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Effect of Ni Content on the Reaction Behaviour and Microstructure of TiB_2-TiC/Ni Cermets Synthesized by MASHS

M. Shahbazi [a], S.A. Tayebifard* [a], M. Razavi [b]

[a] Department of Semiconductor, Materials and Energy Research Center, Karaj, Iran
[b] Department of Ceramic, Materials and Energy Research Center, Karaj, Iran

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ABSTRACT

In this paper TiB_2-TiC/Ni cermets with various Ni (20, 40 and 60 wt %) contents were synthesized by mechanically activated self-propagating high-temperature synthesis (MASHS) and the effects of the addition of Ni were investigated on synthesis parameters and microstructure of the synthesized samples. Raw materials (B_4C, Ti and Ni) were first milled in Ar atmosphere. Powders were then synthesized in the tube furnace. The samples were analyzed by XRD and SEM. Ignition time of the samples was decreased by increasing Ni content. The SEM images show that the microstructure of samples has been fined and the pore size has been decreased by increasing Ni content. The crystallite size of synthesized samples has been calculated by Rietveld method. The average crystallite size of TiB_2 and TiC phase in the sample with 60 wt % Nickel was 53 nm and 22 nm, respectively.

1. INTRODUCTION

Preparation of various borides and carbides by self-propagating high-temperature synthesis (SHS) has been demonstrated in a number of investigations [1-7]. The TiB_2-TiC composites have good properties such as high melting point, high hardness and excellent resistance to corrosion and oxidation [2, 8]. They are used for these applications as a single-phase as well as composite structures. The wear resistance applications are the most important use of TiC and TiB_2. Some researchers have investigated SHS reaction in Ni-Ti-B_4C system. Yang et al reported that the combustion temperature, wave velocities and ceramic particle size decrease with the increase of Ni contents [9]. L. Huang et al investigated the SHS reaction in Ni-Ti-B system [10]. They reported that the size of TiB_2 particles decreases dramatically to 1–2 μm when Ni content increases to 60 wt%.

Nickel based cermets have very good toughness and wear resistance. Furthermore, Ni addition can improve oxidation resistance of the composite. TiB_2 and TiC were used in Ni cermet as the ceramic component. On the other hand, Nickel acts as a binder in TiB_2-TiC/Ni cermet. This is due to good wettability between Ni additive and composite matrix. Moreover, the Ni additive causes an increase in density of composite by the creation of liquid-phase during sintering. The TiB_2-TiC composites have been fabricated by powder metallurgy, mechanical alloying, reactive sintering, and Self-propagating High-Temperature Synthesis (SHS). SHS is an efficient route to synthesis of advanced ceramics. Advantages of SHS process include high purity of the product, short processing time, low-cost and energy requirement [11, 12]. In mechanically activated self-propagating high-temperature synthesis (MASHS), raw materials are activated by milling process. In this step, starting materials are only activated and the process should be stopped before reaction of powders during milling [13, 14]. MASHS is the suitable method for producing nanocrystalline materials. The ignition temperature of TiB_2-TiC synthesis by SHS has been reduced by addition of Ni to the composition because Ni and Ti form eutectic at low melting temperature, which facilitates mass transfer. Additionally, mechanical activation process decreases the ignition time. In this process, the energy of the system increases by forming of dislocation and creation of new surfaces. Consequently, ignition time and temperature have been decreased by increasing the system energy. In this paper, nano-structure TiB_2-TiC/Ni cermet were synthesized by using B_4C, Ti and Ni as raw materials. Phase evolution and microstructure with adjusting Ni content were investigated.

*Corresponding Author's Email: a_tayebifard@yahoo.com (S.A. Tayebifard)

2. EXPERIMENTAL

In this study, starting materials were Ni (99.5%, ≥10ηm, Merck), B_4C (98 %, -200 mesh, Aldrich) and Ti (98%, <150ηm, Merck). Raw materials were blended according to reaction 1.

$$3Ti + B4C + xNi \rightarrow 2TiB2 + TiC + xNi \quad (1)$$

A nickel content (x) of 20, 40 and 60 wt% were used for the experiment. The reactants were activated by the planetary ball mill (Retch PM100) by means of 250 ml stainless steel cup in Ar atmosphere for 3h. Ball to powder ratio and rotation speed were 10/1 and 300 rpm, respectively. In the next step, milled powders were compacted by the uniaxial press using stainless steel die (10mm diameter) under the pressure of 300 MPa (the Green density was about 55-60% theoretical density). The SHS reaction was conducted in the tube furnace under the flow of Ar at about 1000°C. Schematic diagram of the tube furnace and synthesis processis illustrated in Figure 1. Products were analyzed by X-ray diffraction (XRD) (mod.PW1830, Philips Analytical B.V, The Netherlands). The fracture surfaces of samples were investigated by scanning electron microscopy (SEM) (mod.XL30, Philips, The Netherlands at an acceleration voltage of 30kV).

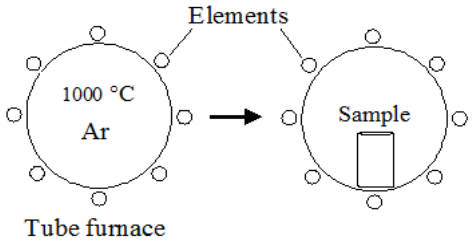

Figure 1.Schematic diagram of tube furnace and synthesis process.

3. THEORY BACKGROUND

The basis of the combustion synthesis is on the heat evolution from the involved reactions. In the SHS process, the maximum temperature that is obtained from reaction under adiabatic condition is called adiabatic temperature (T_{ad}). Adiabatic temperature is an important parameter in combustion synthesis. Knowing the adiabatic temperature of a reaction, one can predict whether or not SHS reaction is executable [15]. Adiabatic temperature of SHS reaction could be calculated by Equation 1 [16]:

$$-\Delta H^0_{298} = \int_{T_0}^{T_{ad}} C_p(\text{products})dT \quad (2)$$

where ΔH^0_{298} and C_p are reaction enthalpy (at 298 K) and heat capacity of the products, respectively. In a semi-experimental study it is demonstrated that the combustion reaction will be self-sustaining if the adiabatic temperature (T_{ad}) of reaction (T_{ad}) is bigger or equal to 1800 k, [17]. The adiabatic temperature of reaction 1 was calculated by Yang et al. [18] for 20, 40 and 60 wt% Ni.

Crystallite size and micro strain were calculated on the basis of Rietveld refinement method by using X'Pert high score plus software (developed by PANalytical BV Company, Almelo, the Netherlands, version 2.0). In this method, peak profile fitting, size broadening, and strain broadening were calculated on the basis of following equations [19]:

$$G_{ik} = \gamma \frac{C_0^{\frac{1}{2}}}{H_k \pi}\left[1 + C_0 X_{ik}^2\right]^{-1} + (1-\gamma)\frac{C_1^{\frac{1}{2}}}{H_k \pi^{\frac{1}{2}}}\exp\left[-C_1 X_{ik}^2\right] \quad (3)$$

$$D_i = \left(\frac{180}{\pi}\right)\frac{\lambda}{(W_i - W_{std})^{0.5}} \quad (4)$$

$$\eta_i = \frac{[(U_i - U_{std}) - (W_i - W_{std})]^{0.5}}{\frac{1}{100}\left[\frac{18}{\pi}\right]^0 4(2\ln 2)^{0.5}} \quad (5)$$

where G_{ik} is the Pseudo-Voigt function, C_0=2, C_1=4ln2, H_k is full width at half maximum of the Kth brag reflection, γ is shape parameter, X_{ik}= $(2\theta_i - 2\theta_k)/H_k$. D_i, η_i, λ, U and W are grain size function, strain function, wavelength, strain parameter and size parameter of peak profile, respectively.

4. RESULTS AND DISCUSSION

Samples containing 20, 40 and 60 wt% Ni have been successfully synthesized at 1000°C. Yang et al. [20] reported that with increasing the Ni content, the ignition temperature would be higher than 1000 °C. This means that for synthesis by SHS method, the sample should be heated over 1000°C whereas in our investigation all samples ($Ti+B_4C+xNi$ and 3h activation) were synthesized at 1000°C or lower. This phenomenon is only explainable by the effects of premechanical activation process. Calculations of Khina [21] shows that point defects and energy storage in sample during mechanical activation are negligible and they depend on physicochemical processes occurring with MA. But in sample without Ni ($Ti+B_4C$) and 3h of activation, the SHS reaction was not occurred at 1000°C. This observation could be described by the effect of Ni addition to the synthesis process by formation of eutectic liquid between Ni, B and Ti phases to form Ni-Ti and Ni-B compounds.

The time from the start of heating to the occurrence of SHS reaction is called ignition time. Results show that ignition times (t_{ig}) were decreased by increasing Ni content (Figure 2). This is due to the formation of Ni-Ti and Ni-B compounds [9]. Furthermore, ignition time has been decreased by increasing the milling time.

The X-ray diffraction patterns of all samples are shown in Figure 3. These patterns show that TiB_2 and TiC phases were successfully formed after MASHS process. Formation of Ni_2B, Ni_3B and Ni_3Ti phases indicates that

the reactions are incomplete. Additionally, it can be observed that some of TiB_2 peaks have been disappeared, and the intensities of TiB_2 and TiC peaks were decreased.

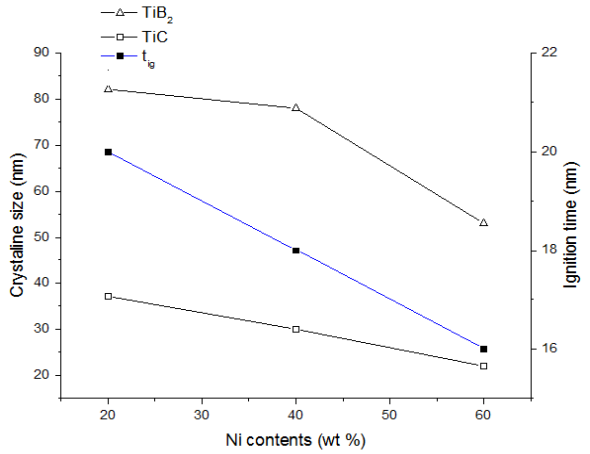

Figure 2.Effect of Ni content on ignition time of samples with 3h activation.

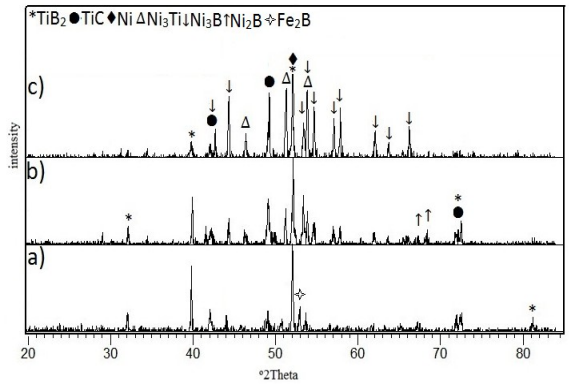

Figure 3.XRD pattern of synthesized products in 1000°C: A) 20 wt% Ni, B) 40 wt% Ni and C) 60 wt% Ni.

Also, Fe_2B phase was formed due to the introduction of Fe impurity from wearing of balls and its reaction with B_4C particles. Fe_2B diffraction lines have been disappeared by increasing the Ni content. In fact, Ni is more reactive than Fe and therefore in the presence of Ni, Ni_3B phase formed instead of Fe_2B phase. Moreover, increasing the Ni could decrease Fe contamination due to decreasing of balls and cups erosion by B_4C particle.

TABLE 1.Crystallite size of the TiB_2 and TiC phases as well as GOF value of Rietveld refinement.

Ni content (wt %)	Milling time(h)	Crystallite size (nm)		Micro strain(%)		Goodness of Fit
		TiB_2	TiC	TiB_2	TiC	
20	3	82	37	0.044	0.074	1.01460
40	3	78	30	0.043	0.122	1.67636
60	3	53	22	0.072	0.194	1.01669
20	1	96	45	0.032	0.081	1.15743
20	6	64	29	0.054	0.149	1.74250

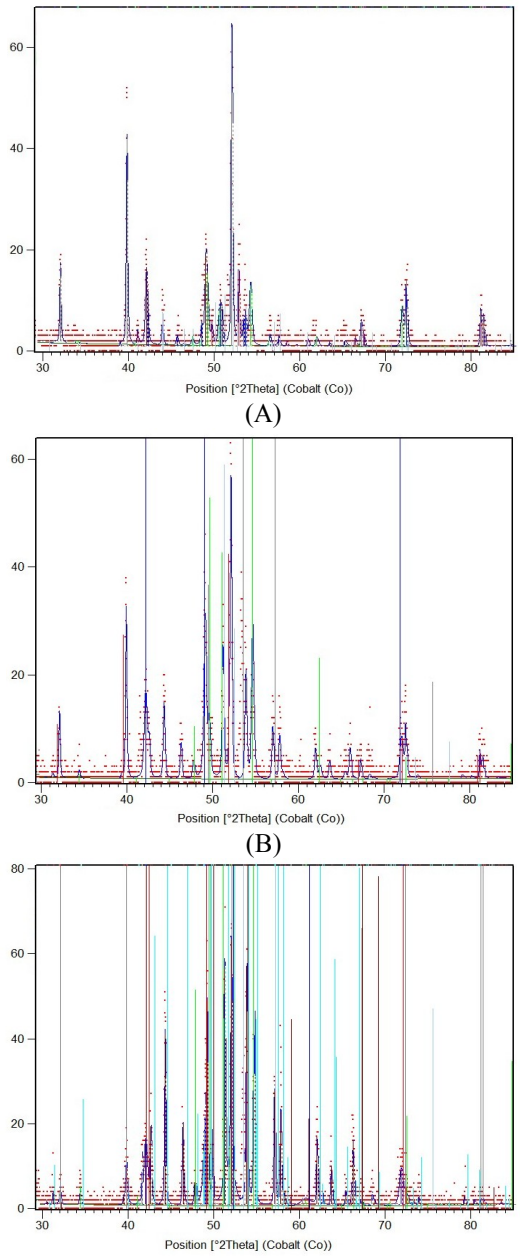

Figure 4. Profile fitting of the cermets with various Ni contents: A) 20 wt% Ni, B) 40 wt% Ni and C) 60 wt% Ni with 3h activation.

Figure 2. shows the crystallite sizes of the samples that have been calculated by the Rietveld method. The refined XRD pattern of samples using X-Pert high score plus software is shown in Figure 4. The solid line demonstrates the calculated intensities. As observed, there is a suitable agreement between the experimental and calculated spectra. In addition, Goodness of fit values after Rietveld refinement are lower than 2 (TABLE 1) indicating that data obtained by refinement are reliable. The crystallite size has been decreased by the addition of Ni. This is due to the dilution effect of

Ni, which decreases the combustion temperature [9, 22]. In other words, the crystallite size has been reduced by decreasing of T_c (increasing the Ni content). The crystallite sizes of TiB_2 and TiC and ignition time of samples are given in TABLE 1. Crystallite size of the samples at various milling times (1 and 6h) containing 20 %wt Ni are shown in TABLE 1.

Microstructures of the fracture surface of the products are shown in Figure 5. Figure 5. (a, b and c) shows that agglomerates have been increased by increasing the Ni content. This phenomenon can be explained by increasing the liquid phase.

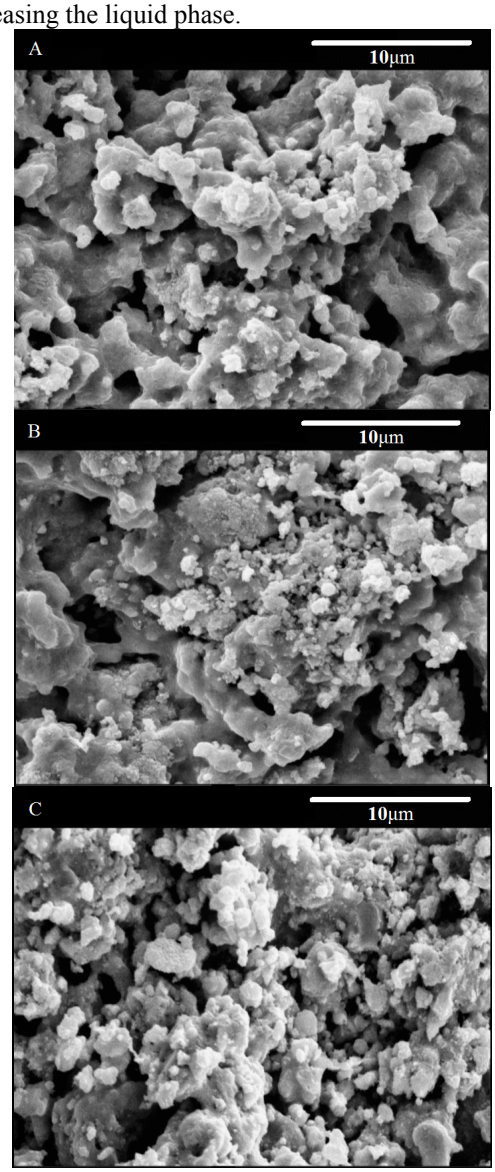

Figure 5. Fracture surface of the cermets with various Ni contents A) 20 wt% Ni, B) 40 wt% Ni and C) 60 wt% Ni with 3h activation.

5. CONCLUSION

TiB_2-TiC/Ni cermets with various Ni contents were synthesized by mechanically activated self-propagating high-temperature synthesis (MASHS) method using Ti, B_4C and Ni as raw materials. The reaction occurred more partially by increasing the amount of Ni. The amount of Ni-Ti and Ni-B compounds was also increased by addition of 40 and 60 wt % Ni. Ignition time (t_{ig}) and crystallite size of the products were decreased by increasing the Ni contents. In addition, the crystallite size of the synthesized phase was decreased by increasing the activation time. Minimum crystallite size of both TiC and TiB_2 phases were obtained in sample containing 60 wt% Ni.

6. ACKNOWLEDGMENTS

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