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# High Temperature Self-Lubricating Materials

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/55645>

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## 1. Introduction

There is an ongoing need for developing high temperature self-lubricating materials to meet the severe conditions of mechanical systems, such as advanced engines which require increasingly high working temperatures (at 1000 °C or above) and long life [1-7]. However, achieving and maintaining low friction and wear at high temperatures have been very difficult in the past and still are the toughest problems encountered in the field of tribology [8,9]. Yet, the efforts to explore novel high temperature self-lubricating materials possessing favorable frictional property and superior wear resistance abilities have never stopped. As a result, great strides have been made in recent years in the fabrication and diverse utilization of new high temperature self-lubricating materials that are capable of satisfying the multifunctional needs of more advanced mechanical systems [10-15]. The following tribological issues addressed in this chapter are presented:

- i. High temperature self-lubricating alloys
- ii. Ni matrix high temperature self-lubricating composites
- iii. Intermetallics matrix high temperature self-lubricating composites
- iv. Ceramic matrix high temperature self-lubricating composites
- v. High temperature self-lubricating coatings.

## 2. High temperature self-lubricating alloys

It is well known that the friction and wear of metal alloys at high temperatures are controlled by their tribochemically generated oxide films [16-20]. Consequently, on a hard metal substrate-formed lubricating soft oxide layer, with low shear strength, results in considerable wear reduction and sometimes a decrease of friction. Hence the idea is reasonable and feasible that realization of self-lubricating property by in situ oxide formation on sliding surface at high temperatures. Peterson M.B. and Li S.Z. applied this concept to develop high temperature self-lubricating alloys, such as Ni-Cu-Re, Co-Cu-Re, and Fe-Re, by lubrication with naturally occurring oxides during the sliding process [19-23].

Meanwhile, the principles of oxide lubrication and to develop alloys based on tribochemically generated oxide films were proposed as to what alloy compositions will produce effective oxide films, what interface temperatures and what operating conditions are necessary and what oxides will be effective[20].

In addition, it is another effective approach to improvement of tribological properties by addition of active elements, such as sulfur and selenium [24,25]. At the interface, heating and sliding produces certain compounds with lubricious properties by tribochemical reaction between the active elements and metal components.

### **3. Ni matrix high temperature self-lubricating composites**

There is a great need in current technology for solid lubricated systems that will perform satisfactorily over a wide range of temperatures. Ni matrix high temperature self-lubricating composites play a significant role in attaining this goal and achieve applications. In the past years, a series of self-lubricating composites based on nickel alloys have been developed by powder metallurgy methods [26-35]. Of these materials, PM212, which was developed by NASA Glenn (previous NASA Lewis) Research Center, shows promise for use over a wide range of temperatures (ranging from room temperature to 900 °C) [26,27]. This material is comprised of metal Ni-Co binder, ceramic  $\text{Cr}_3\text{C}_2$  matrix and solid lubricants  $\text{CaF}_2/\text{BaF}_2$  and Ag. These three components play roles in providing binding, wear resistance and self-lubrication, respectively. Another NASA PM304 (NiCr- $\text{Cr}_2\text{O}_3$ -Ag- $\text{BaF}_2/\text{CaF}_2$ ) possesses well tribological behavior from room temperature to 650 °C [28], however, above 800 °C, the decline in mechanical property degrades its wear resistance. Based on the design view of NASA, many efforts are made to explore new self-lubricating composites based on nickel alloys, such as Nickel alloy-graphite-Ag, Nickel alloy-WC/SiC-PbO, Nickel alloy-Ag- $\text{CeF}_3$ , Nickel alloy-graphite- $\text{CeF}_3$ , Nickel alloy- $\text{MoS}_2$ -graphite, etc. [29-35]. Although the Ni-based high temperature self-lubricating composites attract much attention, their friction and wear properties over a wide temperature range are inferior to those of PM212.

### **4. Intermetallics matrix high temperature self-lubricating composites**

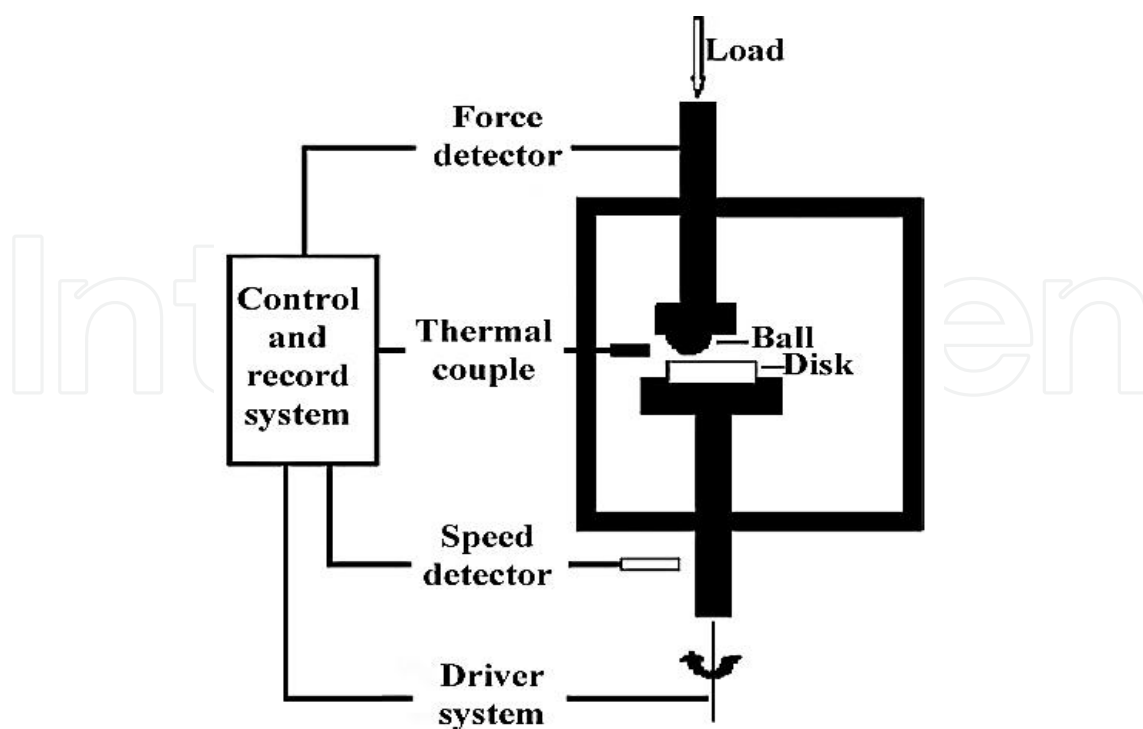
Since the strong internal order and mixed (metallic and covalent/ionic) bonding, intermetallic compounds often offer a compromise between ceramic and metallic properties when hardness and/or resistance to high temperatures is important enough to sacrifice some toughness and ease of processing [36-38]. Since Aoki and Izumi reported the remarkable achievements of ductility in  $\text{Ni}_3\text{Al}$  alloys by B doping in 1979, structural intermetallics and related materials have been actively investigated. Intermetallics have given rise to various novel high temperature self-lubricating materials developments.

#### **4.1. $\text{Ni}_3\text{Al}$ matrix high temperature self-lubricating composites**

$\text{Ni}_3\text{Al}$  is the intermetallic compound that has been most intensively studied from both fundamental and practical points of view [39-47]. In the past years, a great deal of work has been addressed to the study of the effect of alloying elements, mechanical properties,

oxidation and corrosion. The results indicated that  $\text{Ni}_3\text{Al}$  may be an excellent matrix for high temperature self-lubricating composite owing to its high temperature strength, good oxidation resistance and corrosion resistance behavior. However, till now, the tribological behavior of  $\text{Ni}_3\text{Al}$  matrix composite has not been researched systemically.

Recently, a series of  $\text{Ni}_3\text{Al}$  high temperature self-lubricating composites were developed in Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences [15, 48-55]. The self-lubricating composites, which consist of  $\text{Ni}_3\text{Al}$  matrix with Cr/Mo/W, Ag and  $\text{BaF}_2/\text{CaF}_2$  additions, exhibit the low friction coefficient and wear rate at a wide temperature range from room temperature to 1000 °C. Additionally, in order to design and fabricate high temperature self-lubricating composite with excellent tribological property from room temperature to 1000 °C and also explore the friction and wear mechanisms at high temperatures, the effects of solid lubricant and reinforcement on tribological properties of  $\text{Ni}_3\text{Al}$  matrix high temperature self-lubricating composites at a wide temperature range from room temperature to 1000 °C were investigated. The tribological behavior was studied from room temperature to 1000 °C on an HT-1000 ball-on-disk high temperature tribometer. The schematic diagram of HT-1000 ball-on-disk high-temperature tribometer is shown in Fig. 1. The rotating disk was made of the sintered sample with a size of  $18.5 \times 18.5 \times 5$  mm, and the stationary ball was the commercial  $\text{Si}_3\text{N}_4$  or SiC ceramic ball with a diameter of 6 mm. The selected test temperatures were room temperature, 200, 400, 600, 800 and 1000 °C. The tribological tests were carried out at an applied load of 10 or 20 N, sliding speed of 0.2 m/s and testing time of 30 or 60 min. The furnace temperature, which was monitored using a thermocouple, was raised at a heating rate of 10-12 °C/min to the set point.



**Figure 1.** The schematic diagram of HT-1000 ball-on-disk high-temperature tribometer

#### 4.1.1. *Effect of solid lubricant on the tribological behavior*

To obtain high temperature self-lubricating materials with well tribological and mechanical properties, suitable solid lubricant selected is very important. Since no single material can provide adequate lubricating properties over a wide temperature range from room temperature to high temperatures (800 or even 1000 °C), many efforts are made to a synergetic lubricating action of the composite lubricants, namely, the combination of low temperature lubricant and high temperature lubricant [56].

The conventional solid lubricants, such as MoS<sub>2</sub> and graphite, cannot meet the demand on tribological and mechanical properties due to their inadequate oxidation resistance in air above 500 °C. Hexagonal boron nitride (hBN) has been considered an effective solid lubricant for high temperature applications since it has a graphite-like lamellar structure. However, the non-wettability and poor sinterability of hBN would restrict its applications. Except for the above layered lubricants, soft noble metal Ag and Au should be as a promising lubricant for Ni<sub>3</sub>Al at low temperatures (below 450 °C) due to the low shear strength and stable thermochemistry.

It was found that Ag added into the Ni<sub>3</sub>Al matrix composite exhibited no reactants between Ag and other additives detected after the hot-sintering process. Moreover, the composite with Ag had higher strength than those with graphite or MoS<sub>2</sub>. Furthermore, during frictional process, Ag kept favorable thermal stability at low temperatures, whereas oxidation reaction could happen between Ag and other additives in the composite at high temperatures. It is noteworthy that the oxidation products like AgMoO<sub>4</sub> are beneficial to improvement of lubricity.

In a search for even higher temperature solid lubricants for Ni<sub>3</sub>Al, many efforts have been performed on inorganic salts and fluorides of alkali metals [51-53].

Fluorides have shown promise as high-temperature solid lubricants to provide low friction coefficient and wear according to the previous references [57,58]. Ni<sub>3</sub>Al-Cr-Ag-BaF<sub>2</sub>/CaF<sub>2</sub> composites were synthesized by powder metallurgy technique [15,51,59]. XRD results indicated that components in the sintered Ni<sub>3</sub>Al matrix composites did not react on each other and no any new compound formed during the fabrication process. XRD patterns of worn surfaces after frictional tests presented that at 600 °C, BaCO<sub>3</sub> in the form of weak peak appears, and at 800 °C, no BaF<sub>2</sub> peaks present but BaCrO<sub>4</sub> peaks were found. Fluorides served as high temperature lubricants and exhibited a good reduce-friction performance at 400 and 600 °C. However, at 800 °C, BaCrO<sub>4</sub> formed on the worn surface due to the tribo-chemical reaction at high temperatures provided an excellent lubricating property.

Inorganic salts are obvious candidates for consideration owing to low shear strength and high ductility at elevated temperatures. The high temperature lubricious behavior of some sulfates, chromates, molybdates and tungstates has been extensively studied [60-66]. Important early work on high-temperature solid lubricant reported that molybdates appeared to be the promising high-temperature solid lubricants [56]. As a high-temperature

solid lubricant, and similar to  $\text{CaWO}_4$  and  $\text{CaMoO}_4$ ,  $\text{BaMoO}_4$  has scheelite structure and adequate thermophysical properties [67, 68]. However, till now, the lubricious behavior of  $\text{BaMoO}_4$  has not been explored in detail. Recently,  $\text{BaCrO}_4$  has attracted much attention due to its lubricating property at a wide temperature range [62].  $\text{BaCrO}_4$  has an orthorhombic structure, and its thermal data shows that the  $\text{BaCrO}_4$  phase is thermally stable to 850 °C [69,70]. Therefore, they could be expected as promising high-temperature solid lubricants for  $\text{Ni}_3\text{Al}$ .

It can be noted that no  $\text{BaMoO}_4$  peaks presented but Ni, Mo and  $\text{BaAl}_2\text{O}_4$  peaks were found in XRD results of the sintered  $\text{Ni}_3\text{Al}$  matrix composites, and the peaks of Ni, Mo and  $\text{BaAl}_2\text{O}_4$  get stronger with the increase of  $\text{BaMoO}_4$ . This means that the formation of Ni, Mo and  $\text{BaAl}_2\text{O}_4$  results from high-temperature solid state reaction between  $\text{Ni}_3\text{Al}$  and  $\text{BaMoO}_4$  during the fabrication process. However, during the sliding process at high temperatures,  $\text{BaMoO}_4$  re-formed on the worn surfaces. The occurrence of  $\text{BaMoO}_4$  is possible when considering the higher temperature rise at the instantaneous contacting surface in the rubbing process at high temperatures. It could come from the oxidation of Mo and then a reaction with  $\text{BaAl}_2\text{O}_4$ . The frictional results showed that  $\text{Ni}_3\text{Al}$  matrix composites with addition of  $\text{BaMoO}_4$  offered better friction behavior than the monolithic  $\text{Ni}_3\text{Al}$  above 600 °C. The addition of  $\text{BaMoO}_4$  could improve the tribological property, but lead to a decrease in hardness. Below 400 °C,  $\text{Ni}_3\text{Al}$  matrix composites with addition of  $\text{BaMoO}_4$  were non-lubricating, unless at 600°C, re-formed  $\text{BaMoO}_4$  provided a well lubricity.

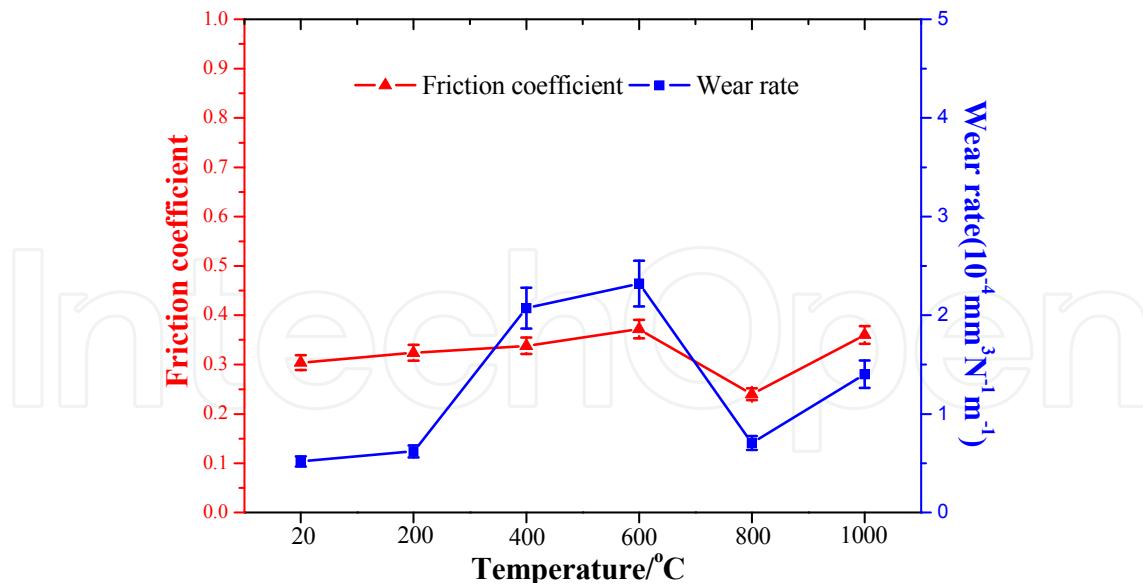
The same as  $\text{BaMoO}_4$ ,  $\text{Ni}_3\text{Al}$  composites with addition of  $\text{BaCrO}_4$  showed the absence of  $\text{BaCrO}_4$  but the formation of  $\text{BaAl}_2\text{O}_4$  during the fabrication process. At high temperatures, it was found the re-formation of  $\text{BaCrO}_4$  on the worn surface. Since  $\text{BaMoO}_4$  and  $\text{BaCrO}_4$  as solid lubricants for  $\text{Ni}_3\text{Al}$  intermetallics only have low friction coefficient at narrow temperature range, they should not be used solely.

#### *4.1.2. Effect of reinforcement on the tribological behavior*

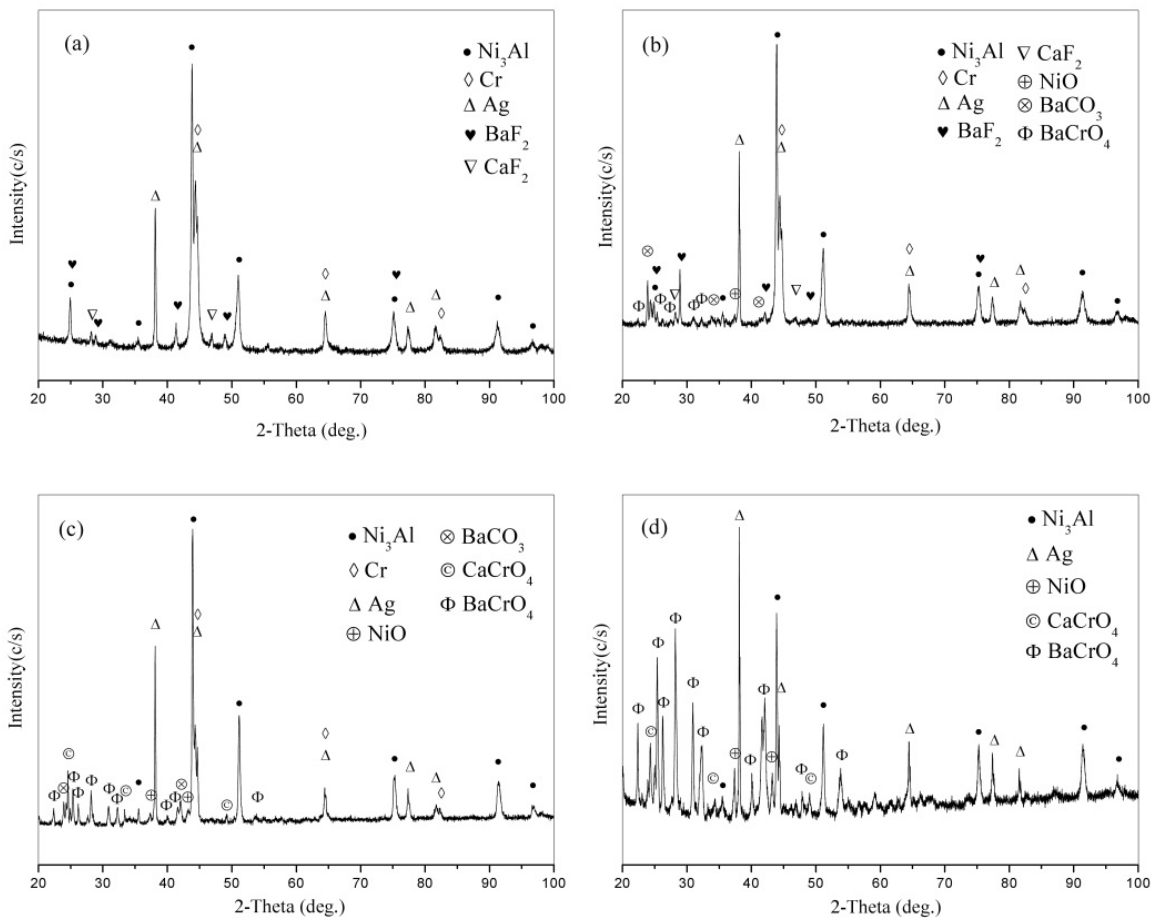
From the point of view of the principle of tribology, the ideal composition of a high temperature solid lubricant material should be composed of high strength matrix, reinforcement and solid lubricant. Reinforcement plays a significantly role in mechanical properties and tribological behavior. Generally, the reinforcement can be classified into two categories: one is the hard ceramic phase, and the other is the soft metal phase. In order to promote the tribological performance of  $\text{Ni}_3\text{Al}$  matrix composites, the different kinds of reinforcements were added.

Titanium carbide is selected as reinforcement because it is a ceramic with high melting point, extreme hardness, low density, moderate fracture toughness, and high resistance to oxidation and corrosion and a very good wettability with  $\text{Ni}_3\text{Al}$  [71-75]. Observations on TiC reinforced  $\text{Ni}_3\text{Al}$  matrix composite showed that the mechanical properties were improved, although the friction and wear performance were not promoted [59].



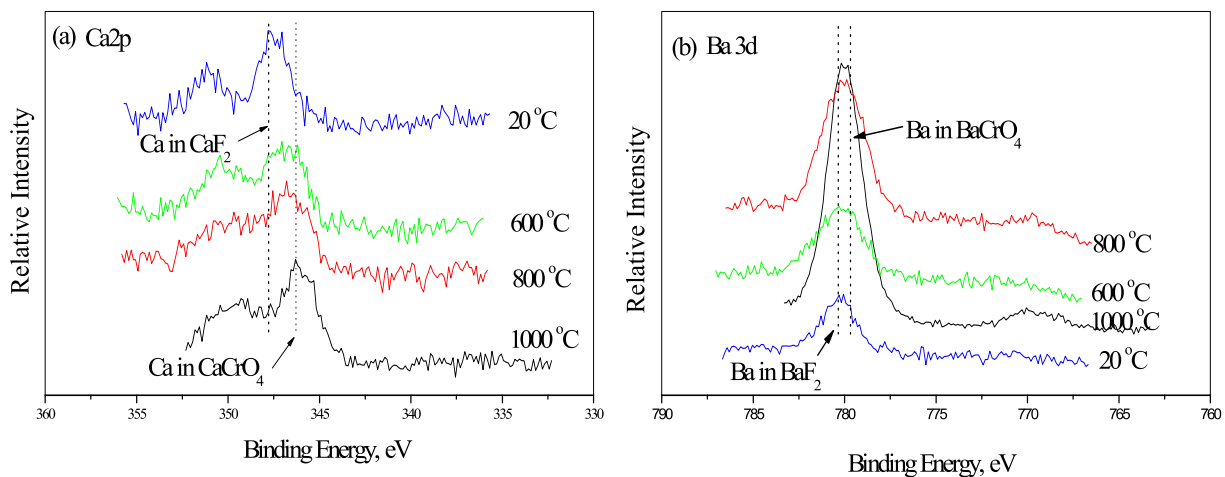


**Figure 2.** Variations of friction coefficients and wear rates of  $\text{Ni}_3\text{Al}-20\%\text{Cr}-12.5\%\text{Ag}-10\%\text{BaF}_2/\text{CaF}_2$  composite at different temperatures (tested at an applied load of 20 N and sliding speed of 0.2 m/s against  $\text{Si}_3\text{N}_4$  ceramic ball)



**Figure 3.** XRD results of the sintered sample: (a) and worn surfaces of  $\text{Ni}_3\text{Al}-20\%\text{Cr}-12.5\%\text{Ag}-10\%\text{BaF}_2/\text{CaF}_2$  composite after tests at different temperatures: 600  $^{\circ}\text{C}$  (b), 800  $^{\circ}\text{C}$  (c) and 1000  $^{\circ}\text{C}$  (d)

Chromium additions to  $\text{Ni}_3\text{Al}$ , as a solution, have been reported the effectiveness of alloying about 8 at% Cr for suppressing the oxygen embrittlement of  $\text{Ni}_3\text{Al}$  alloys at intermediate temperatures [39-42]. Additionally, Cr particles, as reinforcement, can improve the strength of  $\text{Ni}_3\text{Al}$ -Cr composite at low temperatures, whose strength is determined by the strength of the Cr particles and the good bonding between the matrix and Cr reinforcement [76]. The results presented that Cr added to  $\text{Ni}_3\text{Al}$  matrix composite not only enhanced mechanical strength but also ameliorated tribological performance [15]. Further study on the  $\text{Ni}_3\text{Al}$ -Cr-Ag- $\text{BaF}_2/\text{CaF}_2$  self-lubricating composite was carried out by tailoring the composition of the additives [48,51,59]. It was found that  $\text{Ni}_3\text{Al}$ -20%Cr-12.5%Ag-10% $\text{BaF}_2/\text{CaF}_2$  (in weight) composite offered the low friction coefficient 0.24-0.37 and wear rate  $0.52\text{-}2.32 \times 10^{-4} \text{ mm}^3/\text{Nm}$  at a wide temperature range from room temperature to  $1000^\circ\text{C}$  (shown in Fig. 2). Especially at  $800^\circ\text{C}$ , the excellent self-lubricating performance was obtained among the composites.



**Figure 4.** XPS results of worn surfaces of  $\text{Ni}_3\text{Al}$ -20%Cr-12.5%Ag-10% $\text{BaF}_2/\text{CaF}_2$  composite after tests at different temperatures: (a)  $\text{Ca}2p$  3/2 photoelectron peak; (b)  $\text{Ba}3d$  5/2 photoelectron peak

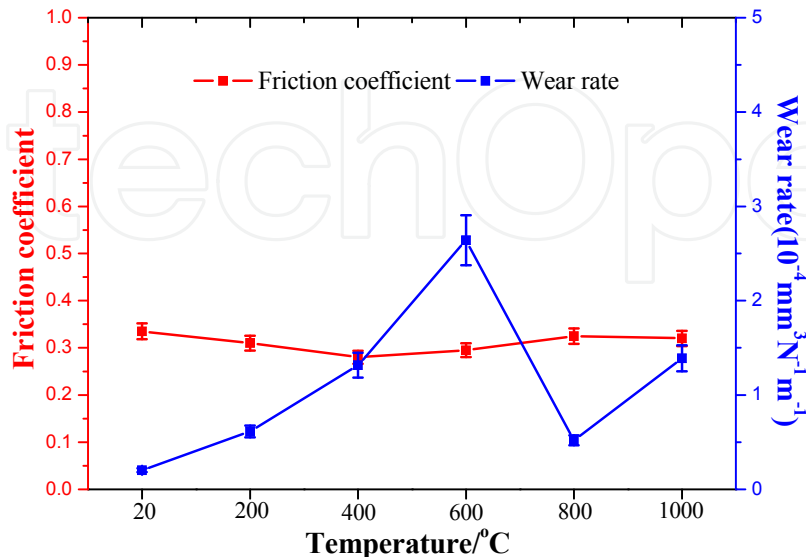
XRD results of the sintered sample and worn surfaces of  $\text{Ni}_3\text{Al}$ -20%Cr-12.5%Ag-10% $\text{BaF}_2/\text{CaF}_2$  composite after tests at different temperatures were represented in Fig. 3. There were no reactants among the  $\text{Ni}_3\text{Al}$ , fluorides, Ag and Cr detected after the hot-sintering process in XRD result of the sintered sample. However, peaks of  $\text{BaCO}_3$  and  $\text{NiO}$  appeared on worn surface at  $600^\circ\text{C}$ , and as did little  $\text{BaCrO}_4$ . Moreover, peaks of chromates get stronger with increase in temperature from  $800$  to  $1000^\circ\text{C}$ , indicating that large amounts of chromates formed on worn surfaces owing to the complex reaction including high temperature reaction and tribo-chemical reaction. Also, XPS results in Fig. 4 demonstrated the formation of chromates on worn surfaces at high temperatures. The favorable self-lubricating property of  $\text{Ni}_3\text{Al}$ - $\text{BaF}_2$ - $\text{CaF}_2$ -Ag-Cr composite at a broad temperature range was attributed to the synergistic effects of Ag, fluorides and chromates formed at high temperatures.

Moreover, another self-lubricating composite  $\text{Ni}_3\text{Al}$ -Mo-Ag- $\text{BaF}_2/\text{CaF}_2$  offers acceptable mechanical strength and excellent tribological properties over a wide temperatures ranging from room temperature to  $1000^\circ\text{C}$ , as shown in Table 1 and Figs. 5 and 6 [49,54,55].

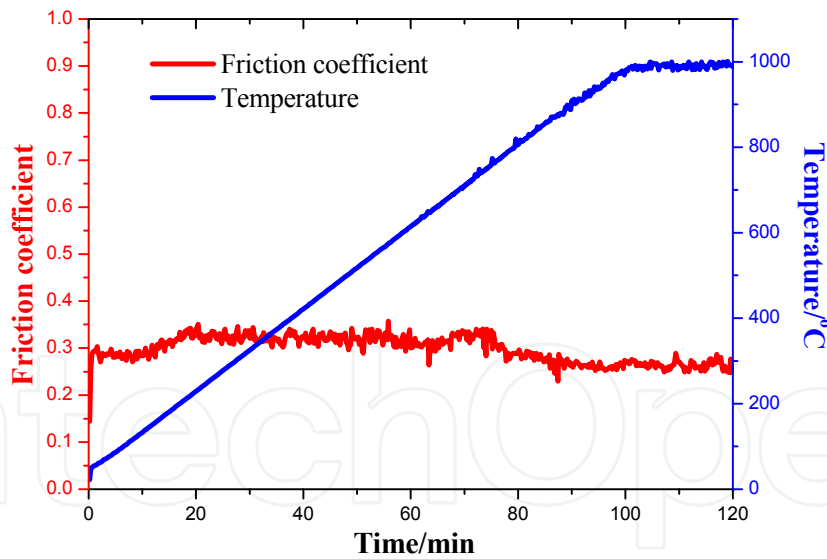


Temperature/°C	20	800	900	1000
Compressive strength/MPa	1200	230	100	43

**Table 1.** Compressive strength of the Ni<sub>3</sub>Al-Mo-Ag-BaF<sub>2</sub>/CaF<sub>2</sub> composite at different temperatures



**Figure 5.** Variations of friction coefficients and wear rates of the Ni<sub>3</sub>Al-Mo-Ag-BaF<sub>2</sub>/CaF<sub>2</sub> composite at different temperatures (tested at an applied load of 20 N and sliding speed of 0.2 m/s against Si<sub>3</sub>N<sub>4</sub> ceramic ball)



**Figure 6.** Evolution of friction coefficient of the Ni<sub>3</sub>Al-Mo-Ag-BaF<sub>2</sub>/CaF<sub>2</sub> composite with sliding time from room temperature to 1000 °C (tested at an applied load of 10 N and sliding speed of 0.2 m/s against Si<sub>3</sub>N<sub>4</sub> ceramic ball)

In addition, tungsten as reinforcement for Ni<sub>3</sub>Al-Ag-BaF<sub>2</sub>/CaF<sub>2</sub> composite is selected based on the premise that fluoride and tungsten are expected to react with oxygen at high temperatures and create tungstate lubricants on the worn surface. As expected, barium and calcium tungstates with lubricious properties contributed to low friction coefficient at elevated temperatures [50].

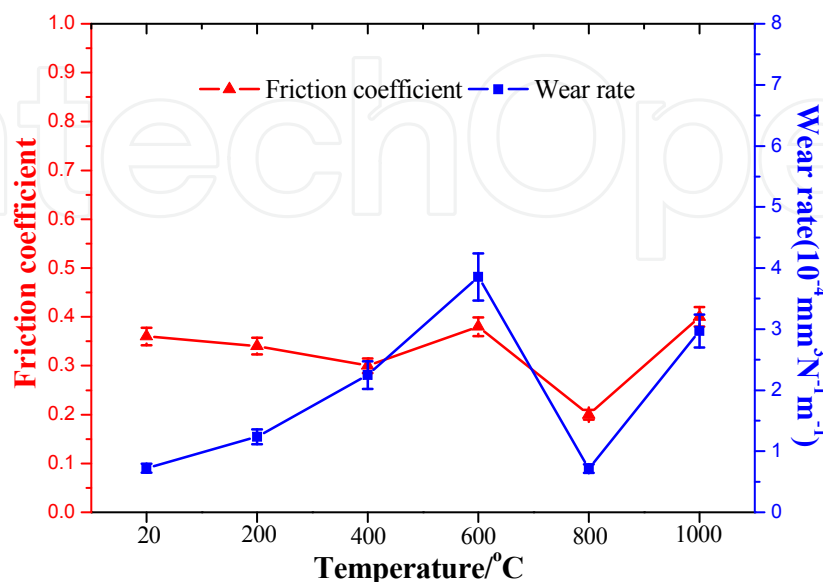
## 4.2. NiAl matrix high temperature self-lubricating composites

Among the intermetallic family, NiAl has been selected for elevated temperature structural applications due to its low density, high oxidation resistance, high melting pointing and high conductivity [77-81]. However, NiAl is not widely used in structural applications due to its poor ductility at ambient temperatures and low strength and creep resistance at elevated temperatures. Alloying is one of effective approach that has been used successfully to improve the room temperature fracture toughness, yield strength and ductility of brittle intermetallics. NiAl-28Cr-6Mo eutectic alloys are regarded as the most logical choice of the multielement system examined to date because of their relatively high melting point, good thermal conductivity and high elevated temperature creep resistance as well as higher fracture toughness [79, 80]. Thus NiAl-28Cr-6Mo alloy may be an excellent matrix for high temperature self-lubricating composite. Recently, NiAl matrix high temperature self-lubricating composites also have been explored [82, 83]. NiAl matrix composite with various high temperature solid lubricants, such as oxide and fluoride, provide excellent lubricating properties at elevated temperatures.

It is well known that the addition of soft oxide is one of effective approach to reduce friction and wear at high temperatures because the softening oxide could offer low shear strength and high ductility and the formation of a glaze film would protect the sliding surface from heavy wear. NiAl, NiAl-Cr-Mo alloy and NiAl matrix composites with addition of oxides (ZnO/CuO) were fabricated by powder metallurgy route [82]. It was found that some new phases (such as  $\text{NiZn}_3$ ,  $\text{Cu}_{0.81}\text{Ni}_{0.19}$  and  $\text{Al}_2\text{O}_3$ ) formed during the fabrication process due to a high-temperature solid state reaction. The results indicated that the monolithic NiAl had high friction coefficient and wear rate at elevated temperatures due to poor mechanical properties. The incorporation of Cr(Mo) not only enhanced mechanical properties evidently but also improved high temperature tribological properties greatly. NiAl matrix composite with addition of ZnO showed superior wear resistance at 1000 °C among the sintered materials, which was due to the formation of the ZnO layer on the worn surface. NiAl matrix composite with addition of CuO exhibited self-lubricating performance at 800 °C, which was attributed to the presence of the glaze layer containing CuO and  $\text{MoO}_3$ . Meanwhile, it had the best tribological properties among the sintered materials at 800 °C.

In addition,  $\text{CaF}_2$  added into NiAl matrix composite exhibited favorable friction coefficient about 0.2 and excellent wear resistance about  $1 \times 10^{-5} \text{ mm}^3/\text{Nm}$  at high temperatures (800 and 1000 °C) [83]. The excellent self-lubricating performance was attributed to the formation of the glaze film on the worn surface, which was mainly composed of  $\text{CaCrO}_4$  and  $\text{CaMoO}_4$  as high temperature solid lubricants. However, the composite had poor tribological performance at low temperatures. Addition of Ag evidently reduced friction coefficient and enhanced wear resistance at low temperatures. It indicated that Ag functioned as a favorable solid lubricant for NiAl intermetallic at low temperatures. However, it was adverse to friction and wear at elevated temperatures because of the decrease in the strength of material. On the whole, NiAl-Cr-Mo- $\text{CaF}_2$ -Ag composite provided self-lubricating properties at a broad temperature range between room temperature and 1000 °C (shown in

Fig. 7) [59]. Especially at 800 °C, the composite offered excellent friction reduction about 0.2 and wear resistance about  $7 \times 10^{-5} \text{ mm}^3/\text{Nm}$  at high temperatures. The low friction coefficient at a wide temperature range could be attributed to the synergistic effect of Ag,  $\text{CaF}_2$ ,  $\text{CaCrO}_4$  and  $\text{CaMoO}_4$ .



**Figure 7.** Variations of friction coefficients and wear rates of NiAl-Cr-Mo-CaF<sub>2</sub>-Ag at different temperatures (tested at an applied load of 10 N and sliding speed of 0.2 m/s against Si<sub>3</sub>N<sub>4</sub> ceramic ball)

## 5. Ceramic matrix high temperature self-lubricating composites

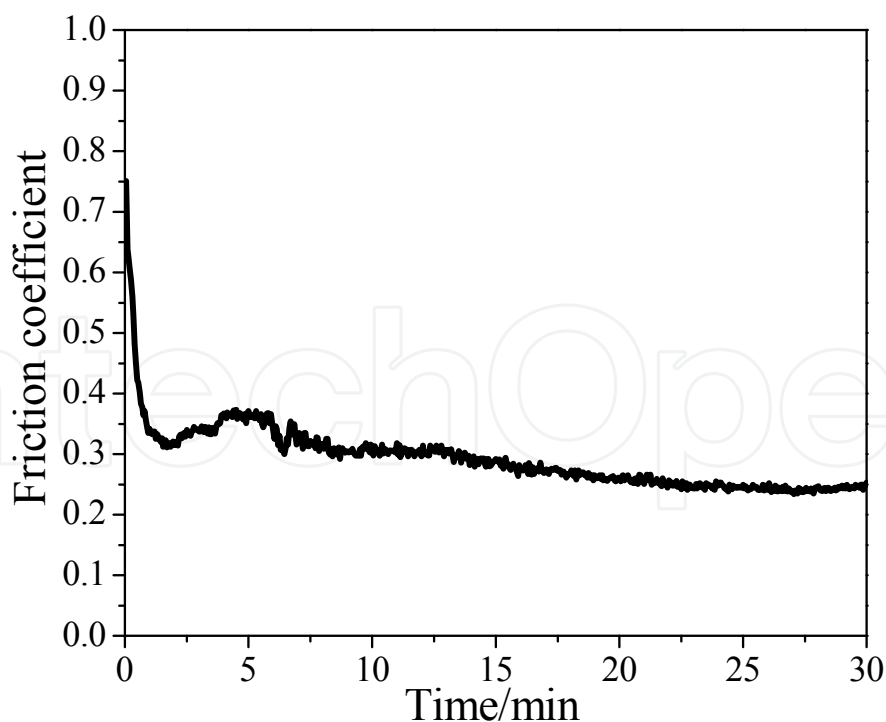
Advanced structural ceramics are expected to be suitable for tribo-systems because of their high hardness and corrosion resistance at high temperature [84,85]. A major challenge in advanced structural ceramics is to develop long-lifetime and reproducible ceramic sliding components for use in mechanical systems that involve high loads, velocities and temperatures. As the friction of unlubricated ceramic surfaces at elevated temperatures is usually high and unacceptable, it is necessary to find ways of effectively lubricating ceramics. Ceramic matrix composites in which solid lubricant is dispersed throughout the structure are advantageous when long lubrication life is required, compared to self-lubricating coatings. In recent years, ceramic matrix high temperature self-lubricating composites have attracted the attention of many researchers.

### 5.1. Zirconia matrix high temperature self-lubricating composites

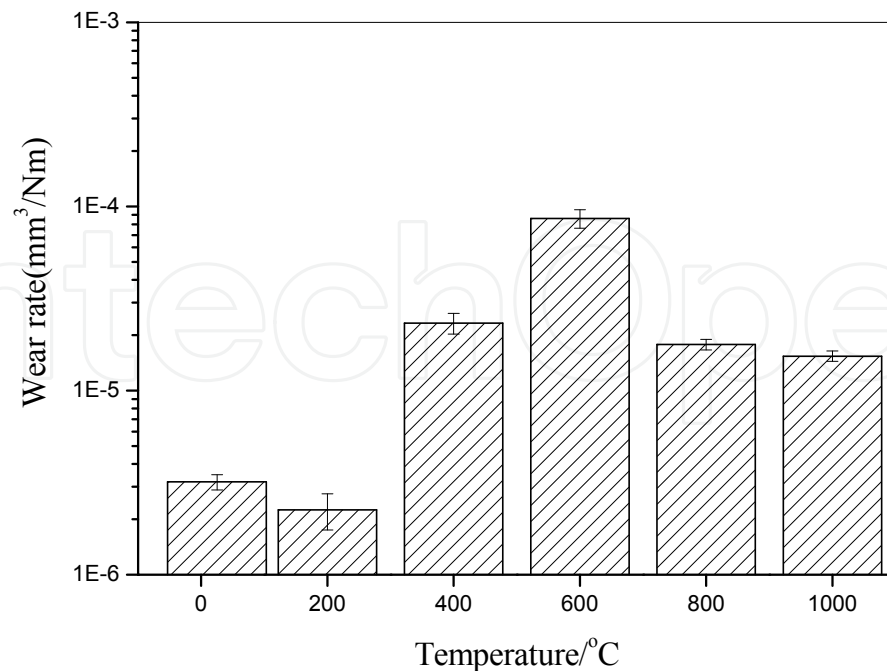
Tetragonal zirconia polycrystals stabilized by yttria present a good combination of fracture toughness and bending strength, which is related to the stress-induced phase transformation of tetragonal  $\text{ZrO}_2$  ( $\text{Y}_2\text{O}_3$ ) into monoclinic symmetry. Therefore, zirconia ceramics are potential candidates for a host of engineering applications, especially at high temperatures. However, the friction coefficient of zirconia ceramics in dry sliding is enough high not to acceptable for engineering applications. Consequently, it is quite necessary to research and develop  $\text{ZrO}_2$  ( $\text{Y}_2\text{O}_3$ ) matrix high temperature self-lubricating composites.

It was reported that the additives of graphite, MoS<sub>2</sub>, BaF<sub>2</sub>, CaF<sub>2</sub>, Ag, Ag<sub>2</sub>O, Cu<sub>2</sub>O, BaCrO<sub>4</sub>, BaSO<sub>4</sub>, SrSO<sub>4</sub> and CaSiO<sub>3</sub> were incorporated into zirconia ceramics, respectively, to evaluate their potentials as effective solid lubricants over a wide operating temperature range [13,86-88]. It was found that the ZrO<sub>2</sub> (Y<sub>2</sub>O<sub>3</sub>) composites incorporated with SrSO<sub>4</sub> exhibited low steady-state friction coefficients of less than 0.2 and small wear rates in the order of 10<sup>-6</sup> mm<sup>3</sup>/Nm at low sliding speed from room temperature to 800 °C. The formation, plastic deformation and effective spreading of SrSO<sub>4</sub> lubricating film were the most important factor to reduce friction and wear rate over a wide temperature range.

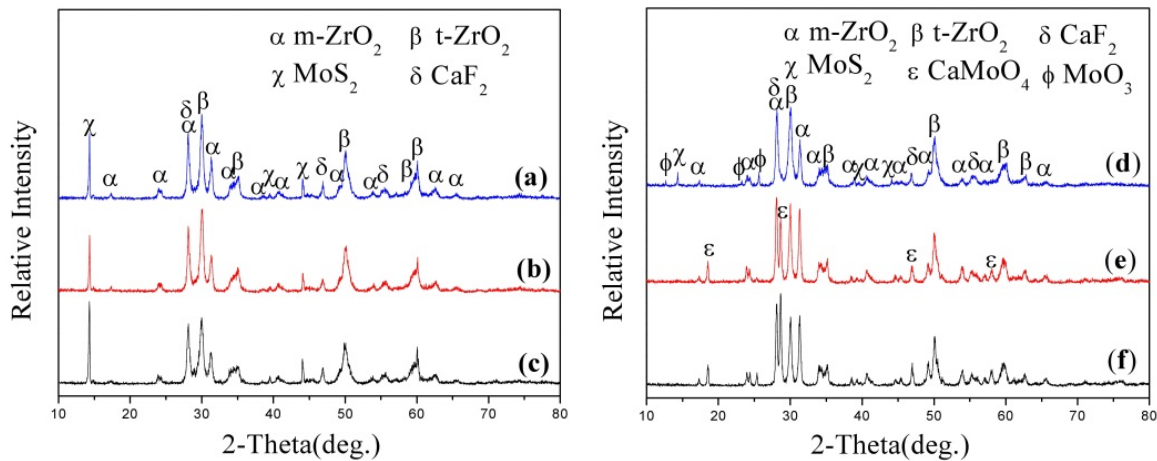
Recently, a ZrO<sub>2</sub> matrix high temperature self-lubricating composite with addition of MoS<sub>2</sub> and CaF<sub>2</sub> as lubricants prepared using hot pressing method was investigated from room temperature to 1000 °C [14,89]. The ZrO<sub>2</sub>-MoS<sub>2</sub>-CaF<sub>2</sub> composites had favorable microhardness (HV 824±90) and fracture toughness (6.5±1.4 MPa m<sup>1/2</sup>), and against SiC ceramic exhibited excellent self-lubricating and anti-wear properties at a wide temperature range. At 1000 °C, the ZrO<sub>2</sub> matrix composite had a very low coefficient of friction of about 0.27 and wear rate of 1.54×10<sup>-5</sup> mm<sup>3</sup>/Nm, as shown in Figs. 8 and 9. The low friction and wear were attributed to a new lubricant CaMoO<sub>4</sub> which formed on the worn surfaces at high temperatures (seen in Fig. 10).



**Figure 8.** Evolution of friction coefficient of the ZrO<sub>2</sub>-MoS<sub>2</sub>-CaF<sub>2</sub> composite with sliding time at 1000 °C (tested at an applied load of 10 N and sliding speed of 0.2m/s against SiC ceramic ball)



**Figure 9.** Variations of wear rates of the ZrO<sub>2</sub>-MoS<sub>2</sub>-CaF<sub>2</sub> composite at different temperatures (tested at an applied load of 10 N and sliding speed of 0.2m/s against SiC ceramic ball)



**Figure 10.** XRD patterns of the ZrO<sub>2</sub>-MoS<sub>2</sub>-CaF<sub>2</sub> composite (a) and its worn surfaces at different temperatures: 200 °C (b), 400 °C (c), 600 °C (d), 800 °C (e) and 1000 °C (f)

## 5.2. Alumina matrix high temperature self-lubricating composites

Alumina is a promising material at high temperature because of its excellent chemical stability and low price. However, tribological experiments of alumina sliding against itself at high temperature show high friction coefficient and wear rate. Solid lubrication becomes necessary to overcome this problem. In order to lubricate alumina ceramics, many efforts have been made in recent years. Among them, alumina matrix composite employed Ag and fluoride as solid lubricants is a successful example [90-92]. The Al<sub>2</sub>O<sub>3</sub>-Ag-CaF<sub>2</sub> composite

exhibited a distinct improvement in wear resistance and frictional characteristics at elevated temperatures. The self-lubricating behavior was dominated by a synergistic effect. The lubricating film as a mixture of Ag and  $\text{CaF}_2$  on friction surfaces was responsible for the reduction of friction and wear at elevated temperature.

### 5.3. Silicon nitride matrix high temperature self-lubricating composites

$\text{Si}_3\text{N}_4$ -based ceramics are potential substitutes for more traditional materials for these specific applications due to their high hardness, excellent chemical and mechanical stability under a broad range of temperatures, low density, low thermal expansion and high specific stiffness [93]. The incorporation of solid lubricants is a goal to further enhance the tribological performance of  $\text{Si}_3\text{N}_4$  [94-98]. The published papers indicated that Cs-compounds are exceptional promises as high temperature lubricants for  $\text{Si}_3\text{N}_4$  ceramic. Cs-compound provided favorable lubrication on  $\text{Si}_3\text{N}_4$  from room temperature to 750 °C, especially with an average value of 0.03 at 600 °C. The synergistic chemical reactions occurred between the cesium compounds,  $\text{Na}_2\text{SiO}_3$ , and the  $\text{Si}_3\text{N}_4$  surface to provide the remarkable performance.

### 5.4. $\text{M}_{n+1}\text{AX}_n$ matrix high temperature self-lubricating composites

The class of refractory oxygen-free compounds possesses a layered structure and a unique combination of metal and ceramic properties, which are generally described by the formula  $\text{M}_{n+1}\text{AX}_n$ , where M is the transition metal, A is the preferentially subgroup IIIA or IVA element of the periodic table, and X is carbon or nitrogen [99-102]. They are characterized by a low density; high thermal conductivity, electrical conductivity, and strength; excellent corrosion resistance in aggressive external media; resistance to high-temperature oxidation; and tolerance to thermal shocks. Additionally, due to their layered structure and by analogy with hexagonal boron nitride and graphite, it is proposed that they are self-lubricating and possesses low friction coefficient. However, in the previous literature on friction and wear,  $\text{M}_{n+1}\text{AX}_n$  phases did not exhibit the expected tribological properties at high temperatures. Although there exists the debate on their intrinsically self-lubricating behavior, they could be appropriate candidate for high temperature self-lubricating matrix due to the combination of metals and ceramics properties [103-107]. In order to lubricate  $\text{M}_{n+1}\text{AX}_n$  phases, many efforts have been made in recent years. Among them,  $\text{M}_{n+1}\text{AX}_n$  matrix composites employed Ag as solid lubricant are the promising materials for high temperature tribological applications [107-111].

## 6. High temperature self-lubricating coatings

High temperature self-lubricating composites with good high temperature anti-oxidation ability have been developed to reduce friction and wear from room temperature to high operating temperatures in many tribological systems. Since it is difficult or impossible for a bulk monolithic material to possess all the above mentioned surface properties [112], much attention has been paid to metallic matrix composite coatings which contain solid lubricants



prepared by various processes, such as PS coatings by plasma spray [11,113], Ni/hBN composite coating by laser cladding [114], adaptive nitride-based coating by unbalanced magnetron sputtering [115], and Ni<sub>3</sub>Al matrix composite coating by powder metallurgy [116].

### 6.1. PS high temperature self-lubricating coatings

In the past 40 years, the PS100, PS200, PS300 and PS400 families of plasma sprayed coatings with self-lubricating behavior were developed at NASA Lewis Research Center (shown in Table 2) [11,113,117-121]. The PS100 family of nickel-glass-solid lubricant-containing coatings pioneered the concept of combining the functions of individual constituents to produce a composite solid lubricant coating. PS200 coatings developed the composite concept, which consisted of a hard nickel-cobalt-bonded chrome carbide matrix and solid lubricants of Ag and BaF<sub>2</sub>/CaF<sub>2</sub> eutectic. The PS300 coating system replaced the harder chrome carbide of PS200 coatings with chrome oxide, eliminating the necessity of costly diamond grinding and providing improved resistance to oxidative changes in high-temperature air. This coating was not very hard but had desirable tribological performance, such as good wear resistance and low friction coefficient, especially at elevated temperature up to 650 °C. NASA has recently developed a new solid lubricant coating, PS400, due to several drawbacks of PS300, namely the need to undergo a heat treatment for dimensional stabilization and poor initial surface finish. These four distinct families of coatings were engineered over the last four decades to address specific tribological challenges encountered in various aerospace systems.

Coating designation	Binder matrix	Harder	Solid lubricants	General attributes
PS100	NiCr	Glass	Ag+Fluorides	Soft-high wear
PS200	Ni-Co	Cr <sub>3</sub> C <sub>2</sub>	Ag+Fluorides	Hard-low wear, (abrasive to counter face dimensionally stable)
PS300	NiCr	Cr <sub>2</sub> O <sub>3</sub>	Ag+Fluorides	Moderate hardness, mildly abrasive to counter face, poor dimensional stability- requires heat treatment
PS400	NiMoAl	Cr <sub>2</sub> O <sub>3</sub>	Ag+Fluorides	Excellent dimensional stability and surface finish, poor initial low temperature tribology

**Table 2.** Comparison of the NASA plasma spray coating

### 6.2. Ni/hBN high temperature self-lubricating composite coating

The non-wettability and poor sinter ability of hBN restrict its applications as a solid lubricant, though it has a graphite-like lamellar structure. Fortunately, the hBN powders electroplated with Ni can improve the wettability with 1Cr18Ni9Ti stainless steel and

sinterability as well [114]. The resulting Ni-coated hBN particulates are then used to prepare a self-lubricating wear-resistant composite coating on the stainless steel substrate with the assistance of laser cladding. Laser cladding Ni/hBN composite coating on the stainless steel substrate was composed of metallic Ni and hBN, and a small amount of B-matrix interphases, and it had high hardness and uniformly distributed constituent phases. The friction and wear behavior of the laser cladding Ni/hBN coating was strongly dependent on test temperature. The coating had good friction-reducing and anti-wear abilities as it slid against the ceramic counterpart at elevated temperatures up to 800 °C, which could be owing to the good lubricating performance of the hBN particles as a kind of high-temperature solid lubricant. The wear rate of the coating increased to some extent as the test temperature rose from 600 °C up to 800 °C, which could be attributed to the decrease in the strength of the coating at excessively high-temperature.

### 6.3. Adaptive nitride-based high temperature self-lubricating coatings

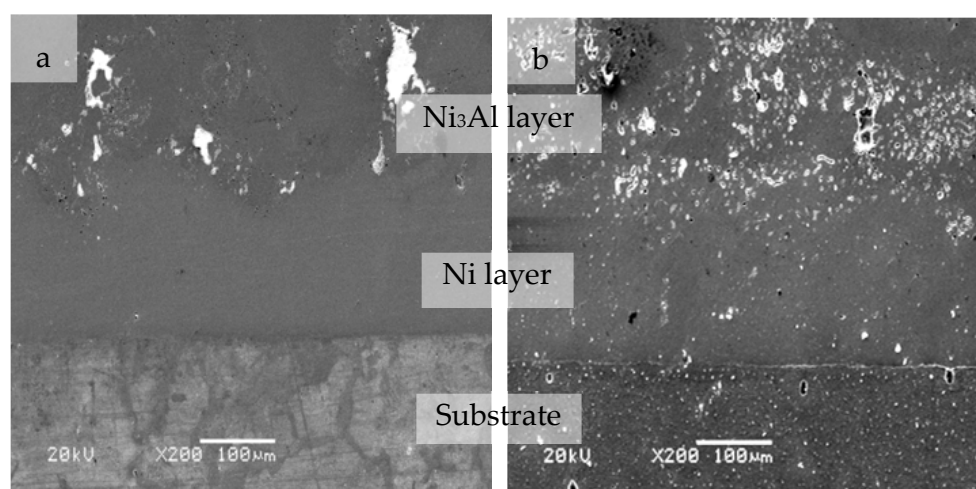
Adaptive tribological coatings have been recently developed as a new class of smart materials that are designed to adjust their surface chemical composition and structure as a function of changes in the working environment to minimize friction coefficient and wear between contact surfaces [12, 122-124]. At a wide temperature range, VN/Ag adaptive tribological coatings produced using unbalanced magnetron sputtering exhibited excellent self-lubricating properties [115]. The friction coefficient was found to vary from 0.35 at room temperature to about 0.15-0.20 in the 700-1000 °C range. After tribotesting, Raman spectroscopy and X-ray diffraction measurements revealed the formation of silver vanadate compounds on the surface of these coatings. In addition, real time Raman spectroscopy and high temperature XRD revealed that silver vanadate, vanadium oxide and elemental silver formed on the surface of these coatings upon heating to 1000 °C. Upon cooling, silver and vanadium oxide were found. Silver reduced the friction coefficient at low temperatures, while the  $\text{Ag}_3\text{VO}_4$  phase provided low friction at high temperatures due to its layered atomic structure.

### 6.4. Intermetallics matrix high temperature self-lubricating composite coatings

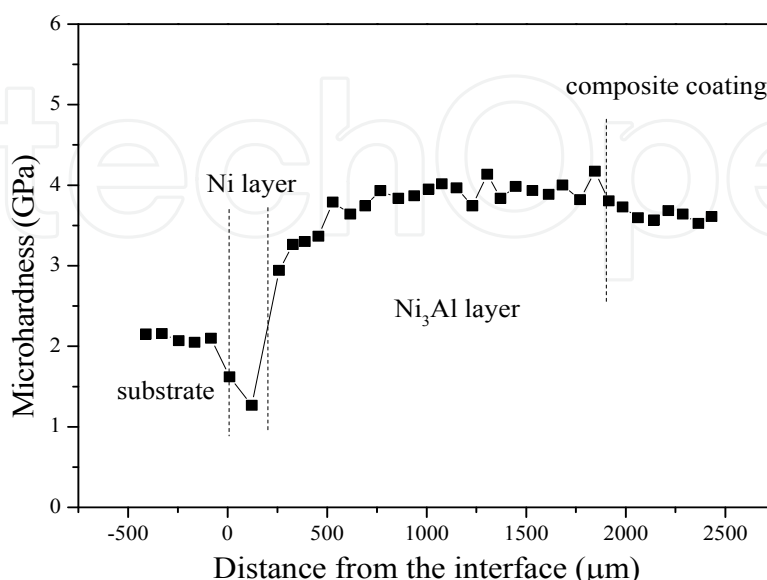
Powder metallurgy is a convenient method to prepare bulk components with fine and dense microstructures. In contrast to the plasma spraying technique, where some components may be lost during the deposition process, the final composition is the same as that of the starting powders. Hence powder metallurgy is applied to prepare the coatings with a fine and dense microstructure.

One of the most attractive engineering properties of  $\text{Ni}_3\text{Al}$  alloys is their increasing yield strength with increasing temperature up to about 650-750 °C. This type of strength behavior suggests that the  $\text{Ni}_3\text{Al}$ -based intermetallic alloys may have good wear properties in the peak-strength temperature range. Consequently, investigations of  $\text{Ni}_3\text{Al}$  intermetallics for tribological coating matrix at high temperatures were initiated.

Recently, a  $\text{Ni}_3\text{Al}$  matrix coating containing Ag, Mo and  $\text{BaF}_2/\text{CaF}_2$  was fabricated by the vacuum hot-pressed sintered technology [116]. Fig. 11 presented the morphology of the interface of the composite coating. A small amount of nickel powders were spread on the surface of the substrate to improve the wettability between the coating and AISI 1045 carbon steel. The  $\text{Ni}_3\text{Al}$  layer on the layer of nickel powder reduced the stress concentration between the substrate and the coating as well as to improve the bonding strength. The mixed composite powders  $\text{Ni}_3\text{Al}$ -Mo-Ag-fluorides were spread on the layer. After sintering, it could be seen that there were no pores and cracks near the interface region and the composite coating layer was well adhered to the substrate (Fig. 11a). The morphology of the interface of the coating (after thermal shock) was shown in Fig. 11b. It showed that the coating did not peel off and even no cracks after the thermal shock, indicating that the coating possesses excellent bonding strength.



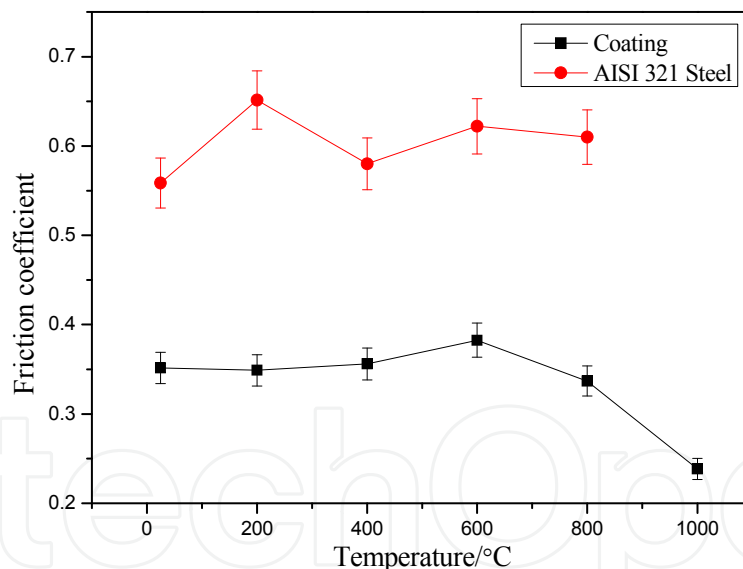
**Figure 11.** SEM micrographs of transverse cross-sections of the  $\text{Ni}_3\text{Al}$ -based composite coating: (a) before thermal shock; (b) after thermal shock.



**Figure 12.** Microhardness profile of the  $\text{Ni}_3\text{Al}$ -based composite coating

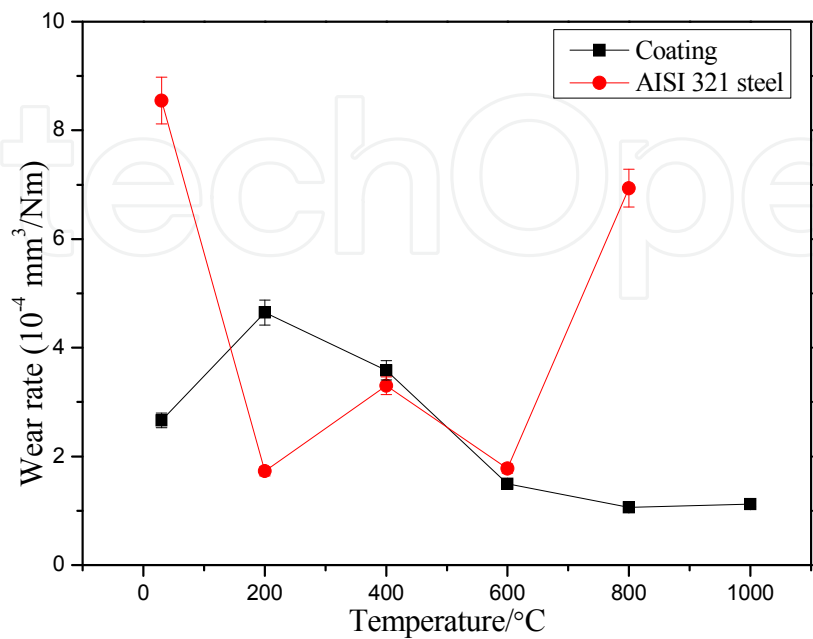
The microhardness depth profile in the transverse cross-section of the composite coating was shown in Fig. 12. It was found that the coating was in three layers according to hardness. The Vickers hardness (HV) of the nickel interlayer was  $1.40 \pm 0.50$  GPa, and that of the  $\text{Ni}_3\text{Al}$  layer is  $3.80 \pm 0.50$  GPa, and at the top surface, the HV is  $3.60 \pm 0.50$  GPa. The result showed that the top layer was not the hardest part of the coating, and the hard  $\text{Ni}_3\text{Al}$  layer provided efficient support in the coating. The multilayer structure of the coating could reduce the stress concentration, and improve the bonding strength.

The average friction coefficients of the coating were presented in Fig. 13. The friction coefficients of the coating were approximately 0.35 from 25 to 800 °C, however, when the temperature reached 1000 °C, the friction coefficients fell to 0.24. In comparison, the friction coefficient of the AISI 321 stainless steel was much higher than that of the coating. Fig. 14 showed the wear rates of the coating at various temperatures in air. Although the wear rates of the coating were higher than that of the AISI 321 stainless steel at the temperature between 200 and 400 °C, but they were lower at room temperature and high temperature (above 600 °C) and remained a stable level.

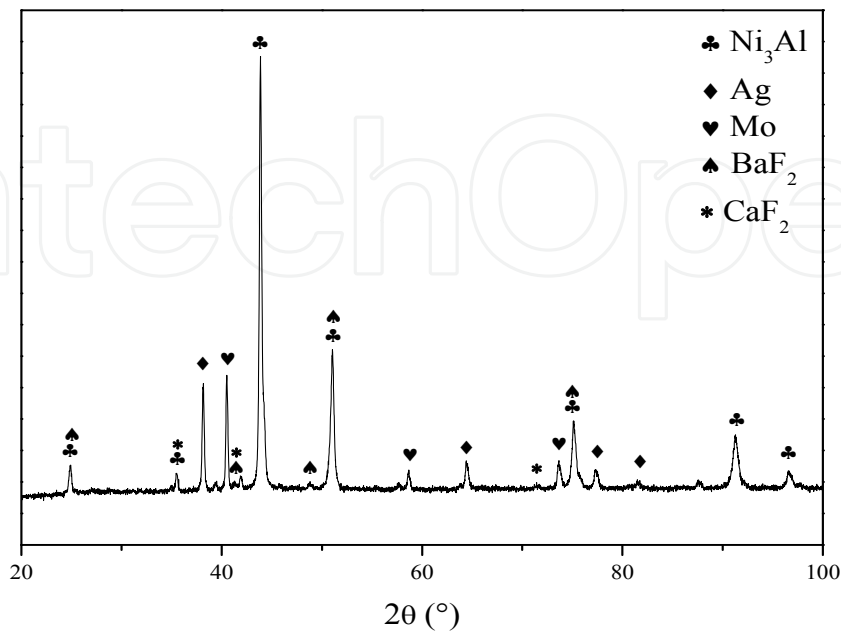


**Figure 13.** Average friction coefficients of the  $\text{Ni}_3\text{Al}$ -based composite coating at temperatures ranging from room temperature to 1000 °C in air (tested at an applied load of 20 N and sliding speed of 0.2 m/s against  $\text{Si}_3\text{N}_4$  ceramic ball)

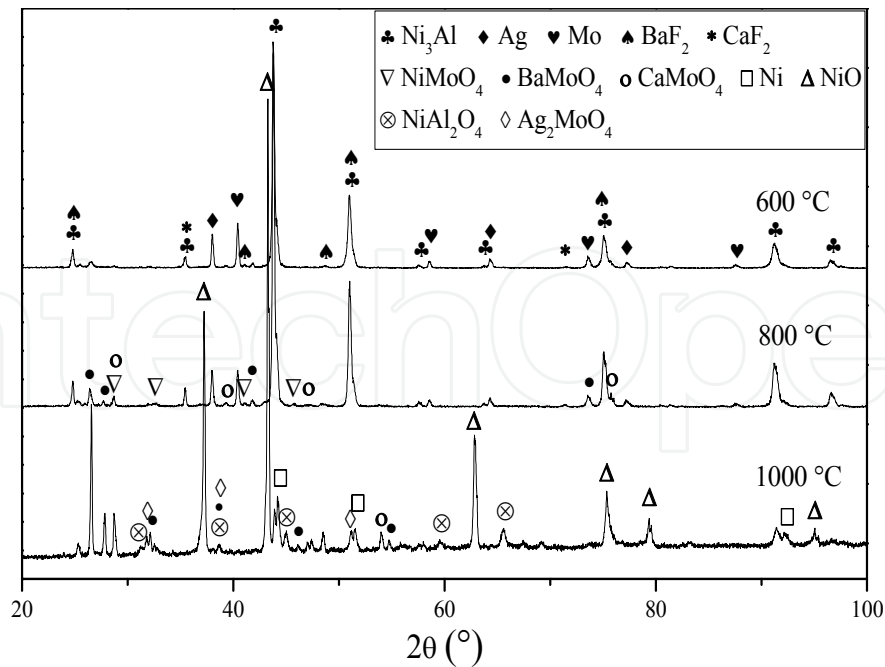
These results proved that the coating offered good self-lubricating property at a wide temperature range from room temperature to 1000 °C. The low friction coefficient of the coating was mainly attributed to Ag and fluorides eutectic at the temperature below 800 °C; at high temperatures, the molybdates, which formed in the tribochemical reaction, acted as effective lubricants (seen in Figs. 15 and 16).



**Figure 14.** Wear rates of the  $\text{Ni}_3\text{Al}$ -based composite coating at temperatures ranging from room temperature to 1000  $^{\circ}\text{C}$  in air (tested at an applied load of 20 N and sliding speed of 0.2 m/s against  $\text{Si}_3\text{N}_4$  ceramic ball)



**Figure 15.** XRD patterns of the sintered  $\text{Ni}_3\text{Al}$ -based self-lubricating composite coating



**Figure 16.** XRD pattern worn surfaces of the  $\text{Ni}_3\text{Al}$ -based composite coating at different temperatures

## 7. Conclusions

There is no doubt that search for newer and better high temperature self-lubricating materials will continue in coming years, since the application conditions of future mechanical systems will undoubtedly be much more demanding than the current ones.

To fulfill engineering application, a general design appraisal of high temperature self-lubricating material can be proposed as follows: low friction (friction coefficient  $< 0.2$ ); high wear resistance (wear rate  $< 10^{-6} \text{ mm}^3/\text{Nm}$ ); and wide temperature range (from room temperature to high temperature of above  $1000^\circ\text{C}$ ).

To meet these requirements, matrix and solid lubricant selected are essential for novel high temperature self-lubricating material.

Intermetallic alloys own the comprehensive mechanical properties for industrial applications by micro- or macro-alloying process. They are now serious candidates for structural applications requiring reduced density, excellent fatigue strength, corrosion/oxidation resistance, and service at temperatures up to  $1000^\circ\text{C}$ . Intermetallic alloys have attracted the attention of many researchers as promising tribomaterials for mechanical components operating under severe or hostile environments.

It should be realized by designers and engineers that there is no “universal lubricant” that can operate at a broad temperature range conditions. A synergetic lubricating action, a mixture of two or more solid lubricants, is one of promising approaches to fabricate high temperature self-lubricating materials. Furthermore, research on novel solid lubricant is also a response to the requirements.



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## Acknowledgement

The authors are grateful to the National Natural Science Foundation of China (51075383) and the National 973 Project of China (2013CB632300) for financial support. And also, we thank Dr. Muye Niu and Lingqian Kong for their help to the paper.

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