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journal homepage: www.elsevier.com/locate/jeurceramsocStability domains of (Ti,W)C and (Ti,W)(CN) during carbothermal reduction of TiO₂/WO₃ mixture at 1500 KHanjung Kwon^{a,b}, Wonbaek Kim^a, Jiwoong Kim^{a,*}^a Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Yuseong-gu, Daejeon, 305–350, South Korea^b Korea University of Science and Technology, Gajeong-ro, Yuseong-gu, Daejeon 305–350, South Korea

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ABSTRACT

Phase stability diagrams for the carbothermal reduction of a mixture of TiO₂ and WO₃ at 1500 K were constructed as a function of the carbon activity, oxygen pressure and characteristics of solution formation. Through this, it was found that the stable domains of carbides/carbonitrides, including (Ti,W)C/(Ti,W)(CN), are larger than the phases that are formed when solid-solution phases are not considered due to their greater stability. The use of a nitrogen atmosphere instead of vacuum expanded the stable domains of the solid-solution phases, indicating that they are made more stable under these conditions. Using these stability diagrams, the reaction sequence of carbothermal reduction can be predicted, and so this study can provide a guideline for preparing tougher carbide/carbonitride (Ti,W)C/(Ti,W)(CN) phases from TiO₂/WO₃ mixtures.

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1. Introduction

Cutting tools are generally fabricated by sintering mixtures of carbide/carbonitride and metallic phases [1,2], as they require a high hardness for machinability in combination with a high fracture toughness to extend the tool's cutting lifetime [1–3]. In other words, a cutting tool can only be used in for a wide range of machining and a long time if the material from which it is made is both hard and tough. Of the various materials that have been used, Ti carbide/carbonitride–Ni/Co composites are usually preferred for finishing work because of the high hardness, excellent wear resistance, and chemical stability provided by the Ti carbide/carbonitride [1,3–5]. However, the relatively low toughness of titanium carbide/carbonitride–Ni/Co compared to WC–Co currently limits its use to this particular machining process. Many studies have therefore looked into ways in which the low toughness of titanium carbide/carbonitride–Ni/Co can be improved [4–9].

It is widely known that the introduction of solid-solution type carbides/carbonitrides into a titanium carbide/carbonitride–Ni/Co composite is a very effective way of improving its inherently low toughness [6–9]. This has, for example, resulted in improved mechanical properties (H_V : 12–13 GPa; K_{IC} : 10–12 MPa·m^{1/2}) in (Ti,W)C/(Ti,W)(CN)–Ni/Co when compared to conventional Ti(CN)–WC–Ni (H_V : ~12 GPa; K_{IC} : 6–7 MPa·m^{1/2}) [6]. In these previous studies, solid-solution type carbides/carbonitrides were obtained through high-energy milling of a mixture of oxides and carbon, followed by heat-treatment in vacuum or nitrogen [6–9]. This heat-treatment induces a carbothermal reduction of the oxides that forms single-phase carbides/carbonitrides, which are subsequently changed to a solid-solution type by reactions between them [10]. This makes the phase stability of the solid-solution carbides/carbonitrides during heat-treatment an important issue, because it determines the conditions needed for synthesis at a given temperature (e.g., the carbon content, oxygen partial pressure, and nitrogen partial pressure).

The likelihood of solid-solution carbides/carbonitrides separating is known to be sensitive to changes in carbon content, oxygen partial pressure, nitrogen partial pressure and temperature [11–16]. As such, the change in the phase stability domains of the solid-solution carbides/carbonitrides with different processing parameters needs to be understood to determine the optimal synthesis conditions. Previous reports have thermodynamically calculated the stability domain of Ti(CN) during the carburization/nitridation of titanium and the carbothermal reduction of titanium oxide [16,17], from which the phase stability diagram of the Ti–TiC–TiN–Ti(CN) system at 1673 K was constructed as a function of carbon activity, nitrogen pressure and the characteristics of solid solution formation [16]. This made it possible

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to determine the conditions needed for stable Ti(CN) formation, and a stability diagram for TiO₂–Ti₃O₅–Ti₂O₃–TiC/Ti(CN) during reduction was also constructed from thermodynamic calculations [17]. Through these studies, the conditions needed for the formation of TiC/Ti(CN) via the carburization/nitridation of titanium and carbothermal reduction of titanium oxide are now known, and the sequence of the latter reaction was verified through the construction of a phase diagram for TiO₂–Ti₃O₅–Ti₂O₃–TiC/Ti(CN) at 1673 K.

Although the mechanical properties of titanium carbide/carbonitride–Ni/Co have been enhanced by replacing TiC/Ti(CN) with solid–solution carbides/carbonitrides, (Ti,M)C/(Ti,M)(CN), the absence of phase domains for these solid–solution carbides/carbonitrides has made it impossible to determine the conditions needed for their preparation. This is further exacerbated by the fact that this is intrinsically different to a simple TiC/Ti(CN) system. This study therefore aims to construct thermodynamic stability diagrams for the Ti–W–C–O–N system based on the Standard Gibbs free energy of formation for stoichiometric (Ti,W)C/(Ti,W)(CN) phases with various Ti:W and C:N ratios that were obtained in a previous study [18]. The stability domains are then constructed with respect to the carbon activity and oxygen partial pressure; and using these, the ideal conditions for the synthesis of stoichiometric (Ti,W)C/(Ti,W)(CN) via the carbothermal reduction of a mixture of TiO₂ and WO₃ in vacuum or a nitrogen atmosphere are evaluated. The effect of W content and N₂ partial pressure on the stability of the (Ti,W)C/(Ti,W)(CN) phases is also investigated using the constructed phase diagrams.

2. Results and discussion

2.1. Equilibrium conditions for Ti–W–C–O–N at 1500 K (No formation of (Ti,W)C/(Ti,W)(CN))

(1) In vacuum

If there is no interaction between Ti and W during the carbothermal reduction of a mixture of TiO₂ and WO₃ in vacuum, then the phase stability diagram of the Ti–W–C–O system can be obtained through a combination of the phase stability diagrams of Ti–C–O and W–C–O shown in Fig. 1(a) and (b), respectively. The equilibrium lines between each phase were calculated on the basis of the Standard Gibbs free energies of formation for oxides and carbides [19], which in the case of the Ti–C–O system were as follows:

$$\text{Ti}_4\text{O}_7 + 0.5\text{O}_2 = 4\text{TiO}_2, \quad 4\Delta G_{\text{T}}^{\text{f,TiO}_2} - \Delta G_{\text{T}}^{\text{f,Ti}_4\text{O}_7} = -RT \ln P_{\text{O}_2}^{0.5}$$

$$4\text{Ti}_3\text{O}_5 + 0.5\text{O}_2 = 3\text{Ti}_4\text{O}_7, \quad 3\Delta G_{\text{T}}^{\text{f,Ti}_4\text{O}_7} - 4\Delta G_{\text{T}}^{\text{f,Ti}_3\text{O}_5} = -RT \ln P_{\text{O}_2}^{0.5}$$

$$3\text{Ti}_2\text{O}_3 + 0.5\text{O}_2 = 2\text{Ti}_3\text{O}_5, \quad 2\Delta G_{\text{T}}^{\text{f,Ti}_3\text{O}_5} - 3\Delta G_{\text{T}}^{\text{f,Ti}_2\text{O}_3} = -RT \ln P_{\text{O}_2}^{0.5}$$

$$2\text{TiO} + 0.5\text{O}_2 = \text{Ti}_2\text{O}_3, \quad \Delta G_{\text{T}}^{\text{f,Ti}_2\text{O}_3} - 2\Delta G_{\text{T}}^{\text{f,TiO}} = -RT \ln P_{\text{O}_2}^{0.5}$$

$$\text{TiO}_2 + \text{C} = \text{TiC} + \text{O}_2, \quad \Delta G_{\text{T}}^{\text{f,TiC}} - \Delta G_{\text{T}}^{\text{f,TiO}_2} = -RT (\ln P_{\text{O}_2} - \ln a_{\text{C}})$$

$$\text{Ti}_4\text{O}_7 + 4\text{C} = 4\text{TiC} + 3.5\text{O}_2, \quad 4\Delta G_{\text{T}}^{\text{f,TiC}} - \Delta G_{\text{T}}^{\text{f,Ti}_4\text{O}_7} = -RT (\ln P_{\text{O}_2}^{3.5} - \ln a_{\text{C}}^4)$$

$$\text{Ti}_3\text{O}_5 + 3\text{C} = 3\text{TiC} + 2.5\text{O}_2, \quad 3\Delta G_{\text{T}}^{\text{f,TiC}} - \Delta G_{\text{T}}^{\text{f,Ti}_3\text{O}_5} = -RT (\ln P_{\text{O}_2}^{2.5} - \ln a_{\text{C}}^3)$$

$$\text{Ti}_2\text{O}_3 + 2\text{C} = 2\text{TiC} + 1.5\text{O}_2, \quad 2\Delta G_{\text{T}}^{\text{f,TiC}} - \Delta G_{\text{T}}^{\text{f,Ti}_2\text{O}_3} = -RT (\ln P_{\text{O}_2}^{1.5} - \ln a_{\text{C}}^2)$$

$$\text{TiO} + \text{C} = \text{TiC} + 0.5\text{O}_2, \quad \Delta G_{\text{T}}^{\text{f,TiC}} - \Delta G_{\text{T}}^{\text{f,TiO}} = -RT (\ln P_{\text{O}_2}^{0.5} - \ln a_{\text{C}})$$

Titanium oxycarbide phase is not considered in the Ti–C–O system because the activities of the solid solutions between TiC and TiO demonstrated a positive deviation from the ideal solution behavior suggesting that the Ti(CO) phase is not stable [20].

The equilibrium lines for the W–C–O system were obtained using:

$$\text{WO}_{2.96} + 0.02\text{O}_2 = \text{WO}_3, \quad \Delta G_{\text{T}}^{\text{f,WO}_3} - \Delta G_{\text{T}}^{\text{f,WO}_{2.96}} = -RT \ln P_{\text{O}_2}^{0.02}$$

$$\text{WO}_{2.9} + 0.03\text{O}_2 = \text{WO}_{2.96}, \quad \Delta G_{\text{T}}^{\text{f,WO}_{2.96}} - \Delta G_{\text{T}}^{\text{f,WO}_{2.9}} = -RT \ln P_{\text{O}_2}^{0.03}$$

$$\text{WO}_{2.72} + 0.09\text{O}_2 = \text{WO}_{2.9}, \quad \Delta G_{\text{T}}^{\text{f,WO}_{2.9}} - \Delta G_{\text{T}}^{\text{f,WO}_{2.72}} = -RT \ln P_{\text{O}_2}^{0.09}$$

$$\text{WO}_2 + 0.36\text{O}_2 = \text{WO}_{2.72}, \quad \Delta G_{\text{T}}^{\text{f,WO}_2} - \Delta G_{\text{T}}^{\text{f,WO}_{2.72}} = -RT \ln P_{\text{O}_2}^{0.36}$$

$$\text{W} + \text{O}_2 = \text{WO}_2, \quad \Delta G_{\text{T}}^{\text{f,WO}_2} = -RT \ln P_{\text{O}_2}$$

$$\text{WO}_{2.72} + \text{C} = \text{WC} + 1.36\text{O}_2, \quad \Delta G_{\text{T}}^{\text{f,WC}} - \Delta G_{\text{T}}^{\text{f,WO}_{2.72}} = -RT (\ln P_{\text{O}_2}^{1.36} - \ln a_{\text{C}})$$

$$\text{WO}_2 + \text{C} = \text{WC} + \text{O}_2, \quad \Delta G_{\text{T}}^{\text{f,WC}} - \Delta G_{\text{T}}^{\text{f,WO}_2} = -RT (\ln P_{\text{O}_2} - \ln a_{\text{C}})$$

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