Physical and Mechanical Properties of Ni-Cr based composites with addition of solid lubricants produced through powder metallurgy process

Wan Farhana Mohamad[1,a], Amir Azam Khan[1], Faiz Ahmad[2] and Abdullah Yassin[1]

[1]*Department of Mechanical and Manufacturing, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia*
[2]*Mechanical Engineering Department, University Technology PETRONAS, 31750 Tronoh, Perak, Malaysia*

Abstract. Ni-Cr based composites with and without the addition of solid lubricants (MoS_2, silver and CaF_2) were prepared by powder metallurgy method. The samples were sintered at two different temperatures, 1000 ^oC and 1200 ^oC. The physical properties such as shrinkage, sintered density and porosity were studied. The microstructures of the Ni-Cr based composites were observed by using SEM analysis while the mechanical properties of the composites were measured by Rockwell Hardness Tester. The results revealed that the increased in sintering temperature improved the shrinkage, sintered density and hardness of the composites while less porosity produced. Ni-Cr based composites with the addition of silver and MoS_2 exhibited better shrinkage, density and porosity. Besides, 5% of MoS_2 addition in the composites improves the hardness of the composites at sintering temperature 1200^oC.
Keywords: solid lubricants, Ni-Cr composites, powder metallurgy, MoS_2, silver, CaF_2

1 Introduction

Giant industries such as automotive and aerospace are having an economical loss due to high maintenance cost for mechanical components. Failure of mechanical components such as bearings and bushings used in the advanced jet engines are caused by friction and wear as subjected to wide temperature range. As for example, the operation temperature of nozzles for turbojet propulsion system is reaching the temperature of 1650^oC [1]. At this high temperature, the liquid lubricant is unstable and tends to lose its lubricating properties. Thus, solid lubricant is preferable compared to the liquid lubricant. Besides, solid lubricant also has advantages compared to liquid lubricants either under the extreme pressure conditions, radiation environment or cryogenic temperature [2].

The incorporation of the solid lubricant in the composites is called self-lubricating composites. The composite is able to form a lubricating film to reduce the effect of friction and wear. The examples of metal used in the self-lubricating composites are iron based, copper based and nickel based composites. Iron based self-lubricating composites are mostly used in the automotive application such as piston ring, clutch, brake system and engine liners [3]. While copper based composites are used for the application of thermal management application due to excellent properties thermal and heat conductivity [4]. Among the metal composites, nickel based composites have become the most attention of researchers for high temperature application. The high cost of refractory metals and complex manufacturing process also make the metal nickel as an option for high temperature application [5].

Nickel Chromium (Ni-Cr) has become one of the leading materials for high temperature application due to its excellent performance at high temperature. A series of nickel based composites has been developed in order to achieve the great need of high temperature solid lubricating system produced through powder metallurgy process [6]. Ni-Cr matrix also acted as a binder and offered excellent high temperature oxidation/corrosion resistance and essential mechanical strength [7], [8]. Nickel itself offers good mechanical properties and anti-oxidizing properties when exposed to air atmosphere at high temperature while chromium offers anti-wear and lubricating properties at high temperature [9] . The strength of the Cr particles can determine the strength and bonding between the matrix and Cr reinforcement.

Efforts have been made in order to enhance the performance of self-lubricating composites with solid lubricants addition. The work is continued in order to develop a perfect combination of matrix and solid lubricant for high temperature system to meet the requirement of advanced technology. In this research work, the author is working on Ni-Cr based composites with the addition of single, dual and multiple solid lubricants in order to obtain an excellent mechanical as

[a] Corresponding author: wanfarhana88@gmail.com

well as tribological properties. The composites are fabricated by powder metallurgy method.

2 Experimental

The Nickel –Chromium (Ni-Cr) composites are based on 80% Ni and 20% Cr. The solid lubricants added are molybdenum disulphide (MoS_2), silver (Ag) and calcium fluoride (CaF_2). All of the raw materials are supplied by Robert Scientific Sdn Bhd. The characterizations of powders were done using Scanning Electron Microscope (SEM) by Hitachi Tabletop TM3030 and X-Ray Fluorescences (XRF) by Bruker S4 Pioneer, USA.

2.1 Preparation of samples

2.1.1 Samples preparations

Ni-Cr based composites have been produced by powder metallurgy method which consists of mixing, compaction and sintering. NC denoted for Ni-Cr based composite (without solid lubricant), NCM (with MoS_2), NCA (with Ag), NCCf (with CaF_2), NCMA (with MoS_2 and Ag), NCMCf (with MoS_2 and CaF_2), NCACf (with Ag and CaF_2) and NCMACf (with MoS_2, Ag and CaF_2). The powder has been weighted by analytical balance based on composition in Table 1. The powder mixture was mixed homogeneously in a ball mill for 30 minutes with the speed of 300 rpm. A mixture of powder was compacted using compression machine with the pressure of 100kN at room temperature. The compacted samples were in a pellet shape with the dimension of 13mm x 5mm. The compacted samples were sintered in a high temperature furnace for 60 minutes. The sintering atmosphere was argon gas with a flow rate of 4 L/min. The compacted samples were sintered at the temperature of 1000 ^oC and 1200 ^oC with a heating rate of 10 ^oC/min.

Table 1. Materials compositions for Ni-Cr based composites.

Samples	Designation	Composition (wt%)			
		80Ni-20Cr	MoS_2	Ag	CaF_2
1 (Pure)	NC	Balance	0	0	0
2 (Single)	NCM	Balance	5	0	0
3 (Single)	NCA	Balance	0	5	0
4 (Single)	NCCf	Balance	0	0	5
5 (Dual)	NCMA	Balance	5	5	0
6 (Dual)	NCMCf	Balance	5	0	5
7 (Dual)	NCACf	Balance	0	5	5
8 (Multiple)	NCMACf	Balance	5	5	5

2.2 Physical Properties

The diameter and height of the sintered samples were measured by using vernier caliper while the mass of the samples was obtained by analytical balance. At least 3 measurements were taken and the average value was measured. The shrinkage, density, and porosity of the samples were calculated using the geometric method (formula).

2.2.1 Shrinkage

The volume of the green and sintered samples in pellet size are calculated by using the formula $V= \pi (d/2)^2h$. The percentage of shrinkage is measured by using formula :

$$\% \text{ of shrinkage} = (V_1 - V_2)/(V_1) \times 100$$

V_1= Volume before sintering

V_2 = Volume after sintering

The measurements of height (h) and diameter (d) were taken 3 times to get the average value.

2.2.2 Density

The density of green and sintered samples is measured before and after sintering. The density, ρ formula is :

$$\rho = m / V$$

m = mass of pellet (g)

V = Volume of pellet (cm^3)

2.2.3 Porosity

The porosity of the composites was measured by formula of:

$$\text{Porosity} = (\rho_{theoritical} - \rho_{sintered}) / (\rho_{theoritical}) \times 100$$

$\rho_{theoritical}$ = theoretical density

$\rho_{sintered}$ = sintered density

2.3 Microstructure and Mechanical Properties

2.3.1 Microstructure

The microstructure of the sintered samples was observed and analyzed by using Scanning Electron Microscope (SEM). The samples were ground with silicon carbide paper and polished with diamond paste as a surface preparation before SEM analysis. The effect of sintering temperature and composition of the composites were studied.

2.3.2 Hardness

The hardness of Ni-Cr based composites was measured by using Mitutoyo Hardness Machine with the diamond indenter at an indentation load of 1471N. At least 10 measurements were taken and the average value is calculated.

3 Results and Discussions

3.1 Characterizations of raw materials

SEM analysis was done to observe the particle shape and distribution while XRF analysis was conducted to determine the purity of the powder. Figure 1 and 2 show the SEM micrograph of the nickel and chromium powder.

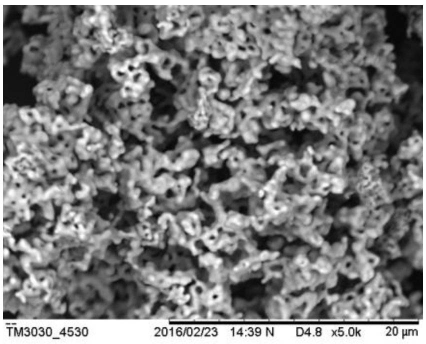

Figure 1. SEM microstructure of nickel powder at a magnification of 5000X.

In Figure 1, SEM analysis with a magnification of 5000X illustrates the nickel powder used in this research. The purity of the nickel powder is 99.1% determined by XRF analysis.

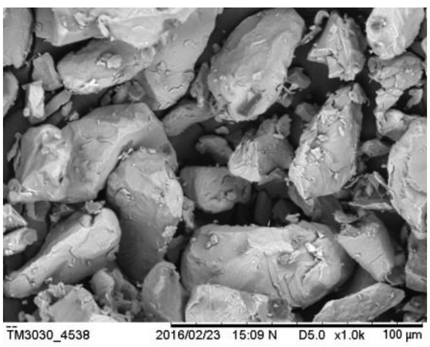

Figure 2. SEM microstructure of chromium powder at a magnification of 1000X.

Figure 2 shows the particle shape and distribution of chromium powder. The particle shape is in the irregular shape. XRF analysis determines the purity of chromium powder is 93.3%. Figure 3-5 shows the SEM microstructure of solid lubricants which are MoS_2, silver and CaF_2.

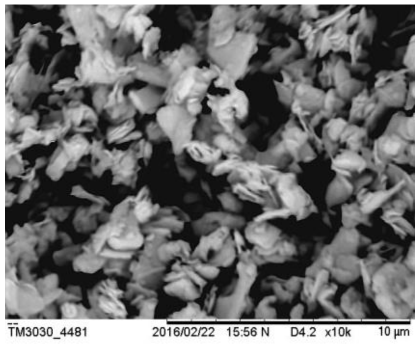

Figure 3. SEM microstructure of MoS_2 powder at a magnification of 10000X.

From the Figure 3, it demonstrates the particle shape of MoS_2 powder which is in flake shape. The purity of the powder is Mo 72% and S 25.1%.

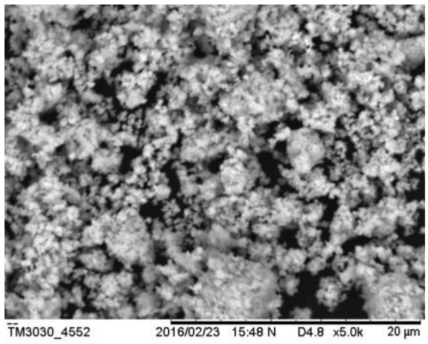

Figure 4. SEM microstructure of silver powder at a magnification of 5000X.

SEM microstructure in Figure 4 shows the particle distribution of silver powder used in the research work.

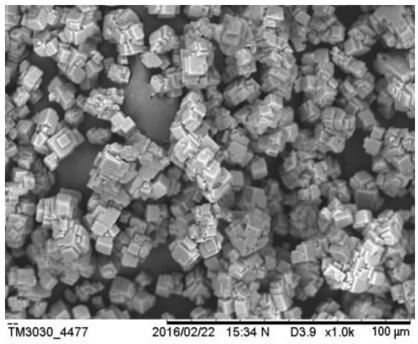

Figure 5. SEM microstructure of CaF_2 powder at a magnification of 1000X.

Based on Figure 5, the micrograph illustrates the stacked crystallize structure of CaF_2. The microstructure in cubic particle shape. The purity of powder is Ca 99.1%.

DOI: 10.1051/matecconf/20178702011

3.2 Characterization of mixed powders.

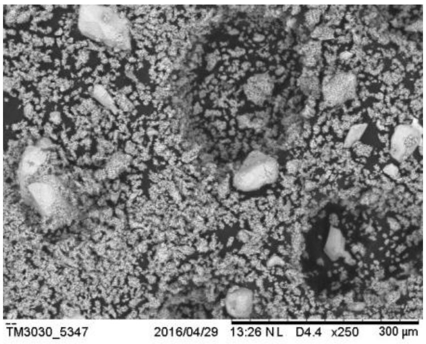

Figure 6. A mixture of Ni and Cr powders after 30 minutes of ball milling.

Figure 6 shows the distribution of Nickel and Chromium powder after mixing by using ball mill machine for 30 minutes. The bigger particles represent chromium powder while the smaller particles represent nickel powder. The mixture was homogeneously distributed throughout the process. Some smaller particles of nickel tend to agglomerate on the chromium surface. After that, the mixture was compacted by a hydraulic press into a pallet shape. The compacted samples were sintered in the tube furnace at the sintering temperature of 1000 °C and 1200 °C for 60 minutes in the argon atmosphere.

3.3 Shrinkage of Ni-Cr based composites

After sintering at high temperature, the compacted samples were subjected to shrinkage. There was a reduction in the volume of compacted samples. Table 2 demonstrates the percentage of shrinkage after sintering at different temperatures. As the sintering temperature increased from 1000 to 1200 °C, the shrinkage of the samples also increased.

Table 2. Percentage of Shrinkage after sintering at 1000 °C and 1200 °C.

Samples	Shrinkage (%)	
	at 1000 °C	at 1200 °C
NC	15.56	32.47
NCM	21.65	35.07
NCA	25.14	38.18
NCCf	24.90	34.77
NCMA	24.83	37.55
NCMCf	22.09	33.79
NCACf	24.35	33.61
NCMACf	20.92	37.50

Based on Table 2, the highest percentage of shrinkage for both temperatures is NCA composites for 25.14% (1000 °C) and 38.18% (at 1200 °C) while the lowest percentage of shrinkage for both temperatures is NC composites for 15.56% (1000 °C) and 32.47% (at 1200 °C). During sintering, the center to center distance between the powder particles is reducing and at the same time, the pore shrinks [10]. The addition of solid lubricant/s increased the percentage of shrinkage of the Ni-Cr based composites. The highest shrinkage were NCA composites at both temperatures. This was due to the smaller particles of silver which filled in the pores and reduced the size of pores. Shrinkage is one of the factors to the increment of sintered density.

3.4 Sintered Density of Ni-Cr based composites

Shrinkage of the composites leads to the densification of the composites. Sintered density is the measurement result for densification. Table 3 illustrates the sintered density of Ni-Cr based composites samples at sintering temperature of 1000 °C and 1200 °C. Sintered density was also enhanced from the sintering temperature of 1000 to 1200 °C.

Table 3. Sintered density of Ni-Cr based composites samples at sintering temperature of 1000 °C and 1200 °C.

Samples	Sintered Density (g/cm^3)	
	at 1000 °C	at 1200 °C
NC	5.59	6.99
NCM	5.67	7.08
NCA	6.07	7.36
NCCf	5.91	6.67
NCMA	6.15	7.23
NCMCf	5.58	6.54
NCACf	6.08	6.94
NCMACf	5.57	6.88

From Table 3, the highest sintered density is achieved by NCA composite followed by NCMA composites at sintering temperature 1200 °C. Increased in density demonstrate that the process of diffusion, densification, recrystallization and grain growth between the particles at the contact area. The result is supported by the percent density graph as shown in Figure 7.

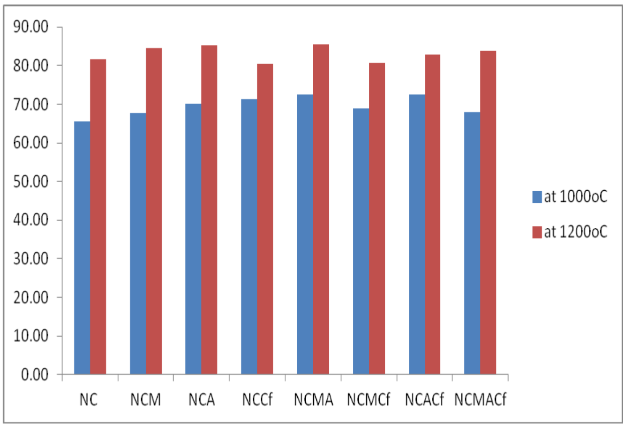

Figure 7. The percent density of Ni-Cr based composites at sintering temperature of 1000 and 1200 °C.

The percent density indicated the densification or pore shrinkage of the composites. During sintering, the particles are diffusing into each other as the temperature rise. Based on Figure 7, the highest percent density was achieved by NCMA followed by NCA and NCM composites at sintering temperature of 1200 °C. Small and fine size of solid lubricant which was silver and

MoS_2 compared to CaF_2 help in the diffusion and densification process during sintering. Then, densification leads to decrease in porosity and increase the particle contact area.

3.5 Porosity in Ni-Cr based composites

As increasing the sintering temperature, the porosity of the Ni-Cr based composites is decreasing. The number of porosities is decreased and the size of pores are reduced. When a higher temperature is applied, the grain of the composite will grow bigger and the pores tend to shrink. Thus, the porosity of the composites is reduced [11]. The reason is the driving force of sintering is increasing when the sintering temperature rises. At the earlier stage of sintering, the driving force is produced by the surface energy which is associated with the internal surface area of the particles. This is where the grains of the composites grow bigger and the pore shrinks. Less porosity is desirable because it will contribute to the positive effect on mechanical properties. Table 4 shows the porosity in the Ni-Cr based composites.

Table 4. Porosity in the Ni-Cr based composites samples after sintering at a temperature of 1000 °C and 1200 °C.

Samples	Porosity (%)	
	at 1000 °C	at 1200 °C
NC	35	18
NCM	32	16
NCA	30	15
NCCf	29	19
NCMA	27	15
NCMCf	31	19
NCACf	27	17
NCMACf	32	16

From Table 4, the lowest porosity is achieved by NCMA composites at both sintering temperature. This is due to the particle size of MoS_2 and Ag which is smaller compared to CaF_2. The particles of MoS_2 and Ag tend to fill in the pores and eventually reduce the size of the pores. The porosity results can be supported by the SEM results in Figures 8-13. The black areas which represent porosity are decreasing as the sintering temperature increased from 1000 to 1200 °C.

3.6 Microstructure of Ni-Cr based composites

Figure 8 and 9 show the microstructure of Ni-Cr based composites without any addition of solid lubricants after sintering at 1000 °C and 1200 °C. The grey phase represents the Nickel matrix while the darker phase represents the Chromium phase. On the other hand, the darkest (black) phase represent the porosity in the composite. More and larger size of pores could be seen in Figure 8 compared to Figure 9. When sintering at a higher temperature, the percentage of shrinkage is bigger, thus, reduce the distance between the particles and shrink the size of pores.

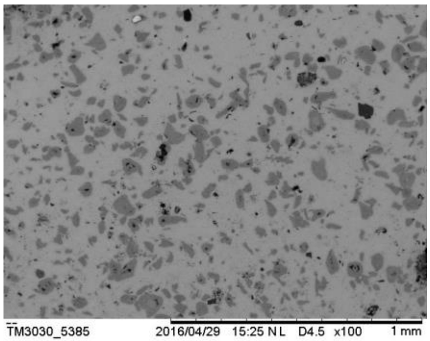

Figure 8. SEM micrograph of NC composite after sintering at 1000 °C.

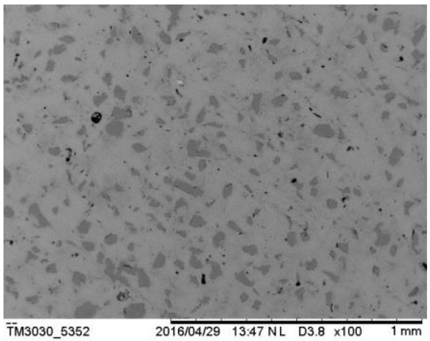

Figure 9. SEM micrograph of NC composite after sintering at 1200 °C.

Figure 10 and 11 show the Ni-Cr based composites with the addition of silver as a solid lubricant. The existence of white phase represents the silver addition in the composite.

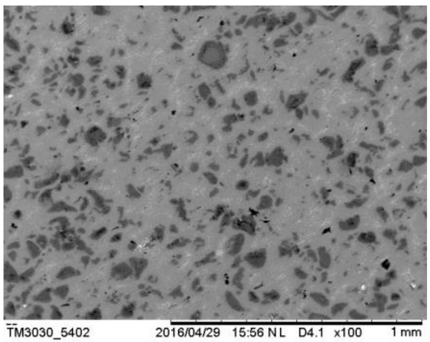

Figure 10. SEM micrograph of NCA composite after sintering at 1000 °C.

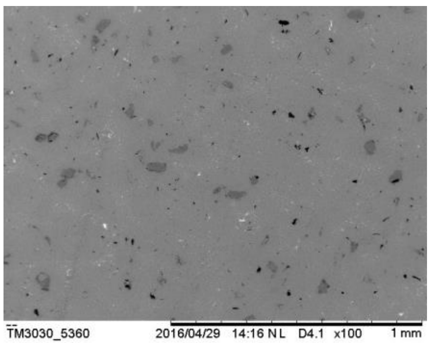

Figure 11. SEM micrograph of NCA composite after sintering at 1200 °C.

Figure 12 and 13 demonstrate the microstructure of Ni-Cr based composites with the addition of dual solid lubricant which are MoS_2 and silver.

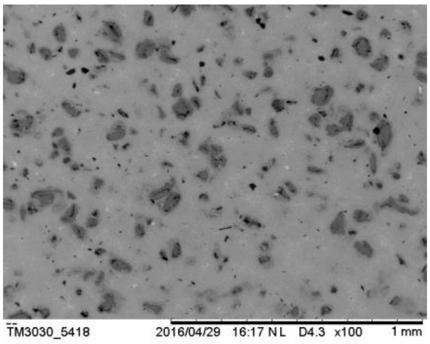

Figure 12. SEM microstructure of NCMA composites sintering at 1000 ^oC.

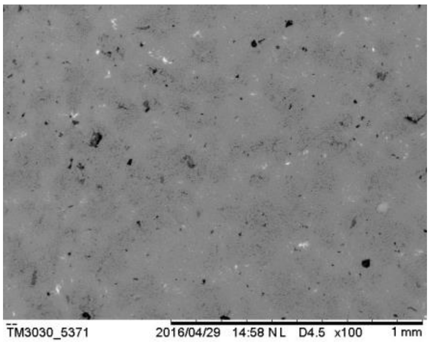

Figure 13. SEM microstructure of NCMA composites sintering at 1200 ^oC.

3.6 Hardness of Ni-Cr based composites

Higher shrinkage, enhancement of density and reduction of porosity will contribute to better mechanical properties. The hardness of the composites were listed in Table 5.

Table 5. The hardness of Ni-Cr based composites samples after sintering at temperature of 1000 ^oC and 1200 ^oC.

Samples	Hardness (HRC)	
	at 1000 ^oC	at 1200 ^oC
NC	42.6	51.5
NCM	36.8	52.1
NCA	35.1	48.5
NCCf	37.5	44.0
NCMA	41.9	57.1
NCMCf	35.8	46.4
NCACf	36.0	44.8
NCMACf	32.0	57.5

Based on Table 5, at sintering temperature of 1000 ^oC, the highest hardness is attained by the Ni-Cr composites. As we added the solid lubricants, the hardness of all Ni-Cr based composites is decreasing. However, at a higher sintering temperature of 1200 ^oC, the hardness of all of the composites containing MoS_2 are increasing (NCM, NCMA and NCMACf). 5% addition of MoS_2 as solid lubricant helps in improving the mechanical properties of the composite. A suitable amount of solid lubricant addition is important in order to enhance mechanical properties of the composites [12].

The highest hardness achieved by NCMACf composites after sintering at 1200 ^oC with a value of 57.5 HRC. The lowest hardness also achieved by NCMACf composites after sintering at 1000 ^oC with a value of 32 HRC. The main reason is the sintering temperature play the main role in the reinforcement and strengthening of the composites. At sintering temperature of 1000 ^oC, the addition of solid lubricant such as MoS_2, Ag and CaF_2 is not fully forming a good bonding of grain boundary. Thus, the grain growth between the particles is less thus the strengthening of the particles is also low compared to sintering at a higher temperature (1200 ^oC) [13].

4 Conclusions

1. The increment in sintering temperature from 1000 ^oC to 1200 ^oC enhanced the shrinkage, density and hardness while reduced the porosity of Ni-Cr based composites.

2. Ni-Cr based composites which contain silver and MoS_2 (NCA and NCMA) achieved better physical properties such as shrinkage, density and porosity due the fine size of these solid lubricants compared to CaF_2. The fine size of solid lubricant helped in filling the pores and thus increased the densification of the composites.

3. The mechanical properties of Ni-Cr based composites are improving with the increasing sintering temperature and addition of MoS_2. The addition of 5% MoS_2 in Ni-Cr based composites improved their hardness. A suitable amount of solid lubricant addition was helpful to enhance the mechanical properties.

4. Further research will be conducted on the wear properties of Ni-Cr based composites with the single, dual and multiple solid lubricants in order to achieve a composite with excellent mechanical as well as wear properties.

Acknowledgement

The author would like to thank UNIMAS DPP grant for providing financial support of this research work.

References

[1] M. B. Peterson, S. LI, and S. F. Murray, "Wear-resisting Oxide Films for 900°C," *J.Mater.Sci.Technol*, **13**, 99–106, (1997).

 DOI: 10.1051/matecconf/20178702011

[2] K. Miyoshi, “Solid Lubricants and Coatings for Extreme Environments : State-of-the-Art Survey,” (2007).

[3] A. Vadiraj, M. Kamaraj, and V. S. Sreenivasan, “Effect of solid lubricants on friction and wear behaviour of alloyed gray cast iron,” **37**, 569–577, (2012).

[4] S. Huang, Y. Feng, K. Ding, G. Qian, H. Liu, and Y. Wang, “Friction and wear properties of Cu-based self-lubricating,” *Acta Metall. Sin.*, **25**, 391–400,(2012).

[5] M. Suzuki, M. Moriyama, M. Nishimura, and M. Hasegawa, “Friction and wear of self-lubricating composites at temperatures to 450 °C in vacuum,” *Wear*, **162–164**, 471–479, (1993).

[6] Q. Bi, S. Zhu, and W. Liu, “High Temperature Self-Lubricating Materials,” in *Tribology in Engineering*, (2013).

[7] M. Xue, “High temperature oxidation and wear behaviour of powder metallurgically developed Ni-Cr-W-Al-Ti-MoS2 composite,” *Sci. York*, **16**, 111–115, (2009).

[8] C. H. Ding, P. L. Li, G. Ran, Y. W. Tian, and J. N. Zhou, “Tribological property of self-lubricating PM304 composite,” *Wear*, **262**, 575–581, (2007).

[9] E. Y. Liu, Y. M. Gao, W. Z. Wang, X. L. Zhang, X. Wang, G. W. Yi, and J. H. Jia, “Effect of the synergetic action on tribological characteristics of Ni-based composites containing multiple-lubricants,” *Tribol. Lett.*, **47**, 399–408, (2012).

[10] C. Suiyuan, W. Jing, L. Yijie, L. Jing, and L. Changsheng, “Synthesis of New Cu-based Self-lubricating Composites with Great Mechanical Properties,” *J. Compos. Mater.*, **45**, 51–63, (2010).

[11] L. F. Güleryüz, S. Ozan, R. İpek, and D. Uzunsoy, “Production of B 4 C p reinforced magnesium metal matrix composites by powder metallurgy,” **1**, 51–58, (2012).

[12] X. Dangsheng, “Lubrication behavior of Ni–Cr-based alloys containing MoS2 at high temperature,” *Wear*, **251**, 1094–1099, (2001).

[13] F. Li, J. Cheng, Z. Qiao, J. Ma, S. Zhu, L. Fu, J. Yang, and W. Liu, “A Nickel-Alloy-Based High-Temperature Self-Lubricating Composite with Simultaneously Superior Lubricity and High Strength,” *Tribol. Lett.*, **49**, 573–577, (2013).