Journal of the European Ceramic Society 22 (2002) 2401–2407

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Formation of ternary carbide Co_6W_6C by mechanical activation assisted solid-state reaction

Takeshi Tsuchida*, Naruki Morita

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University,
North 13 West 8, Kita-ku, Sapporo, 060-8628 Japan

Received 14 June 2001; received in revised form 4 December 2001; accepted 28 December 2001

Abstract

The powder mixtures of Co/W/C = 6/6/1–1/1/2 in molar ratio were mechanically activated by grinding in a planetary ball mill and subsequently heated at 800–1100 °C in argon atmosphere. Ternary carbide, Co_6W_6C, was obtained from the sample of Co/W/C = 7/7/2 which was ground for 4 h and heated at 1100 °C. In contrast, from most of the samples ground for 1–3 h, WC was mainly formed accompanying Co_6W_6C, Co_2W_4C and $Co_3W_9C_4$, and from the unground samples, these carbides were hardly formed. From the results concerning the effects of mixing ratio, grinding time and heating temperature of the Co/W/C powder mixtures on the formation of ternary carbides, it was found that the formation of Co_6W_6C strongly depends on the mixing homogeneity, the intimate contact and the activated state of the Co, W and C grains, finely ground by ball milling. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Carbides; Co_6W_6C; Mechanical activation; Milling

1. Introduction

Recently, studies on the formation and properties of carbides involving two or more metals have been noted because these carbides are expected to have novel properties as compared with individual monometal carbides. For example, the magnetic properties of $R_2Fe_{12}C_x$ (R = rare earth metals)[1] and Mn_3MC (M = Ga and Al),[2,3] and the electrical properties of Ti_3MC_2 (M = Si and Ge) [4] have been reported. In general, however, it is very difficult to produce ternary or more complex carbides at temperatures below the melting points of the starting materials, mainly because of the difficulty in mixing the constituent powder particles homogeneously.

It is well known that mechanical activation enhances the reactivity of solids, as well as their mixing homogeneity and remarkably lowers the reaction temperature. However, a major drawback of this process is powder contamination from milling equipment (vial, balls and grinding medium) during grinding. In order to reduce powder contamination, the mechanical activation by prolonged grinding must be primarily avoided. Therefore, a process that combines short-time mechanical activation and subsequent heat treatment at lower temperatures, which is sometimes called mechanical activation assisted solid-state reaction, is a traditional, but still important process to synthesize useful materials at lower temperatures. Consequently, the application of this process for the preparation of ternary carbides is of significance and very interest. In such a reaction system, besides, the use of graphite as a reactant can be expected to minimize contamination of the powder, because of its excellent lubricant ability. And so far we have studied the low-temperature formation of Fe_3M_3C (M = Mo, W) assisted by mechanical activation.[5]

In the present study, we discuss the optimal conditions and reaction mechanism for the formation of ternary carbide, Co_6W_6C, in which the powder mixtures of Co/W/C with different molar ratios were mechanically activated by grinding and subsequently heated at temperatures ranging from 800 to 1100 °C.

2. Experimental procedures

The procedures of mechanical activation of the metal–graphite powder mixtures have been described in

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* Corresponding author. Tel./fax: +81-11-706-6578.
E-mail address: tsuchida@eng.hokudai.ac.jp (T. Tsuchida).

PII: S0955-2219(02)00016-X

detail in previous papers.[5,6] Co and W metals (each particle size below 45 and 150 μm, 99.9% purity, Kojundo Chemical Laboratory) and natural graphite (mean flake size 5 μm, 97% carbon, 2% ash and 1% volatile component, Nippon Kokuen Industry) were used as starting materials. These powders were mixed in various molar ratios of Co/W/C = 6/6/1, 4/4/1, 7/7/2, 3/3/1, 2/2/1, 1/1/1, 1/1/2 in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany), and then ground for 1–6 h. The grinding was interrupted every 15 min and a sample was scraped from the balls and the side walls of the jar and then reloaded to continue grinding. A 25 ml jar and seven balls of tungsten carbide (12 mm diameter) were used for the grinding. The weight ratios of powder to balls were 4:9–2:5 for the samples of Co/W/C = 6/6/1–1/1/2. The ground sample was taken out of the jar, and then heated up to 800–1100 °C at a heating rate of 10 °C min^{-1} in a flowing argon of 86 ml min^{-1} in a TG–DTA-2000 apparatus (Mac Science). Powder X-ray diffraction (XRD) patterns were obtained with a RINT-1000 (Rigaku Denki) using Fe-filtered CoK_α radiation. Optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out with a VH-7000 digital HD microscope (Keyence) and a JSM-5410-SEM–EPMA–WDX combined microanalyzer (Jeol). Transmission electron microscopy (TEM) was carried out with a JEM-2000ES electron microscopy (Jeol). Elemental analysis was also carried out using energy dispersive X-ray spectroscopy (623M-3SST-EDX, NORAN) with 5 nm beam diameter. Prior to microscopic observation, the powder sample was dispersed in ethanol by ultrasonication, and was placed as a drop on a glass plate or a brass stub or a copper mesh and then dried.

3. Results and discussion

Figure 1 shows the XRD patterns of the samples of Co/W/C = 7/7/2 which were ground for 0 (unground) ~6 h. As can be seen from the XRD pattern of the unground sample, Co consisted of both the cubic and hexagonal phases initially. Then it transformed from cubic structure to hexagonal structure by grinding, the latter peak apparently decreased in intensity and broadened with increasing grinding time. The 002 peak of graphite disappeared after the grinding of 1 h. These results indicate the size diminution and the increase in the lattice strain of Co metal particles, and the disappearance of the stacking order of the graphite layers and the formation of disordered carbon with finely divided grains.[6] In contrast to this, the 110 and 200 peaks of W remarkably increased in intensity with grinding time. Particularly the 200 peak reached to a maximum after the grinding of 3 h and then decreased. It seems to correspond to the fact that the cleavage plane of W is {100} planes. Similar behavior was also observed in the XRD patterns for the ground samples with other molar ratios.

The ground samples were heated up to 1100 °C in a TG–DTA apparatus in flowing argon. On heating the 0, 1, 4 and 6 h-ground samples of Co/W/C = 7/7/2, the weight losses of 0.2, 0.8, 2.9 and 3.5 wt.%, respectively, were initiated at around 950, 300, 280 and 260 °C in the TG curves. These weight losses result from the oxidation reaction of graphite with a trace amount of oxygen, which remained in a TG–DTA apparatus, nevertheless it was purged with argon before and during heating.[7] In fact, the weight loss of the sample increased with increasing grinding time and began at lower temperature, depending on the reactivity of carbon disordered by mechanical activation. In addition, it was also observed that the surface of the sample was covered with a blue product layer of $CoWO_4$ after heating in a TG–DTA apparatus. Therefore, this surface oxide was removed prior to all the XRD measurements.

Fig. 2 shows the XRD patterns for the Co/W/C = 7/7/2 samples, which were ground for 6 h and then heated at 800–1100 °C for 30 min in TG–DTA runs. The ternary carbide Co_6W_6C appeared at 800 °C together with WC, increased with increasing heating temperature. At 1000 °C, different ternary carbides, Co_2W_4C and $Co_3W_9C_4$, also appeared, but disappeared at 1100 °C and the Co_6W_6C phase occurred preferentially with a small amount of Co_7W_6. From the SEM microphotographs of Co_6W_6C formed at 1100 °C, the grains, having a polydispersed size distribution from a few μm to 20 μm, were observed. So far, it is reported by Pollock and Stadelmaier[8] that Co_6W_6C and Co_2W_4C were synthesized by heating of the mixture of Co/W/C with comparable mixing ratio at 1100 °C for 75 h and then 1000 °C for 200 h. Compared to this, it seems to be noteworthy that ternary carbide Co_6W_6C began to form at a temperature as low as 800 °C by the present process combined with mechanical activation and subsequent heat treatment.

The XRD results for the Co/W/C samples with various molar ratios, which were ground for 1–4 h and then heated at 1100 °C for 30 min, are summarized in Table 1. The unground samples, although are not shown in Table 1, did not form any carbides on heating at 1100 °C, except that a trace of WC and $Co_3W_9C_4$ was detected for the samples of Co/W/C = 4/4/1 and 7/7/2. From Table 1 it can be seen that in most of the 1–3 h-ground samples WC exclusively formed accompanying three kinds of ternary carbides, Co_6W_6C, Co_2W_4C and $Co_3W_9C_4$, and Co_7W_6, its amount depending on the sample. In contrast, in only the sample of Co/W/C = 7/7/2, Co_6W_6C formed preferentially, and was obtained as a single phase in the sample ground for 4 h. Interestingly, in the sample ground for 6 h, as can be seen in Fig. 2, Co_6W_6C formed not as a single phase, but together with Co_7W_6. As already described, this sample

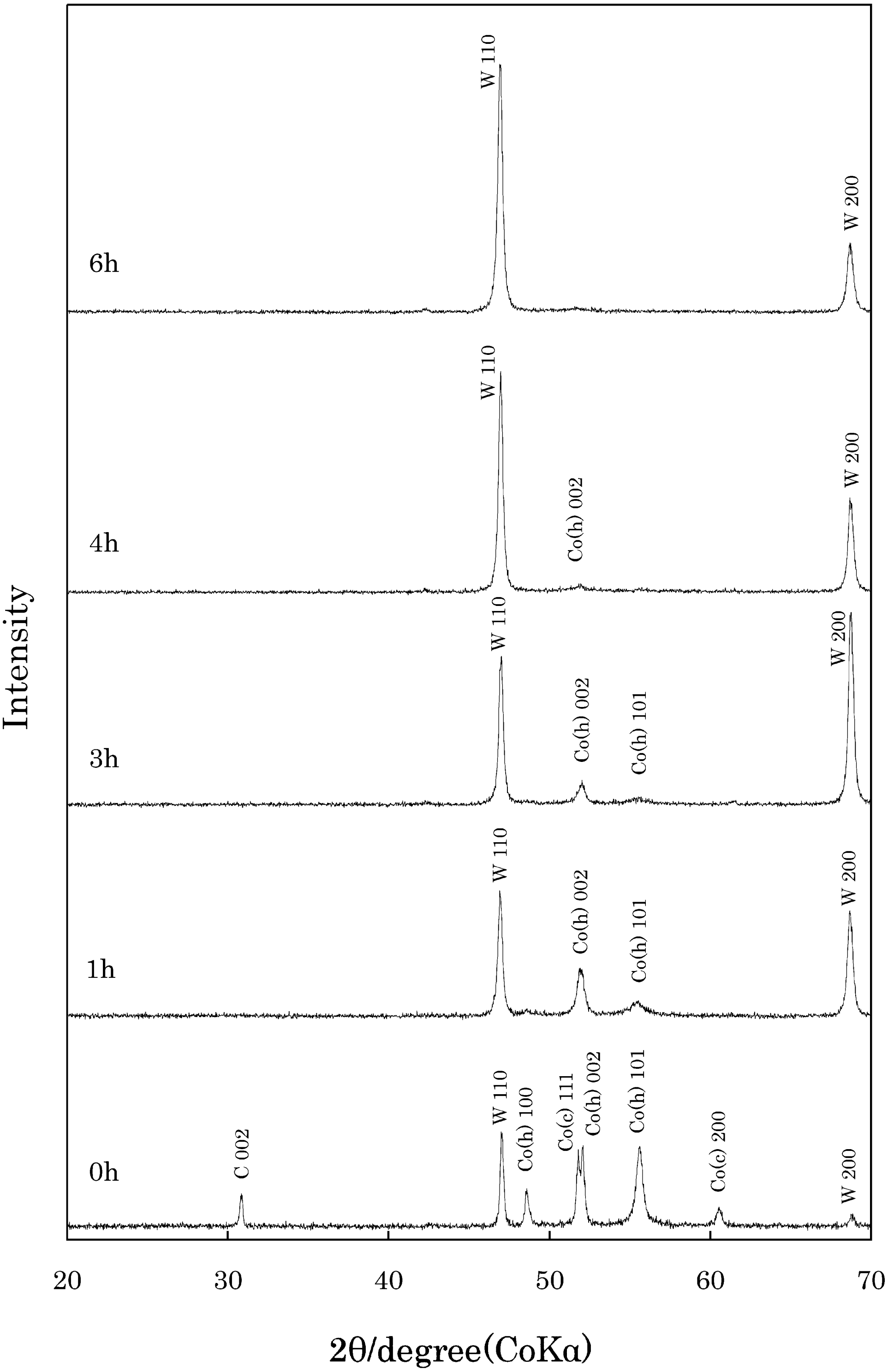

Fig. 1. The XRD patterns of the samples of Co/W/C = 7/7/2 which were ground for 0–6 h.

showed the weight loss of 3.5 wt.% due to the oxidation of carbon above 260 °C in TG curve. Therefore, a decrease in carbon content in the sample seems to have led a suitable condition to the formation of Co_7W_6. In the carbon rich sample of Co/W/C = 1/1/2, WC and $Co_3W_9C_4$ formed. From the dependence of the product phase on the mixing ratio and grinding time of the Co/W/C powder, it can be considered that the optimal mixing ratio, the mixing homogeneity and the activated state of the Co, W and C particles finely divided by grinding is needed to form Co_6W_6C, which is further discussed below.

From the optical microphotographs of the unground sample of Co/W/C = 7/7/2, it was observed that there is

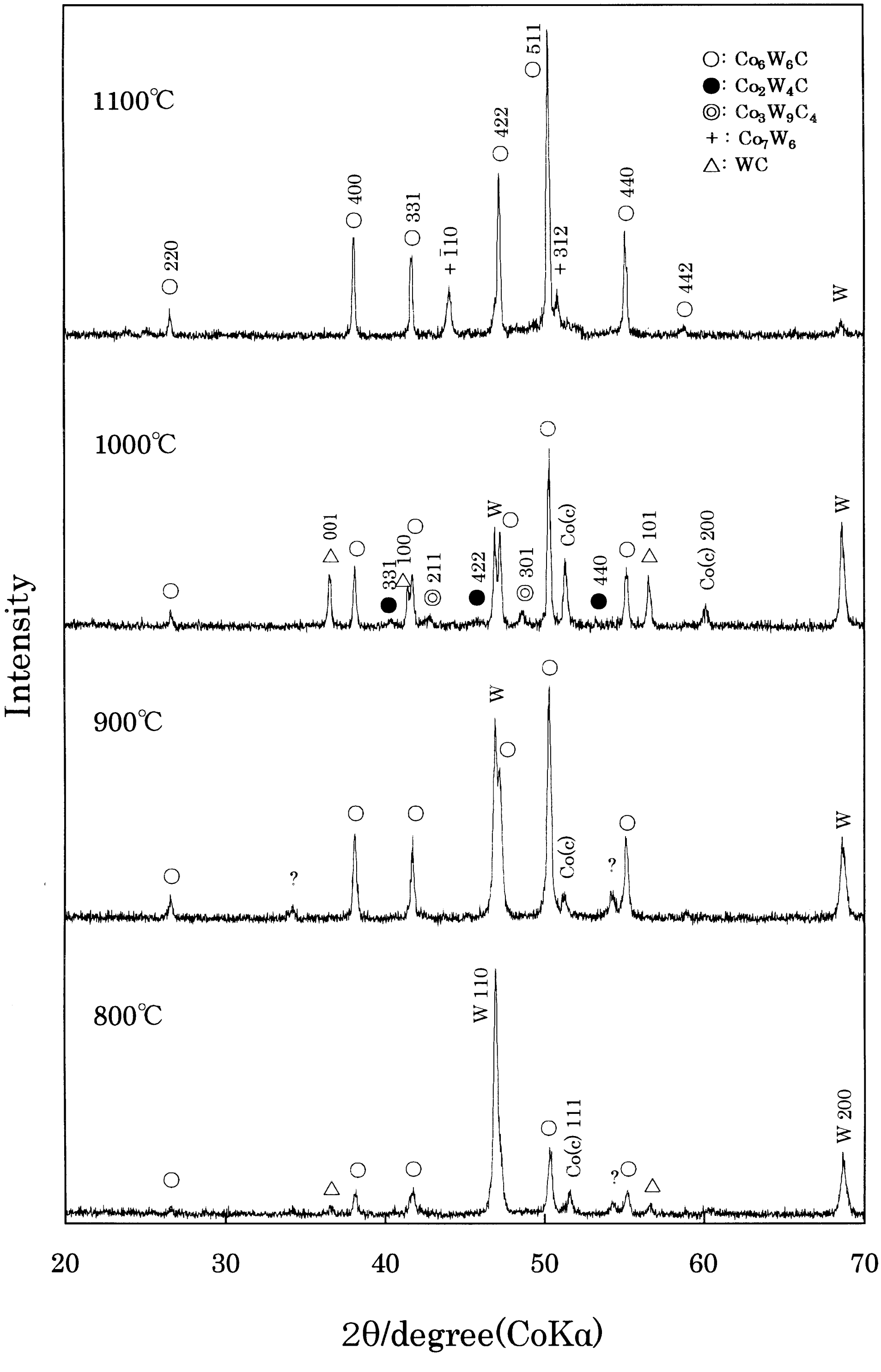

Fig. 2. The XRD patterns of the samples of Co/W/C = 7/7/2, which were ground for 6 h and then heated at 800–1100 °C for 30 min, respectively.

neither a homogeneous distribution nor an intimate contact among the component particles of Co, W and C. However, after grinding of 4 h, the particle sizes of the three components decreased remarkably and their mixing homogeneity was much improved. The SEM–EPMA observation shown in Fig. 3 is available to investigate the mixing homogeneity of the ground components. In the sample of Co/W/C = 7/7/2 ground for 1 h [Fig. 3(a)], a homogeneous distribution among the particles of Co, W and C components can not be seen, which would provide rather favorable circumstances for the formation of cobalt and tungsten carbides, respectively. In fact, the

Table 1
The XRD results of the product phases obtained in the Co/W/C samples with different molar ratios, which were ground for 1–4 h and then heated at 1100 °C for 30 min

Co/W/C	1 h-Grinding	2 h-Grinding	3 h-Grinding	4 h-Grinding
6/6/1	$WC \gg Co_7W_6 > Co_6W_6C > Co_3W_9C_4, Co_2W_4C$	$WC, Co_6W_6C > Co_3W_9C_4, Co_7W_6 > Co_2W_4C$	$WC > Co_6W_6C, Co_3W_9C_4$ $Co_2W_4C > Co_7W_6$	
4/4/1	$WC > Co_6W_6C > Co_3W_9C_4, Co_2W_4C$	$WC > Co_6W_6C > Co_3W_9C_4, Co_2W_4C$	$WC, Co_6W_6C > Co_3W_9C_4, Co_2W_4C, Co_7W_6$	
7/7/2	$WC, Co_6W_6C > Co_3W_9C_4, Co_2W_4C$	$Co_6W_6C > WC > Co_3W_9C_4, Co_2W_4C$	$Co_6W_6C \gg WC > Co_3W_9C_4, Co_2W_4C$	Co_6W_6C
3/3/1	$WC > Co_7W_6 > Co_6W_6C > Co_2W_4C$	$WC > Co_6W_6C > Co_7W_6 > Co_2W_4C$	$WC > Co_6W_6C > Co_7W_6, Co_2W_4C$	
2/2/1	$WC \gg Co_6W_6C$	$WC \gg Co_6W_6C$	$WC \gg Co_6W_6C, Co_7W_6$	
1/1/1	$WC \gg Co_6W_6C, Co_7W_6$	$WC > Co_7W_6 \gg Co_6W_6C$	$WC > Co_7W_6 \gg Co_6W_6C$	$WC > Co_7W_6 \gg Co_6W_6C$
1/1/2	$Co_3W_9C_4 > WC$	$WC > Co_3W_9C_4$	$WC > Co_3W_9C_4$	

free energy of the formation of WC (in unit per one mole of W, according to the reaction $W + C = WC$) was calculated to be -38 to -34 kJ mol^{-1} in the temperature range of 100 to 1100 °C.[9] According to the phase diagram for the Co–C system,[10] the α-Co solid solution containing $\leqslant 4.2$ at.% C form and decompose into, ε-Co (~ 0 at.% C) and graphite at 422 °C. Consequently, a preferential formation of WC can be suggested under the present experimental conditions. On the other hand, in the 4 h-ground sample in Fig. 3(b), a good homogeneous distribution among the finely divided grains of Co, W and C components is observed. Therefore, such a creation of homogeneous distribution and intimate contact among these fine particles is considered to be essential to the formation of ternary carbide, Co_6W_6C. The values of the free energy of the formation of Co_6W_6C, Co_2W_4C and $Co_3W_9C_4$ have not been reported yet, but they may be comparable to that of WC. Furthermore, it is well known that mechanical activation creates numerous structural defects, which enhance the solid-state reaction between the components of the initial powder mixture and lead to the formation of metastable or amorphous compounds. If an amorphous Co_6W_6C phase, though it can not be detected by X-ray, was formed during the mechanical activation, it might act as a preferred nucleation site during recrystallization by heat treatment. This assumption may be verified by transmission electron microscopic (TEM) observation.

Fig. 4 shows the TEM microphotographs of the Co/W/C = 7/7/2 sample ground for 4 h. The results of elemental analysis by EDX from the eight spots shown in the photographs are given in Table 2. From Fig. 4 and Table 2, some features can be pointed out as follows. In the particles shown by 2, 3 and 4, the elements of $\geqslant 90\%$ C, $\leqslant 10\%$ Co and $\leqslant 12\%$ W were detected. Carbon also existed preferentially at the peripheral region of the particles (the light grey area in the figure), where the aggregate of extremely small, thin particles can be seen. In these particles, the breaking down of graphite grains into nanocrystallites was often observed and the introduction of lattice defects, such as shearing and turbostratic stackings of 002 planes into the crystallites, can be sufficiently expected. On the other hand, in the dark, large particles ($\geqslant 200$ nm) numbered 5, 6 and 8, both elements of Co and W are mainly present, but the atomic ratios between them are not constant, maybe indicating that the formation of Co–W alloys by mechanical activation is uncertain. Consequently, it seems to be reasonable to assume that the formation of amorphous Co_6W_6C phase occurs initially in the former aggregates as a mechanochemical reaction, and it acts as a preferred nucleation site during recrystallization by subsequent heat treatment, and then the reaction propagates progressively into the latter aggregates containing larger particles. Because, it is well known that the reactivity of the nanosized particles, such as disordered carbon formed by mechanical grinding, is extremely high.

4. Summary

In order to discuss the optimal conditions and reaction mechanism for the formation of the ternary carbide, Co_6W_6C, by mechanical activation assisted solid-state reaction, the powder mixtures of Co/W/C = 6/6/1–1/1/2 were ground for 1–6 h in a planetary ball mill and were subsequently heated at 800–1100 °C. A single phase of Co_6W_6C formed from the powder mixtures of Co/W/

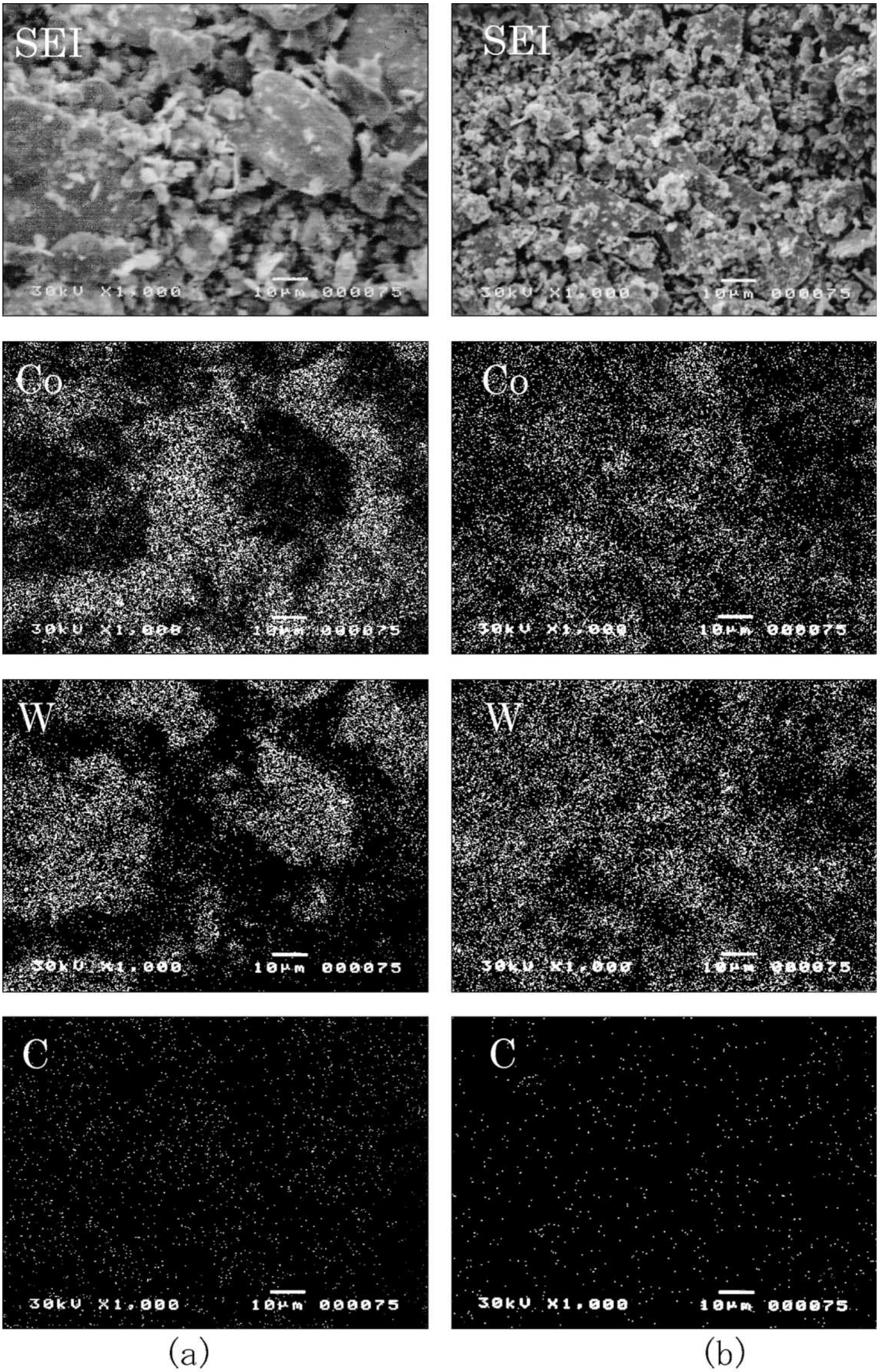

Fig. 3. The seconday electron images (SEI) and associated elemental maps of the samples of Co/W/C = 7/7/2 ground for (a) 1 h and (b) 4 h.

C = 7/7/2 ground for 4 h, whereas WC formed mainly from the other powder mixtures ground for 1–3 h. From the results obtained, it was found that the formation of Co_6W_6C strongly depends on the mixing homogeneity, the intimate contact and the activated state of the particles of Co, W and C components finely ground by ball milling.

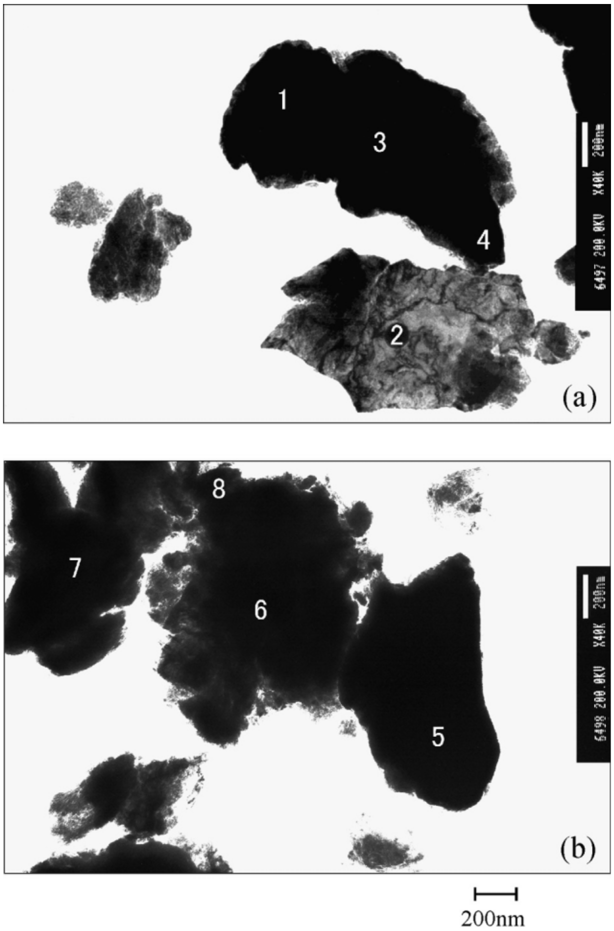

Fig. 4. The TEM microphotographs of the sample of Co/W/C = 7/7/2 which was ground for 4 h. The numbers in the photographs indicate the spots subjected to elemental analysis by EDX. The results are given in Table 2. The scale bar is 200 nm.

Table 2
The results of elemental analysis (at.%) by EDX from the eight spots shown in Fig. 4

	1	2	3	4	5	6	7	8
C	39.2	96.0	85.1	87.3	0.0	7.7	20.5	38.5
Co	5.7	0.2	9.6	1.1	31.3	62.8	73.1	40.7
W	55.1	3.8	5.3	11.6	68.7	29.5	6.4	20.8

Acknowledgements

The authors are grateful to Mr. K. Sugawara for his useful discussion and assistance in measuring the TEM.

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