Sintered 316L/Cu/h-BN composites

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Abstract
Sintered 316L/h-BN composites show high potential as self-lubricating materials, which can be applied as moving parts where lube oils and greases are not applicable and inaccessible for maintenance. The past production of such composites by sintering faced two problems. Firstly - interaction between 316L matrix and h-BN resulting in loss of h-BN content and its lubricity. And secondly - poor 316L matrix integrity. This work employed two approaches to solve such problems. The first approach was the use of nitrogen-containing atmosphere for sintering, to retard 316L matrix and h-BN interaction. And the second approach, was copper addition to promote sintering of 316L powder particles. Sintered self-lubricating 316L/Cu/h-BN composites were produced from mixtures of 3 different 316L/Cu matrices (made by additions of 2.0, 4.0 and 6.0 wt.% copper powder to 316L powder) and 15 vol.% of h-BN powder. Green compacts of powder mixtures were sintered under cracked ammonia (75 vol.% hydrogen + 25 vol. % nitrogen) at 1300°C for 60 minutes. The sintered composites were cooled in a Linn high temperature sintering furnace. It was found that copper additions led to the decrease of densities of sintered 316L/Cu/h-BN composites, compared to that of sintered 316L/h-BN composite, due to porosity left behind by copper powder melting and dissolution. Tensile strengths of sintered 316L/Cu/h-BN composites were improved when copper contents were 4 and 6 wt.% There was no intergranular phase, the evidence of 316L matrix and h-BN interaction in all experimental sintered composites. Microstructural observation by scanning electron microscopy (SEM) also revealed that h-BN flakes still existed in pores of sintered composites. The unreacted h-BN flakes are expected to provide lubricity of sintered composites.

Keywords: Sintering, self-lubricating composites, 316L/Cu/h-BN, mechanical properties
1. Introduction

Self-lubricating components are widely used with many applications such as bearings, gears, seals and connectors [1]. These components are able to extend service life, and reduce the maintenance operation of moving components, by releasing and forming a lubricant film on a contact surface [2]. The lubricant film prevents direct contact between two rubbing surfaces, even under high loads, resulting in reducing wear and heat in relative motion.

Among various types of self-lubricating components, a self-lubricating composite is suitable for such an application. Sintering a mixture of metal powder and solid lubricant is a traditional method for processing a self-lubricating composite. Sintered materials are usually porosity, by nature. The pore formation is due to the presence of cusp-shape voids, generated at powder particle corners in a powder compact [3-6]. This porosity is considered as an ideal site for impregnating a solid lubricant, to form a self-lubricating composite.

Various types of solid lubricants including molybdenum disulfide, graphite, dichalcogenide and boron nitride [7]. Molybdenum disulfide [8] and graphite [9] are widely used in many self-lubricating composites, generally produced by sintering. However, these materials experience one major problem, which involves their decomposition under high sintering temperatures. Hexagonal boron nitride (h-BN), which has high thermal and chemical stability, is considered for this research because it has good lubricating properties due to its crystal structure similar to that of graphite. Due to the lubricating potential of h-BN, it was introduced to sintered stainless steel 316L matrix by ‘the press and sinter’ process [10].

A previous study of sintered 316L/h-BN composites revealed that there was an intergranular boride phase formed in the materials. The intergranular boride phase resulted from a reaction between boron from h-BN decomposition and iron-based powder particles. The interaction between 316L matrix and h-BN resulted in a loss of h-BN content and its lubricity. However, it has been found that the intergranular boride phase, formed with very small amounts under a pure hydrogen atmosphere [11, 12]. With the presence of nitrogen in cracked ammonia (75 % hydrogen and 25 % nitrogen) atmosphere, it is expected that the interaction between h-BN and stainless steel 316L matrix to form borides, will be minimized.

A recent discovery found that the sintering atmosphere of cracked ammonia could retard h-BN decomposition and subsequent boride formation, but the sintered composite materials still had inferior mechanical properties due to poor 316L matrix integrity [13]. This work employed two approaches to solve such problems. The first approach was to use a cracked ammonia atmosphere for sintering, to retard 316L matrix and h-BN interaction. The second approach was to add copper, which was expected to promote the liquid phase sintering of 316L powder particles.

2. Experimental procedure

2.1 Materials preparation

The materials employed for this investigation included 316L stainless steel powder, solid lubricant powder (15 Vol.% h-BN) and copper powder (2, 4, 6 wt.%). were prepared by using a tumbling mixer with a speed of 40 rpm. Powder mixtures were then compacted into green parts with a green density of 6.5 g/cm³. Green compacts were sintered under cracked ammonia at 1300°C for 60 minutes and cooled in a Linn high temperature sintering furnace at the rate of 0.1°C/s.

2.2 Materials characterization

Sintered density was determined by using the Archimedes method. Microstructural observation was performed by following a standard metallography method. The sintered specimens were cut and polished down to 1 μm and etched with 2% Nital. To observe the general microstructure, an optical microscopy (OM). Scanning electron microscopy (SEM) technique was performed on the specimens. For observing the decomposition of h-BN energy, a dispersive spectroscopy (EDS) mapping technique was used.
Mechanical properties of the sintered specimens were tested by using a universal testing machine and hardness tester.

3. Results and Discussion

3.1 Microstructure

The experimental sintered Cu-bearing composites showed porosity higher than that of the sintered Cu-free 316L specimen (Figure 1). Microstructures of sintered 316L/Cu/h-BN composites with various Cu contents 0-6 wt% showed in Figure 1. The experimental sintered Cu-bearing composites showed porosity higher than that of the sintered Cu-free 316L specimen. It was found that copper additions led to the decrease of densities of sintered 316L/Cu/h-BN composites (Figure 4, due to porosity left behind by copper powder melting and dissolution). It was difficult to identify solid lubricant h-BN particles by observation under OM technique and SEM SE mode (in the top row of Figure 2). Differentiation of matrix, pore and h-BN was available by using SEM SE mode (in the bottom row of Figure 2). No free copper was detected in experimental sintered composites. EDS mapping analysis was performed on a sintered composite added with h-BN (Figure 3). The results clearly showed the coexistence of nitrogen (N) and boron (B) atoms.

High porosity in the experimental sintered composites (Figure 4) is due to copper (Cu) dissolution into 316L matrix. The pores left behind by Cu dissolution are not remedied or refilled. Cu is supposed to become liquid during heating and sintering. During cooling the liquid Cu is expected to solidify and fill empty pores in a sintered composite. However, no free copper is detected in any sintered composites. There are two possible ways related to undetectable free Cu. The first is that solubility of Cu in 316L matrix is higher than expectation. The second is that the dissolved Cu precipitate as nano Cu particles in 316L matrix. Since these nano Cu particles cannot be detected by the equipment used in this work and the formation of nano Cu particles in 316L matrix was already reported in some research works [14, 15], the nano Cu precipitation is highly possible for undetectable free Cu in the sintered composites.

The h-BN retention in the experimental sintered composites is strongly supported by the evidences given in the bottom row of Figure 2 and the EDS analysis result given in Figure 3. In previous works [10, 16, 17], the interaction between h-BN and 316L matrix results in formation of intergranular boride phase, which affects tribological property of sintered 316L/h-BN composites. The formation of intergranular boride phase retarded by employing cracked ammonia sintering atmosphere has been recently reported in [13]. Thus, the h-BN retention in the experimental sintered composites strongly confirms the hypothesis that cracked ammonia sintering atmosphere can prevent h-BN decomposition, even it is in contact with Fe-based materials at high temperatures. The mechanism responsible for h-BN decomposition is proposed here as the reversible reaction.
During heating and sintering, if BN is allowed to decompose the reaction products are free B and nitrogen gas. The high concentration of nitrogen gas due to cracked ammonia atmosphere (75 % H₂ and 25 % N₂) will cause reversible reaction, which yields BN again. Due to such reversible reaction, the B amount dissolved in 316L is very small. Consequently, the eutectic melting according to Equation (2) hardly occurs.

\[ \text{Fe} + \text{Fe}_2\text{B} \rightarrow \text{Liquid} \]  \hspace{2cm} (2)

In case that very small amount or no liquid is formed, solidification to form the intergranular boride phase will be limited or not occur. Microstructures of the sintered composites hardly show the intergranular boride. Moreover, close observation by SEM also reveals h-BN particle flake shape (Figure 5), which confirms the h-BN retention in the experimental sintered composites.
**Figure 2.** SEM micrograph (SE in the top row and BSE in the bottom row) of sintered 316L/h-BN composites.

**Figure 3.** EDS mapping analysis of a sintered 316L/h-BN composite.
3.2 Mechanical Properties

Tensile strength and elongation of sintered 316L/Cu/h-BN composites improved with increasing copper content whereas the drop of hardness was found in 2 and 4 wt. % Cu additions (Figure 6). The overall mechanical properties of the sintered composites are still low. The main reason for poor mechanical properties is high porosity left behind by Cu dissolution. It was expected in this work that Cu addition would help improving sintered density by liquid phase sintering, by which liquid Cu would fill empty pores and wet grain boundaries between 316L grains. However, there is no evidence for free Cu in all sintered composites. It is possible that the added Cu contents may be too low to form free Cu, which improves sintered density and mechanical properties of sintered composites. Further work is necessary, to obtain liquid phase sintering in this kind of sintered composites.
4. Conclusions

1) Under a cracked ammonia atmosphere and at sintering temperatures of 1300°C, h-BN was still encapsulated in pores of sintered composites. The remaining h-BN, indicated by the absence of intergranular boride phase, was confirmed by EDS analysis. The hypothesis, in which nitrogen-containing sintering atmosphere retards h-BN decomposition and boride formation, was proved. The unreacted h-BN flakes were expected to provide lubricity of sintered composites.

2) Copper additions led to the decrease of densities of sintered 316L/Cu/h-BN composites, compared to that of sintered 316L/h-BN composite, due to porosity left behind by Cu powder melting and dissolution.

3) Tensile strengths of sintered 316L/Cu/h-BN composites were improved when Cu contents were 4 and 6 wt.%. It was possible that the Cu addition improved mechanical properties of sintered composites due to the solution strengthening by copper.

Acknowledgments

This work is funded by the project P1951261 supported by National Science and Technology Development Agency (NSTDA). The first author is also financially supported by TAIST-Tokyo Tech scholarship. The authors are grateful for supports from Thailand National Metal and Materials Technology Center (MTEC) and King Mongkut's Institute of Technology Ladkrabung (KMITL).

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