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Instability of solid–liquid interface in transitional metal–carbide systems

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Abstract The instability of solid–liquid interface (ISLI) during the liquid-phase sintering was studied using carbide–Ni composites. Of the various transitional metal carbides TiC of 4th period is the only carbide that exhibits a strong ISLI with negative curvatures in molten Ni. No ISLI was observed for other carbides in the 5th and 6th periods. The origin of ISLI is strain developed at the interface between the carbides and the newly formed solid solutions. The difference in the size of the atoms involved can be used to predict the formation of a carbide–Ni solid solution when the Hume-Rothery rules are applied. Aside from the size factor, other factors in the rules are not effective in predicting this phenomenon.

Introduction

The tendency to reduce surface energy is a major driving force in the sintering of a single-phase system. Therefore, grain morphologies are typically spherical or at least flat. However, in some special cases, negative curvatures are also found. This phenomenon is referred to as chemically induced grain migration (CIGM) and especially in the liquid-phase sintering it is called instability of the solid–liquid interface (ISLI).

Many reports have appeared on the driving force for CIGM [1–8]. These studies indicate that a large part of the total driving force for CIGM can be attributed to the presence of strain energy at the coherent interface layer. Chae et al. [4] reported ISLI in a TiC–Fe system. Later Chun et al. [5] also studied ISLI using a TiC–Mo–Ni system. They concluded that the strain was induced by the formation of a coherent layer, which is a solid solution rim formed from the carbide and binder phases. However, CIGM is not always observed in all systems.

It was found that CIGM, narrowly speaking, ISLI was not commonly observed in carbide–metal systems during sintering. It is generally thought that the formation of a solid-solution rim is a necessary condition for ISLI. In this study various carbide–Ni composites were prepared and their microstructures were investigated. In addition, the parameters in Hume-Rothery rules such as atomic size, electro-negativity, electron valence, and crystal structure, were examined with these carbide–metal composite systems.

Experimental procedure

The starting raw materials were Group IVA, VA, and VIA transitional metal carbides with nickel as the binder phase. Table 1 lists the average particle size and manufacturers of the various materials. Specimens were prepared by means of an infiltration technique. The ratio between the Ni infiltrant and carbide skeleton was 1:1 in vol%. The skeleton and infiltrant powders were prepared separately by wet-mixing with acetone and paraffin and, were dried in an oven at 100 °C for 24 h. Disk compacts of the infiltrant and skeleton powders were prepared using a pressure of 125 MPa. The Ni infiltrant was placed on the top of the skeleton in an alumina crucible. Infiltration was performed in a graphite resistance vacuum furnace at 1510 °C for 1 h. The vacuum level and

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Table 1 Average particle size and manufacturers of initial powders

	Particle size(μm)	Manufacturer
TiC	1.00	Treibacher
ZrC	2.40	H.C. Starck
HfC	1.61	Kennametal
VC	1.10	HCST
NbC	1.75	Treibacher
TaC	1.12	Treibacher
Cr_3C_2	1.75	Kennametal
Mo_2C	1.42	Kennametal
WC	1.88	Xiamen
Ni	4.00	INCO

heating rate were 10^{-2} torr and 10 °C/min, respectively. Specimens were polished with 6 and 1 μm diamond pastes for microscopic examination. The microstructures of the specimens were observed by scanning electron microscopy (SEM, Model JMS-5600, Japan Electronic Optics Laboratory, Japan). XRD Analyses were done using a X-ray Diffractometer (M18XHF-SRA, MAC Science Co.) with Si as a standard.

Results and discussion

Microstructures of various systems without ISLI

Figure 1 shows the microstructures of the specimens without ISLI, which were obtained after infiltration and heat-treatment at 1510 °C for 1 h. All those were from 5th-period metal–carbide systems. Similar microstructures were obtained from 6th-period carbides. Ni infiltrated into the skeletons without any difficulties. However, numerous cracks often appeared in the binder phase. The size of carbide particles varied substantially as shown in Fig. 1a–c. However, most carbide particles had an angular form, with no negative curvature.

The metal carbides in the same group tend to show similar particle morphology in the Ni binder. However, the kinetics of particle growth is different depending on the group in the periodic table. For example, HfC of IVA grew more rapidly than ZrC even though the initial particle size of the HfC was smaller than that of ZrC. On the other hand, Mo_2C, which is in the same period as ZrC, grew much faster than WC. It is closely related to the tendency of those carbides to dissolve in the Ni melt, which is a function of the solubility limit in Ni and thermodynamic stability of the carbides [9].

Microstructure of systems with ISLI

Figure 2 shows the microstructures of the specimens obtained from the 4th-period transitional metal carbides. In these systems, carbide particles with negative curvatures can be seen. The TiC–Ni system shows a particularly strong ISLI phenomenon. However, only a limited ISLI is observed in Cr_3C_2–Ni system if any at all. Both systems also showed the same cracking tendency in the binder phases as shown in the Mo_2C–Ni of Fig. 1. Unlike the TiC–Ni system, VC–Ni shows no evidence of any negative curvature. The IVA, VA, and VIA transitional metal carbides in the 4th period were found to grow much faster (30–100 μm) than the other carbides in the 5th and 6th periods (5–10 μm).

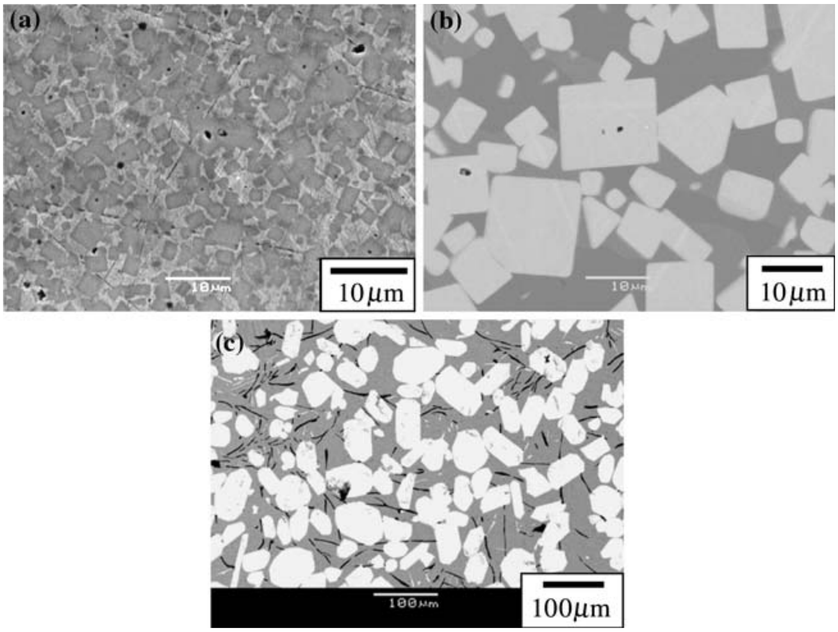

Fig. 1 SEM micrographs of (**a**) ZrC–50Ni, (**b**) NbC–50Ni, and (**c**) Mo_2C–50Ni (vol%), heat-treated at 1510 °C for 1 h

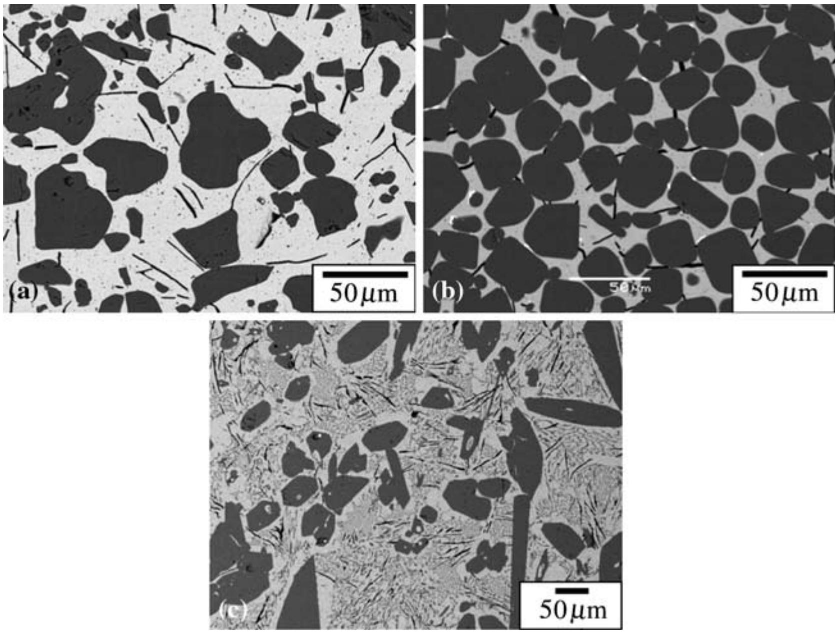

Fig. 2 SEM micrographs of (**a**) TiC–50Ni, (**b**) VC–50Ni, and (**c**) Cr_3C_2–50Ni (vol%) heat-treated at 1510 °C for 1 h under vacuum

As reported by other researchers, the main cause of ISLI is the strain energy developed at the particle interface. When the systems are exposed to >1300 °C, carbides dissolve in the metal binder (Ni). They subsequently precipitate as rim phases in the form of a solid solution, resulting in particle growth. If the rim of a solid solution forms a coherent or semi-coherent interface, misfit strain will be generated between the original carbide and the rim phase. Thus, the formation of a solid solution is a necessary condition for carbides to have a negative curvature. In addition, the strain energy developed at the interface should be large enough to compensate for the increase in free energy due to the increased surface area.

Analyses with XRD

An XRD analysis was done to better understand the tendency toward solid solution formation by measuring the shifts in the main peaks. As summarized in Table 2, all carbide systems demonstrate clear peak shifts. A heat treatment of carbides was done separately in the absence of Ni at 1510 °C to find the effects of carbon loss and strain relief in the carbides. The loss of carbon in the carbides, in general, decreases the lattice constants while the strain relief increases these values. With the exception of TaC strain relief appeared to have a greater effect on peak shifts than that of carbon loss, resulting in an increase in lattice parameters.

A comparison was made between the data for heat-treated carbides with and without Ni, since this might indicate the role of Ni at 1510 °C on the peak shift. The peak shifts to high diffraction angles (2θ) were observed for TiC, Cr_3C_2, and WC. The shifts to high angles could be interpreted as a tendency of the carbides to form solid solutions readily with Ni. The TiC–Ni system, which demonstrates a strong ISLI, shows a decrease in lattice constants as the result of forming a solid solution. In the case of Cr_3C_2–Ni, the shift was less than that of TiC–Ni. This could imply that Cr_3C_2–Ni has a reduced tendency to form solid solutions compared to TiC–Ni and a limited ISLI is observed in Cr_3C_2–Ni. The behavior of WC–Ni is not well understood at present, since the WC of an hcp structure would not form a solid solution with Ni of fcc.

Other carbides such as VC, ZrC, NbC, HfC, TaC, and Mo_2C showed peak shifts to low angles. Based on the XRD results and growth behavior of their carbides (Fig. 1), these carbides can be said to be reluctant to form solid solutions with Ni. Even if these systems form solid solutions with Ni, the interface at the carbide/solid solution rim might be a semi- or incoherent boundary in nature, which will provide little driving force for ISLI.

Application of Hume-Rothery rules

The nature of bonding in the carbides used in this investigation is known to be largely a mixture of covalent and metallic bonding with little ionic tendency. If a solid solution were formed, nickel would substitute for metal atoms in the carbides. According to the Hume-Rothery rules, atomic size, electro-negativity, electron valence, and crystal structure are known to be important factors in solid solutions formation. Carbides were investigated with Hume-Rothery rules in terms of their ability to form a solid solution with Ni.

Table 2 Peak shifts of major peaks of various carbide–metal systems (2θ)

Carbides	A JCPDS	B Raw powder	C 1510 °C heat-treatment w/o Ni (C–B)	D 1510 °C sintering with Ni (D–C)
TiC	41.710	41.673	41.400 (–0.273)	41.657 (+0.257)
VC	43.490	43.415	43.360 (–0.055)	43.340 (–0.020)
Cr_3C_2	50.077	50.051	50.027 (–0.024)	50.054 (+0.027)
ZrC	33.040	33.054	33.034 (–0.020)	32.755 (–0.279)
NbC	34.730	34.822	34.633 (–0.189)	34.458 (–0.175)
Mo_2C	39.392	39.530	39.466 (–0.064)	39.229 (–0.237)
HfC	33.437	33.456	33.213 (–0.243)	33.212 (–0.001)
TaC	34.855	34.927	35.065 (0.138)	34.607 (–0.458)
WC	48.266	48.355	48.118 (–0.237)	48.550 (+0.432)

Table 3 Atomic radii and size factors of 4, 5, 6 group transition metal atoms and nickel atom

	Atomic radius(nm) (A)	Most common valence (V)	Crystal structure of carbide	Electro-negativity (E)	ΔA(nm)	ΔV	ΔE	Atomic size factor (%)
Ni	0.149	2	FCC	1.91	–	–	–	–
Ti	0.176	4	B1	1.54	0.027	2	0.37	15.34
Zr	0.206	4	B1	1.33	0.057	2	0.58	27.67
Hf	0.208	4	B1	1.3	0.059	2	0.61	28.37
V	0.171	5	B1	1.63	0.022	3	0.28	12.87
Nb	0.198	5	B1	1.6	0.049	3	0.31	24.75
Ta	0.200	5	B1	1.5	0.051	3	0.41	25.5
Cr	0.166	3	Orthorhombic	1.66	0.017	1	0.25	10.24
Mo	0.190	4	Hexagonal	2.16	0.041	2	0.25	21.58
W	0.193	4	Hexagonal	2.36	0.044	2	0.45	22.8

In Table 3 the differences in atom size between carbides and nickel are shown under a size factor. Other factors are also listed for comparison. The size factor was determined by (atomic size of the metal in the carbide–atomic size of nickel)/(atomic size of the metal in the carbide). The size difference between impurity and host atoms must be under ~15% for a solid solution to form [10]. The 5th and 6th period metal atoms (Zr, Hf, Mo, Nb, Ta, and W) have size factors of over 15% with nickel while 4th period metal atoms (Ti, V and Cr) have size factors under ~15%. VC has the best conditions among the carbides of this study to form a solid solution with Ni. However, the tendency of VC to form a solid solution with Ni was small from XRD data and this system failed to show ISLI. Main peak of VC in XRD data is from (4 0 0) plane and the lattice spacing of this plane is smaller than that of other planes. This could be why the tendency to form a solid solution with Ni is not big as much as the case of TiC, Cr_3C_2 and ISLI is not observed in VC–Ni system. However, all these factors including electro-negativity, electron valence and crystal structure do not provide clear predictive information on the formation of solid solutions.

Summary and conclusions

The instability of solid–liquid interface (ISLI) during liquid-phase sintering was studied using carbide–Ni composites. Summary and conclusions of this investigation follows.

(1) Of the various transitional metal carbides TiC of the 4th period is the only carbide that exhibits a strong ISLI with negative curvatures in molten Ni. The Cr_3C_2–Ni system shows a limited tendency to develop ISLI. Other carbides in 5th and 6th periods show no detectable ISLI.

(2) VC has the best conditions among the carbides of this study to form a solid solution with Ni. The small lattice spacing of (4 0 0) plane of VC could hinder a solid solution formation with Ni and negative curvature, ISLI.

(3) Hume-Rothery rules did not provide clear predictive information on the formation of solid solutions in various carbide–metal systems.

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