Effect of Milling on the Carbothermal Reduction of Oxide Mixture for (Ti,W)C-Ni

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The effect of high-energy milling on the phase transformation and carbothermal reduction was examined using an oxide mixture, TiO₂-WO₃-NiO-C, with a process to synthesize (Ti,W)C cermets. Due to the high energy involved in the mill raw, anatase TiO₂ transformed first to TiO₂-II and then to rutile, while WO₃ transformed to a high-pressure WO₃-HP and hexagonal WO₃ phase. The co-existence of WO₃ and TiO₂ enhanced the formation of a nano-crystalline or amorphous phase. The (Ti,W)C phase was formed mainly at 1150°C from TiC and WC formed in the early stages. These results were further examined using XRD, the Rietveld method and mass spectroscopy.

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1. Introduction

Titanium carbide and carbo-nitride are excellent materials in cutting tool applications, and are used in a wide range of cutting operations.¹⁾ TiC- and Ti(CN)-based cermets are used in high-speed final or semi-final cutting tools in place of WC-Co alloys.^{2,3)} However, the applications of such cermet systems are limited due to the low toughness of the cermets. The low toughness was ascribed to the complicated microstructure of TiC- or Ti(CN)-based cermets and the poor wettability of the Ni binder phase on the carbides. WC addition to a TiC-Ni or Ti(CN)-Ni system is effective in improving the toughness and is decreasing the particle growth rate.^{4,5)}

Cermets consisting of only (Ti,W)C- or (Ti,W)(CN)-type solid-solution phase microstructures have been pursued since the 1980s. Recently, (Ti,W)C- or (Ti,W)(CN)-type solid-solution phase microstructure was reported by Park *et al.*⁶⁾ They reported that a solid-solution phase could be produced from an oxide mixture with greatly improved toughness compared with conventional TiC-based cermets. In addition, the temperature for the carbothermal reduction of the oxide mixture was reduced to <1300°C through high-energy milling, which is remarkably lower than the conventional temperatures used (1700~2000°C).

This study examined the effect of high-energy milling on the phase transformation of milled oxide mixture using the Rietveld method. This is in contrast to previous studies that reported a phase transformation with only one or two milled compounds such as TiO₂, V₂O₅, ZrO₂, and metals (Ni, Al, and Ti) using this method.⁷⁻¹⁰⁾ The milling efficiency and phase transformation of the oxide mixture and individual oxides was also compared. The overall results were related to the carbothermal reduction and final phase formation process.

2. Experimental Procedure

The (Ti,W)C-Ni powders were synthesized using anatase-TiO₂ (99+% purity, 43 µm ave. particle size, Aldrich), NiO (99% purity, 45 µm ave. particle size, Sigma-Aldrich) and WO₃ (99+% purity, 20 µm avg. particle size, Aldrich). The oxides were mixed with carbon black to achieve the target composition, (Ti_{0.93}W_{0.07})C-20 mass%Ni, TiC-15 mass%, WC-20 mass%Ni. The carbon content was found not only to reduce all the oxides except for NiO to form CO but also to carburize the solid solution carbide, (Ti,W)C.

The oxide/carbon mixture was subjected to high-energy ball milling using a planetary mill (Pulverisette 5, Fritsch, Germany). Tungsten carbide balls were mixed with the oxide/carbon mixture at a ball-to-powder ratio (BPR) of 40:1 by weight. Four WC-coated bowls were used, and each bowl contained 25 grams of the oxide mixture. All milling was carried out at a speed of 250 rpm for periods of 5, 10 and 20 h. The (Ti,W)C-Ni powder was prepared by carbothermal reduction at 1200° or 1300°C for 1 h.

The specimens were analyzed by X-ray diffraction (M18XHF-SRA, Macscience, Japan) with Si as the standard. The crystallite size and phase transformation after milling the oxide mixture were investigated using the Rietveld and integral breadth methods after eliminating the instrumental broadening factor. The amount of gas evolution during carbothermal reduction was measured using a mass spectrometer (QMS 403, NETZSCH, Germany) under helium flow.

3. Results and Discussion

3.1 Milling effect on phase transformation

Figure 1 shows the sequential XRD profiles of TiO₂-WO₃-NiO-C mixtures with respect to the high-energy milling time. In general, the intensities of the profiles were relatively low, even after 5 h milling (Fig. 1(a)), while many peaks combined with time (Fig. 1(c)). Figure 1(d) shows the final phases, (Ti,W)C and Ni, obtained from the carbothermal reduction of the powder shown in Fig. 1(c) at 1300°C for 1 h.

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Fig. 1 XRD profiles of TiO_2 - WO_3 - NiO -C mixtures after planetary milling for (a) 5 h, (b) 10 h, (c) 20 h, and (d) after carbothermal reduction of (c) at 1300°C for 1 h.

Fig. 2 Phase Diagram of TiO_2 as a function of temperature and pressure.¹⁴⁾

In the initial stage of milling, new phases appear, such as rutile TiO_2 and a high-pressure TiO_2 -II phase (Fig. 1(a) and (b)). In addition, TiO_2 -II forms preferentially over rutile. In the late stage, rutile grows dominantly by consuming TiO_2 -II (Fig. 1(b) and (c)). Apparently, raw anatase TiO_2 transformed to two new phases that are stable at high temperature and/or high pressure. The sequence of phase transformation, anatase to TiO_2 -II to rutile, has already been reported in the literature for the milling of anatase TiO_2 . The impact induced from the milling actions is regarded as the main reason for high pressure TiO_2 -II synthesized during milling.^{11–13)}

This result is consistent with the phase diagram shown in Fig. 2 where the anatase and TiO_2 -II phases change into rutile under high pressures and temperatures.¹⁴⁾ Based on Figs. 1 and 2, it can be said that raw anatase TiO_2 transforms to TiO_2 -II first and then to rutile when the temperature of the vessels and impact are high enough in the planetary mill.

This result implies that high pressures ($>2500\text{ MPa}$) and temperatures ($>500^\circ\text{C}$) prevail during milling, which allows such transformations.

The milling efficiency of the planetary mill was compared with that of the attrition mill, which is commonly used for powder preparation. Attrition milling was performed with the same quantity of oxide mixture (100 gram) in a vessel under the same milling conditions as the planetary mill: speed of 250 rpm with a BPR of 40:1. Figure 3 shows the XRD results of the powder after attrition milling. A high level of crystallinity of various phases was observed without complete alloying, even after 20 h attrition milling.

In the attrition mill, rutile appears first after 5 h milling, which is followed by TiO_2 -II after 10 h milling. The attrition mill in this study does not provide sufficient impact to form TiO_2 -II. Instead, the TiO_2 -II phase forms at a relatively low pressure due to an increase in vessel temperature (Fig. 2). Both phases are retained in the powder attrition-milled for 20 h. However, the intensity of these phases is not significant compared with those of the other phases in the system.

Rietveld analysis was also performed to examine the phase transformations in more detail in that it is a reliable technique for the estimation of the grain size of these phases. The Rietveld analysis for the overlapped peaks is shown in Fig. 4. Table 1 shows the phases present in the powder milled by the attrition and planetary mills for 20 h. It also lists their space group, crystal structure and final grain size of the phases found from the planetary mill. This analysis reconfirms that there are three different types of TiO_2 in the system. The possible presence of srilankite TiO_2 was also noted in the powder milled using the planetary mill. WO_3 transforms to a high-pressure WO_3 -HP and hexagonal WO_3 in the planetary mill, whereas $\text{W}(\text{CO})_6$ was found in the attrition mill. The transformation can vary significantly according to the milling techniques or impact.

Fig. 3 XRD profile of $\text{TiO}_2\text{-WO}_3\text{-NiO-C}$ mixtures after attrition milling for (a) 5 h, (b) 10 h, (c) 20 h and (d) 20 h with Co_3O_4 in place of NiO (planetary milling).

Fig. 4 Rietveld analysis about the overlapped XRD profiles of $\text{TiO}_2\text{-WO}_3\text{-NiO-C}$ mixtures after planetary milling for 20 h.

Figures 1 and 3 show the broadening of the peaks for the various phases in the system. They suggest that all phases are nano-crystalline after 5 h milling. The results of the Scherrer's method revealed the size of crystallites milled using the attrition technique exceeds the limit of the method (>100 nm). However, the average size of rutile in the planetary mill <10 nm while that of raw anatase was $43\text{ }\mu\text{m}$ initially and was milled to ~ 30 nm (Table 1).

3.2 Compositional effect on milling efficiency

It is interesting to find that NiO remained unmixed, which is in contrast to the other oxides, as shown in Figs. 1 and 3. This might be due to its crystal structure and mechanical properties. The melting points of TiO_2 , WO_3 and NiO are 1800 , 1473 and 1960°C , respectively. The highest melting point of NiO among the oxides is often related to its strong bond strength, which causes high hardness. However, the

Table 1 Microstructural parameters of the powder after attrition and planetary milling for 20 h.

Starting materials		Powder after attrition milling		Powder after planetary milling		
Phase	Crystallite size, μm	Phase	Phase	Crystallite size, nm	Crystal system	Space group
$\text{TiO}_2\text{-Anatase}$	43	$\text{TiO}_2\text{-Anatase}$	$\text{TiO}_2\text{-Anatase}$	21.7	Tetragonal	I41/amd
		$\text{TiO}_2\text{-II}$	$\text{TiO}_2\text{-II}$	31.2	Orthorhombic	Pbcn
		$\text{TiO}_2\text{-Rutile}$	$\text{TiO}_2\text{-Rutile}$	7.6	Tetragonal	P42/mnm
$\text{WO}_3\text{-mono}$	20	$\text{WO}_3\text{-mono}$	$\text{WO}_3\text{-mono}$	*	Monoclinic	P21/n
		$\text{WO}_3\text{-HP}$	$\text{WO}_3\text{-HP}$	*	Monoclinic	P21/c
		$\text{W(CO)}_6\text{-Pnma}$	$\text{WO}_3\text{-hex}$	*	Hexagonal	P6/mmm
NiO	45	NiO	NiO	52.7	Cubic	Fm3m
C	1.65	C	C	3.3	Hexagonal	P63mc

*Fraction of the phase was less than 5 mass% and therefore the grain value is not reliable, BPR=ball-to-powder weight ratio.

hardness values of NiO and TiO₂ are found to be about the same as 5.5 and 5.5~6 GPa, respectively. It seems to rule out the influence of mechanical properties of NiO as a possible cause for unaccountable milling behavior of NiO.

The crystal structure aspect of NiO was examined as another possible reason for the immiscibility issue. NiO has a cubic structure that belongs to the space group, Fm3m, which is different from that of the other phases, Pabc. A different oxide, Co₃O₄ with a cubic structure that belongs to space group, Fd3m, was used in place of NiO for comparison. As shown in Fig. 3(d) peak broadening was noted with much lower peak intensity. The mixing tendency was superior to NiO, resulting in a homogeneous nano-crystalline or amorphous phase. The melting point of Co₃O₄ is 900°C, indicating that it has lower bond strength than NiO. Based on the information above, it is likely that the milling behavior of NiO is largely attributed to the relatively high mechanical strength of NiO more than the difference in crystal structure among constituent oxides in the system.

No phase transformation was observed from NiO. This is only because NiO has the lowest amount of oxygen among the Ni-O compounds. There are four different types of nickel oxides, NiO, NiO₂ of C2/m and R-3m, and Ni₂O₃.¹⁵⁻¹⁷ All nickel oxides will change to NiO first in a reducing atmosphere. The melting points of NiO₂ of C2/m and R-3m, and Ni₂O₃ are presumed to be the same as that of NiO since they are dissociated into NiO. The dissociation of unstable Ni₂O₃ is known to occur ~600°C.¹⁸ These facts support our assertion above.

The use of rutile TiO₂ as a raw oxide, instead of anatase, was examined to determine the effect of the transformation on the reduction process. The result, after 20 h milling, is shown in Fig. 5. In the case of rutile, the milling impact was less than that of anatase. Using the (012) peak of NiO as a reference, the intensity ratios of the TiO₂ (120) peak to NiO (012) peak were 0.73 and 1.02 in the cases of anatase and rutile, respectively (Fig. 5). The milling behavior of NiO is assumed to be more or less inert to the kind of TiO₂. The use of anatase lowers effectively the crystallinity of the

rutile TiO₂ phase formed after milling. This demonstrates that the two different starting TiO₂ oxides take different paths to arrive at nano-crystalline rutile. The anatase phase initially becomes disordered to some extent in structure by mechanical impact and then begins forming nano-crystalline rutile via TiO₂-II.

Mass spectroscopy also demonstrates that when anatase is used, the reduction begins at a ~100°C lower temperature than with rutile. There was no further transformation of TiO₂ observed when rutile was used even if the size of rutile was smaller than that of anatase. Based on these results, the use of anatase is an important factor for lowering the crystallinity of the system and inducing a proper phase transformation.

The effect of other oxides in inducing relevant transformations was investigated by examining the milling behavior of the individual oxides with carbon. The same amount of the individual oxide was milled with the same amount of carbon as that of the oxide mixture. That is, for the milling of the individual oxide mixture, such as TiO₂, WO₃ and NiO along with C, the same volume ratio of milling ball to powder was used instead of the weight ratio to mix the TiO₂-WO₃-NiO-C powder. The volume ratios were recalculated to weight ratios later.

When a mixture of TiO₂/C was milled for 20 h, anatase phase transformed completely to rutile, as shown in Fig. 6(a). However, the crystallinity was much higher than that of the oxide mixture. Figure 6(b) and (c) show that partial reduction occurred when WO₃ or NiO was milled with C, resulting in WO₂ and hexagonal Ni. Compared with the result shown in Fig. 1, WO₃ can be alloyed effectively in the form of nano-crystalline or amorphous phases in the presence of other oxides such as TiO₂. This confirms that the NiO/C mixture has the least milling and miscibility among oxides. The presence of WC in this system was due to contamination from the milling media.

3.3 Carbothermal reduction of milled oxide mixture

Figure 7 shows the evolution of CO/CO₂ gas measured using a mass-spectrometer from the oxide mixtures milled for 5, 10, and 20 h. The temperature range for the reduction was varied with respect to the milling time. While the onset temperature of the CO/CO₂ gas evolution is ~530°C for the powder milled for 5 h, CO/CO₂ gas is released at ~500 and 450°C in case of 10 and 20 h milling, respectively. A thermodynamic calculation shows that CO₂ is more stable at a lower temperature than CO. According to the Ellingham diagram,¹⁹ the coexistence of CO and CO₂ gases prevails up to ~1130°C with unmilled oxides if the total pressure is maintained at 1×10^5 Pa. In this case, the temperature decreases to ~500°C, even if the reduction environment is much different from the standard state. With the milled powder of this study, the CO evolution was completed at a lower temperature, 1200°C, with increasing milling time (Fig. 7(c)). Therefore, the level of crystallinity and extent of phase transformation during milling determine the temperature needed to complete the reduction.

Figure 8 shows the changes in weight and the thermal behavior of the milled oxide mixture obtained by TG-DSC. The first discrete drop in TG (see the arrow) was attributed

Fig. 5 XRD patterns of the oxide mixture milled for 20 h using (a) anatase TiO₂ and (b) rutile TiO₂.

Fig. 6 XRD patterns of (a) anatase TiO_2 +C, (b) WO_3 +C and (c) NiO +C after 20 h planetary milling.

Fig. 7 Gas evolution of CO/CO_2 during carbothermal reduction of $\text{TiO}_2+\text{WO}_3+\text{NiO}+\text{C}$ mixture after high-energy milling for (a) 5 h, (b) 10 h, and (c) 20 h.

Fig. 8 Mass change and heat flow during carbothermal reduction measured by TG-DSC.

Table 2 The phases observed after carbothermal reduction at various temperatures for 1 h.

	500°C	800°C	1000°C	1100°C	1150°C
Phases	TiO_2 -Rutile	TiO_2 -Rutile	TiC	TiC	TiC
confirmed from	WC	Ti_4O_7	Ti_4O_7	Ti_3O_5	$(\text{Ti},\text{W})\text{C}$
XRD analysis	Ni	Ti_3O_5	Ti_3O_5	Ti_2O_3	WC
		WC	WC	WC	Ni
		Ni	Ni	Ni	

to the reduction of NiO , which was confirmed by mass spectrometry for the NiO/C mixture. Since then, there was a continuous decrease in the oxide mixture until it reached 1200°C. This is in line with the result shown in Fig. 7. In order to have accurate analyses for the reactions, the oxide mixture, which had been milled for 20 h, was heat treated at various temperatures for 1 h. Table 2 summarizes the XRD results of the mixture. The results show that the rutile phase was continuously reduced into a suboxide, TiO_{2-x} , until it reached 1000°C. Various suboxides appeared and were reduced at a faster rate than rutile. This can indicate the relative stability of the oxides examined in this study.

In addition, differential scanning calorimetry (DSC) shows two distinct endothermic reactions that are completed in the vicinity of 1000°C and 1150°C, respectively in Fig. 8. According to Table 2, TiC begins forming in the vicinity of 1000°C while the formation of WC is almost complete at ~800°C. Since the thermal gravimetry (TG) results indicates no more weight loss from 1150°C, it is believed that $(\text{Ti},\text{W})\text{C}$ formation occurs at this temperature from TiC and WC, which had already formed below 1150°C.²⁰⁾

4. Summary and Conclusions

This study examined the effect of high-energy milling on the phase transformation of a milled oxide mixture, TiO_2 -

WO₃-NiO-C. The effect of the mixture on the milling efficiency was related to the carbothermal reduction and final phase formation process. In high-energy milling, raw anatase TiO₂ transforms first to TiO₂-II and then to rutile in the form of a nanocrystalline phase, while WO₃ transforms to a high-pressure WO₃-HP and hexagonal WO₃. The presence of the WO₃ phase helps form a nano-crystalline or amorphous phase with TiO₂ due to its low bond strength and brittle nature. TiC begins to form in the vicinity of 1000°C while the formation of WC is almost complete at ~800°C. (Ti,W)C formation occurs mainly at 1150°C from TiC and WC, which have formed previously.

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