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Synthesis of titanium-chromium nitride composites by millimeter-wave sintering

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New composites of Ti-Cr-N system were synthesized using a high power millimeter-wave heating method. Ti-Cr-N composites were synthesized from the powder mixtures containing metallic Ti and Cr_2N under nitrogen atmosphere by 28 GHz millimeter-wave radiation. The composites consisted of (Ti,Cr)N, Cr_2N with some amount of metallic Cr, and their hardness ranged from 9 GPa to 15 GPa, depending on the nitrogen pressure during sintering. In these composites, quite high oxidation resistance was found from their small weight gains less than 5 g/m^2 in oxidation experiment in air at 1000 °C for 60 min.. It was also indicated that a high pressure nitrogen environment is advantageous for the millimeter-wave syntheses of nitride composites with high oxidation resistance.

1. Introduction

Recently, extensive application of millimeter-wave heating has been expected by several successful results on the sintering of some ceramics instead of 2.45 GHz microwaves usage [1–4]. Since 1980s, sintering of ceramics by the microwaves has been developed and it has indicated that there are numerous advantages such as rapid and uniform heating, and higher densification at lower temperature in the sintering process and so on. Irrespective of these advantages, however, some problems are associated with insufficiency in the direct heating for low dielectric-loss ceramics and difficulty of designing a multi-mode applicator with uniform electromagnetic field for avoiding so-called "thermal runaway" [5]. On the other hand, usage of millimeter-wave radiation is quite suitable for solving these problems. In comparison with 2.45 GHz microwave heating, a higher power absorption and a weaker temperature dependence of dielectric loss rate are brought by the usage of millimeter-wave [5].

Another problem for wide application of microwave heating is its difficulty to metallic materials due to scarce absorption of radiation. However, possibility for heating metallic powders was reported [6] in 2.45 GHz microwave heating, from which we have considered to apply 28 GHz millimeter-wave heating for synthesizing nitride ceramics from the powder mixtures containing metallic materials.

Among various engineering nitride ceramics, TiN is one of the widely available nitrides as well as Si_3N_4, and it is widely used for hard coating [7]. In some cases, it is also used as bulk ceramics fabricated by conventional sintering and hot pressing methods [8, 9]. TiN ceramics is not so easily consolidated without metallic additives and, in general, high pressure condition of several GPa is needed for obtaining highly densified TiN ceramics. Although TiN ceramics is enough to satisfy high oxidation resistance, these are not always enough to be used for severe environment. In the current investigations on protective coatings [10], syntheses of multicomponent coatings, for example, containing AlN [11] have been performed for the purpose of improving these oxidation resistances.

In order to improve the inherent properties of single phase TiN ceramics, composites of TiN have been produced by other refractrory ceramics such as TiB_2 or Si_3N_4 [12–15]. Especially, composites of TiN and TiB_2 have been fairly investigated using various processing such as hot pressing, SHS and electrical discharge methods. It has been reported in these papers that fracture toughness is improved by TiB_2 addition [12] and, in some papers, the addition of TiB_2 is reported to be effective for suppressing of grain growth of TiN [13].

The purpose of present report is not to synthesize highly hard ceramics such as $TiN + TiB_2$ composites, but to fabricate a composite nitride with high oxidation and abrasive wear resistances. In this point it is interesting that chromium nitride coatings show excellent properties for tribological application [16]. Besides, the formation of sesquioxide by oxidizing chromium nitrides is expected to be effective for improving their oxidation resistant property. From these motivations, the millimeter-wave synthesis of nitride composites of Ti-Cr-N system has been tried by using mixtures of metal and nitride powders as the starting materials.

2. Experimental procedures

Ti powder (The Nilaco Corporation, Tokyo, Japan) of 99.3% purity and Cr_2N powder (Kojundo Chemical

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Laboratory Co., Ltd.) of 99% purity were used as the starting materials. These powders were mixed in ethanol. The content of Ti powder in the mixtures was 51 mol%. After drying, the mixed powder was put into graphite dies coated with BN and calcined pellet-like specimens were obtained using pulsed high current heating method. The calcination was performed at 550 °C for 5 min. under a pressurized condition of 55 MPa. The vacuum condition during the calcination was kept to be below 10 Pa.

Sintered bodies of titanium-chromium nitride composites were produced by millimeter-wave heating equipment, which consists of 28 GHz gyrotron millimeter-wave generator and multi-mode type chamber (Fuji Denpa Kogyo Ltd., Type FGS-10-28). In order to examine the influence of the change of N_2 gas pressure on properties of sintered samples, the millimeter-wave sintering of calcined specimens was mainly performed at 1350 °C for 20 min. under several N_2 gas pressures. For some cases, the millimeter-wave sintering was done at 1300 °C. The heating rate was fixed at approximately 25 °C/min. and all specimens were cooled down in the chamber after sintered.

Microwave sintering is principally different from conventional one by electric furnace. On the former process, heat is generated internally within the material through the interaction between microwave and sample. In this case it is important to inhibit radiant heat loss from the sample at high temperature, for which Al_2O_3 fibrous and fiber board were used as thermal insulation materials.

Microstructures of synthesized composites were examined by observing polished surfaces of the samples with scanning electron microscopy (SEM). Elemental distributions in these surfaces were analyzed with electron probe microanalysis (EPMA) method. The crystalline phases were identified by X-ray diffraction (XRD) method. Hardness of these composites was measured with a Vickers hardness tester under a condition of 4.9 N load and the 20 sec. holding time. Oxidation resistance of the composites was examined by weight gain after heating in air at 1000 °C for 60 min.

3. Results and discussion

3.1. Influence of sintering temperature on microstructures

XRD patterns of sintered composites for the powder mixture of 51 mol% Ti and Cr_2N are shown in Fig. 1. The samples were sintered at 1300 °C and 1350 °C under the nitrogen pressure of 0.11 MPa. The XRD

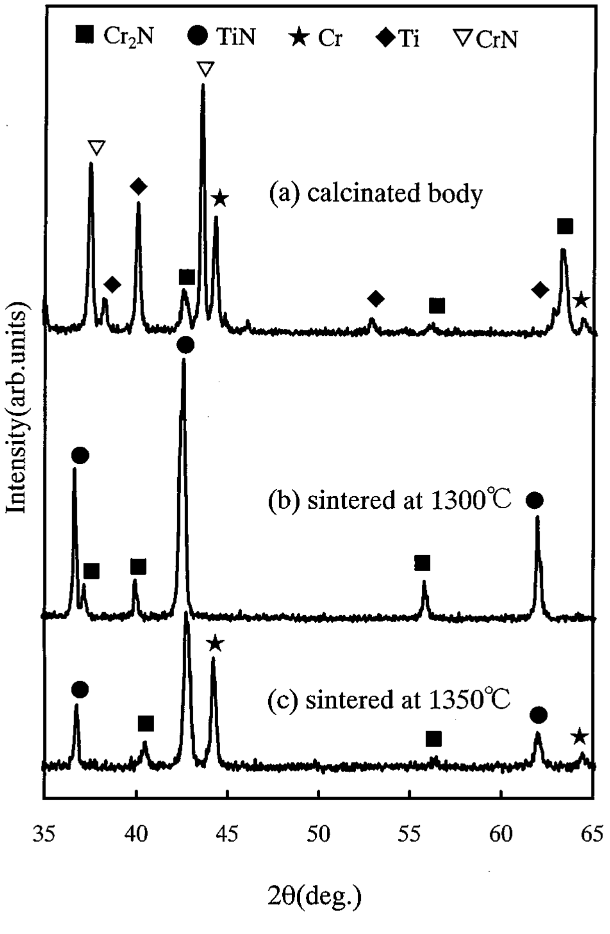

Figure 1 X-ray diffraction patterns obtained from the Ti-Cr-N composites with 51 mol% Ti calcined by pulsed high current method and sintered by 28 GHz millimeter-wave radiation.

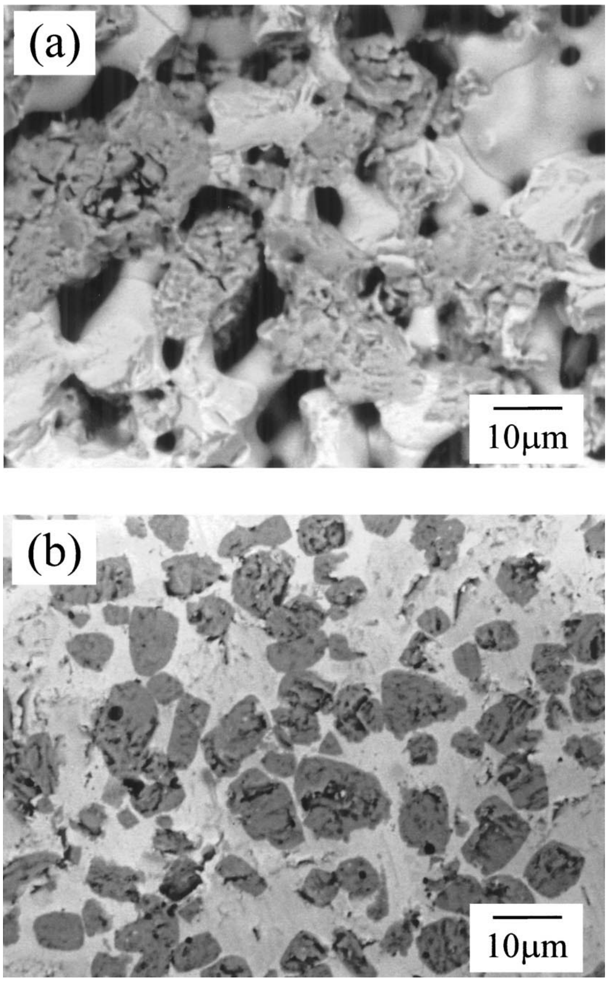

Figure 2 Microstructural photographs of Ti-Cr-N composites with 51 mol% Ti sintered at (a) 1300 °C and (b) 1350 °C by 28 GHz millimeter-wave radiation. (By comparing weight gains due to water absorption with sample weights, the porosity of these samples was roughly estimated to be (a) around 18% and (b) below 1.0%, respectively. As indicated in the text, however, it is difficult to estimate the true densities, especially because of no estimation of close pores and phase compositions.)

pattern of the calcinated body is also shown in this figure. Though coexistence of metallic Cr and Ti is found in the calcinated body, sintered bodies by millimeter-wave heating at 1300 °C consist of TiN and Cr_2N phases only. When sintering temperature was raised to 1350 °C, metallic Cr phase was identified in the sintered body. The formation of metallic Cr phase is perhaps attributed to the decomposition of Cr_2N.

SEM photographs of polished surfaces of the same specimens with those for XRD measurement are shown in Fig. 2. Porous structure is observed in the sintered composite at 1300 °C, whereas densified structure is found in the composite at 1350 °C. These observations made us confirm that densification of the composite proceeded at a sintering temperatures between 1300 °C and 1350 °C. The densification is attributed to the melting of Cr_2N phase. However, the precise densification

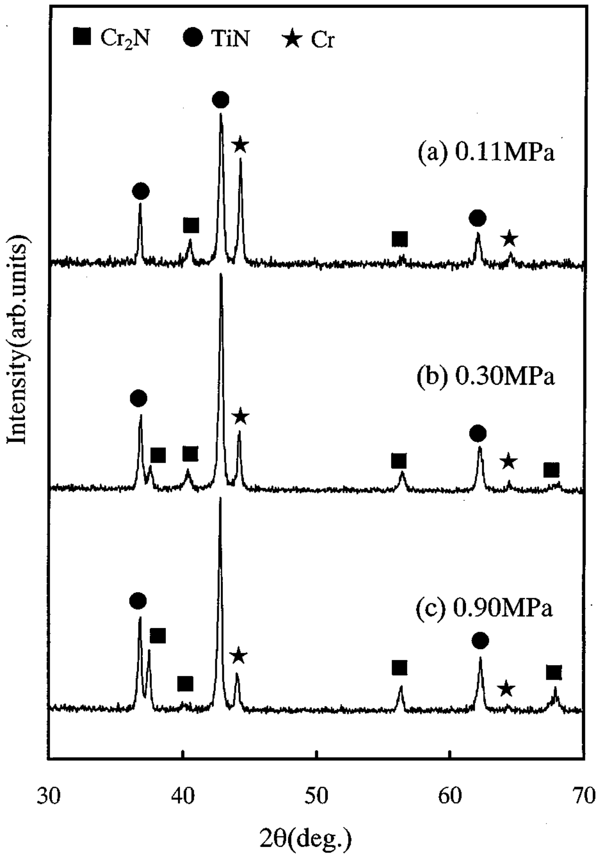

Figure 3 X-ray diffraction patterns obtained from Ti-Cr-N composites with 51 mol% Ti sintered under several N_2 gas pressures by 28 GHz millimeter-wave radiation.

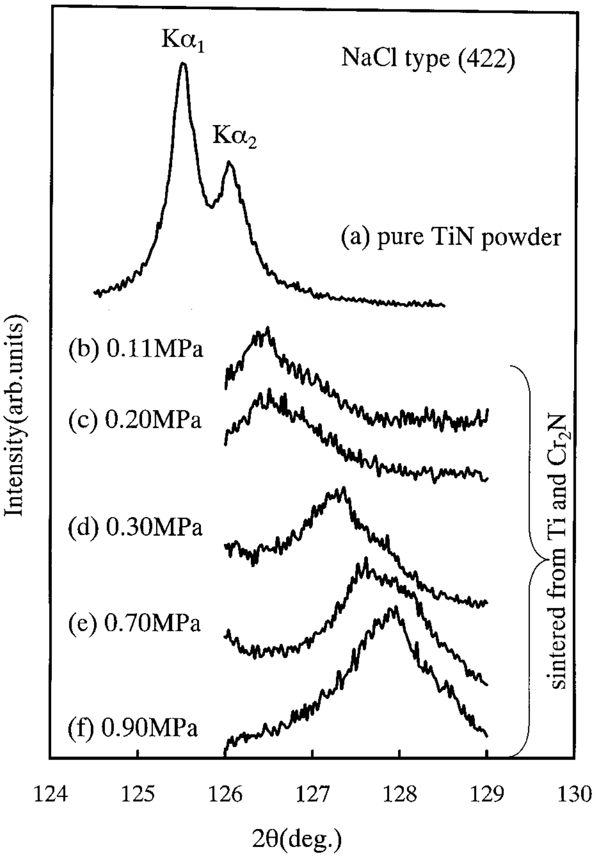

Figure 5 X-ray diffraction patterns of (422) planes of NaCl(Bl) lattice obtained from the Ti-Cr-N composites with 51 mol% Ti which were sintered under the various nitrogen pressures by millimeter-wave radiation.

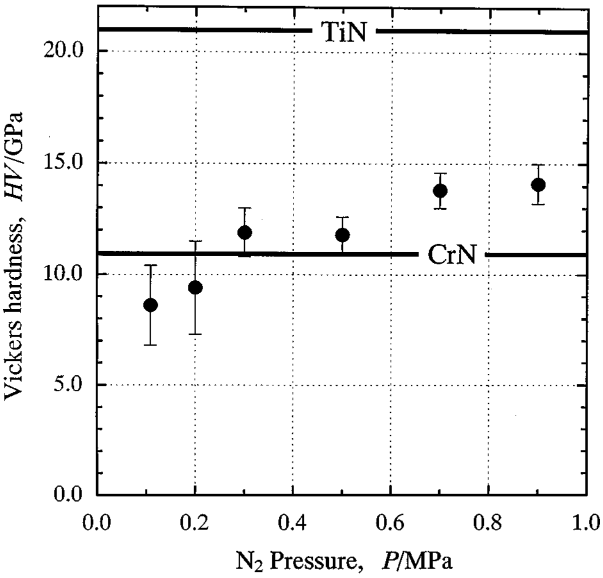

Figure 4 Dependence of Vickers hardness of Ti-Cr-N composites with 51 mol% Ti on the nitrogen pressure in the millimeter-wave sintering.

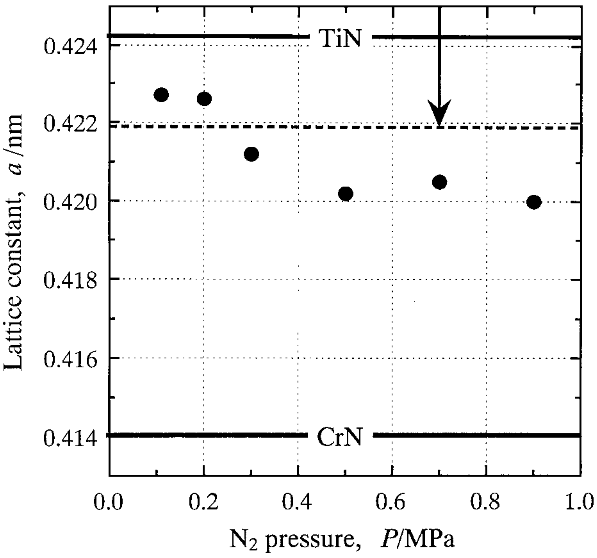

Figure 6 Dependence of lattice constant of NaCl-type nitride on the nitrogen pressure during millimeter-wave sintering.

of respective sintered composite could not be estimated because it was difficult to determine the precise compositions and contents of the identified phases. In this study, densification of these composites was examined by absorption of water into the samples. The water absorption ratio, which is calculated by the weights of dried and moistened composites, was examined as a function of the soaking time, and in the composites sintered at 1350 °C, the ratio decreased with increasing soaking time in the range below 1% (by about 0.1% when the soaking time was 20 min., for example). For the composites sintered at 1300 °C, on the other hand, the ratio indicated a decrease of about 4% till the soaking time was 60 min. and less than 1% when the soaking time reached 100 min.

3.2. Effect of nitrogen pressure on microstructure

Influence of the pressure variation of nitrogen during millimeter-wave heating was examined in the range between 0.11 MPa to 0.90 MPa, fixing the sintering temperature and holding time at 1350 °C and 20 min, respectively. XRD patterns of the sintered composites are shown in Fig. 3. It is found that the amount of metallic Cr decreases with increasing the pressure. Vickers hardness of these composites also increases with the pressure, as shown in Fig. 4 and the values at high nitrogen pressures are plotted between that of pure TiN and CrN. On the other hand, the water absorption ratio for these composites did scarcely depend on the nitrogen pressure, suggesting no influence on the densification. Accordingly, the increment of hardness of the composites under the pressurization is attributed to the decrement of metallic chromium, as indicated by XRD data in Fig. 3.

Subsequently, the dissolution of Cr into TiN phase was examined by measuring the change of XRD peak position of titanium nitride phase in the sintered composites because the dissolution of Cr into TiN is important factor on the improving the oxidation resistance of single phase. In this study, the XRD peak due to (422) plane of NaCl-type phase was selected from the requirement of both the sensitivity and the resolution

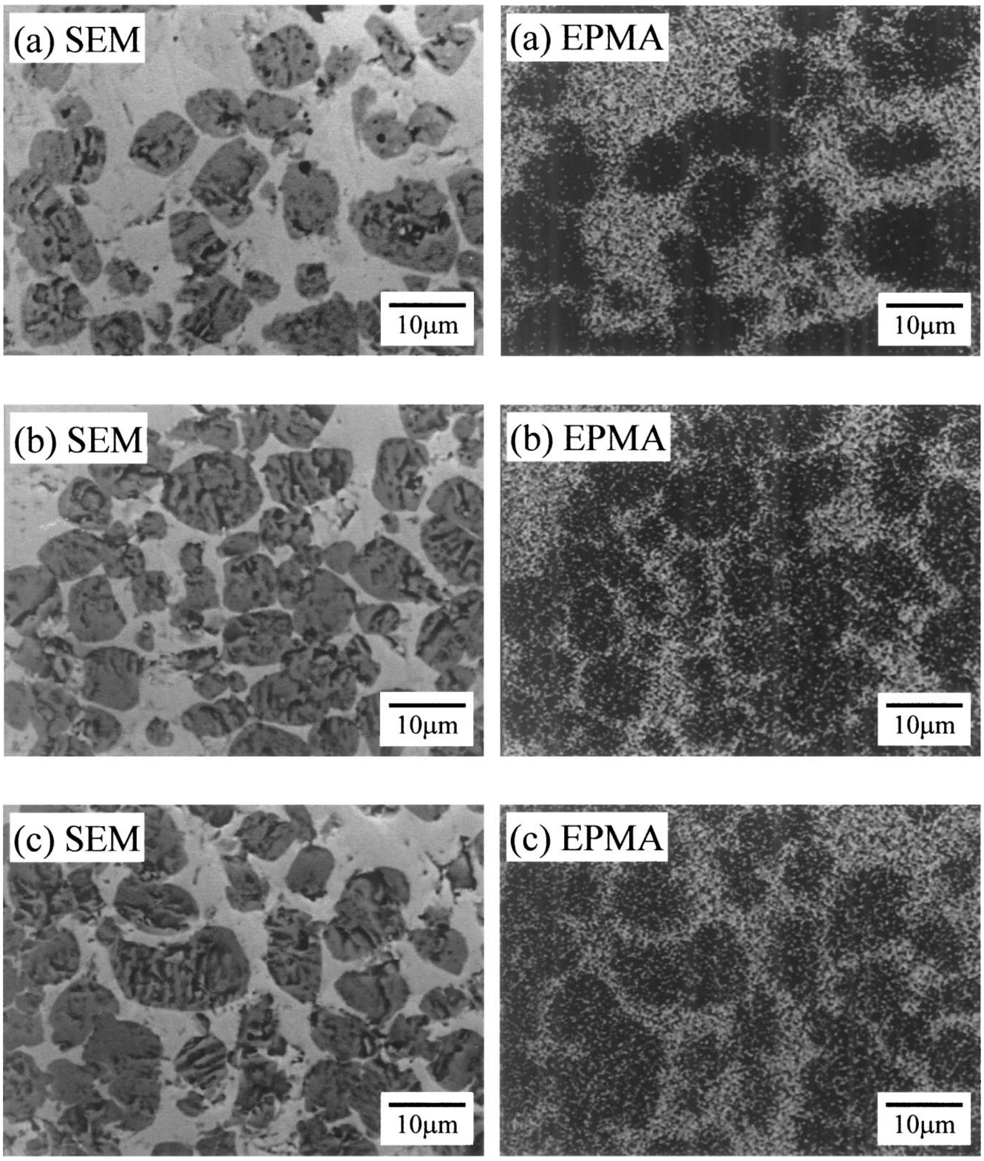

Figure 7 SEM photographs and chromium distributions (by EPMA) of Ti-Cr-N composites with 51 mol% Ti sintered under several nitrogen pressures by millimeter-wave radiation. (The presence of chromium on the maps by EPMA is shown by white dots. (a) 0.11 MPa N_2, (b) 0.30 MPa N_2, (c) 0.90 MPa N_2).

for observing the peak shift. As shown in Fig. 5, two (422) peaks due to Kα_1 and Kα_2 x-rays are observed in the pure TiN, while these peaks in the sintered composites are observed as only one peak on account of the overlap of the broadened two peaks. The peak position shifts from about 125 degree to a higher diffraction angle, with increasing the nitrogen pressure. Calculating the lattice constant from the peak position, as given in Fig. 6, it is found that the lattice constant of the B1 nitride phase changes from 0.423 nm to 0.420 nm, with increasing the nitrogen pressure. The lattice constants of stoichiometric TiN and CrN with B1 structure are also drawn by the straight lines in Fig. 6. The lattice constant of the non-stoichimetric B1-type $Ti_{1-x}N$ with the largest compositional deviation is also drawn by dotted line. As we can easily find from Fig. 6, the observed lattice constant becomes smaller than that of $Ti_{1-x}N$ with increasing the nitrogen pressure. The decrease of the lattice constant of the B1 nitride phase in the sintered composites is attributed to both non-stoichiometric effect and the dissolution of Cr into titanium nitride lattice. Because the partial nitrogen pressure in this experiments was not so low to produce large non-stoichiometric effect, the decrease of lattice constant is mainly attributed to the increase of the dissolved content of Cr into the B1 nitride phase.

The dissolution of Cr into the B1 nitride phase is also clearly observed in Fig. 7, which shows SEM photographs obtained from the polished surfaces of these composites and gives chromium distributions in the same regions analyzed with EPMA method. Especially, for the composite sintered at 0.9 MPa nitrogen, a fairly high content of Cr is observed in titanium nitride grains, which are surrounded by Cr_2N phase, on the planar map of Cr content for the composite sintered at 0.9 MPa nitrogen, suggesting a fairly dense dissolution of Cr into titanium nitride grains.

3.3. Oxidation resistance

Oxidation resistance of the composites was examined by heat treatment at 1000 °C for 60 min. (3600 Ks) in air. Weight gains of the composites during heat treatment are shown in Fig. 8. The composites sintered at 0.90 MPa nitrogen pressure shows higher oxidation resistance than those sintered at 0.11 MPa. The weight gain for the former composite is about one-fifth of the latter. This discrepancy in oxidation resistance seems to arise from microstructural difference between these composites. As shown in Fig. 7, it is clearly found that the grains of titanium nitrides in the composites sintered under 0.90 MPa N_2 contain a higher chromium content than those under 0.11 MPa N_2, in which a better oxidation resistance is obtained. Additionally, XRD measurement was done for examining the formation of TiO_2 phases on the surfaces of these composites heat-treated at 1000 °C for 60 min. in air. It is observed in Fig. 9 that a smaller amount of TiO_2 phase is formed in the composites sintered at 0.90 MPa N_2. This is a proof for better oxidation resistance of the composites sintered under 0.90 MPa N_2 environment because the formation of TiO_2 phase is not so effective for oxidation barrier.

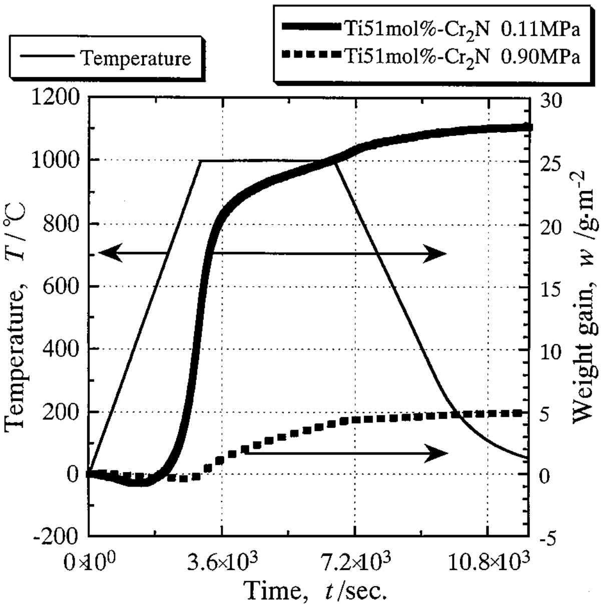

Figure 8 Time-dependence of weight gains of Ti-Cr-N composites with 51 mol% Ti exposed in air at 1000 °C.

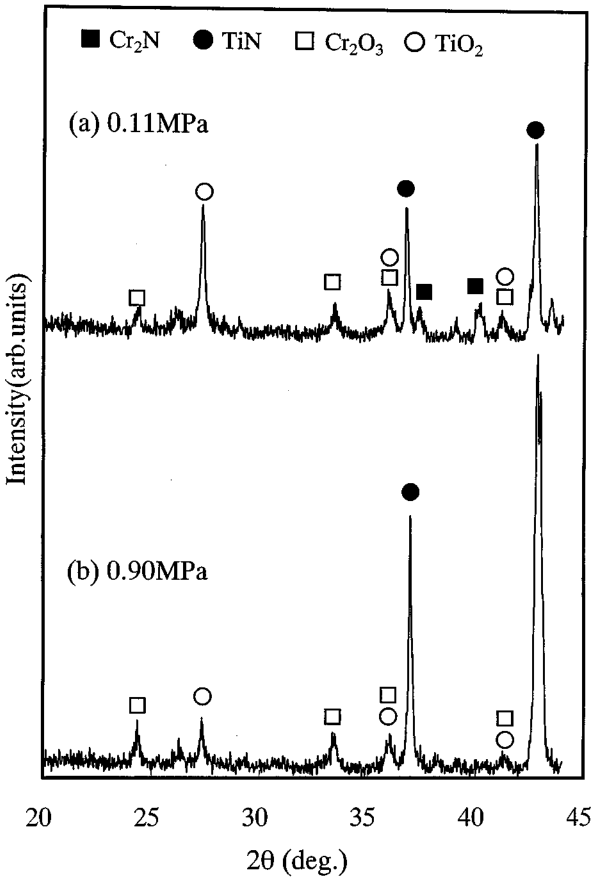

Figure 9 X-ray diffraction patterns obtained from Ti-Cr-N composites with 51 mol% Ti exposed in air at 1000 °C.

4. Summary

Synthesis of new ceramic composites of Ti-Cr-N system was tried by sintering powder mixtures of metallic Ti and Cr_2N under nitrogen atmosphere with a high power millimeter-wave heating method. It was found by XRD analysis that the sintered composites were identified to be multiphase mixture of TiN, Cr_2N and some amount of metallic Cr. Their hardness and oxidation resistance showed a fairly strong dependence on the amount of remnant metallic Cr, which was suppressed by increasing the pressure of nitrogen during sintering. Depending on the composition of constituent phases and nitrogen pressure, the hardness of these nitride composites ranged from 9 GPa to 15 GPa. The composites suppressed to be small amount of metallic Cr showed a high oxidation resistance, which was indicated from extremely small weight gain less than 5 g/m^2 obtained from the oxidation experiment in air under 1000 °C for 60 min.. The millimeter-wave heating under a high pressure nitrogen was found to be applicable for synthesizing new nitride composites even from the powder mixtures containing considerable amount of metallic component.

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