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Electronic Supplementary Information

Low-Temperature Decomposition and Segregation on a Surface in Carbide-Containing Solid Solutions of the Zirconium-Niobium-Carbon System and in Related Ternary Systems

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Calculation details

Dependence of the size of precipitated particles on the composition of the solid solution can be taken into account as follows: The minimal size of the precipitated particle of the impurity component is $D_{\min} = (\sqrt{2}/2)a$, i.e., $D_{\min\,B}(x{=}0) = (\sqrt{2}/2)a_B$ and $D_{\min\,A}(x{=}1) = (\sqrt{2}/2)a_A$. In the range $0.5 \le x \le 1$, when x decreases from 1 to x_b (the content of the impurity component A increases from 0 to $(1-x) \le (1-x_b)$), the size of the precipitated particles D_A increases to some limiting value and does not change with a further decrease in x from x_b to 0.5. Thus, to a first approximation, the change in the size of precipitated particles with changing composition in the range $0 \le (1-x) \le 0.5$ (or, which is the same, $0.5 \le x \le 1.0$) can be represented as

$$D_A(x) = D_{\min\,A}\{[1 + m(1-x)][1 - f_H(x-x_b)] + [1 + m(1-x_b)]\, f_H(x-x_b)\}, \qquad \text{(S1)}$$

where x_b = const is the boundary content of the second component, corresponding to the limiting size of the particles of the precipitated phase; and $f_H(x-x_b) = \begin{cases} 1, \text{if } x \le x_b \\ 0, \quad \text{if} > x_b \end{cases}$ is the Heaviside function. Analogously, for the range $0 \le x \le 0.5$, in which component B is an impurity, we can obtain the symmetric expression for the size D_B of phase B:

$$D_B(x) = D_{\min\,B}\{(1 + mx)[1 - f_H(1-x-x_b)] + [1 + m(1-x_b)]\, f_H(1-x-x_b)\}, \qquad \text{(S2)}$$

where $f_H[(1-x)-x_b) = \begin{cases} 1, \text{if } x \le x_b \\ 0, \quad \text{if} > x_b \end{cases}$. Inasmuch as component B is an impurity at $x < 0.5$ and component A is an impurity at $x > 0.5$, the general equation for $D(x)$ can be written as

$$D(x) = D_{\min\,A}\{[1 + m(1-x)][1 - f_H(x-x_b)] + [1 + m(1-x_b)]\, f_H(x-x_b)\}[1 - f_H(x-0.5)] +$$

$$+ D_{\min\,B}\{(1 + mx)[1 - f_H(1-x-x_b)] + [1 + m(1-x_b)]\, f_H(1-x-x_b)\} f_H(x-0.5). \qquad \text{(S3)}$$

In the formula (3), $D_{\min\,A}$ and $D_{\min\,B}$ are the minimum sizes of the precipitated particles; x_b is the boundary content of the second component; m is parameter characterizing growth rate of particles; and $f_H(x-0.5) = \begin{cases} 1, \text{if } x \le 0.5 \\ 0, \text{if } x > 0.5 \end{cases}$.

Table S1. Parameters B_{0s} and B_{1s} of mutual exchange energy $B_s = B_{0s} + xB_{1s}$ of the solid phase for carbide solid solutions of some pseudobinary $(ZrC_y)_{1-x}(NbC_{y'})_x$ systems

Pseudobinary system	B_{0s} (kJ·mol[-1])	B_{1s} (kJ·mol[-1])
HfC - NbC	$-0.781 + 0.471\times10^{-3}T - 0.012\times10^{-6}T^2$	$15.000 - 1.436\times10^{-3}T + 0.031\times10^{-6}T^2$
HfC - TaC	$3.125 - 0.422\times10^{-3}T + 0.001\times10^{-6}T^2$	$18.806 - 0.893\times10^{-3}T$
$ZrC_{0.98}$ - TaC	$9.885 + 0.291\times10^{-3}T - 0.001\times10^{-6}T^2$	$14.738 - 1.900\times10^{-3}T - 0.012\times10^{-6}T^2$
$VC_{0.88}$ - TaC	$33.312 - 4.157\times10^{-3}T + 0.011\times10^{-6}T^2$	$-3.479 + 1.577\times10^{-3}T - 0.006\times10^{-6}T^2$
$VC_{0.88}$ - NbC	$40.367 - 4.196\times10^{-3}T - 0.058\times10^{-6}T^2$	$-9.661 + 1.629\times10^{-3}T + 0.016\times10^{-6}T^2$