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Simultaneous synthesis and densification of TiC/Ni–Al composites

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The process of combustion synthesis was used to produce ceramic–metal composite materials consisting of titanium carbide (TiC) and an intermetallic alloy of the Ni–Al system. The samples were produced by rapidly heating a mixture of elemental Ti, C, Ni, and Al powders in a graphite die up to the ignition temperature. By applying mechanical pressure during or immediately following the combustion reaction, products of greater than 99% theoretical density were obtained. The residual porosity and microstructural development were characterized using optical microscopy, and X-ray diffraction methods. The nature and composition of the product phases can be controlled by variations in the ratios of the starting reagents, level of mechanical pressure, addition of diluents, and the inclusion of dopants. By varying the combustion synthesis parameters, the properties of the product can be tailored to meet specific application needs. Apparent applications of such composites include cutting tools, wear parts, structural components, armour, etc.

1. Introduction

The use of a combustion reaction to synthesize a refractory material was first considered by Walton and Poulos [1] who produced cermet materials using thermite reactions. Little further development took place until the late 1960s when Merzhanov and co-workers (e.g. [2–9]) began work on self-propagating combustion reactions. This work by Merzhanov led to the development of a process, for producing a variety of refractory materials, which they called "self-propagating high-temperature synthesis (SHS)" or, more simply, combustion synthesis. In this process, materials which have sufficiently high heats of reaction may be synthesized in a combustion wave, which after ignition, spontaneously propagates throughout the reactants converting them into the products. A wide variety of materials have been produced by this method including carbides [9, 10], borides [3, 11], nitrides [12–18], intermetallics [19–22], and composite materials [23–27].

One of the major drawbacks in the combustion synthesis of refractory materials is the highly porous nature of the products. This porosity is caused by three basic factors: (1) the molar volume change inherent in the reaction, (2) the porosity present in the unreacted sample, and (3) adsorbed gases which are present on the reactant powders. In the reaction between Ti and C to form TiC, for example, the product is approximately 23% more dense than the reactants. Furthermore, the unreacted powders are generally cold pressed to the 50%–70% density range. Thus, without densification occurring one could not expect to obtain a product of greater density than approximately 50%. Maksimov *et al.* [23] and Holt and Munir [10] have also found that adsorbed gases greatly contribute to the porosity of the final product. This is due to the massive expansion which takes place as these gases are rapidly heated from ambient temperature up to the combustion temperature. Because of the porosity of these products the majority of the materials produced are used in powder form. If dense materials are desired the powders then generally must undergo some type of densification process such as sintering or hot pressing. The ideal production process would combine the synthesis and densification steps into a one-step process.

One of the characteristics of combustion synthesis reactions is the high temperatures achieved in the combustion wave (e.g. approximately 3000 K for the combustion of Ti and C). As a result, if pressure could be applied during or immediately following combustion while the product mass is still at an elevated temperature, then it might be possible to synthesize and densify the product simultaneously. Various methods of applying pressure have been incorporated into experimental designs to accomplish this production process. Rice *et al.* [28] used a rolling mill technique on the TiB_2–Al_2O_3, TiC–Ti, and TiB_2–TiC systems. Miyamoto and co-workers [29–31] used a high-pressure (3 GPa) anvil apparatus and a process which they called "high-pressure self-combustion sintering (HPCS)" to densify a variety of ceramic materials. Both Holt [32] and Takano *et al.* [33] applied hot isostatic pressing (HIP) technology to the

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combustion synthesis of materials in the Ti–B system. By far the simplest method applying pressure to the combustion synthesis reaction is the use of hot-pressing apparatus. This technique has been used by Holt and Munir [10], Richardson *et al.* [34], and Riley and Niiler [35]. Alternatively, use has been made of a liquid phase formed during a reaction to enhance densification [21, 23, 26, 27] or to allow for the formation of cast products [36].

In this paper the use of a low-pressure hot-pressing technique to produce dense ceramic–metal composites will be demonstrated by results from work on the Ti–C–Ni–Al system. This system was selected because strongly exothermic reactions occur in both the Ti–C and Ni–Al systems and because of interest in composite materials consisting of TiC and an intermetallic alloy of Ni and Al for various structural, cutting tool, and armour applications.

2. Experimental procedure

Small particle sizes of Ti, Al, Ni and C were used in all of the combustion experiments. The Ti, had an average particle size of 11 μm. A spectrochemical analysis showed the principle impurities to be Zr 5000 p.p.m., Al 2000 p.p.m., Ca 1000 p.p.m., Si 100 p.p.m., Mn 100 p.p.m., Mg 100 p.p.m. The Ni powder had an average particle size of 83 μm and major impurities were found to be Co 100 p.p.m., Cu 2 p.p.m., Al 1 p.p.m. The Al powder had an average particle size of 9.9 μm with major impurities Fe 100 p.p.m., Si 30 p.p.m., Ga 10 p.p.m., Cu 10 p.p.m., Mn 10 p.p.m. Amorphous furnace black was selected for use because this form of C is much more reactive than graphite. Monarch 905 furnace black was used, which is a very fine (0.01 μm) powder. Table I contains a summary of the surface area and average particle size data for the reagents used.

TABLE I Characterization of reagent powders

Reagent	Mean particle size (μm)	(Surface area ($m^2 g^{-1}$)
Ti (Alfa)	11.0	0.48
Ni (EM Scientific)	83.0	0.06
Al (ALCOA)	9.9	1.10
C (Cabot)	0.01	230

Reagent powder mixtures were prepared for the following three basic reactions

$$\mathrm{Ti} + \mathrm{C} + x(\mathrm{Ni} + \mathrm{Al}) \qquad (1)$$

$$\mathrm{Ti} + \mathrm{C} + x(3\mathrm{Ni} + \mathrm{Al}) \qquad (2)$$

$$50\,\mathrm{wt}\,\%(\mathrm{Ti} + \mathrm{C}) + 50\,\mathrm{wt}\,\%(y\mathrm{Ni} + z\mathrm{Al}) \qquad (3)$$

where x ranged from 12.5–75 wt % while y and z were such that the proper stoichiometry existed in the mixture to form each of the Ni–Al compounds known to exist (see Fig. 1). It should be noted that the Ni–Al part of both the reagents and products will be referred to as the "binder". The reagent powders were weighed out in the proper stoichiometric proportions keeping a constant equimolar ratio of Ti to C but varying both the amounts of Ni and Al and the ratio of Ni to Al in the binder. The powder batches were mixed in a glass jar for 30 min on a mechanical shaker and were inspected periodically to ensure that even mixing was occurring.

The powder mixture was then poured into a cylindrical graphite die that had been fitted with a 254 μm (10 mil) graphoil liner. This liner served both to protect the die and to promote the escape of gases during combustion. The graphite die was equipped with double-acting graphite rams which were machined so that there was a clearance of 83 μm (5 mil) after insertion of the graphoil liner. The powder mixture was cold pressed at a pressure of 20.7 MPa (3000 p.s.i.) where it achieved a density of approximately 50% theoretical. The die assembly was then inserted into the hot-pressing apparatus as shown schematically in Fig. 2. The graphite die was heated at approximately 1500 K min^{-1} by placing a potential across the copper plates and allowing the current flow to heat resistively the die. A thermocouple was inserted into a hole in the side of the die so that the approximate die temperature at ignition could be monitored. When ignition occurred the hydraulic rams were compressed to the desired pressure. This pressure was held for approximately 1–2 min (until the die was not red hot).

3. Results and discussion

3.1. Temperature profiles

Fig. 3a shows a temperature profile measured during the combustion of the mixture shown in Equation 1 where x has a value of 50 wt %. In this experiment an 80 μm (3 mil) W–Re thermocouple was placed into a small hole in the bottom of the sample opposite the end where ignition occurred. The output voltage of the thermocouple was monitored using a Hewlett Packard multiprogrammer system developed by Dunmead and Holt [37]. Here, it can be seen that this reaction between solids is typified by a relatively sharp rise from ambient temperature up to a peak combustion temperature of approximately 2200 °C followed by cooling to a plateau at approximately 1800 °C, a slight increase in temperature and then further cooling back to ambient temperature. The heating rate realized in the zone of sharpest temperature increase was calculated to be of the order of $5 \times 10^4\,\mathrm{K\,s^{-1}}$. The temperature profile found in Fig. 3b is a magnification of the zone of rapid temperature rise found in Fig. 3a. This profile is shown to point out the complicated nature of the temperature distribution in the combustion wave. The intricacies of the combustion wave are, however, beyond the scope of this paper and are currently the subject of further research.

The temperature profile in Fig. 3a indicates that the compact remains at an elevated temperature well after the combustion front has passed. As can be seen in Fig. 1, the phase in the Ni–Al system with the highest melting point is the 1:1 compound, NiAl, which has a melting point of 1638 °C. The compact remains above this temperature for approximately 23 s, and thus a liquid phase must exist for at least this amount of time. As a result of the existence of this liquid phase the

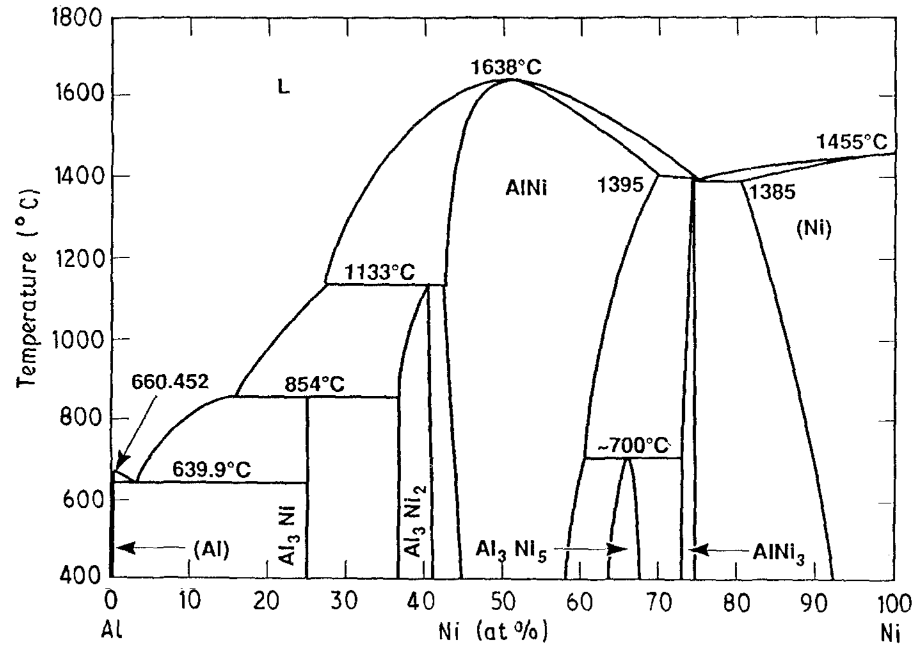

Figure 1 Phase diagram for the Ni–Al system.

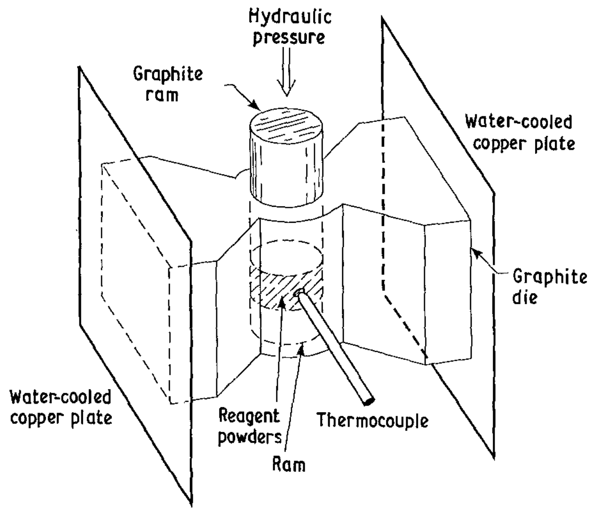

Figure 2 Schematic diagram of the combustion/compaction apparatus used.

application of pressure during this time should result in the densification of the product.

3.2. Binder composition

3.2.1. X-ray diffraction

Table II shows the results of X-ray diffraction (XRD) work carried out on the products of combustion of the mixtures shown in Equation 3. It should be pointed out that all of these reactions were carried out in the hot-pressing apparatus under a mechanical pressure of 20.7 MPa (3000 p.s.i.). In this series of experiments the Ni to Al ratio in the binder was varied so that the stoichiometric relationships of all seven compounds of the Ni–Al system (Ni, Ni_3Al, Ni_5Al_3, NiAl, Ni_2Al_3, $NiAl_3$ and Al) were represented. As can be seen in Table II, when the binder composition was Ni, 3Ni + Al, Ni + Al, and 2Ni + 3Al the product contained only TiC and the Ni–Al phase with the same stoichiometry as was in the reactants. When, however, the binder composition was 5Ni + 3Al, the product consisted of TiC, NiAl, and Ni_3Al. This can be explained by looking at the phase diagram in Fig. 1 and noting that Ni_5Al_3 decomposes on heating at approximately 700 °C into NiAl and Ni_3Al. As the compact cools, the kinetics of the peritectoid reaction

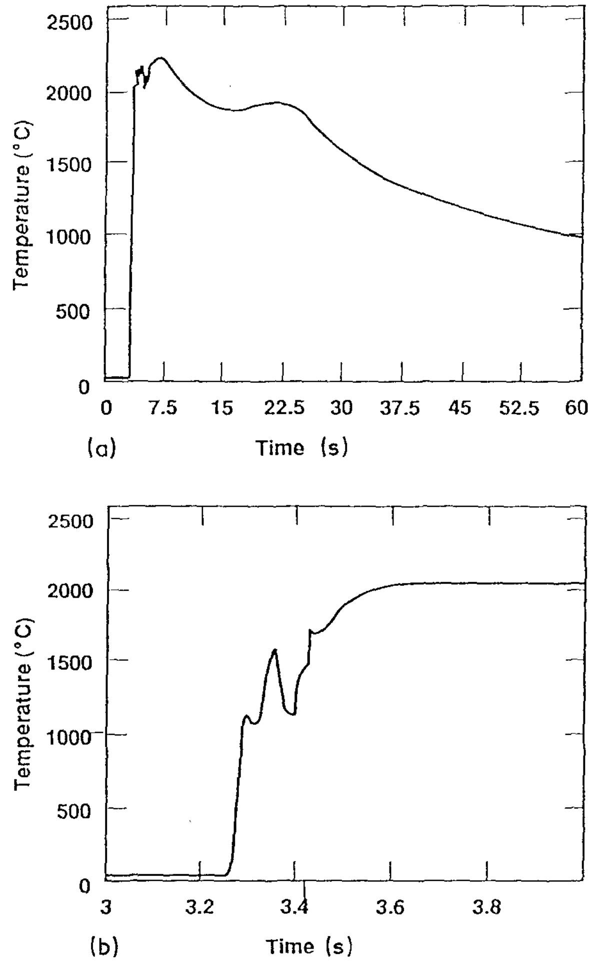

Figure 3 Temperature profiles measured for the combustion of 50 wt % (Ti + C) + 50 wt % (Ni + Al), (a) as-measured, and (b) magnified view of the combustion front.

TABLE II X-ray diffraction results for reactions of the form 50 wt % (Ti + C) + 50 wt % (*x*Ni + *y*Al)

Binder	TiC	Ni	Ni_3Al	Ni_5Al_3	NiAl	Ni_2Al_3	$NiAl_3$	Al	$TiAl_3$
Ni	M	M	–	–	–	–	–	–	–
3Ni + Al	M	–	S	–	–	–	–	–	–
5Ni + 3Al	M	–	S	–	S	–	–	–	–
Ni + Al	M	–	–	–	S	–	–	–	–
2Ni + 3Al	S	–	–	–	–	M	–	–	–
Ni + 3Al	S	–	–	–	–	M	m	–	m
Al	m	–	–	–	–	–	–	m	M

M, major phase; S, secondary phase; m, minor phase.

between solids NiAl and Ni_3Al to form Ni_5Al_3 are slow enough that the phases present in the higher temperature two-phase field are quenched in. It is also apparent from Table II that the compositions with high Al content (Ni + 3Al and Al) result in complex phase relationships including the formation of $TiAl_3$.

3.2.2. *Residual porosity*

The effect of the binder composition on the residual porosity was also studied and the results are shown in Fig. 4. Here, it can be seen that the sample which contained Ni + Al as the binder contains the least amount of porosity (0.3%) in the product. Because NiAl has the highest heat of formation of any of the Ni–Al compounds, this particular reaction would also be expected to have the highest combustion temperature. As a result there is probably more liquid phase present for a longer period of time during the reaction and thus, more densification occurs. As an example of the homogeneity of the porosity found in these products, Fig. 5 shows a low magnification micrograph of a sample which contained 75 wt % (Ti + C) and 25 wt % (Ni). This sample was found to have a porosity of 3.9 % and as can be seen in the micrograph the pores are very small and well distributed.

3.3. Binder content

3.3.1. *Residual porosity*

The effect of the amount of binder in the compact on the residual porosity of the final product was studied for two sets of samples in which the product was either a TiC–NiAl or TiC–Ni_3Al composite. Fig. 6 shows the results of this work for a set of experiments where a mechanical pressure of 20.7 MPa (3000 p.s.i.) was applied. Here, it can be seen that in general there is a slight decrease in the level of porosity as the amount of binder in the compact increases. This is probably a result of an increase in the quantity of liquid phase present during the reaction. From Fig. 6 it is also evident that at low binder contents the identity of the binder has little effect on the residual porosity in the product. At higher binder contents, however, the compacts which contain NiAl as the binder have consistently lower levels of porosity than those which contain Ni_3Al. As was previously explained this is due to differences in the heat of formation of NiAl ($-71\,650\ \mathrm{J\,mol^{-1}}$) and Ni_3Al ($-37\,550\ \mathrm{J\,mol^{-1}}$). The compacts containing NiAl will have higher combustion temperatures which favour densification.

3.3.2. *Microstructure*

Fig. 7 shows optical micrographs of the combustion product of 50 wt % (Ti + C) and 50 wt % (Ni + Al) at two different magnifications. This sample had a mechanical pressure of 20.7 MPa (3000 p.s.i.) applied immediately following combustion resulting in a residual porosity of 0.3 %. The spherical TiC grains (55 vol %) in this sample were found to average 1.2 μm and the microhardness was measured to be 930 $\mathrm{kg\,mm^{-2}}$. It is interesting to note that the TiC grains in this sample

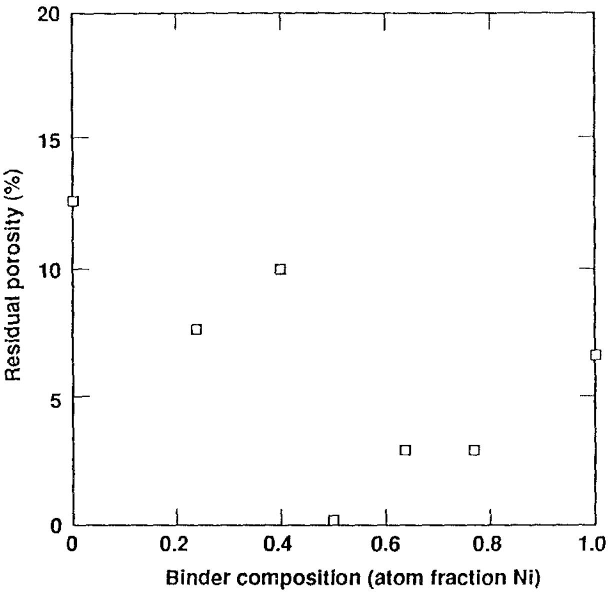

Figure 4 Residual porosity of 50 wt % (Ti + C) + 50 wt % (*y*Ni + *z*Al) samples combusted under 20.7 MPa (3000 p.s.i.).

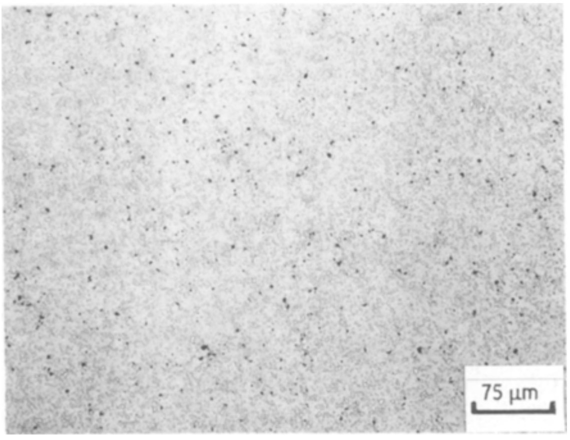

Figure 5 Optical micrograph of combustion product of 75 wt % (Ti + C) + 25 wt % (Ni) combusted under 20.7 MPa (3000 p.s.i.).

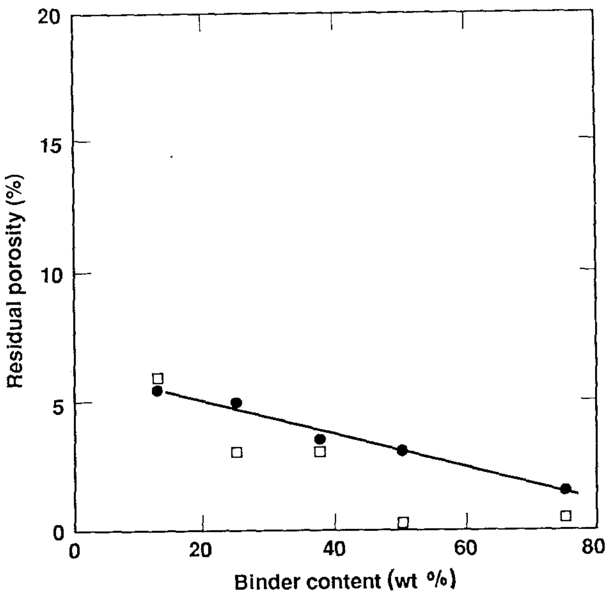

Figure 6 Residual porosity of samples containing varying amounts of (□) (Ni + Al) or (●) (3Ni + Al) as the binder combusted under 20.7 MPa (3000 p.s.i.).

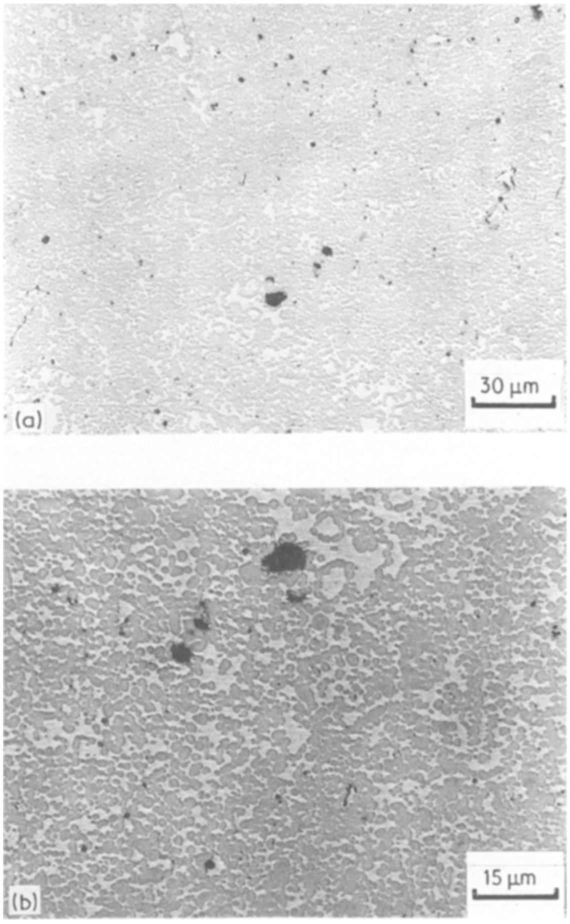

Figure 7 Optical micrographs of the combustion product of 50 wt % (Ti + C) + 50 wt % (Ni + Al) under 20.7 MPa (3000 p.s.i.) at (a) × 500 and (b) × 1000.

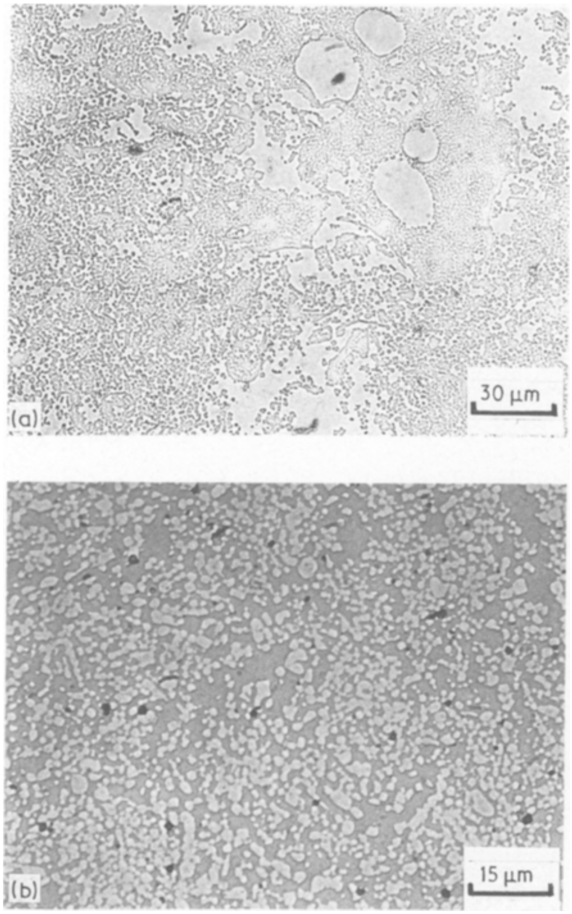

Figure 8 Optical micrographs of the combustion product of 50 wt % (Ti + C) + 50 wt % (3Ni + Al) under 20.7 MPa (3000 p.s.i.) at (a) × 500 and (b) × 1000.

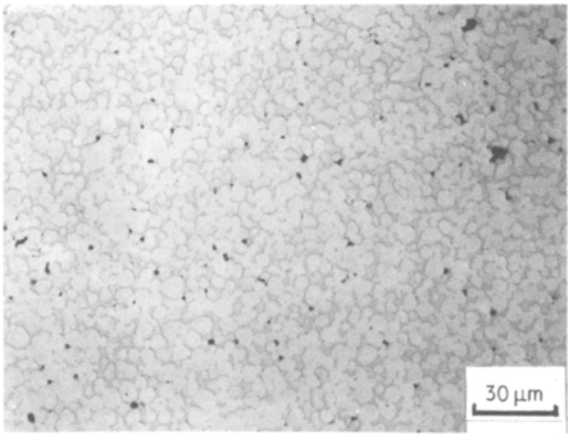

Figure 9 Optical micrograph of the combustion product of 75 wt % (Ti + C) + 25 wt % (Ni + Al) under 20.7 MPa (3000 p.s.i.) at × 500.

appear as if they were precipitated from a melt. Fig. 8 shows optical micrographs of the combustion product of 50 wt % (Ti + C) and 50 wt % (3Ni + Al) at two different magnifications. This sample was combusted under the same conditions as that shown in Fig. 7. Here, the product was found to have a residual porosity of 3.0 %, an average grain size of 1.1 µm, and microhardness of 1111 kg mm^{-2}. Fig. 9 shows an optical micrograph of the combustion product of 75 wt % (Ti + C) and 25 wt % (Ni + Al). Again the combustion was under the same conditions as the previous two samples resulting in a residual porosity of 5.7 %. The average grain size of the TiC was found to be 5.9 µm and the microhardness was measured to be 1916 kg mm^{-2}.

In order to gain some insight into the mechanism of formation of these composites a sample identical to that shown in Fig. 7 was combusted in which graphite fibres were substituted for the carbon black. The reagent mixture was difficult to mix and the sample was harder to ignite than with the carbon black. When examining the microstructure, however, no evidence was found that the fibres had ever existed. The grain size, porosity, and microhardness were virtually identical in the two samples. These results indicate that during the reaction the carbon is dissolved into a melt and then the TiC precipitates out, but further research is needed in this area.

Fig. 10 shows the effect of the amount of binder (both NiAl and Ni_3Al) on the average grain size of TiC in the product. All of these specimens had a mechanical pressure of 20.7 MPa applied immediately after ignition. Here, it can be seen that in general the grain size decreases with an increase in the amount of binder. This can be explained by noting that the combustion temperature will decrease with an increase in the amount of binder. Because grain growth is exponentially dependent upon temperature one would expect the samples which contain more binder to possess smaller TiC grains. This figure also shows that for samples which contain a similar amount of the two different binders the samples with the Ni_3Al binder have consistently smaller TiC grains. This is again attributed to the lower combustion temperatures in these samples due to the lower heat of formation of Ni_3Al.

3.4. Applied pressure

Fig. 11 shows the effect of the amount of applied pressure on the level of porosity in the product for samples which contain 50 wt % of either NiAl or Ni_3Al as the binder. Here, it can be seen that the application of pressures as low as 6.9 MPa (1000 p.s.i.) has dramatic effects on the level of porosity. This graph also shows that, as expected, an increase in the amount of applied pressure results in a decrease in the residual porosity for both binders.

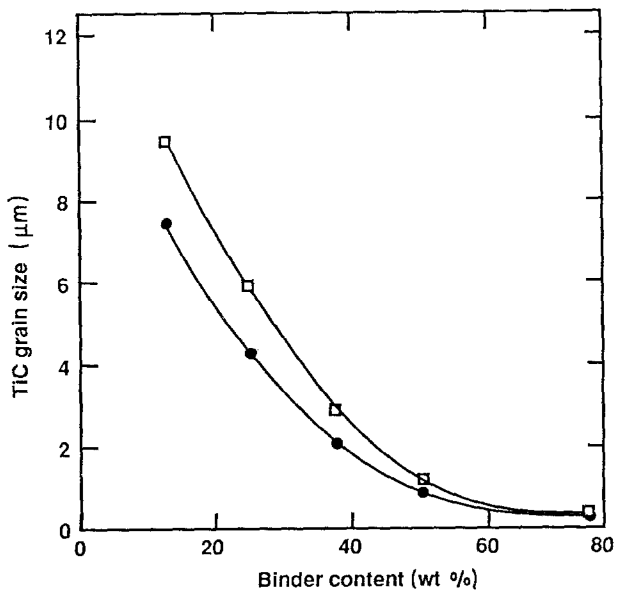

Figure 10 TiC grain size of samples containing varying amounts of (□) (Ni + Al) and (●) (3Ni + Al) at the binder combusted under 20.7 MPa (3000 p.s.i.).

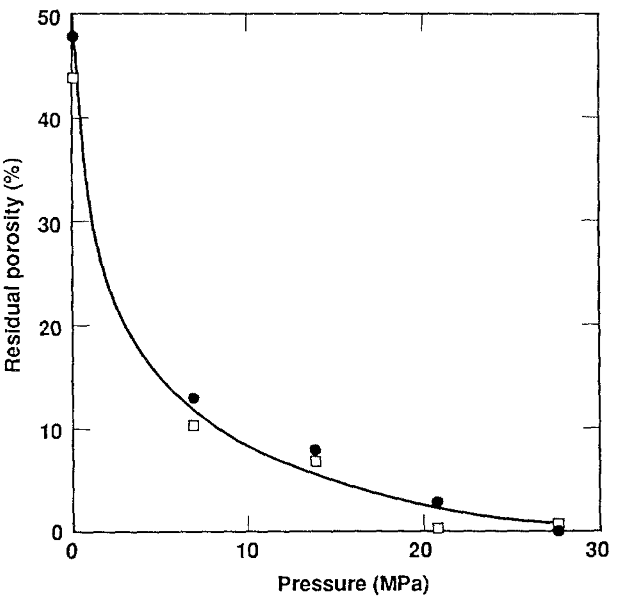

Figure 11 Residual porosity for samples containing both (□) (Ni + Al) and (●) (3Ni + Al) as the binder combusted under various pressures.

4. Conclusion

By using a simple hot-pressing apparatus, certain refractory materials may be synthesized and densified in a one-step combustion process. Specifically, composite materials consisting of TiC–Ni, TiC–NiAl, and TiC–Ni_3Al can be produced at near theoretical density using a combustion synthesis process under relatively low mechanical pressures. It was also shown that very fine-grained materials can be produced in this way and that the grain size can be controlled by changes in the amount of the binder. By adjusting the synthesis conditions it is possible to tailor the properties of the product and to develop further a viable materials production process.

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