Injection Moulding and Heat Treatment of Ni-Cr-Si-B Alloy Powder

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ABSTRACT

Injection moulding, debinding, sintering and heat treatment of Ni-Cr-Si-B alloy powder of high hardness value have been studied. A binder system comprised of two polymers, a major component of water soluble polyethylene glycols (PEGs) and a minor component of very finely dispersed polymethyl methacrylate (PMMA) derived from an emulsion was employed. Mixing of a number of different feedstocks was carried out manually. Following the identification of the optimum binder composition (20 wt. % PMMA, 80 wt. % PEGs) and solid loading (65 Vol. %), several test specimens were injection moulded for further processing. The PEGs were removed by leaching with water. The PMMA was removed by pyrolysis, prior to the sintering stage. Samples were sintered to ~ 99 % of theoretical density. With careful control of the various processing parameters, including sintering temperature and time, cooling rate and heat treatment conditions, good mechanical properties including high hardness of HR_C ~57 were attained. In an attempt to reduce the process cycle time, the sintering ramp was modified to include solutionising and oil-quenching in a single sintering cycle. The hardened samples were tempered at temperatures from 250 to 350 °C for 2 hours. Scanning electron microscopy was used to reveal the micro-structural changes during various sintering and heat-treatment stages.

Key Words: Debinding, Polyethylene Glycols, Polymethy Methacrylate, Leaching, Sintering

1. INTRODUCTION

During the past two decades Metal Injection Moulding (MIM) has evolved as a versatile mass production method for a wide range of complex-shaped metal components. To obtain feedstock for injection moulding, the metal powder is mixed with a polymeric binder by high shear mixing at a volume loading typically between 50 and 70 vol. %. Then, the feedstock is injected into a die cavity where it solidifies and the required shape is formed. The polymeric binder is removed prior to sintering the metal powder compacts. Binder removal is a critical processing step and plays a central role in the success of MIM parts production because the risk of defects forming in the components is particularly high during the debinding stage. Multicomponent binder systems, where the polymers are removed by solvents or degrade at different points of a thermal debinding cycle, have shown considerable potential for minimising debinding defects. Finally, the debinded parts are sintered to high density to obtain near net shape components [1, 2].

Due to their good sinterability fine powders with a particle median around 10 µm is generally preferred for manufacturing parts via MIM route Traditional press and sintering uses metal powders with a particle median from 50-100 µm and a sieve cut of 200-300 µm. Cost of the powder will be the major consideration because coarse powders are relatively cheaper than fine ones. However, coarser powders have lower sintering activity, and less ability to fill thin sections. Lower material cost will be especially important for larger components where the material represents a relatively high cost proportion compared to smaller components. Maybe a

significant material cost reduction can expand the total market of MIM and thus compete with larger components produced by investment casting, forging and machining [3, 4].
The aim of the present study was to explore the possibility of injection moulding of a cheap and relatively coarse Ni-Cr-Si-B alloy powder with high hardness values. Due to its high hardness this powder can be used for manufacturing of various types of tools.

2. EXPERIMENTAL

Ni-Cr-Si-B alloy of high hardness value was selected for this study. The properties, such as chemical composition of the powder together with typical hardness value, density and solidus temperature, obtained from manufacturer's own data sheets, are given in the Table 1.

Table 1:- The chemical composition, hardness value, density and solidus temperature of the Ni-base alloy used for the present study.

Si %	S %	Cr %	Fe %	B %	Ni %	Hardness (HR_C)	Density mg m^{-3}	Solidus Temp., °C
4.4	0.01	15.6	3.35	3.1	Bal.	60	7.9	965

Scanning electron microscopy was used to examine the morphology of the said powder particles. The Coulter LS130 Particle Size Analyzer was used to measure the particle size distribution of the powder. A binder system comprised of two polymers, a major component of water soluble polyethylene glycols (80 wt. % PEG_{1000}) and a minor component of very finely dispersed polymethyl methacrylate (20 wt. % PMMA) derived from an emulsion was used. A 65 vol. % powder loading was used for preparing the feedstock. The feedstock was mixed in two steps. In the first step, the powder was gradually added and mixed into the emulsion to ensure a homogeneous mix (Mixture 1). The PEG was dissolved in warm water and mixed into the Mixture 1and then dried at ~60 °C. It was frequently mixed during drying and then cooling to room temperature to avoid de-mixing. The mixture was then hot extruded using the injection moulding machine. The extruded mixture was chopped into small pieces of ~ 4 to 5 mm in size for easy loading into injection moulding machine. Simple bar-shaped specimens having dimensions 5 x 5 x *55* mm were injection moulded.
Based on the experiences and observations of the previous study on debinding [5,6], leaching of the moulded specimens was done in warm water (~ 60 °C) for about 3 hours, and then the specimens were dried at 60 °C for one hour. Finally, the leached and dried specimens were thermally debinded and sintered under various gas atmospheres. The densities of the sintered samples were measured. The hardness was measured on the C scale using a Rockwell Hardness Tester. The samples for microscopic examination were prepared using standard metallographic techniques. Optical and scanning electron microscopy was used to study the pore morphology and etched structures.

3. RESULTS AND DISCUSSION

A representative scanning electron micrograph of the powder is shown in Figures 1, which shows that powder particles were spherical in shape having some internal voids. The particle size distribution for the said powder is given in Table 2 and plotted in Figure 2. It is considered that mixing as slurry and using emulsion containing very fine PMMA particles resulted in uniform

feedstock. Hot extrusion of the feedstock helps in reducing the entrapped air in the feedstock. Sound moulings were obtained when moulding was carried out in the temperature range of 140-150 °C and pressure 45-50 MPa.

Table 2: The cumulative particle size distribution of the alloy powder (percent finer than).

Size (µm) Finer than	43	37	28	20	13
Percent, %	90	75	50	25	10

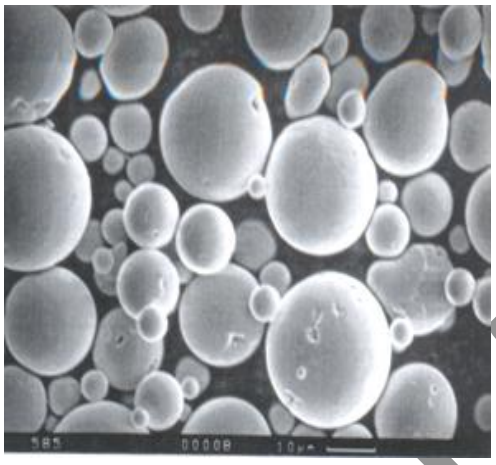

Figure 1: A scanning electron micrograph of the powder showing spherical shape particles having small pores.

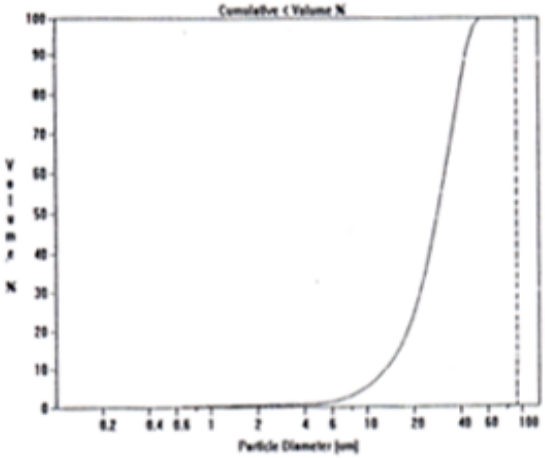

Figure 2: The cumulative volume percent and particle size distribution of the powder.

Leaching of the moulded samples for three hours in warm water (~ 60 °C) was found to be sufficient to remove PEGs and to open-up pore channels for subsequent thermal debinding. The leached samples were dried at 60 °C for one hour.

Unfortunately, no literature on sintering of this powder was found, although it was assumed that liquid phase sintering would occur because of the presence of relatively low melting point eutectics involving silicide and boride phases. Therefore, trial and error methods were used to develop a suitable sintering cycle to obtain the desired properties. Initially various heating cycles under different atmospheres were studied. Based on certain observations during initial experimentation, the following thermal debinding and sintering cycles were investigated for different specimens. Pure argon gas atmosphere was used in all cases.

Cycle No. 1	**Cycle No. 2**
a) Heating at a rate of 6 °C/min. up to 450 °C, b) Held at 450 °C for 10 minutes, c) Heating at a rate of 6 °C/min. from 450 to 985 °C, d) Held at 985 °C for 90 minutes, and e) Cooled in the furnace with the power switched off.	a) Heating at a rate of 8.5 °C/min. up to 450 °C, b) Held at 450 °C for 10 minutes, c) Heating at a rate of 10 °C/min. from 450 to 995 °C, d) Held at 995 °C for 45 minutes, and e) Furnace cooled.

Cycle No. 3	**Cycle No. 4**
a) Heating at a rate of 10 °C/min. up to 1015 °C, b) Held at 1015 °C for 45 minutes, and c) Furnace cooled.	a) Heating at a rate of 5 °C/min. up to 400 °C, b) Held at 400 °C for 15 minutes, c) Heating at a rate of 10 °C/min. from 400 to 1000 °C, d) Held at 1000 °C for 30 minutes, and e) Furnace cooled.

The following observations were made during the present study:

1) During initial experimentation, while sintering under a nitrogen atmosphere or in still air, the powder was not properly sintered and the final specimens were very brittle. This is probably due to the formation of nitrides or oxides at the sintering temperatures.
2) Sintering under pure Ar, Ar-2 % H_2 and a pure hydrogen atmosphere gave better results with the sintered bars being much less brittle.
3) Sintering of the specimens at the solidus temperature (965 °C) for 30 minutes gave very low density (about 85 % of the theoretical density). However, a specimen sintered at 965 °C for *5* hours under pure hydrogen atmosphere, followed by heating at a rate of 2 °C/min. up to 975 °C and holding at this temperature for 10 minutes and finally cooling with furnace, gave about 98 % of the theoretical density, Figure 3.

Based upon the above observations, the thermal debinding and sintering was carried out in one step in the same furnace under pure argon gas atmosphere. The results of different heating cycles are given below:

Cycle No. 1)

No cracking or distortion was observed in the sintered part. The density of the sintered sample was about 98.5 % of the theoretical value. The HR_C hardness values measured at three different points were 57, 57 and 57, which shows a very uniform hardness, hence, uniform properties. The microstructure of a polished surface is shown in Figure 4.

Cycle No. 2)

No cracking or distortion was observed in the sintered part. The density of the sintered sample was about 98 % of the theoretical value. The HR_C hardness values measured at three different points were 51, 51 and 52, which shows a very uniform hardness and, hence, uniform microstructure and properties. A microstructure of the polished surface is shown in Figure 5.

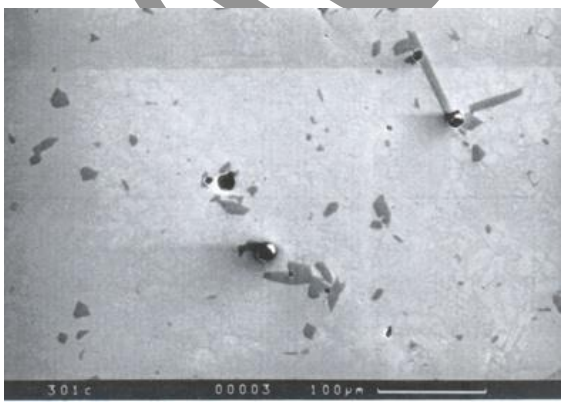

Figure 3: SEM micrograph of a specimen sintered at 965 °C for 5 hours followed by heating at 975 °C for 10 minutes, showing sintered homogenization and some near-spherical porosity.

Figure 4: SEM of a sintered specimen, debinded and sintered using Cycle No 1.

Cycle No. 3)
The samples were distorted and the edges of the square bar were rounded, indicating excessive melting.

Cycle No. 4)
No cracking or distortion was observed in the sintered part. The density of the sintered sample was about 99 % of the theoretical value. The HR_C Hardness values measured at three different points were 57, 57.5 and 58. The microstructure of the polished surface is shown in Figure 6.

The samples having hardness HR_C 57 and tempered at 300 to 350 °C gave hardness about HR_C 54 – 55, but it is considered that this treatment will improve the toughness.

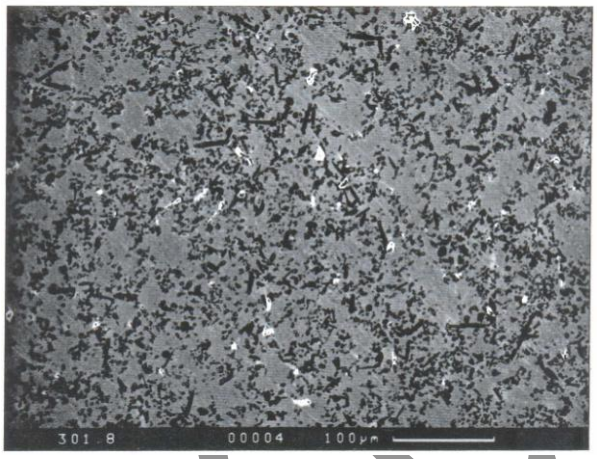

Figure 5: SEM of a sintered specimen, debinded and sintered using Cycle No 2.

Figure 6: SEM of a sintered specimen, debinded and sintered using Cycle No 4.

CONCLUSIONS

Based on the observation made during the present experimentation, the following conclusions can be drawn:

1. Sound moulings were obtained when moulding was carried out in the temperature range of 140-150 °C and pressure 45-50 MPa.
2. Water leaching removed the major binder component (i.e. 80 vol. % PEG) and the remaining binder can be easily removed by thermal treatment.
3. While sintering under a nitrogen atmosphere or in still air, the powder was not properly sintered and the final specimens were very brittle. This is probably due to the formation of nitrides or oxides at the sintering temperatures.
4. Sintering under pure Ar, Ar-2 % H_2 and a pure hydrogen atmosphere gave better results with the sintered bars being much less brittle.

5. Liquid phase sintering was observed because of the presence of relatively low melting point eutectics involving silicide and boride phases. This resulted in a high sintered density, i.e. about ~ 99 % of the theoretical density.
6. Sintering above 1000 °C, the samples were distorted and the edges of the square bar were rounded, indicating excessive melting.
7. Samples sintered at 1000 °C for 30 minutes and furnace cooled attained a density of about 99 % of the theoretical value. The HR_C Hardness values measured at three different points were 57, 57.5 and 58, hence uniform hardness and uniform properties

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