

On the disappearance of Mo₂C during low-temperature sintering of Ti(C,N)-Mo₂C-Ni cermets

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In order to seek a better understanding of the mechanisms leading to the disappearance of Mo₂C during the sintering of Ti(C,N)-based cermets at or below 1200 °C, the sintering reactions occurring in ternary phase mixtures Ti(C,N)-Mo₂C-Ni and their associated binary counterparts Ni-Mo₂C, Ti(C,N)-Mo₂C and Ni-Ti(C,N) at 1200 °C were investigated by X-ray diffraction analysis. It was shown that the decrease and disappearance of Mo₂C during the sintering of Ti(C,N)-Mo₂C-Ni cermet composites at or below 1200 °C are dictated by the relative amount of Mo₂C to Ni, through enhanced dissolution of Mo₂C in Ni by the presence of Ti(C,N). The reprecipitation of (Ti,Mo)(C,N) onto Ti(C,N) grains does not occur to a large extent under these conditions. On average, when the ratio of Mo₂C to Ni is below or around 0.3, all of the Mo₂C phases present in the Ti(C,N)-Mo₂C-Ni alloys can be dissolved in Ni after 1 h at 1200 °C. However, when the ratio is well over 0.3, only partial dissolution of Mo₂C can be observed even when the alloys are sintered at 1200 °C for 10 h. Both Mo₂C and Ti(C,N) can be dissolved in Ni in the solid state, but the dissolution of Mo₂C in Ni in the Ti(C,N)-Mo₂C-Ni alloys is enhanced by the presence of Ti(C,N), hence N, compared to the dissolution of Mo₂C in the Ni-Mo₂C alloys. Negligible phase interactions are detected between Ti(C,N) and Mo₂C when sintered at 1200 °C for up to 5 h, either with or without Ni presence. © 1999 Kluwer Academic Publishers

1. Introduction

TiC- and Ti(C,N)-based cermets belong to a class of hard, wear-resistant materials produced by sintering pressed powder mixtures at a temperature where the metal binder phase is present as a liquid. They are widely used in the metal industry as cutting tools. With the growing use of parts cast or forged to near-net shape, which has been shifting the machining tasks from heavy roughing to semifinishing/finishing in a single set-up, it is expected that the use of cermets will further be increased [1]. This is because TiC- and Ti(C,N)-based cermets possess superior wear resistance and chemical stability at high cutting speeds, hence the ability to produce finishes fine enough to eliminate final grinding.

The sintering of Ti(C,N)-Mo₂C-Ni and TiC-Mo₂C-Ni cermet composites generally involves two different stages, namely the solid-state and liquid-phase sintering. In most cases, the latter stage has been the focus of concern, because major sintering reactions and densification primarily develop in this stage. As is known, Mo₂C or Mo was introduced into TiC-based cermets initially from the finding that Mo₂C or Mo enhances the wetting of TiC to Ni by forming a (Ti,Mo)C shell outside the TiC particles [2]. Later, it was further noticed that the addition of Mo₂C or Mo could also

bring about refinement of the TiC or Ti(C,N) grain size [3–6], and significantly improve the deformation resistance of TiC-based cermets [6]. To this end, the ratio of Mo/(Mo+Ni) is generally controlled in the range of 0.1–0.2 [7]. So in various commercial TiC- and Ti(C,N)-based cermets, a certain amount of Mo₂C, usually in the range of 10 to 25% (wt%), is added to the powder mixtures. After sintering, Mo₂C disappears with Mo existing in the binder Ni and as a mixed carbide (Ti,Mo)C or carbonitride (Ti,Mo)(C,N) rim around the TiC or Ti(C,N) particles. The disappearance of Mo₂C and the related sintering reactions are thus crucial to understanding the sintering of these materials. Previously it was believed that the disappearance of Mo₂C occurred during the liquid phase sintering stage. Suzuki *et al.* [6] proposed that Mo₂C and TiC dissolved in liquid Ni followed by reprecipitation of (Ti,Mo)C or (Ti,Mo)(C,N) onto large remnant TiC or Ti(C,N) particles. On the other hand, Moskowitz and Plummer [8] reported that diffusion of Mo from the liquid Ni into TiC occurred during sintering to form the characteristic core-rim structure.

Recently, it has been shown that during the sintering of TiC- and Ti(C,N)-based cermets, the Mo₂C phase disappeared completely at or below 1200 °C [9–12],

well before any liquid Ni was formed. Several different mechanisms have been proposed accordingly. Nishigaki and Doi [9, 13] proposed that Mo_2C merged into the lattice of TiC to form TiC- Mo_2C solid solutions at temperatures above 1000 °C. Hachisuka [10] pointed out that Mo_2C dissolved in TiC at temperatures below 1200 °C in the form of $\zeta\text{-MoC}$, which then led to the formation of (Ti,Mo)C. Andren *et al.* [11] concluded that Mo_2C dissolved in Ni below 1200 °C and then re-precipitated onto TiC particles in the form of (Ti,Mo)C, forming a TiC-(Ti,Mo)C core-rim structure. After liquid phase sintering, they reported that this (Ti,Mo)C rim phase was still present in the microstructure, which they referred to as an “inner rim” structure in order to distinguish it from the rim phase formed during liquid phase sintering. More recently, Yang and Lee [12] reported that the disappearance of Mo_2C below 1200 °C was a result of Ti diffusing from Ti(C,N) into the neighbouring hexagonal Mo_2C phases, which then transformed into Mo-rich cubic (Mo,Ti)(C,N).

This work reports our experimental results on various phenomena occurring during low temperature sintering of Ti(C,N)- Mo_2C -Ni cermet composites and their associated binary counterparts Ni- Mo_2C , Ti(C,N)- Mo_2C and Ni-Ti(C,N). The emphasis is placed on the mechanisms leading to the disappearance of the Mo_2C phase.

2. Experimental details

As-received pure $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ (particle size, 1–5 μm), Mo_2C (1.5–2.5 μm) and Ni (2.2–3 μm) powders supplied by H. C. Starck GmbH & Co. KG, Germany, were used in this work. All of the phase mixtures, i.e. Ni- Mo_2C , Ti(C,N)- Mo_2C , Ni-Ti(C,N) and TiCN- Mo_2C -Ni, of desired compositions were first blended in a rotating blender at 60 rpm for 24 h. Then, each mixture was pressed into rectangular briquettes (dimensions, 50.8 × 6.25 × 4.0 mm) in a steel mold under a pressure of 154 MPa. Sintering was carried out

in a vacuum of 10^{-4} mbar or better. Unless otherwise stated, the sintering temperature adopted was 1200 °C with a heating rate of 10 °C/min. After sintering, the briquettes were cooled in the furnace to room temperature with an average cooling rate of 7 °C/min from 1200 to 600 °C and 2 °C/min thereafter. In order to eliminate the surface contamination effect possibly encountered during sintering, a layer 0.3–0.4 mm in thickness was polished off the surfaces of all sintered briquettes.

The X-ray diffraction was conducted on a Japan Shimadzu XRD-6000 X-Ray Diffractometer. The quantitative analysis of the phase concentration of interest (C_0) in each phase mixture was based on the spiking method [14], where C_0 is given by

$$C_0 = \frac{I_1 C_1}{I_2 - I_1} \quad (1)$$

in which I_1 is the intensity of a diffraction line from the sample, I_2 the intensity of the same line after the sample has been spiked, and C_1 the difference in the phase concentration before and after the sample is spiked. Equation 1 assumes a linear change in intensity with concentration, namely the absorption coefficient of the spiked material is the same as that of the sample.

3. Results

3.1. Ternary Ti(C,N)- Mo_2C -Ni alloys

Three compositions of Ti(C,N)- Mo_2C -Ni phase mixtures were designed to study the reported disappearance phenomena of Mo_2C at or below 1200 °C during the sintering of these alloys: (a) $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -10Ni, (b) $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -30Ni, and (c) $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -10 Mo_2C -30Ni (wt %). Figs 1–3 demonstrate the XRD patterns of the three alloys after different lengths of time at 1200 °C, respectively. The change in the Mo_2C content in each alloy is plotted in Fig. 4. From Figs 1 and 2 it can be found that, for alloys containing 15%

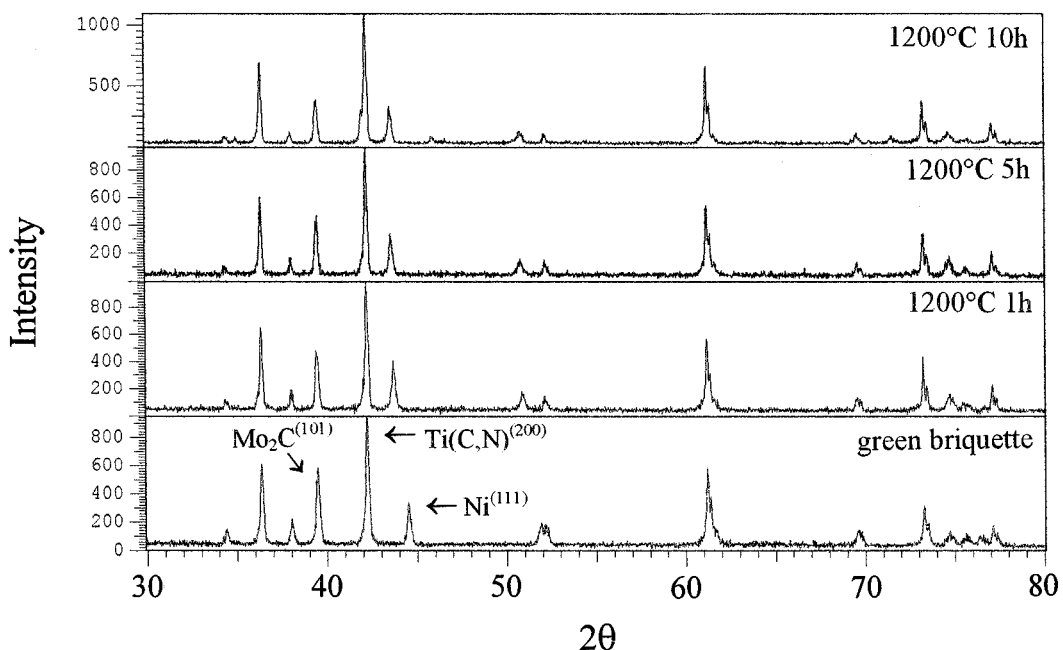


Figure 1 XRD patterns for the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -10Ni (wt %) or $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -9.5 Mo_2C -6.5Ni alloy (vol %) sintered at 1200 °C for different lengths of time.

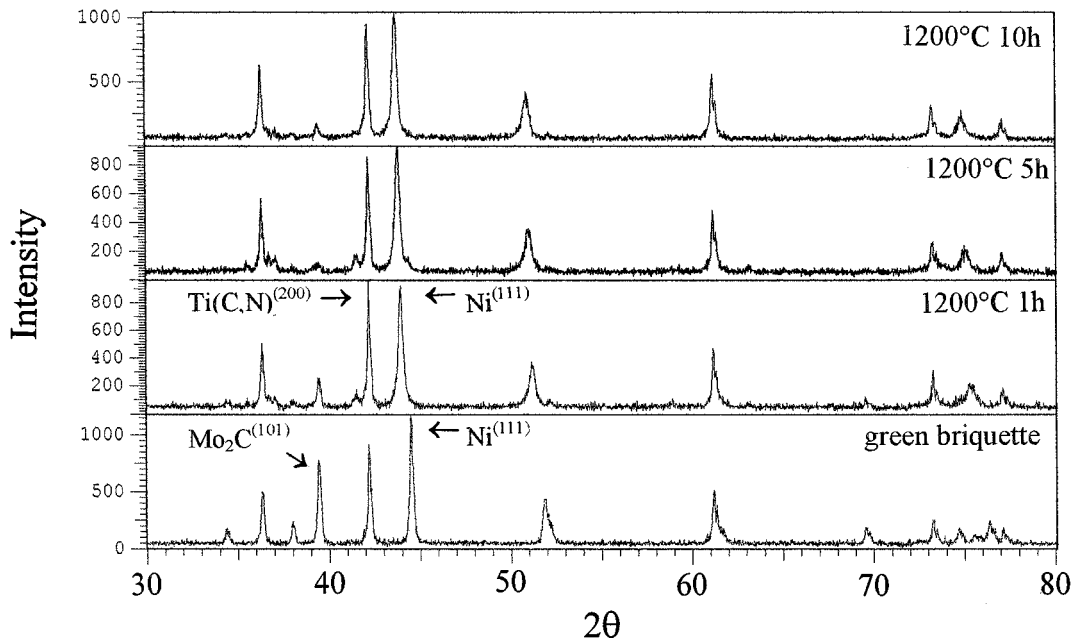


Figure 2 XRD patterns for the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -30Ni (wt %) or $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -10.5 Mo_2C -21.5Ni alloy (vol %) sintered at 1200 °C for different lengths of time.

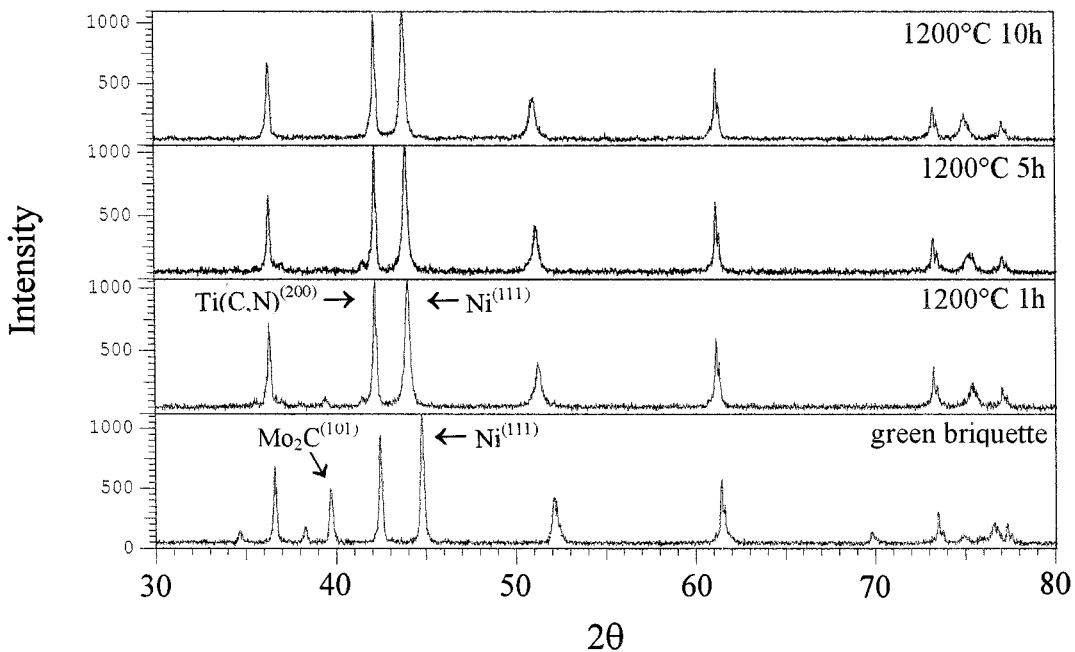


Figure 3 XRD patterns for the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -10 Mo_2C -30Ni (wt %) or $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -7 Mo_2C -21Ni alloy (vol %) sintered at 1200 °C for different lengths of time.

of Mo_2C and 30% or less of Ni, Mo_2C does not disappear as a phase component at or below 1200 °C, even when the alloys are sintered at 1200 °C for up to 10 h. However, on the other hand, for the alloy with only 10% of Mo_2C and 30% of Ni, a substantial amount of the Mo_2C phase disappeared after 1 h at 1200 °C, and complete disappearance of the Mo_2C phase was observed after 10 h at temperature (see Fig. 3). The above results suggest that the relative amount of Mo_2C to Ni in the $\text{Ti}(\text{C},\text{N})$ - Mo_2C -Ni alloy plays a significant role in the stability of the Mo_2C phase during the sintering of these materials. For example, with 30% of Ni present in the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -30Ni mixture, the Mo_2C content dropped abruptly from 15 to 5.54%

after 1 h at 1200 °C (see curve 2 in Fig. 4). By contrast, the Mo_2C content in the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -10Ni alloy declined only from 15 to 11.94% in the first hour at 1200 °C and stayed at about 9.16% even after 10 h at temperature (see curve 1 in Fig. 4). It can be deduced that if the Mo_2C content in the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -30Ni and $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -15 Mo_2C -10Ni alloys is less than 9.46%, i.e. (15–5.54)% and 3.06%, i.e. (15–11.94)% respectively, or the Ni phase is more than 30%, most or even all of the Mo_2C phases will disappear in both alloys after 1 h at 1200 °C as observed in the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ -10 Mo_2C -30Ni alloy (see Figs 3 and 4). The relative amount of Mo_2C to Ni is therefore an important parameter for the decrease and disappearance

of Mo_2C during the sintering of $\text{Ti}(\text{C,N})$ -based cermets and will be discussed later in detail.

To understand the possible effect of the various components on the disappearance of Mo_2C during the sintering of $\text{Ti}(\text{C,N})$ - Mo_2C -Ni alloys, the sintering reactions occurring in relevant binary phase mixtures are studied. The results can be summarised below.

3.2. Component binary alloys

3.2.1. $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ phase mixture

A $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ phase mixture was prepared in this study. As shown in Fig. 5, the relative intensity of the XRD peak for $\text{Mo}_2\text{C}^{(101)}$ (the strongest XRD peak

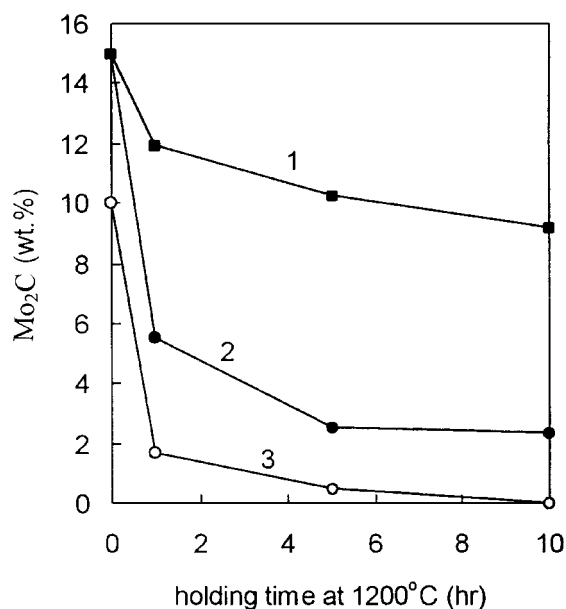


Figure 4 Change in the amount of Mo_2C in different $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - Mo_2C -Ni alloys with sintering time at 1200°C : curve 1, $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ - 10Ni ; curve 2, $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ - 30Ni ; curve 3, $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $10\text{Mo}_2\text{C}$ - 30Ni (wt %).

for Mo_2C) exhibited little variation in this mixture when sintered at 1200°C for up to 5 h. It implies that no appreciable reduction has occurred in the amount of Mo_2C during the sintering process. The position of the XRD peak for $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ also remained almost unchanged. For instance, the 2θ value for the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})^{(200)}$ peak (the strongest XRD peak for $\text{Ti}(\text{C,N})$) was 42.0228° in the green briquette; after 5 h at 1200°C , it was diffracted to be 42.0223° . Therefore, one may conclude that in the absence of Ni, no appreciable change occurs in the phase composition of the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ alloy during sintering at 1200°C . Nevertheless, it should be pointed out that the above result should not be interpreted as the two phases being in thermodynamic equilibrium at 1200°C . It is possible that there is a driving force to form $(\text{Ti},\text{Mo})(\text{C,N})$ but the kinetics is much too slow at 1200°C if Ni is not present as a diffusion path.

3.2.2. Ni- $24\text{Mo}_2\text{C}$ phase mixture

In this experiment, a Ni- $24\text{Mo}_2\text{C}$ phase mixture was prepared. This mixture is equivalent to a Ni- 22.5Mo alloy with the Mo content just below the room-temperature solubility of Mo in Ni, i.e. about 23 wt % as judged from the Ni-Mo phase diagram [15]. Fig. 6 shows the XRD patterns of the mixture after different lengths of time at 1200°C . Note that the relative intensity of the XRD peak for $\text{Mo}_2\text{C}^{(110)}$ decreased sharply after 1 h at 1200°C but changed only little on further sintering. The position of the XRD peak for Ni showed a similar trend of change. In the as-compacted state, the 2θ value for the $\text{Ni}^{(111)}$ peak (the strongest XRD peak for Ni) was diffracted to be 44.4608° . After 1 h at 1200°C , it dropped to 44.0052° . Then, it changed only slightly, being equal to 43.9751° after 5 h at 1200°C .

Fig. 7 depicts the change in the Mo_2C content in the Ni- $24\text{Mo}_2\text{C}$ alloy with sintering time at 1200°C . The amount of Mo_2C decreased fairly abruptly from 24 to 13.46% after 1 h at 1200°C , but much slowly

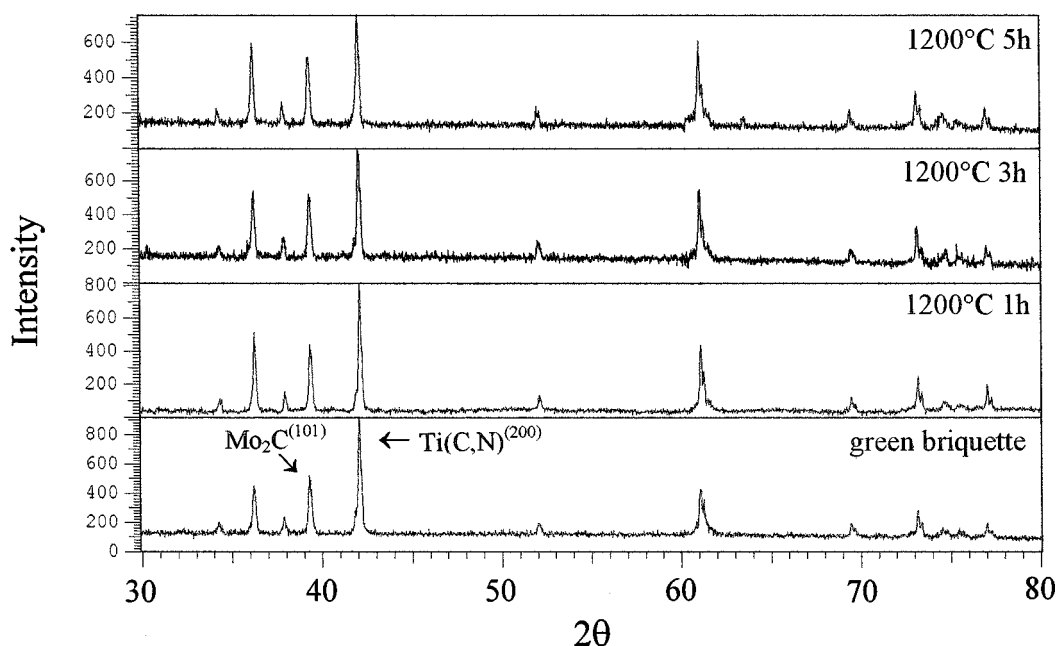


Figure 5 XRD patterns for the $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $15\text{Mo}_2\text{C}$ (wt %) or $\text{Ti}(\text{C}_{0.5},\text{N}_{0.5})$ - $10\text{Mo}_2\text{C}$ alloy (vol %) sintered at 1200°C for different lengths of time.

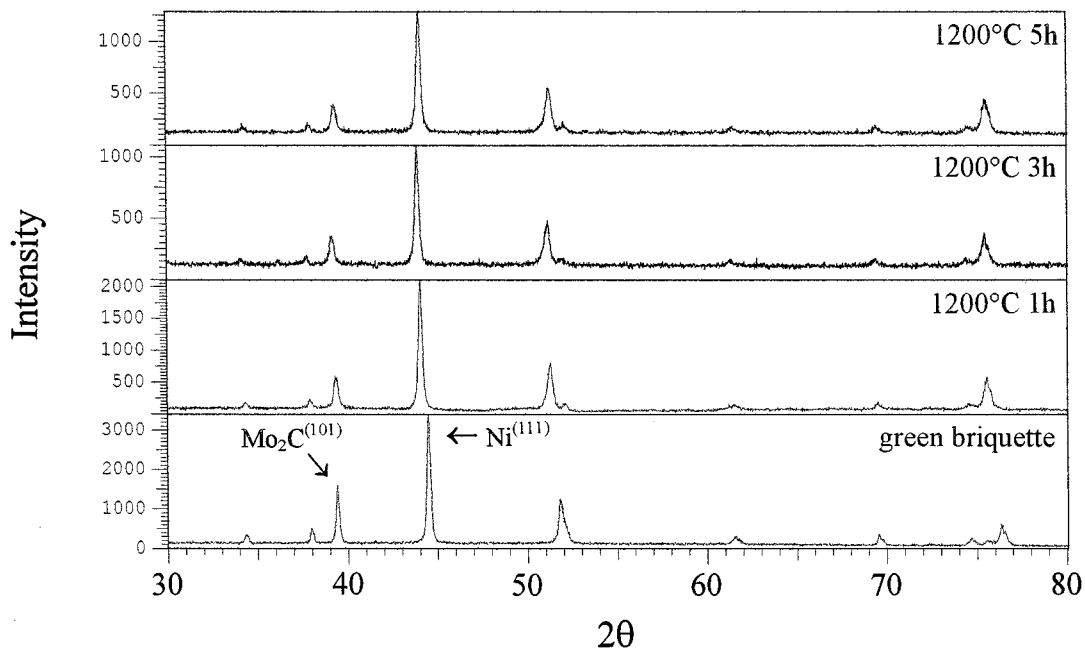


Figure 6 XRD patterns for the Ni-24Mo₂C (wt %) or Ni-15Mo₂C alloy (vol %) sintered at 1200 °C for different lengths of time.

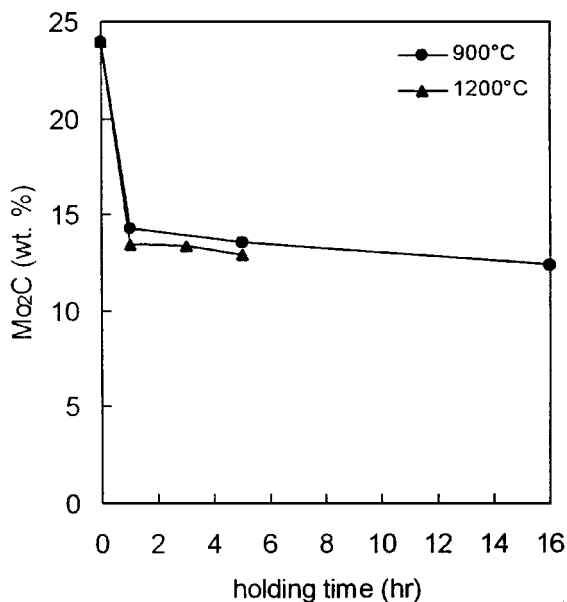


Figure 7 Change in the amount of Mo₂C in the Ni-24Mo₂C (wt %) alloy with sintering time.

thereafter and registered a value of 12.88% after 5 h at temperature. Since no other phases were detected by the XRD except for Ni and Mo₂C (see Fig. 6), the decline in the Mo₂C content in this mixture can be completely attributed to the dissolution of Mo₂C in Ni. Corresponding to the reduction in the amount of Mo₂C shown in Fig. 7, there is only about 10.35 wt % of Mo present in Ni after 5 h at 1200 °C. This figure is much lower than the room-temperature solubility of Mo in Ni (i.e. 23 wt %), let alone the solubility at 1200 °C (i.e. 37 wt %). One possible explanation for the above is that the solubility of Mo in Ni in the Ni-Mo₂C system is determined by the equilibrium reaction $2[\text{Mo}]^{\text{Ni}} + [\text{C}]^{\text{Ni}} \rightleftharpoons \text{Mo}_2\text{C}$ in the presence of Ni.

Also shown in Fig. 7 is the change in the amount of Mo₂C with sintering time at 900 °C. It is interest-

ing to note that the amount of Mo₂C dissolved in Ni at 900 °C and 1200 °C are comparable. This indicates that the dissolution of Mo₂C in Ni reached about saturation after 1 h at 900 °C. This is consistent with earlier observations that the disappearance of Mo₂C during the sintering of the TiC- and Ti(C,N)-based cermets began to develop even at 800 or 900 °C [9–12].

3.2.3. Ni-8.4Ti(C_{0.5},N_{0.5}) phase mixture

A Ni-8.4Ti(C_{0.5},N_{0.5}) phase mixture was prepared in this study. The Ti content in this mixture, i.e. 6.58 wt %, equals the solubility of Ti in Ni at 600 °C by the Ti-Ni phase diagram [15]. Fig. 8 shows the XRD patterns of the mixture sintered at 1200 °C for different lengths of time, and Fig. 9 the variation in the amount of Ti(C_{0.5},N_{0.5}) with sintering time. Clearly, Ti(C_{0.5},N_{0.5}) can also be dissolved in Ni at or below 1200 °C. After 1 h at 1200 °C, the Ti(C_{0.5},N_{0.5}) content in the Ni-8.4Ti(C_{0.5},N_{0.5}) alloy declined from 8.4 to 4.58% (see Fig. 9). This reduction is however much less than the amount of Mo₂C dissolved in Ni after 1 h at 1200 °C (see Fig. 7). Similar to the case of Mo₂C, increasing the sintering time from 1 to 5 h does not enhance further dissolution of Ti(C_{0.5},N_{0.5}) significantly. Note also that no other phases (e.g. TiNi₃) were found in the specimens sintered except for the original Ni and Ti(C_{0.5},N_{0.5}) (see Fig. 8). The reduction in the Ti(C_{0.5},N_{0.5}) content in the Ni-8.4Ti(C_{0.5},N_{0.5}) phase mixture was thus entirely a result of dissolution.

4. Discussion

Comparing Fig. 7 with Fig. 4 one can find that with 76% of Ni present in the Ni-24Mo₂C alloy, the Mo₂C content showed a decline by 10.54% after 1 h at 1200 °C (see Fig. 7), equivalent to an average reduction of 1.38% of Mo₂C per 10% of Ni present. However, in the ternary phase systems studied, the decline in the

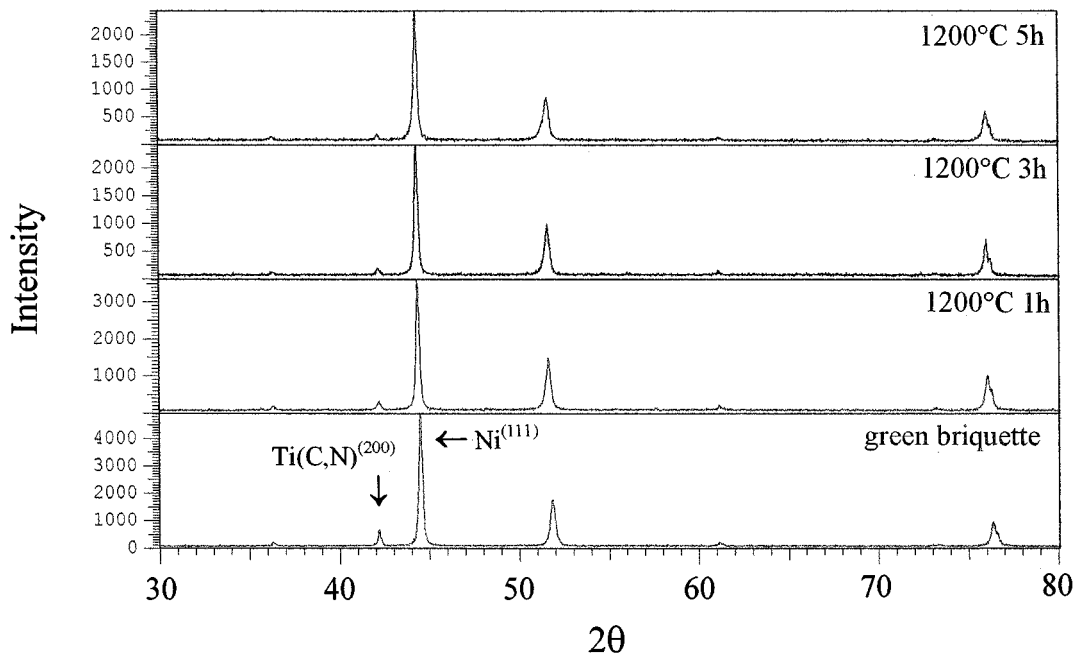


Figure 8 XRD patterns for the Ni-8.4Ti(C_{0.5}N_{0.5}) (wt %) or Ni-13.5Ti(C_{0.5}N_{0.5}) alloy (vol %) sintered at 1200 °C for different lengths of time.

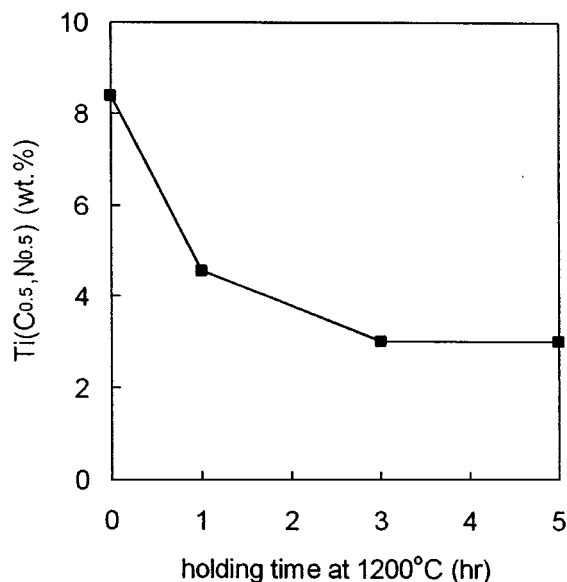
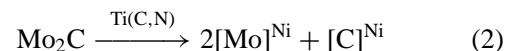


Figure 9 Change in the amount of Ti(C_{0.5}N_{0.5}) in the Ni-8.4Ti(C_{0.5}N_{0.5}) (wt %) alloy with sintering time at 1200 °C.

Mo₂C content was 3.06% in the Ti(C_{0.5}N_{0.5})-15Mo₂C-10Ni alloy, and 9.46 and 8.33% in the Ti(C_{0.5}N_{0.5})-15Mo₂C-30Ni and Ti(C_{0.5}N_{0.5})-10Mo₂C-30Ni alloys, respectively (see Fig. 4). Therefore, on average, for the three Ti(C_{0.5}N_{0.5})-Mo₂C-Ni alloys studied, every 10% of Ni causes about a 3% decline in the Mo₂C content. In other words, all the Mo₂C phases present in the Ti(C_{0.5}N_{0.5})-Mo₂C-Ni alloys can disappear after 1 h at 1200 °C when the ratio of Mo₂C to Ni is less than 0.3 in these alloys. This is much higher than the 1.38% decline for every 10% of Ni in the binary Ni-24Mo₂C alloy studied. As there is negligible phase interaction occurring between Ti(C,N) and Mo₂C at 1200 °C (see Fig. 5), the two most possible mechanisms underlying the difference in the reduction of Mo₂C content then can be attributed to either dissolution and reprecipitation

or enhanced dissolution of Mo₂C in Ni. In the former mechanism, Mo₂C and Ti(C,N) are partially dissolved in Ni, and then reprecipitate onto existing Ti(C,N) particles in the form of (Ti,Mo)(C,N). In the latter, it is possible that the dissolution reaction of Mo₂C in Ni is significantly promoted by the presence of Ti(C,N) [9], namely



Firstly, let us assume that the reduction in the Mo₂C content in the Ti(C_{0.5}N_{0.5})-Mo₂C-Ni alloys is controlled by the dissolution and reprecipitation mechanism. Then, along with the precipitation of (Ti,Mo)(C,N) from Ni onto the Ti(C,N) particles, the Mo content in Ni will continue to decrease. This, in turn, will lead to a continuous but steady dissolution of Mo₂C in Ni, hence the eventual disappearance of the Mo₂C phase. This, however, is not the case observed for the Ti(C_{0.5}N_{0.5})-15Mo₂C-10Ni and Ti(C_{0.5}N_{0.5})-15Mo₂C-30Ni alloys studied (see curves 1 and 2 in Fig. 4). Fig. 10a presents a view of the microstructure of the Ti(C_{0.5}N_{0.5})-15Mo₂C-30Ni alloy after 10 h at 1200 °C, where there still remain 2.31% of Mo₂C phases in this alloy. Note the absence of the characteristic Ti(C,N)-(Ti,Mo)(C,N) core-rim structure. Also, no characteristic core-rim structures were detected for the Ti(C,N)-10Mo₂C-30Ni alloy after 10 h at 1200 °C (Fig. 10b), although in this case all the Mo₂C phases were dissolved after the heat treatment. The above observation is consistent with the XRD results shown in Figs 1–3, which show no obvious broadening of the XRD peaks for Ti(C,N) under all the sintering conditions used (the presence of a (Ti,Mo)(C,N) rim would probably broaden the Ti(C,N) peaks due to the effects of its smaller crystallite sizes, inhomogeneous solid solutions of Mo in Ti(C,N), and dislocations caused at the core-rim interface [14]. Such broadening effect may be

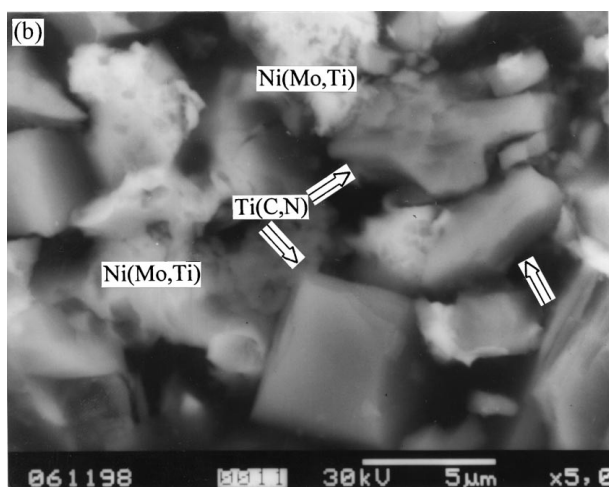
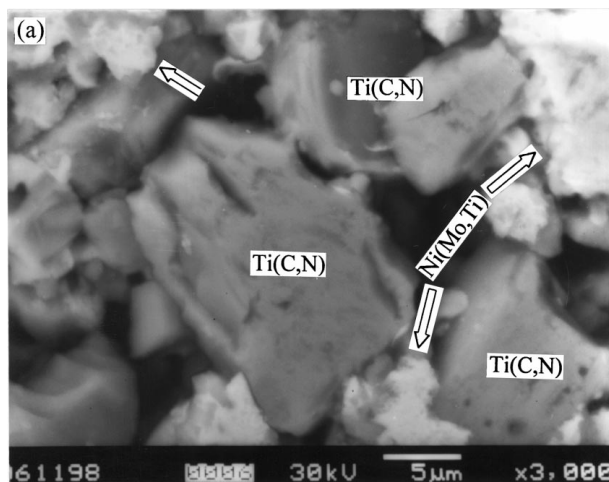


Figure 10 Back-scattered electron micrographs showing the microstructures of (a) the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}15\text{Mo}_2\text{C-}30\text{Ni}$ alloy and (b) the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}10\text{Mo}_2\text{C-}30\text{Ni}$ alloy. Both were sintered at 1200°C for 10 h. In (a) there still remains 2.31% of Mo_2C while in (b) all the Mo_2C phases have been dissolved.

detected when the volume fraction of rim is up to a certain extent in the microstructure).

Now let us assume that the reduction in the Mo_2C content in each alloy shown in Fig. 4 is a result of enhanced dissolution. Note the rate of decline in the amount of Mo_2C at 1200°C in all the three $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-Mo}_2\text{C-Ni}$ alloys studied. It dropped fairly abruptly in the first hour of the sintering but only gradually thereafter. For example, the average rate of decline of Mo_2C content in the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}15\text{Mo}_2\text{C-}30\text{Ni}$ alloy was 9.46%/h for the first hour (see curve 2 in Fig. 4), 0.755%/h between 1 and 5 h, and 0.042%/h only between 5 and 10 h. This trend of decline coincides well with the trend of dissolution for both Mo_2C and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ in the $\text{Ni-}24\text{Mo}_2\text{C}$ and $\text{Ni-}8.4\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ mixtures studied (see Figs 7 and 9).

This is in qualitative agreement with the shift in the $\text{Ni}^{(111)}$ peak in the XRD results as shown in Figs 1–3, 6 and 8. Note that in all these figures, the shift in the $\text{Ni}^{(111)}$ peak is very conspicuous after 1 h at 1200°C but becomes less significant on continued sintering. The shift in the $\text{Ni}^{(111)}$ peak in the XRD spectra is a result of the dissolution of Mo and Ti in Ni, which affects the lattice

parameter of Ni. According to the reduction of Mo_2C shown in Fig. 4, it can be calculated that the Mo content in Ni will be in the range of 20–22.5 wt% after 1 h at 1200°C . This is almost level with the room-temperature solubility of Mo in Ni (i.e. 23 wt%), but still much lower than the solubility of Mo in Ni at 1200°C (i.e. 37 wt%). As shown by a number of investigators, the solubility of Mo in Ni increases rapidly with increasing total N or TiN/Ti(C,N) content in the $\text{TiC-Mo}_2\text{C-Ni}$ alloys [9, 11, 13, 16]. In particular, Nishigaki and Doi [9] reported that the addition of 5% of TiN to the $\text{TiC-Mo}_2\text{C-Ni}$ alloy increased the binder Mo content by a factor of 4. The present results are thus consistent with enhanced dissolution of Mo_2C in Ni being the predominant mechanism responsible for the decrease and disappearance of Mo_2C during the sintering of the $\text{Ti}(\text{C,N})\text{-Mo}_2\text{C-Ni}$ alloys at or below 1200°C .

5. Conclusions

1. Both Mo_2C and $\text{Ti}(\text{C,N})$ can dissolve in Ni in the solid state. The dissolution of Mo_2C and/or $\text{Ti}(\text{C,N})$ in Ni occurs largely in the first hour during sintering at 1200°C . The rate of dissolution decreases abruptly thereafter for both Mo_2C and $\text{Ti}(\text{C,N})$.

2. Negligible phase interactions were detected between $\text{Ti}(\text{C,N})$ and Mo_2C when sintered at 1200°C for up to 5 h, either with or without Ni presence.

3. The dissolution of Mo_2C in Ni is enhanced by the presence of $\text{Ti}(\text{C,N})$, hence N in the $\text{Ti}(\text{C,N})\text{-Mo}_2\text{C-Ni}$ alloys, compared to dissolution of Mo_2C in the $\text{Ni-Mo}_2\text{C}$ alloys, when sintering is carried out at 1200°C or below.

4. The disappearance of Mo_2C during solid state sintering of $\text{Ti}(\text{C,N})\text{-Mo}_2\text{C-Ni}$ phase mixtures at 1200°C or below is mainly through solid solution in Ni and that reprecipitation of $(\text{Ti,Mo})(\text{C,N})$ onto $\text{Ti}(\text{C,N})$ grains does not occur to a large extent under these conditions.

5. On average, when the ratio of Mo_2C to Ni is below or around 0.3, most or even all of the Mo_2C phases present in the $\text{Ti}(\text{C,N})\text{-Mo}_2\text{C-Ni}$ alloys can be dissolved in Ni after 1 h at 1200°C . However, when the ratio is well over 0.3, only partial dissolution of Mo_2C can be observed even 10 h at 1200°C .

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