

Retarded growth of nano-sized carbide particles in liquid metals at 1500°C: Nitrogen effect

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Abstract

The nano-crystalline solid-solution carbide powders were prepared by carbo-thermal reduction after high-energy planetary milling of proper oxide mixture. Then, particle growth behaviors of nano-crystalline transitional metal carbides such as $(\text{Ti}, \text{M}_1)(\text{CN})$, $(\text{Ti}, \text{M}_1, \text{M}_2)(\text{CN})$ and $(\text{Ti}, \text{W}, \text{M}_1, \text{M}_2)(\text{CN})$ were investigated and compared each other when those carbides were present in a Ni or Co melt at 1500°C. From experiments it is found that the growth of $(\text{Ti}, \text{M}_1)(\text{CN})$, $(\text{Ti}, \text{M}_1, \text{M}_2)(\text{CN})$ and $(\text{Ti}, \text{W}, \text{M}_1, \text{M}_2)(\text{CN})$ in a liquid melt was significantly retarded compared to other single-phase carbides such as WC or TiC. In order to elucidate the mechanisms of their growth retardation, we studied the roles of solutes and nitrogen gas in the melt. We calculate the formation energy of these carbides to evaluate their thermal stabilities at high temperatures.

1. Introduction

WC-Co, a major material has several excellent properties for cutting applications such as ultra high melting point, thermal stability, excellent mechanical properties and so forth. However, a major problem of the material is WC-Co is composed of strategic materials, as a result, numerous attempts have been conducted. As a respect of that, TiC- or Ti(CN)-based cermets are representative materials. TiC- or Ti(CN)-based cermets have been designed for this purpose and have been used in high precision machining operations [1, 2]. Unfortunately, even though cermets have a number of excellent properties (high temperature stability, chemical stability, good thermal conductivity and so on) cermets materials have serious problem, low toughness.

In an effort to solve the problem, secondary carbides, such as WC, TaC, NbC, and Mo_2C were added into the cermets materials. This method effectively improved the toughness by increasing the density (sinterability) and forming core-rim structure [3, 4], especially, it was found that the rim phases are responsible for the toughening [5]. Recently, to achieve the toughening of cermets, coreless solid solution cermets or solid solution core-rim structure cermets without sing carbide phase were developed and microstructure control is getting more attention [6, 7].

Traditionally, control of microstructure is a important part of structural materials. In particular, nano-structure is issued during past decade. However, in the case of cermets, even though using nano-particles to produce cermets, it is hard to retain nano-sized carbide particles during sintering process because of dissolution and precipitation [4]. S. Park et. al., [8] produced nanocrystalline $(\text{Ti}, \text{M}_1, \text{M}_2)(\text{CN})$ -20Ni cermets powders and sintered cermets bodies with nano-sized carbonitride grains. However, the reason that how can retard the grain growth during liquid phase sintering is still veiled.

In present study, we elucidate the reason that how can retard the grain growth during liquid phase sintering as a respect of Gibbs formation energy of solid solution. In particular, nitrogen effect on the formation energy was revealed in present study. To obtain the formation energy, we employed VASP (Vienna ab initio simulation package) [9, 10] and Debye approximation [11-13].

2.1 Experiment

Proper amount of oxide mixture were mixed and milled using a planetary mill (Fritsch Pulverisette 7, Germany) at a speed of 250 rpm for 20 h. To obtain the carbides and carbonitrides carbo-thermal reduction at 1350 to 1400°C for 2 h was used in vacuum furnace with nitrogen atmosphere. Thereafter, carides and carbo nitrides and Ni mixture sintered at 1500°C for 1 h in vacuum atmosphere.

The powders were characterized by X-ray diffraction (D-MAX2500-PC, Rigaku, Japan) with monochromatized Cu-K radiation ($\lambda = 1.5418 \text{ \AA}$). Microstructures of sintered samples were observed by FE-SEM (JSM-6330F, JEOL, Japan).

2.2 Calculation methods

The 1st principles pseudo-potential total energy method, the formation enthalpy of various transition carbides and nitrides solid solution were calculated at zero-temperature. According to thermodynamic principles, the formation enthalpy is equal to formation energy at zero-temperature. Also, if the system is held at a fixed T and P, the equilibrium state is obtained from non-equilibrium Gibbs free energy minimization.

$$G = E(x) + PV(x) + A_{\text{vib}}(x, T) + E_{\text{ele}}(x, T)_{\text{ele}}, \quad (1)$$

Where x is configuration vector which implies geometric data, PV is hydrostatic pressure term, A is vibrational Helmholtz free energy and E_{ele} is electronic excitation. Also, Gibbs free energy of formation is

$$\Delta G^f = \sum G^{\text{solution}} - \sum G^{\text{elements}} \quad (2)$$

To calculate Gibbs free energy of mixing, as a first step we employed ideal solid solution model. To obtain zero-temperature E-V data, we used VASP engine. Both unit cell model and supercell model were employed. To optimize model structure the Monkhorst Pack (11 x 11 x 11) and (5 x 5 x 5) k-points used for unit and super cell model, respectively. To improve the accuracy of the results, we employed a cutoff of 400 eV for structure optimization and 500 eV for obtaining EOS (Equation of state). Bulk moduli for Debye temperature calculation were calculated using the Birch-Murnaghan EOS (BM5) [14].

$$E(V) = a + bV^{-n/3} + cV^{-2n/3} + dV^{-3n/3} + eV^{-4n/3} \quad (3)$$

To obtain Debye temperature of several kinds of transition carbides and nitrides, following equation is used in present calculations.

$$\theta_D = \frac{\hbar}{3^{1/3}k_B} \left(\frac{9\rho N_A}{4\pi(M/N_{\text{unit}})} \right)^{1/3} V_m \quad (4)$$

Detailed calculations were listed in M. Blanco et. al. [15].

3. Results and Discussion

To obtain the grain growth behavior of several kinds of solid solution grains 8 kinds of compositions were employed in present research (Table 1.)

Comp	Ti ^{4a}	W ^{4a}	Nb ^{4a}	Mo ^{4a}	C ^{4b}	N ^{4b}	Ni ^{bind}	Co ^{bind}
A	0.95	0.05	0	0	0.5	0.5	20	0
B	0.95	0	0.05	0	0.5	0.5	20	0
C	0.95	0	0	0.05	0.5	0.5	20	0
D	0.94	0	0.03	0.03	0.5	0.5	20	0
E	0.94	0	0.03	0.03	0.5	0.5	0	20
F	0.91	0.03	0.03	0.03	0.5	0.5	20	0
G	0.91	0.03	0.03	0.03	0.5	0.5	0	20
H	0.91	0.03	0.03	0.03	1.0	0	20	0

Table 1. 8 compositions for observing microstructure of cermets (Ti₁M₁M₂M₃)(C,N)-20Ni/(Co).; 4a and 4b indicate 4a and 4b site in B1 structure, respectively.

Powders have similar specific surface area range of D ($D = 6/(A\rho)$): D is 200 ~ 500nm. ($H = \sim 900$ nm)

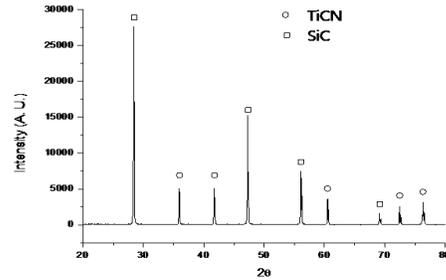


Fig. 1 XRD profile of (Ti_{0.91}W_{0.03}Mo_{0.03}Nb_{0.03})(C_{0.5}N_{0.5}) solid solution powder.

Figure 1 shows the XRD profile of (Ti_{0.88}W_{0.04}Mo_{0.05}Nb_{0.03})(C_{0.5}N_{0.5}) solid solution powder after reduction process at 1400°C for 2 h. There are no other peaks without Ti-based solid solution peaks, it indicates that the target solid solution powders were able to obtain using high-energy ball milling process and carbo-nitriding reduction process.

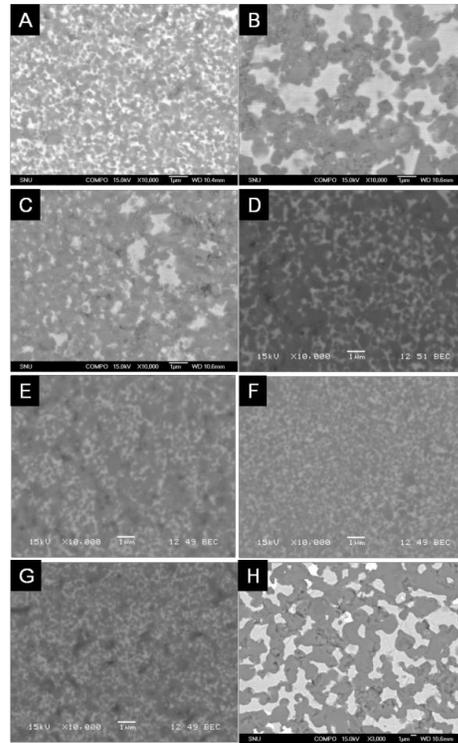


Fig. 2 Microstructure of 8 compositions (A - H).

Figure 2 shows the microstructure of 8 compositions cermets. Except H (carbides), the other compositions (carbo-nitrides) have the nano-sized grains. Compared H to the other compositions (A - G), nitrogen affects strong influence on the

grain growth retardation. Also, microstructure of A to G compositions show that grain growth behavior depends on 4a site metal and binder composition.

To elucidate nitrogen effect on growth retardation, Gibbs free energy of Formation difference was calculated at 1500 °C in Fig. 3.

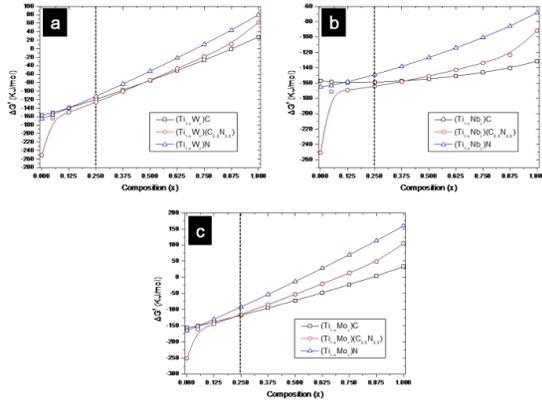


Fig. 3 Nitrogen effect on the formation Gibbs free energy of Ti-based solid solution carbide, nitride and carbo-nitrides at 1500 °C.

Figure 3 represents nitrogen effect on the formation Gibbs free energy of binary Ti-based solid solution carbide, nitride and carbo-nitride. Generally, Ti-based B1 structure materials have the solubility limit for secondary carbide about 15 to 35 at. % at 1500 °C. Therefore, the left side of vertical dashed line is considered in present study. When the nitrogen contains in Ti-based solid solution, formation Gibbs free energy is decreased. However the nitrogen content is over the certain point (a: ~0.125, ~0.5, b: ~0.125, ~0.375, c: ~0.06, 0.25) nitrogen cannot decrease the formation energy. The formation Gibbs free energy means stability of certain phase. Generally, the ratio of the dissolution rates of grains in cermet system has been estimated using the following equation [16].

$$Q_{MC} = S_G w_G m_{tG} \Delta t, \quad (5)$$

where Q_{MC} represents the concentration of carbide, or carbo-nitride grains, S_G the average specific surface area of grains, w_G the amount of grains in the system, m_{tG} the dissolution rate of grains and Δt the dissolution time. The stability is strongly related to m_{tG} , if system has low stability, m_{tG} is higher than that of the high stability system. In the view of this fact, nitrogen is able to reduce m_{tG} , that is able to retard dissolution process of grains. Therefore, assuming all affecting factors are same except m_{tG} , comparing H in Fig. 2 to other compositions, the formation Gibbs free energy plays very important roles in grain grow retardation. However, nitrogen content exceeds critical point, retardation effect of nitrogen is decreased. Also, Figure 3 implies that solute

materials in Ti-based B1 structure solid solution exceed certain content, grain growth retardation effect of nitrogen is vanished because formation Gibbs free energy is higher than carbide system.

4. Conclusion

The grain growth retardation effect of nitrogen at 1500 °C during liquid phase sintering was investigated in present study. Compared to carbide system and carbo-nitride system, notable grain growth retardation was observed in carbide system. We calculated Gibbs free energy of formation of binary solid solution system using VASP ab initio calculations. Gibbs free energy of formation is able to express the degree of dissolution rate, because Gibbs free energy of formation means stability of certain phase. Nitrogen was able to reduce Gibbs free energy of formation, that is nitrogen can increase the system stability. According to this, dissolution rate of grains was reduced, notably. However, the grain growth retardation effect of nitrogen can vanish in certain solute content or amount of nitrogen in the system.

5. References

- [1] R. Kieffer, P. Ettmayer and Freundhofeier, 'New sintered nitride and carbonitride hard metals' Powder. Metall. 25, 1335-42, 1971.
- [2] R. Kieffer, P. Ettmayer and Freundhofeier, 'Modern devices in powder metals' New York: Plenum Press; 5, 201-14, 1971.
- [3] S. Kim, K. Min and S. Kang, 'Rim structure in Ti(C_{0.7}N_{0.3})-WC-Ni cermets' J. Am. Ceram. Soc., 86, 1761-66, 2003.
- [4] S. Ahn and S. Kang, 'Formation of core/rim structures in Ti(C,N)-WC-Ni cermets via a dissolution and precipitation process' J. Am. Ceram. Soc. 83, 1489-94, 2000.
- [5] J. Jung and S. Kang, 'Effect of ultra-fine powders on the microstructure of Ti(CN)-xWC-Ni cermets' Acta. Mater. 52, 1379-1386, 2004.
- [6] J. Kim, M. Seo and S. Kang, 'Microstructure and mechanical properties of Ti-based solid- solution cermets' Mater. Sci. Eng. A 528, 2517-2521, 2011.
- [7] J. Kim and S. Kang, 'Microstructure evolution and mechanical properties of (Ti_{0.93}W_{0.07})C-xWC-20Ni cermets' Mater. Sci. Eng. A 528, 3090-3095, 2011.
- [8] S. Park, Y. Kang H. Kwon and S. Kang, 'Synthesis of (Ti,M₁,M₂)(CN)-Ni nanocrystalline powders' Int. J. Refract. Met. Had Mater. 24, 115-121, 2006.
- [9] G. Kresse and J. Hafner, "Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium", Phys. Rev. B 49 (1994) 14251.
- [10] G. Kresse J. Furthmuller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set", Phys. Rev. B 54 (1996) 11169.
- [11] M. Blanco, E. Francisco and V. Luana, 'Gibbs: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model' Comput. Phys. Commun. 158 (2004) 57-72.

- [12] S. Shang, Y. Wang, D. Kim and Z. Liu, 'First-principles thermodynamics from phonon and Debye model: Application to Ni and Ni₃Al' *Comp. Mater. Sci.* 47 (2010) 1040-1048.
- [13] M. Falkowski, A. Kowalczyk, M. Timko, J. Sebek, E. Santava, M. Reiffers and M. Mihalik, 'Specific heat of CeNi₄Si compound' *J. Magn. Magn. Mater.* 316 (2007) e474-e476.
- [14] S. Shang, Y. Wang, D. Kim and Z. Liu, 'First-principles thermodynamics from phonon and Debye model: Application to Ni and Ni₃Al' *Comp. Mater. Sci.* 47, 1040-1048, 2010.
- [15] M. Blanco, E. Francisco and V. Luana, 'Gibbs: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model' *Comput. Phys. Commun.* 158, 57-72, 2004.
- [16] S. Ahn and S. Kang, 'Effect of various carbides on the dissolution behavior of Ti(C_{0.7}N_{0.3}) in a Ti(C_{0.7}N_{0.3})-30Ni system' *Int. J. Refract. Met. Hard Mater.* 19, 539-545, 2001.