Calcium Fluoride a Potential Solid Lubricant for Green Tribology and Sustainability

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Abstract Development of materials has been of great concern for scientists and researchers since ancient times. Lubrication is one such area where lot of work has been carried out by many researchers, especially in the area of solid lubrication. The emergence of solid lubricants has increased the lubrication potential of liquid lubricants many fold times. The term self-lubricating composites have been coined due to the association of solid lubricants with many base materials such as ceramics and metals. Various solid lubricants such as graphite, molybdenum disulphide and boron nitride have been tried by researchers, and amongst these lubricants, fluorides hold an important place. This paper presents a brief overview of solid lubricants along with a detailed description of calcium fluoride and their usage as solid lubricants in various materials, especially in metals and ceramics.

Keywords Wear · Friction · CaF_2 · Solid lubricant

1 Introduction

In the growing environmental concerns, energy demands have led to the development of green tribology. Green tribology, an emerging field in the area of tribology, deals with environmental aspects of tribology [1]. Out of the various principles of green tribology as proposed by Nasonovskyi and Bhushan [2], self-lubrication or elimination of liquid lubricants is an important one. There is widespread involvement of lubrication in various sliding applications, and without lubrication, the life of the contact materials decreases to larger extents. The science of contact surfaces, i.e. tribology would not have been originated without lubrication. Improper lubrication has led to huge energy consumption. It has been reported by scientists and researchers that wear and friction at the contact surfaces resulted in 23% of total energy consumption. Out of this, 20% is consumed to overcome friction and rest 3% for remanufacturing. Globally, saving in this regard amounts to 1.4% of the GDP on annual basis [1].

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The researchers have explored that the parts of passenger cars, e.g. brakes, engine, etc. consume one-third of the energy from fuel to overcome friction. As reported by researchers, 21.5% of the fuel energy is utilized in causing the motion of the vehicle excluding friction due to brakes. With the advent of new ways and means of lubrication, losses due to friction in passenger cars can be reduced by 18% in the short term and by 61% in the long term [2]. Moreover, in case of paper mills, the consumption of energy to overcome friction in moving parts amounts to 15–25%, and the new technological advancements in the area of lubrication will result in reducing friction losses up to 11 and 23.6% in short term and long term, respectively. Similarly, in case of heavy-duty vehicles, energy utilized to overcome friction is around 26% of the fuel energy, which can be reduced to 14% by using technological innovations [3–5]. These statistics show that lubrication is inevitable due to the continuous use of sliding parts. In view of the above discussion, it is evident that there is a need is to explore better methods of lubrication.

This paper summarizes the role of solid lubricants in minimizing frictional properties and brings forth the role of fluorides as a solid lubricant. The paper focuses on the work carried out by researchers where they have used calcium fluoride as a solid lubricant and have obtained good results.

2 Solid Lubricants

Contrary to liquid lubricants, solid lubricants are solid materials that have been used to decrease the tribological properties at the contact surfaces of the sliding parts by preventing direct contact between the materials. These lubricants can be categorized as greases, free-flowing powders, additives in various oils/coatings, etc. [6]. The contact surfaces have many asperities with peaks and valleys which cause friction and wear. These peaks and valleys are levelled by the solid lubricants resulting in reduced friction and wear. Moreover, the type of lubrication offered by solid lubricants is boundary lubrication. While comparing with liquid lubrication, solid lubrication results in least contamination, corrosion resistance, dry lubrication, etc. In addition, solid lubricants can also survive in different temperatures and in typical conditions. Contrary to liquid lubrication, solid lubrication is sustainable, as it does not require changing of the lubricant, thereby having little impact on the environment as the lubricant spilled to the environment poses serious threats. These factors have given impetus to the use of solid lubricants. Dry and clean lubrication, resistance to contamination, protection against corrosion, lubrication at various conditions and temperatures, etc. are some of the significant characteristics of solid lubricants due to which such lubrication is frequently being adopted [7]. Solid lubricants are generally classified as lamellar solids, soft metals, oxides, halides, sulphides, alkali earth metals, organic materials, etc. [8].

Various techniques have been used for incorporating solid lubricants into other materials such as stir casting, powder metallurgy, pulse laser deposition, magnetron sputtering, ion-beam mixing and ion-beam-assisted deposition [9–12].

3 Fluorides

High-temperature lubrication has been of great concern for scientists and researchers. Various lubricants could not perform at high temperatures such as graphite and molybdenum disulphide. Researchers have always looked for lubricants, which could perform at both room and high temperature. Fluorides such as calcium fluoride (CaF_2) and barium fluoride (BaF_2) have played an important role, especially for high-temperature applications, i.e. for temperatures above 500 °C (1000 °F). Amongst fluorides, CaF_2 has been used extensively and still is being explored either alone as a solid lubricant or with other lubricants/fluorides. The adhesiveness of CaF_2 has made it a suitable candidate for solid lubrication [13, 14]. The thermal stability of various fluorides of calcium, barium, magnesium, aluminium, etc. has been studied at temperatures ranging from 100 to 1000 °C. The purpose of the study was to explore the possibilities of using fluorides as solid lubricant at different temperatures. The experiments carried out in air and hydrogen atmosphere have revealed that the thermal stability of zinc sulphide at temperatures from 500 to 1000 °C is higher than that of barium, calcium and magnesium fluorides. It has also been observed that sulphides of zinc decompose fully in air at 500 °C and in hydrogen and water vapour at 900 °C [15]. The hardness of fluorides of barium and calcium (CaF_2 and BaF_2) has been studied by researchers at temperatures ranging from 25 to 670 °C. The findings have shown fluoride eutectic as a good lubricant for high temperatures as it undergoes brittle to ductile transition at about 400–500 °C [16].

CaF_2 has a strong chemical, physical and microstructural influence on the tribological behaviour of contact surfaces. The structure of CaF_2 is same as that of graphite, molybdenum disulphide, i.e. it has a lamellar structure with hexagonal pattern in every plane, and these planes are connected by weak forces that shear easily at certain temperatures and thus lubricates. The efficacy of liquid lubricants in certain applications involving high temperatures or vacuum environments becomes very low, and thus, in those applications high-temperature solid lubricants like CaF_2 play an important role [17].

The low solubility of CaF_2 in water and its capability to resist radiations have placed it amongst the safe materials to be used in radiation exposure also. CaF_2 has shown good compatibility and enhanced tribological properties with many matrices. However, researchers have also reported decrease in mechanical properties, and some have confirmed increased hardness due to addition of CaF_2 [18–20].

The improvement in tribological properties against decrease in mechanical properties had made study of CaF_2 of great significance. CaF_2, being high-temperature solid lubricant, has also performed even at room temperature. This makes study of these materials most important as researchers are trying hard to find solid lubricants which could perform both at room as well as at high-temperature applications [21]. There is not much work being carried out with CaF_2 as solid lubricant. The succeeding section presents the research carried out using CaF_2 as solid lubricant with metals and ceramics.

4 CaF_2-Reinforced Metal Matrix Composites

Researchers have investigated many composites with metals as base matrix and CaF_2 as solid lubricant. The results were interesting due to the improvement in tribological properties. Wear and friction characteristics of sintered steels reinforced with titanium carbide, manganese sulphide and calcium fluoride have been investigated at high temperature. The results have shown improved lubricating characteristics with CaF_2 [22]. Fe–W–CaF_2 composites were fabricated using powder metallurgy, and their mechanical and tribological properties were investigated. Grain refinement resulting due to addition of CaF_2 along with intermetallic formations led to increased hardness. The wear and friction testing carried out at high temperature revealed decreased wear rate with increase friction at high speeds. The increase in friction at high speeds is due to the dominance of hard iron oxides over CaF_2 [23]. Researchers have developed iron base composite with molybdenum (15 wt%) and CaF_2 (6 and 9 wt%) as solid lubricant using powder metallurgy and have found that at high temperatures, there is an increase in mechanical properties such as hardness, impact strength and rupture strength, which is due to the high concentration of CaF_2 [24]. Using compaction and sintering, Fe-based composites were fabricated with FeS, ZnS, BaF_2, CaF_2 and BN as solid lubricants. Amongst all these developed composites, CaF_2 reinforced composite have shown low coefficient of friction and wear rate which is attributed to the decreasing shear strength of CaF_2 at high temperatures [25]. Sintered Fe-Mo-based composites were developed using CaF_2 as a solid lubricant, and the composites were subjected to mechanical and tribological testing at room and high temperature of 600 °C. The weight percentage of Mo and CaF_2 was varied and different composites were prepared. From the results, it was observed that reinforcing CaF_2 in Fe-10Mo matrix has enhanced mechanical as well as tribological properties. Composite with Fe–10Mo–8CaF_2 has shown raised mechanical along with tribological properties at both room and high temperature [26]. Composites with Fe–Cu–C as base and CaF_2 as solid lubricant have also been developed by the researchers and have been evaluated at room and high temperatures. Interestingly, the results have revealed that CaF_2 can offer increased tribological properties at room as well as high temperatures. However, a slight decrease in some physical and mechanical properties was observed with the increase in CaF_2 contents such as density and compression strength [27, 28]. Moreover, the wear and friction of the Fe–Cu–C as base matrix have been enhanced using CaF_2 as a solid lubricant [29]. The authors have evaluated the composites at high speeds, and improvement in the tribological properties have been reported. Fe-based impregnated diamond bit matrix was reinforced with CaF_2 and hBN, high-temperature solid lubricants. The composites were fabricated by powder metallurgy route and the volume percentage of the lubricants used was 2, 4, 6, 8 and 10. The objective was to study mechanical and tribological properties of the developed composites and draw a comparison between the usages of both high-temperature lubricants. Findings have shown that in general, increasing the lubricant content degrades the mechanical properties; however, the impact of CaF_2 in decreasing mechanical behaviour is less significant as compared to hBN. A slight decrease in hardness was observed in CaF_2-added composite to that of hBN-added composite. Similarly, the wear loss of hBN-added composites was more than that of CaF_2-added ones. Moreover, the worn surface of CaF_2-added composite was better than that of hBN-added composite [30]. The mechanical and tribological properties of nickel base bearings developed using hot isostatic pressing have also been studied. Bearings were fabricated with nickel alone and nickel with CaF_2. CaF_2 was used in these bearings as a solid lubricant. The bearings were developed for high-speed printing machines, and the results have shown interesting outcomes. Intense friction films were observed for bearings made from nickel and CaF_2. These films formed at the contact surface resulted in low friction and enhanced wear resistance, 3.2–6 times more as compared to the bearings with nickel only [31].

5 CaF_2-Reinforced Ceramic Composites

Ceramics have been explored by many researchers in various applications and have obtained good results [32–34]. In order to obtain high tribological performance at elevated temperature of Titanium–Aluminium (TiAl) intermetallic alloy, CaF_2 was mixed with NiCr–Cr_3C_2, and finally, coatings of NiCr–Cr_3C_2–CaF_2 were fabricated on TiAl alloy using laser cladding process. From the wear and friction studies, it was found that the coating with NiCr–Cr_3C_2–40CaF_2 has shown low friction and wear rate [35]. The authors have developed coatings of cobalt alloy, titanium carbide (TiC) and CaF_2 on the copper specimen. The ratio of the coating material was fixed as Co alloy alone and variations in the proportions of Co alloy with TiC and CaF_2 powders. The coatings were fabricated on Cu specimen using laser cladding. It was observed that fine spherical particles of TiC along with spherical particles of CaF_2 dispersed uniformly in the Co matrix. The tribological tests revealed that introduction of CaF_2 and TiC in the coating resulted in reduced friction and wear rate of the fabricated composites [36]. A wear-resistant composite was fabricated using Al_2O_3 and CaF_2 using laser cladding. Al_2O_3 alone and Al_2O_3–30 wt% CaF_2 were tested for wear resistance at room temperature, and Al_2O_3–CaF_2 composite was found to exhibit better wear resistance than monolithic Al_2O_3. A unique microstructure comprising of isolated spherical CaF_2 particles in plate-like framework of Al_2O_3 was developed, and uniform distribution of the solid lubricant was observed in the inter-framework regions [37]. There was a need to develop silicon carbide-based self-lubricating composites which should operate up to a temperature of 900 °C. The researchers have developed two composites, with SiC alone and with combination of SiC and CaF_2. These composites were investigated for tribological properties and results showed raised friction and wear rate in SiC-based composites, whereas composites fabricated with SiC and CaF_2 have shown reduced friction and wear rate. This reduction in friction and wear of SiC+ CaF_2 up to 700 °C are due to the smearing of calcium fluoride on the contacting surfaces, and at 900 °C, CaF_2 reacted with silica, and thus, improvement in wear behaviour was observed [38]. CaF_2 has been tried with various ceramics to enhance their tribological properties. CaF_2 has been reinforced in Al_2O_3/TiC composites in 5, 10 and 15 vol% using powder metallurgy route. The results have shown that addition of CaF_2 has resulted in decrease of the flexural strength, fracture toughness and hardness as compared to the base matrix. Coefficient of friction also decreased with the increase in CaF_2; however, the wear rate was observed to decrease up to 10 vol% CaF_2, and beyond 10 vol%, wear rate increases rapidly [39]. Due to the capability of enhancing wear and friction, CaF_2 was again tried by researchers with Al_2O_3 and TiC, but this time, the processing was slightly changed. Al_2O_3/TiC composites were prepared using cold pressing and sintering, and one more composite was prepared using CaF_2. Layered structure was developed by cold pressing, i.e. between the layers of Al_2O_3/TiC, there was introduced a layer of Al_2O_3/TiC/CaF_2. The friction and wear testing of these composites revealed low coefficient of friction and high wear resistance of the prepared Al_2O_3/TiC/CaF_2–Al_2O_3/TiC laminated composite as compared to that of Al_2O_3/TiC ceramic. The worn surface of the Al_2O_3/TiC/CaF_2–Al_2O_3/TiC laminated composites was found to improve and thus resulted in enhanced wear resistance. During the study, Al_2O_3/TiC/CaF_2 layer in the laminated composite was also observed to be more compact than Al_2O_3/TiC [40]. BaF_2/CaF_2 was used with Ag and Ti_3SiC_2 in a TiAl matrix and the composites were prepared using Spark Plasma Sintering at 1100 °C under a pressure of 40 MPa in pure Ar atmosphere. The proportions of BaF_2, CaF_2, Ag and Ti_3SiC_2 were varied in the composites. The objective was to investigate the tribological behaviour against Si_3Ni_4 over a temperature range from room temperature to 600 °C. The investigation depicted enhanced wear and friction behaviour which was ascribed to the synergetic effect of Ag, Ti_3SiC_2 and BaF_2/CaF_2 lubricants [41]. The lubricating potential of combined CaF_2 and BaF_2 has been investigated by fabricating a composite coating. The coating consists of base matrix as WC-Co, and copper along with both fluorides reinforced using powder metallurgy process. The weight percentage of CaF_2 and BaF_2 was kept constant at the rate of 19 wt% and 31 wt%, respectively. The findings have revealed that coatings with CaF_2 and BaF_2 exhibited raised compactness, low coefficient of friction and low wear loss. The study also reflected the capability of these solid lubricants to prevent decarburization and decomposition of the composite [42]. On the same lines, BaF_2/CaF_2 has been tried with NiCr–Cr_2O_3–Ag–CaF_2/BaF_2 coatings, and good results were obtained [43]. Ceramics such as ZrO_2 (Y_2O_3) were tried with 10 wt% of MoS_2 and 10 wt% of CaF_2 using powder metallurgy. The results of the study have shown the usefulness of such composites at both room as well as high temperatures, e.g. at room/low temperature, MoS_2 has shown good tribological behaviour, whereas at high temperatures, an intermetallic $CaMoO_4$ was formed which acted as an effective solid lubricant [44]. Table 1 summarizes various compositions, which have been discussed in this chapter.

Table 1 Compositions

S. No.	Details of the composite	Year	Reference
1	Fe–FeS/ZnS/BaF_2/CaF_2/BN	1968	[25]
2	Fe–Mo–CaF_2	1976	[24]
3	SiC–CaF_2	2001	[38]
4	CaF_2/Al_2O_3	2002	[37]
5	Fe–CaF_2/MnS/TiC	2004	[22]
6	NiCr–Cr_2O_3–Ag–CaF_2/BaF2	2005	[43]
7	Al_2O_3–TiC–CaF_2	2006	[39]
8	Fe–Mo/CaF_2	2009	[26]
9	Al_4C_3–TiC–CaF_2	2009	[35]
10	WC–Co–Cu–BaF_2/CaF_2	2010	[42]
11	Fe–W–CaF_2	2012	[23]
12	Co-based alloy–TiC–CaF_2	2013	[36]
13	Al_2O_3/TiC/CaF_2–Al_2O_3/TiC	2013	[40]
14	ZrO_2 (Y_2O_3)–MoS_2–CaF_2	2013	[44]
15	Ni–CaF_2	2014	[31]
16	Ti_3SiC_2–BaF_2/CaF_2	2014	[41]
17	Fe–Cu–C	2017, 2018	[27–29]
18	Fe–hBN/CaF_2	2018	[30]

6 Conclusion and Future Scope

The expenditure of energy in overcoming friction and the importance of solid lubricants have been discussed in the present work. Solid lubricants play a vital role in minimizing friction in the regimes where liquid lubrication is not suitable. Apart from this, solid lubricants have also been used to enhance the lubrication capability of the liquid lubricants. The paper also focuses upon the importance of fluorides especially CaF_2 as a high-temperature solid lubricant, which has also proved its worth at room temperature. Since there is not much work carried out with CaF_2 as solid lubricant, the usage of CaF_2 in combination with other low- and high-temperature lubricants has also not been explored much. Thus, there is a scope for further research where more materials with CaF_2 can be explored. This gives a space for researchers to develop more composites with combined lubricants. In fact, CaF_2 can also be tried with liquid lubricants and nano-CaF_2 powders with different matrices.

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References

1. Zhang SW (2013) Green tribology: fundamentals and future development. Friction 1(2):186–194
2. Nosonovsky M, Bhushan B (eds) (2012) Green tribology: biomimetics, energy conservation and sustainability. Springer, New York
3. Holmberg K, Erdemir A (2017) Influence of tribology on global energy consumption, costs and emissions. Friction 5(3):263–284
4. Holmberg K, Andersson P, Nylund NO, Mäkelä K, Erdemir A (2014) Global energy consumption due to friction in trucks and buses. Tribol Int 78:94–114
5. Holmberg K, Siilasto R, Laitinen T, Andersson P, Jäsberg A (2013) Global energy consumption due to friction in paper machines. Tribology International 62:58–77
6. Sharma SM, Anand A (2016) Solid lubrication in iron based materials–a review. Tribol Ind 38(3)
7. Vasil'ev YN, Kolyaev IA (2011) On the friction mechanism of solid lubricants. J Fric Wear 32(5):324
8. Menezes PL, Nosonovsky M, Kailas SV, Lovell MR (2013) Friction and Wear. Tribology for Scientists and Engineers: from basics to advanced concepts. Springer, New York, pp. 43–91
9. Holmberg K, Ronkainen H, Matthews A (2000) Tribology of thin coatings. Ceram Int 26(7):787–795
10. Anand A, Haq MIU, Vohra K, Raina A, Wani MF (2017) Role of green tribology in sustainability of mechanical systems: a state of the art survey. Materi Today Proc 4(2):3659–3665
11. Singh N, Mir IUH, Raina A, Anand A, Kumar V, Sharma SM (2018) Synthesis and tribological investigation of Al-SiC based nano hybrid composite. Alexandria Eng J 57(3):1323–1330
12. Haq MIU, Anand A (2018) Dry sliding friction and wear behaviour of Hybrid AA7075/Si3N4/Gr self lubricating composites. Mat Res Expr
13. Milojević S, Pešić R, Taranović D (2015) Tribological Principles of constructing the reciprocating machines. Tribol Ind 37(1)
14. Kostornov AG, Fushchich OI, Chevychelova TM, Kostenko AD, Karpets MV (2014) Tribological characteristics of the iron-based composite at 500 °C. Powder Metall Metal Ceram 53(7–8):411–416
15. Miroshnikov VN, Shevchuk YF (1973) Choice of solid lubricants. Powder Metall Metal Ceram 12(10):844–847
16. Deadmore DL, Sliney HE (1987) Hardness of CaF_2 and BaF_2 solid lubricants at 25–670 °C. National Aeronautics and Space Administration, Lewis Research Center
17. Sliney HE (1991) Solid lubricants
18. Bolton JD, Gant AJ (1993) Phase reactions and chemical stability of ceramic carbide and solid lubricant particulate additions within sintered high speed steel matrix. Powder Metall 36(4):267–274
19. Muthuraja A, Senthilvelan S (2015) Abrasive wear performance of tungsten carbide based self-lubricant cutting tool material. Int J Refract Metals Hard Mater 51:91–101
20. Sliney HE (1973) High temperature solid lubricants: when and where to use them
21. Vadiraj A, Kamaraj M, Sreenivasan VS (2011) Wear and friction behaviour of alloyed gray cast iron with solid lubricants under boundary lubrication. Tribol Int 44(10):1168–1173
22. Zuomin L, Childs THC (2004) The study of wear characteristics of sintered high speed steels containing CaF_2, MnS and TiC additives at elevated temperature. Wear 257(3–4):435–440
23. Kostornov AG, Fushchich OI, Gorban VF, Chevychelova TM, Kostenko OD (2012) Effect of dry friction parameters on the tribosynthesis of secondary structures on composite antifriction iron-based material. Powder Metall Metal Ceram 51(7–8):412–419
24. Fedorchenko IM, Shevchuk YF, Miroshnikov VN, Borisenko VA (1976) Elevated-temperature mechanical properties of sintered iron-base materials containing calcium fluoride additions. Soviet Powder Metall Metal Ceram 15(3):238–242
25. Shevchuk YF, Zozulya VD, Khrienko AF (1968) Friction of materials with additions of substances acting as solid lubricants. Powder Metall Metal Ceram 7(12):985–988

26. Han J, Jia J, Lu J, Wang J (2009) High temperature tribological characteristics of Fe–Mo-based self-lubricating composites. Tribology letters 34(3):193–200
27. Sharma SM, Anand A (2017) Friction and wear behaviour of Fe–Cu–C based self lubricating material with CaF_2 as solid lubricant. Ind Lubric Tribol 69(5):715–722
28. Anand A, Sharma SM (2017) High temperature friction and wear characteristics of Fe–Cu–C based self-lubricating material. Trans Indian Inst Metals 70(10):2641–2650
29. Sharma SM, Anand A (2018) Effect of speed on the tribological behaviour of Fe–Cu–C based self lubricating composite. Trans Indian Inst Metals 71(4):883–891
30. Li C, Duan L, Tan S, Zhang W, Pan B (2018) Effect of CaF_2 and hBN on the mechanical and tribological properties of Fe-based impregnated diamond bit matrix. Int J Refrac Metals Hard Mater 75:118–125
31. Roik T, Gavrish A, Kyrychok P, Vitsuk Y, Askerov M (2014) Physical, mechanical and tribotechnical properties of new composite bearings for printing equipment. Zeszyty Naukowe/Wyższa Szkoła Oficerska Wojsk Lądowych im. gen. T, Kościuszki
32. Singh RP, Singhal S (2017) Rotary ultrasonic machining of macro ceramic: an experimental investigation and microstructure analysis. Mater Manuf Process 32(9):927–939
33. Kataria R, Singh RP, Kumar J (2016) An experimental study on ultrasonic machining of tungsten carbide-cobalt composite materials. AIMS Mater Sci 3(4):1391–1409
34. Singh RP, Singhal S (2018) Experimental study on rotary ultrasonic machining of alumina ceramic: microstructure analysis and multi-response optimization. Procee Inst Mech Eng Part L: J Mater Design Appl 232(12):967–986
35. Liu XB, Shi SH, Guo J, Fu GY, Wang MD (2009) Microstructure and wear behaviour of $\gamma/Al_4C_3/TiC/CaF_2$ composite coating on γ-TiAl intermetallic alloy prepared by Nd: YAG laser cladding. Appl Surf Sci 255(11):5662–5668
36. Yan H, Zhang J, Zhang P, Yu Z, Li C, Xu P, Lu Y (2013) Laser cladding of Co-based alloy/TiC/CaF_2 self-lubricating composite coatings on copper for continuous casting mold. Surf Coat Technol 232:362–369
37. Wang HM, Yu YL, Li SQ (2002) Microstructure and tribological properties of laser clad CaF_2/Al_2O_3 self-lubrication wear-resistant ceramic matrix composite coatings. Scripta Materialia 47(1):57–61
38. Shuaib M, Davies TJ (2001) Wear behaviour of a REFEL SiC containing fluorides up to 900 °C. Wear 249(1–2):20–30
39. Jianxin D, Tongkun C, Zeliang D, Jianhua L, Junlong S, Jinlong Z (2006) Tribological behaviours of hot-pressed Al_2O_3/TiC ceramic composites with the additions of CaF_2 solid lubricants. J Eur Ceram Soc 26(8):1317–1323
40. Yang X, Cheng J, Song P, Wang S, Yang L, Wang Y, Mao K (2013) Wear behaviour of cold pressed and sintered Al_2O_3/TiC/CaF 2–Al_2O_3/TiC laminated ceramic composite. Acta Metallurgica Sinica (English Letters) 26(2):157–166
41. Shi X, Yao J, Xu Z, Zhai W, Song S, Wang M, Zhang Q (2014) Tribological performance of TiAl matrix self-lubricating composites containing Ag, Ti_3SiC_2 and BaF_2/CaF_2 tested from room temperature to 600 °C. Mater Des 53:620–633
42. Yuan J, Zhu Y, Ji H, Zheng X, Ruan Q, Niu Y, Zeng Y (2010) Microstructures and tribological properties of plasma sprayed WC–Co–Cu–BaF_2/CaF_2 self-lubricating wear resistant coatings. Appl Surf Sci 256(16):4938–4944
43. Kim G, Choi H, Han C, Uhm S, Lee C (2005) Characterization of atmospheric plasma spray NiCr–Cr2O3–Ag–CaF2/BaF2 coatings. Surf Coat Technol 195(1):107–115
44. Kong L, Bi Q, Niu M, Zhu S, Yang J, Liu W (2013) ZrO_2 (Y_2O_3)–MoS_2–CaF_2 self-lubricating composite coupled with different ceramics from 20 to 1000 °C. Tribol Int 64:53–62