not observed earlier in carbide solid solutions.

DISCUSSION

The initial solid solutions are homogeneous. Therefore the formation of the second phase after annealing and the precipitation of ZrC carbide grains on the surface of the samples can be associated only with the decomposition of the solid solutions.

In order to determine the solid-phase decomposition region in the phase diagram of the ZrC_y-NbC_y pseudobinary system, we calculated the phase equilibria in this system at temperatures below 1300K. The calculations were performed using the subregular solution model^[4]. According to calculations, the ZrC_y and NbC_y carbides at any carbon content within the homogeneity regions of the cubic phase form a continuous series of solid solutions at $T > 1200\text{K}$. However, at lower temperatures, there exists a solid-state decomposition region in this system^[4,5]. As the carbon content decreases, the maximum decomposition temperature of the solid solution increases from $T_{\text{decomp}}^{\text{max}} = 843\text{K}$ for

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the ZrC_{1.0}-NbC_{1.0} section to $T_{\text{decomp}}^{\text{max}} = 1210\text{K}$ for the ZrC_{0.60}-NbC_{0.70} section. The asymmetry of the decomposition region and shift of its vertex in the ZrC_y-NbC_y pseudobinary sections toward the NbC_y niobium carbide (66.8 mol.% NbC_y at y=1.00 and 53.6 mol.% NbC_y at y=0.70) indicates that, at temperatures $T < T_{\text{decomp}}$, the solubility of ZrC_y in niobium carbide is several times less than that of NbC_y in zirconium carbide.

The presence of decomposition region is necessary but not sufficient condition for the segregation.

The diffusion decomposition of solid solutions can occur through two mechanisms^[6]. The first mechanism is the spinodal decomposition proceeding throughout the bulk of the solution. The second mechanism is the fluctuation nucleation of phases and their subsequent growth. Spinodal decomposition is not realized most likely due to the low temperatures at which the diffusion mobility of atoms in the crystal is too small to provide spatial separation of the phase with a predominant content of niobium carbide and ZrC phase. In the case of fluctuation nucleation, the growth of new-phase grains in the surface layer is facilitated as a result of the favorable effect of the interfacial energy. Thus, the formation of the zirconium carbide phase becomes possible even at a relatively low temperature.

The segregation of the second phase becomes possible when its content exceeds the solubility limit. The calculations of the immiscibility region boundaries demonstrated that (ZrC)_{1-x}(NbC)_x solid solutions with $(1-x) \geq 0.01$ at $T < 700\text{K}$ are supersaturated with ZrC. Consequently, in the (ZrC)_{1-x}(NbC)_x solid solutions containing ~1 mol% ZrC or more, the necessary condition of segregation is met at $T < 700\text{K}$. The sufficient conditions of surface segregation depend on the segregation energy and diffusion.

In the regular solution approximation, the models of an equilibrium state of the solid solution surface^[7-9] suggest that the bulk and surface phases coexist in a solid under equilibrium conditions. Let us consider an A-B system in which A is the solute and B is the solvent. As applied to our system ZrC_y-NbC_y, the niobium carbide is the solvent and the zirconium carbide is the solute; i.e., $A \equiv \text{ZrC}_y$ and $B \equiv \text{NbC}_y$. For the A-B system, the atomic concentration of the solute in the

surface phase, $x_{\text{A-surf}}$, is

$$X_{\text{A-surf}} = X_{\text{B-surf}} (X_{\text{A-bulk}} / X_{\text{B-bulk}}) \exp(-\Delta H_{\text{seg}} / k_{\text{B}} T), \quad (1)$$

where $x_{\text{A-bulk}}$ and $x_{\text{B-bulk}}$ are the atomic concentrations of the solute and solvent in the bulk phase, respectively, $x_{\text{B-surf}} = 1 - x_{\text{A-surf}}$ and ΔH_{seg} is the segregation energy of the solute A. By substituting experimental values $x_{\text{ZrC-surf}} \approx 0.985$, $x_{\text{ZrC-bulk}} \approx 0.013$, and $T = 700\text{K}$ into eq.(1), we obtain the surface segregation energy of ZrC: $\Delta H_{\text{seg-exp}} \approx -50 \text{kJ}\cdot\text{mol}^{-1}$.

According to^[8,9], the segregation energy ΔH_{seg} includes the interfacial energy ΔH_{int} , the energy of pair interatomic interactions ΔH_{bin} , and the strain energy ΔH_{str} ; i.e., $\Delta H_{\text{seg}} = \Delta H_{\text{int}} + \Delta H_{\text{bin}} + \Delta H_{\text{str}}$. The interfacial energy can be represented as

$$\Delta H_{\text{int}} = (\gamma_{\text{A}} - \gamma_{\text{B}}) s_{\text{B}} N_{\text{A}}, \quad (2)$$

where γ_{A} and γ_{B} are the specific interfacial energies of solute A and solvent B, respectively; $s_{\text{B}} = (M/\rho N_{\text{A}})^{2/3}$ is the surface area per solvent molecule; M is the molecular mass of the solvent; and ρ is the density of the solvent. For the ZrC - NbC system at $T = 1773\text{K}$, we have $\gamma_{\text{A}} \equiv \gamma_{\text{ZrC}} = 2.13 \text{J}\cdot\text{m}^{-2}$ and $\gamma_{\text{B}} \equiv \gamma_{\text{NbC}} = 2.60 \text{J}\cdot\text{m}^{-2}$ ^[10], and s_{B} is equal to 0.0793nm^2 for NbC_{1.0}. Therefore, the ΔH_{int} energy in the ZrC-NbC system is equal to $-22.4 \text{kJ}\cdot\text{mol}^{-1}$. This value of ΔH_{int} is a rough estimation because the accuracy of determining the γ energies for carbides is low (~40%).

The energy of pair interactions in the case of solid solutions can be represented as $\Delta H_{\text{bin}} = -G_{\text{s}}^{\text{e}} / (z x_{\text{A-bulk}} x_{\text{B-bulk}})$ where G_{s}^{e} is the excess free energy of mixing and z is the coordination number of the crystal lattice in which the substitutional solid solution is formed. For the solid phase, $G_{\text{s}}^{\text{e}} = x_{\text{A}} x_{\text{B}} B_{\text{s}}$ where B_{s} is the interchange energy^[4]. It follows that $\Delta H_{\text{bin}} = -B_{\text{s}}/z$. In the (ZrC)_{1-x}(NbC)_x solid solutions with a FCC metal sublattice, the coordination number z is equal to 6 and the calculated interchange energy $B_{\text{s}} \approx 15 \text{kJ}\cdot\text{mol}^{-1}$ ^[5] therefore the energy of pair interatomic interactions $\Delta H_{\text{bin}} \approx -2.5 \text{kJ}\cdot\text{mol}^{-1}$.

The solute strain energy ΔH_{str} is associated with the difference in sizes of the substituted atoms in the solid solution and can be expressed in the form^[9,11]

$$\Delta H_{\text{str}} = -24\pi N_{\text{A}} [KGR_{\text{A}}R_{\text{B}}(R_{\text{A}} - R_{\text{B}})^2] / (4GR_{\text{B}} + 3KR_{\text{A}}) \quad (3)$$

where $K = 2.28 \times 10^{11} \text{Pa}$ is the bulk modulus of the solute ZrC, $G = 2.20 \times 10^{11} \text{Pa}$ is the shear modulus of the solvent NbC, and R_{A} and R_{B} are the effective atomic (ionic) radii of the substituted atoms of the solute and solvent, respectively ($R_{\text{Nb}} = 0.064 \text{nm}$ and $R_{\text{Zr}} = 0.072 \text{nm}$ for the ions Nb⁵⁺ and Zr⁴⁺ with the coordination number $z=6$). This yields a value of the strain

energy $\Delta H_{\text{def}} \approx -6.4 \text{ kJ}\cdot\text{mol}^{-1}$ for the $\text{ZrC}_y\text{-NbC}_y$ solid solutions.

The theoretical energy of segregation of zirconium carbide from the $(\text{ZrC})_{1-x}(\text{NbC})_x$ solid solution with inclusion of the calculated contributions ΔH_{int} , ΔH_{bin} and ΔH_{str} is approximately equal to $-31.3 \text{ kJ}\cdot\text{mol}^{-1}$ and substantially differs from the experimental value $\Delta H_{\text{seg}}^{\text{exp}} \approx -50 \text{ kJ}\cdot\text{mol}^{-1}$. The overestimated theoretical energy ΔH_{seg} can be explained by an approximate estimate of the interfacial energy ΔH_{int} , which makes the largest contribution to the segregation energy ΔH_{seg} .

According to [12], when the new phase precipitates on the surface and $\alpha \equiv x_{\text{A-surf}}/x_{\text{A-bulk}} \gg 1$, the surface concentration of segregant A is

$$x_{\text{A-surf}}(t) = x_{\text{A-surf}} \{1 - \exp(-Dt/\alpha^2 d^2) \operatorname{erfc}[(Dt/\alpha^2 d^2)^{1/2}]\} \quad (4)$$

where $x_{\text{A-surf}}(t)$ and $x_{\text{A-surf}}$ are the contents of compound A on the surface at time t and after attaining the equilibrium, respectively; D is the diffusion coefficient of solute A at the temperature T ; d is the thickness of the surface layer of a new phase; and $\alpha = \text{const}$ is the maximum coefficient of the surface enrichment with solute A at $t \rightarrow \infty$. The function $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$ is the complementary probability integral. With due regard for Eq.(1), Eq.(4) takes the form

$$x_{\text{A-surf}}(t) = x_{\text{B-surf}} (x_{\text{A-bulk}}/x_{\text{B-bulk}}) \exp(-\Delta H_{\text{seg}}/k_B T) \times \{1 - \exp(-Dt/\alpha^2 d^2) \operatorname{erfc}[(Dt/\alpha^2 d^2)^{1/2}]\}. \quad (5)$$

At $t \rightarrow \infty$ and in the absence of evaporation, the segregant content asymptotically tends to the equilibrium content $x_{\text{A-surf}} = x_{\text{B-surf}} (x_{\text{A-bulk}}/x_{\text{B-bulk}}) \exp(-\Delta H_{\text{seg}}/k_B T)$ which depends only on the solid solution composition and the segregation energy. According to the estimates made from Eq.(5), in the $(\text{ZrC})_{0.01}(\text{NbC})_{0.99}$ solid solution at temperature from 500 to 700K and the segregation energy $\Delta H_{\text{seg}} = -31.3 \text{ kJ}\cdot\text{mol}^{-1}$, the equilibrium (at $t \rightarrow \infty$) concentration of ZrC in the surface phase, $x_{\text{ZrC-surf}}$, lies in the range from ~ 0.80 to ~ 0.98 . This is in good agreement with the experimental value, which is no less than 0.97.

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