Tribological Behavior and Self-Healing Properties of Ni$_3$Al Matrix Self-Lubricating Composites Containing Sn-Ag-Cu and Ti$_3$SiC$_2$ from 20 to 800 °C

Yuchun Huang $^{1,*}$, Haishu Ma $^1$, Yubo Meng $^1$ and Xiyao Liu $^{2,3}$

$^1$ School of Mechanical Engineering, Henan University of Engineering, No. 1, Xianghe Road, Zhengzhou 451191, China; haishuma@haue.edu.cn (H.M.); myb0201@126.com (Y.M.)
$^2$ State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China; lxylx199076163.com
$^3$ School of Mechatronic Engineering, Xi’an Technological University, 2 Xuefuzhong Road, Xi’an 710021, China
* Correspondence: yuchunhuang@haue.edu.cn

Abstract: As a high-temperature structural material, Ni$_3$Al matrix composites are often used to manufacture basic mechanical components that need to be used in high-temperature conditions. To meet the increasing demand for metal matrix composites with an excellent tribological performance over a wide temperature range, Ni$_3$Al matrix self-lubricating composites containing Sn-Ag-Cu and Ti$_3$SiC$_2$ (NST) were synthesized via laser-melting deposition. Dry sliding friction tests of NST against Si$_3$N$_4$ ball were undertaken from 20 to 800 °C to investigate the tribological behavior and wear-triggered self-healing properties. The results show that the tribological behaviors of NST are strongly dependent on the testing temperature and self-healing properties. At low and moderate temperatures from 20 to 400 °C, as the Sn-Ag-Cu flows into the cracks and is oxidized during sliding friction, while the cracks on the worn surface are filled with oxides consisting mainly of Al$_2$O$_3$, SnO$_2$ and CuO. At higher temperatures of 600 and 800 °C, the cracks are filled by the principal oxides of Al$_2$O$_3$, TiO$_2$ and SiO$_2$ due to the partial decomposition and oxidation of Ti$_3$SiC$_2$. Compared with other testing temperatures, the recovery ratio relative to the Ni$_3$Al base alloy of the cracks on the worn surface of NST is the highest at 400 °C, which is about 76.4%. The synergistic action mechanisms of Sn-Ag-Cu and Ti$_3$SiC$_2$ on the crack self-healing from 20 to 800 °C play a significant role in forming a stable solid lubricating film, improving the anti-friction and wear resistance of NST. The results provide a solution allowing for metal matrix composites to achieve excellent lubrication stability over a wide temperature range by virtue of the crack self-healing properties.

Keywords: sliding wear; self-lubricating composites; self-healing properties; wear mechanism

1. Introduction

Recently, researchers around the world have shown great interest in self-healing composites because such self-healing properties might increase their service life, reducing maintenance costs and improving product safety and reliability [1]. Self-healing composites can repair stress cracking caused by fatigue wear [2]. These self-healing properties are an effective mechanism by which materials can delay mechanical damage, which can enhance their mechanical and tribological performances [2,3].

To realize the self-healing properties of metal matrix composites, the current methods adopted by domestic and foreign scholars mainly include precipitation self-healing, shape-memory-alloy-based self-repairing and the addition of a healing agent to the composites [3,4]. Yang et al. [5] analyzed the self-regulating tribological function of titanium alloy with a MgAl microchannel. The results indicated that the Al$_2$O$_3$ and graphene could enhance the self-recovery performance of the friction interface, resulting in a good self-healing morphology of the worn surface material. Lucci et al. [6] discussed the self-healing properties of a metal matrix
composite. The results showed that the alloy healing agent with a low melting point flowed into the crack after melting, which allow for the self-healing of the crack. Oladijo et al. [7] analyzed the self-healing properties of aluminum hybrid composites. The results showed that the difference in the self-healing effect could be attributed to the difference in the interfacial bonding of the materials [7]. Zhou et al. [8] studied the tribological performances and self-repairing functionality of Ti6Al4V matrix composites at 25–600 °C. The results showed that Ag and multilayer graphene precipitated onto the microcrack along with the spreading of a lubricating film, which would contribute to the self-repairing of the worn surface material.

As an excellent high-temperature structural material, Ni3Al matrix composites have good mechanical properties and outstanding oxidation resistance at high temperatures [9,10], rendering them applicable in the manufacture of basic mechanical components such as forging dies, valves, turbocharger parts, and piston heads of internal combustion engines [11]. To meet the increasing demand for metal matrix composites with an excellent tribological performance under working conditions with a wide temperature range, this provides a feasible way to further develop Ni3Al matrix self-lubricating composites with self-healing properties over a wide temperature range. Recently, Mn+1AXn phase ceramics have been regarded as ideal additive agents to realize the self-healing of crack damage due to their remarkable ability to form stable oxides with good adhesion and high relative volume expansion [12]. Zhai et al. [2] have researched the tribological performances of the nickel aluminum bronze/Ti3SiC2. The results indicated that the decomposition and oxidation of Ti3SiC2 promoted crack self-healing, which could contribute to the enhancement of tribological properties. The Mn+1AXn phase has excellent high-temperature oxidation resistance and can improve the high-temperature tribological performance of the composite [13,14]. In addition, the relative volume expansion that occurs due to the oxidation of Ti3SiC2 at high temperatures is more prominent than those of other MAX phases [2]. Therefore, Ti3SiC2 can be used as a perfect healing agent for metal matrix composites at high temperatures. As a soft metal, the addition of Sn-Ag-Cu to metal matrix composites can provide the materials with good self-lubricating properties at low and moderate temperatures [15–17].

Here, the self-healing properties of Ni3Al matrix self-lubricating composites containing Sn-Ag-Cu and Ti3SiC2 (NST) prepared via laser melting deposition (LMD) were studied from room temperature (20 °C) to 800 °C. The effects of testing temperature, physical and chemical evolutions of Sn-Ag-Cu and Ti3SiC2 on the tribological performance and self-healing properties of NST were systematically discussed. It is expected that the NST will show extraordinary lubrication stability over a wide temperature range by virtue of its crack self-healing properties.

2. Experimental Details

2.1. Materials Preparation

The main compositions of Ni3Al-based alloy (NBA) are shown in Table 1. Starting materials for NBA, Sn-Ag-Cu and Ti3SiC2 are commercial powders (Changsha Tianjiu Metal Materials Co., Ltd., Changsha, China) with the average sizes of 5–20 µm. Referring to the previous experimental studies of Liu et al. [18] and Xu et al. [19], to obtain good lubrication and mechanical composite properties, the addition ratios of Sn-Ag-Cu and Ti3SiC2 in the matrix were determined to be 10 wt.% and 12 wt.%, respectively. The compositions and microhardness of the as-prepared samples are shown in Table 2. The element ratio of Sn, Ag and Cu was determined to be 50:40:10 [18,20]. The initial powder was prepared according to the corresponding adding ratio and mixed evenly using a common planetary ball mill. Finally, the spherical powder was prepared by a centrifugal atomization equipment (LD-QW/500, Hebei Jingye Additive Manufacturing Co., Ltd., Shijiazhuang, China). Figure 1 shows the flow chart for the preparation process of NST.
via LMD. Referring to relevant studies [21–23], the optimum process parameters for LMD obtained after multiple parameter tests are listed in Table 3. According to the lubricant addition ratios and LMD process parameters, the NBA, NST, NT and NS samples were prepared using 3D printing equipment (RC-LDM-8060, Nanjing Yuchen Laser Technology Co. Ltd., Nanjing, China). The dimensions of the samples were 25 mm × 25 mm × 10 mm. To obtain a low surface roughness (0.15 ± 0.02 µm), the surfaces of the NBA, NST, NT and NS were mechanically polished.

Table 1. Chemical compositions of Ni3Al-based alloy (wt.%).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>Mo</th>
<th>Cr</th>
<th>Zr</th>
<th>B</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>8.0–8.5</td>
<td>6.5–7.0</td>
<td>5.5–6.0</td>
<td>0.1–0.3</td>
<td>0.03–0.05</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2. Compositions and microhardness of the as-prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Compositions (wt.%)</th>
<th>Microhardness (HV1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBA</td>
<td>Ni3Al-based alloy</td>
<td>561.2 ± 10.2</td>
</tr>
<tr>
<td>NST</td>
<td>Ni3Al-based alloy-10 wt.% Sn-Ag-Cu-12 wt.%Ti3SiC2</td>
<td>615.4 ± 9.5</td>
</tr>
<tr>
<td>NS</td>
<td>Ni3Al-based alloy-10 wt.% Sn-Ag-Cu</td>
<td>545.5 ± 10.0</td>
</tr>
<tr>
<td>NT</td>
<td>Ni3Al-based alloy-12 wt.%Ti3SiC2</td>
<td>682.5 ± 11.3</td>
</tr>
</tbody>
</table>

Figure 1. The flow chart for the preparation process of NST via LMD.

Table 3. Process parameters for laser-melting deposition.

<table>
<thead>
<tr>
<th>LMD Process</th>
<th>Laser Power (W)</th>
<th>Scanning Velocity (mm/s)</th>
<th>Laser Beam Diameter (mm)</th>
<th>Scanning Distance (mm)</th>
<th>Layer Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process parameters</td>
<td>2000</td>
<td>7.2</td>
<td>6</td>
<td>3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

2.2. Friction Testing and Material Characterization Methods

The friction tests of NBA, NST, NT and NS samples were executed with a multi-function tribometer (MFT-5000, Rtec, San Jose, CA, USA) for 60 min at 20, 200, 400, 600 and 800 °C. Si3N4 ball was selected as the counter-pair due to its low thermal expansion coefficient and excellent oxidation resistance in a wide temperature range [24]. The sliding speed was 0.2 m/s [25]. The applied load was 12 N [26]. The friction radius was 5 mm. The friction coefficients of the samples were recorded by the device. The wear rates W of the samples were calculated as $W = V/(P \times S)$, where $V$, $P$ and $S$ were the wear volume, applied load and total sliding distance, respectively. As presented in Figure 2b, to obtain the wear volume of the samples, a 2D cross-sectional profile was measured by a profilometer (ST400,
Nanovea Corporation, Irvine, CA, USA) along the line AA (see Figure 2a). The depth and width of the wear scar of NST after friction and wear tests at 20 °C were 22 µm and 1.2 mm, respectively. The friction tests were repeated thrice to obtain the mean value.

Figure 2. Typical 3D profile (a) and 2D cross-sectional profile (b) of the wear scar.

X-ray diffraction (XRD; D/MAX-RB RU-200B, Rigaku, Tokyo, Japan) was used to identify the phase constitutions of the NBA, NS, NT and NST. The microhardness of each sample was obtained by an HVS-1000 Vickers hardness tester (Beijing times peak Technology Co.Ltd., Beijing, China) with a load of 1 kg and a dwell time of 8 s. The morphologies of the worn surfaces of the NBA, NS, NT and NST were investigated by an electron probe microanalyser (EPMA; JAX-8230, JEOL Ltd., Tokyo, Japan). The elemental compositions of the worn surfaces were acquired using an energy-dispersive spectroscopy (EDS; GENESIS 7000, JEOL Ltd., Japan). To analyze the phase composition of the worn surface, a Raman spectrum (InVia, Renishaw, Gloucester, UK) analysis was performed. The method of cooling fracture was adopted to obtain the cross-section structures of wear scars. The as-prepared samples were incised down to a residual thickness of about 1–1.5 mm at the relative side of the wear scars. After being incised, the samples were cooled for 30 min using liquid nitrogen. The cooled samples were broken by the low shearing force in a dust-free environment. The cross-sectional morphologies of the NBA and NST were characterized using scanning electron microscopy (SEM; JSM-IT300, JEOL Ltd., Japan).

3. Results and Discussion
3.1. Phase Characterization

Figure 3 presents the XRD patterns of NBA, NS, NT and NST samples. The results show that all samples are mainly composed of the Ni₃Al phase, which is the main component of the matrix materials. At the same time, a Ti₃SiC₂ phase can be found in the NT and NST samples. Ti₃SiC₂ has a high melting point and high-temperature chemical stability [25], which ensures its stability in the samples’ preparation process. The lubricating phases of Sn, Ag and Cu can be found in the NS and NST samples.

Figure 3. XRD patterns of NBA, NS, NT and NST.
3.2. Friction and Wear Performance

Figure 4 shows the friction coefficients and wear rates of NBA, NS, NT and NST sliding against Si$_3$N$_4$ ball at 12 N-0.2 m/s for 60 min at different temperatures. As presented in Figure 4a, the friction coefficient of each sample decreases from 20 to 400 °C. At 400 °C, the friction coefficient of NST is 0.22, which is similar to that of NS. As the temperature increases to 800 °C, the friction coefficient of NST increases to 0.29, which is similar to that of NT. As presented in Figure 4b, the wear rate of each sample decreases from 20 to 400 °C. At 400 °C, the wear rate of NST is 6.2 × 10$^{-6}$ mm$^3$N$^{-1}$m$^{-1}$, which is similar to that of NS. At 600 and 800 °C, the wear rate of NST increases to 8.7 × 10$^{-6}$ and 1.25 × 10$^{-5}$ mm$^3$N$^{-1}$m$^{-1}$, respectively, which is similar to that of NT. Compared with NBA, NS and NT, NST shows lower friction coefficients (0.22–0.29) and wear rates (0.62–1.25 × 10$^{-5}$ mm$^3$N$^{-1}$m$^{-1}$) from 20 to 800 °C due to the synergistic action mechanism of Sn-Ag-Cu and Ti$_3$SiC$_2$ on the crack self-healing.

Figure 4. Friction coefficients (a) and wear rates (b) of NBA, NS, NT and NST at 20, 200, 400, 600 and 800 °C.

Figure 5 shows the dynamic friction coefficients of NST varying with the sliding time at 200, 400, 600 and 800 °C. The fluctuations in the friction coefficients with the sliding time at 400 and 600 °C are more stable than those obtained at 200 and 800 °C, due to the excellent crack self-healing properties of NST at 400 and 600 °C, which improves the tribological performances of the NST. Moreover, the testing temperatures have a certain influence on the duration of the running-in process of NST. Compared with other testing temperatures, the duration of the running-in process of NST at 400 °C is shorter, which can be attributed to the formation of a more stable solid lubricating film on the friction contact surface of NST within a shorter friction time.

Figure 5. Dynamic friction coefficients of NST varying with the sliding time at 200, 400, 600 and 800 °C.

3.3. Self-Healing Behavior and Mechanism

Figure 6 presents the worn surface morphologies of NBA, NS, NT and NST at 400 °C. As presented in Figure 6a, obvious furrows and some cracks indicate that the main wear...
mechanisms of NBA at 400 °C are a mixture of abrasive wear and fatigue wear [27]. As presented in Figure 6c, obvious spalling and cracks indicate that the main wear mechanism of NT at 400 °C is fatigue wear [27]. As presented in Figure 6b,d, a relatively complete lubrication film and a few cracks appear on the worn surfaces of NS and NST. Figure 6e,f shows the EDS results of the areas marked by boxes A and B in Figure 6d. The element contents of O, Sn and Ag in the crack-healing region B are obviously higher than those of region A at the edge of the worn surface of NST. This demonstrates that the Sn-Ag-Cu flows into the crack and is partially oxidized at 400 °C, which can promote the crack self-healing of NST.

Figure 6. Cont.
Figure 6. Worn surface morphologies of NBA, NS, NT and NST at 400 °C (a–d); EDS results of the areas marked by boxes A and B in Figure 5d: box A at the edge zone of the worn surface (e), box B at the crack healing area (f).

Figure 7 presents the worn surface morphologies of NBA, NS, NT and NST at 600 °C. As presented in Figure 7a,b, obvious spalling and some cracks indicate that the main wear mechanisms of NBA and NS at 600 °C are fatigue wear [27]. As presented in Figure 7c,d, relatively complete lubrication film and fine cracks can be observed on the worn surfaces of NT and NST. At 600 °C, the anti-friction performance of the worn surfaces of NT and NST may be attributed to the slippage between the layered structures of Ti₃SiC₂, which can contribute to the dispersal of shear stress and the formation of a solid lubrication film [19]. The major wear mechanisms of NT and NST are plastic deformation and slight oxidative wear [24]. At 600 °C, the oxidized layer can reduce the direct contact between the friction pairs, providing an excellent self-lubricating effect [8]. Figure 7e,f shows the EDS results of the areas marked by boxes A and B in Figure 7d. The element contents of O, Ti and Si in the crack healing region B are obviously higher than those of region A at the edge of the worn surface of NST. The differences in element contents can probably be ascribed to the aggregation and oxidation of the Ti₃SiC₂ with a multilayer structure on the friction contact surface under the action of sliding friction, promoting crack healing and the formation of solid lubrication film of NST.

Figure 7. Cont.
The average crack widths on the worn surfaces of NBA, NS, NT and NST are listed in Table 4. At 400 °C, the recovery ratios relative to NBA of the cracks on the worn surfaces of NS, NT and NST are about 73.2, 40.8 and 76.4%, respectively. The crack recovery ratios of NS and NST are close at 400 °C. In addition, at 600 °C, the recovery ratios of the cracks on the worn surfaces of NS, NT and NST are about 34.2, 77.3 and 75.4%, respectively. The crack recovery ratios of NT and NST are close at 600 °C. It can be concluded that the additions of Sn-Ag-Cu and Ti$_3$SiC$_2$ to the NST play a significant role in the crack self-healing that occurs at 400 and 600 °C, respectively.

The effect of crack healing of the NST is evaluated by the recovery ratio $\lambda$, and $\lambda$ can be calculated by Equation (1) \[28,29\].

$$\lambda = \frac{W_{NBA} - W_{NST}}{W_{NBA}}$$

where $W_{NBA}$ and $W_{NST}$ are the average values of crack widths on the worn surfaces of NBA and NST, respectively.

The average crack widths on the worn surfaces of NBA, NS, NT and NST are listed in Table 4. At 400 °C, the recovery ratios relative to NBA of the cracks on the worn surfaces of NS, NT and NST are about 73.2, 40.8 and 76.4%, respectively. The crack recovery ratios of NS and NST are close at 400 °C. In addition, at 600 °C, the recovery ratios of the cracks on the worn surfaces of NS, NT and NST are about 34.2, 77.3 and 75.4%, respectively. The crack recovery ratios of NT and NST are close at 600 °C. It can be concluded that the additions of Sn-Ag-Cu and Ti$_3$SiC$_2$ to the NST play a significant role in the crack self-healing that occurs at 400 and 600 °C, respectively.
Table 4. Crack widths on the worn surfaces of NBA, NS, NT and NST and crack recovery ratio relative to NBA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>NBA</th>
<th>NS</th>
<th>NT</th>
<th>NST</th>
<th>NBA</th>
<th>NS</th>
<th>NT</th>
<th>NST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>400</td>
<td>600</td>
<td></td>
<td></td>
<td>281</td>
<td>194</td>
<td>75</td>
<td>52.5</td>
</tr>
<tr>
<td>Crack width (nm)</td>
<td>237.5</td>
<td>63.7</td>
<td>140.5</td>
<td>56</td>
<td>292.5</td>
<td>192.5</td>
<td>66.5</td>
<td>72</td>
</tr>
<tr>
<td>Average value (nm)</td>
<td>-</td>
<td>73.2%</td>
<td>40.8%</td>
<td>76.4%</td>
<td>-</td>
<td>34.2%</td>
<td>77.3%</td>
<td>75.4%</td>
</tr>
</tbody>
</table>

Figure 8 presents the worn surface morphologies of NST at 200 and 800 °C. As shown in Figure 8a, obvious furrows and some cracks can be observed at 200 °C, which results in an increase in the surface roughness and frictional resistance of the worn surface of NST [22]. The main wear mechanism of NST at 200 °C is abrasive wear [27]. As presented in Figure 8b, obvious spalling and oxides indicate that the main wear mechanisms of NST at 800 °C are adhesive wear and oxidative wear [24]. As the temperature increases to 800 °C, the loose oxidative layer results in a rough worn surface, which is consistent with the high wear rate of oxidation wear [30]. The EDS result shown in Figure 8d also confirms that the O content of the worn surface material of NST is higher at 800 °C compared with other testing temperatures. At 800 °C, a lubricating film with rich multi-metal oxides is formed due to the high-temperature oxidation, which plays an important role in anti-friction and wear resistance during high-temperature friction [31]. In addition, excessive oxidation leads to the spalling of the lubricating film under cyclic friction contact stress at 800 °C, which will increase the wear rate of NST.

Figure 9 presents the typical worn surface morphologies of Si3N4 balls against the NST at 200, 400, 600 and 800 °C. As presented in Figure 9a, some furrows are visible on the worn surface of Si3N4 ball at 200 °C, indicating that the main wear mechanism is abrasive wear at 200 °C. As presented in Figure 9b, some flaky transfer film can be seen on the worn surface of Si3N4 ball at 400 °C. The transfer film produced by the NST during dry friction can play an antifriction role [32]. As presented in Figure 9d, a lot of wear debris can be found on the
worn surface of Si$_3$N$_4$ ball at 800 °C. As the testing temperature increases to 800 °C, due to the excessive oxidation of the worn surface material, the lubrication film is easy to flake off under cyclic friction contact stress, resulting in a lot of wear debris adhering to the worn surface of the Si$_3$N$_4$ ball.

![Figure 9. Typical worn surface morphologies of Si$_3$N$_4$ balls against the NST at 200 (a), 400 (b), 600 (c) and 800 °C (d).](image)

Figure 9 shows the Gibbs free energy ($\Delta G^\circ$) used to form the oxides, which can be used to determine the precedence of oxidation of NST during sliding friction [2]. It can be seen that the Gibbs free energy of Al used to form the Al$_2$O$_3$ is the lowest. Therefore, under low and moderate temperatures, it can be inferred that the preferred oxides are mainly Al$_2$O$_3$, followed by SnO$_2$. In addition, it can be deduced that the oxides preferentially formed at high temperatures are mainly Al$_2$O$_3$, followed by TiO$_2$ and SiO$_2$.

![Figure 10. The Gibbs free energy used to form the oxides and elastic modulus of the oxides.](image)
The prediction of the oxidation sequence of the main elements in NST shows the selective oxidation of Al₂O₃, SnO₂, TiO₂ and SiO₂, as demonstrated by the XRD results of worn surfaces of NST at 400 and 600 °C, as presented in Figure 11. The XRD results show that there are some oxides of Ni₂O₃, Al₂O₃, SnO₂ and CuO at 400 °C. At 600 °C, the main oxides are Al₂O₃, SnO₂, TiO₂, SiO₂, NiO and NiAl₂O₄. The oxides generated by partial oxidation of the worn surface material of NST at 400 and 600 °C can contribute to crack self-healing. In addition, during high-temperature friction, the tribochemistry reactions of the solid lubricants produce various oxides with a lubrication effect on the worn surface, which have good anti-friction effects [33]. In addition, TiC and TiO₂ with high hardness can reinforce the lubricating film of NST [34,35], improving the wear resistance of NST at high temperatures. Furthermore, as shown in Figure 10, the SnO₂, CuO, TiO₂ and Al₂O₃ have a higher elastic modulus when compared with the NST matrix, which can prevent the premature fracture or spalling of the solid lubrication film [36]. Relevant research [37,38] also showed that these compounds had a good anti-friction effect under high temperatures, which would reduce the friction coefficient of NST during sliding friction.

![Figure 11. XRD results of worn surfaces of NST at 400 (a) and 600 °C (b).](image)

Relevant studies have shown that materials with crack self-healing properties need to exhibit fluidity to cracks and adhesion to crack surfaces to achieve crack-filling [39]. Therefore, it can be inferred that the oxidation of Sn, Cu and Ti₃SiC₂ may be a vital reason for the self-healing behavior of cracks. The chemical equations for calculating the relative volume expansion generated by the generation of principal oxides are as follows:

\[
Sn + O_2 \rightarrow SnO_2
\]

\[
2Cu + O_2 \rightarrow 2CuO
\]

\[
Ti_3SiC_2 + 6O_2 \rightarrow 3TiO_2 + SiO_2 + 2CO_2
\]

\[
V_{R/Sn} = \frac{V_{SnO_2} - V_{Sn}}{V_{Sn}} = \frac{M_{SnO_2} \times \rho_{Sn}}{M_{Sn} \times \rho_{SnO_2}} - 1 = 32.9\%
\]

\[
V_{R/Cu} = \frac{V_{CuO} - V_{Cu}}{V_{Cu}} = \frac{M_{CuO} \times \rho_{Cu}}{M_{Cu} \times \rho_{CuO}} - 1 = 77.8\%
\]

\[
V_{R/Ti_3SiC_2} = \frac{3V_{TiO_2} + V_{SiO_2} - V_{Ti_3SiC_2}}{V_{Ti_3SiC_2}} = \frac{(3M_{TiO_2} \times \rho_{SiO_2} + M_{SiO_2} \times \rho_{TiO_2}) \times V_{Ti_3SiC_2}}{\rho_{TiO_2} \times V_{SiO_2} \times V_{Ti_3SiC_2}} - 1 = 93.4\%
\]

The relative volume expansions generated by the oxidation of Sn, Cu and Ti₃SiC₂ are 32.9%, 77.8% and 93.4%, respectively. This confirms that the formation of oxides such as SnO₂, CuO, TiO₂ and SiO₂ promotes the self-healing of NST by filling the cracks.
Figure 12 presents the Raman spectra of the worn surfaces of NST at 400 and 600 °C. As shown in Figure 12a, at 400 °C, the main oxides of Al$_2$O$_3$, SnO$_2$, CuO and Ni$_2$O$_3$ are found on the worn surface of NST at 400 °C, in agreement with the XRD results. It can be concluded that the lubricating phase Sn-Ag-Cu is partially oxidized at 400 °C, which is helpful for the crack self-healing of NST. As shown in Figure 12b, rich oxides consisting of Al$_2$O$_3$, SnO$_2$, CuO, TiO$_2$ and SiO$_2$, NiO and NiAl$_2$O$_4$ are formed at 600 °C. During the high-temperature friction, the Al element in the NST preferentially oxidized to Al$_2$O$_3$, which has a certain anti-wear effect at high temperatures [31]. These oxides promote crack self-healing during sliding friction, thus improving the tribological properties of NST from 20 to 800 °C.

In addition, Figure 13 presents the representative cross-sectional morphologies of NBA and NST at 400 and 600 °C. As shown in Figure 13a,c, no obvious solid lubricating film can be seen in the cross-section of NBA. Some cracks with average widths of about 10.9 and 35.6 nm can be seen in the cross-sections of NBA at 400 and 600 °C, respectively. As shown in Figure 13b,d, obvious solid lubricating films can be observed in the cross-section of NST. A few fine cracks with average widths of about 3.2 and 5.9 nm can be seen in the cross-sections of NST at 400 and 600 °C, respectively. Some self-healing areas can be seen at the ends of the cracks on the cross-sections of NST. As shown in Table 5, the recovery ratios relative to NBA of the cracks on the cross-sections of NST at 400 and 600 °C are approximately 70.6% and 83.4%, respectively. Figure 14 shows the EDS profiles of the regions marked in boxes in Figure 13b,d. Positions A and C are located in the matrix of NST. Positions B and D are located in the crack self-healing areas. As presented in Figure 14a,b, the element contents of Sn, Cu and O in position B are higher than those in position A. This suggests that Sn-Ag-Cu flows into the crack and is easy to oxidize at 400 °C, promoting the crack self-healing of NST. As presented in Figure 14c,d, the element contents of Ti, Si and O in position D are higher than those in position C. The EDS results further confirm the thermal decomposition and oxidation of Ti$_3$SiC$_2$ at 600 °C, which significantly contribute to the crack self-healing property of NST.
Figure 12. Raman spectra of the worn surfaces of NST at 400 (a) and 600 °C (b).

In addition, Figure 13 presents the representative cross-sectional morphologies of NBA and NST at 400 and 600 °C. As shown in Figure 13a,c, no obvious solid lubricating film can be seen in the cross-section of NBA. Some cracks with average widths of about 10.9 and 35.6 nm can be seen in the cross-sections of NBA at 400 and 600 °C, respectively. As shown in Figure 13b,d, obvious solid lubricating films can be observed in the cross-section of NST. A few fine cracks with average widths of about 3.2 and 5.9 nm can be seen in the cross-sections of NST at 400 and 600 °C, respectively. Some self-healing areas can be seen at the ends of the cracks on the cross-sections of NST. As shown in Table 5, the recovery ratios relative to NBA of the cracks on the cross-sections of NST at 400 and 600 °C are approximately 70.6% and 83.4%, respectively. Figure 14 shows the EDS profiles of the regions marked in boxes in Figure 13b,d. Positions A and C are located in the matrix of NST. Positions B and D are located in the crack self-healing areas. As presented in Figure 14a,b, the element contents of Sn, Cu and O in position B are higher than those in position A. This suggests that Sn-Ag-Cu flows into the crack and is easy to oxidize at 400 °C, promoting the crack self-healing of NST. As presented in Figure 14c,d, the element contents of Ti, Si and O in position D are higher than those in position C. The EDS results further confirm the thermal decomposition and oxidation of Ti3SiC2 at 600 °C, which significantly contribute to the crack self-healing property of NST.

Figure 13. Representative morphologies of cross-sections of NBA (a,c) and NST (b,d) at 400 and 600 °C.

Table 5. Average values of crack widths on the cross-sections of NBA and NST and crack recovery ratio of NST relative to NBA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>NBA</th>
<th>NST</th>
<th>NBA</th>
<th>NST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>400</td>
<td>600</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>Crack width (nm)</td>
<td>9.1</td>
<td>2.8</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Average value (nm)</td>
<td>10.9</td>
<td>2.8</td>
<td>3.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Recovery ratio relative to NBA</td>
<td>70.6%</td>
<td>83.4%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 13. Representative morphologies of cross-sections of NBA (a, c) and NST (b, d) at 400 and 600 °C.

Figure 14. EDS profiles of the box labeled areas presented in Figure 13b,d: area A (a), area B (b), area C (c) and area D (d).

Figure 15 presents the schematic diagrams of the crack self-healing of wear scar of NST during sliding friction from 20 to 400 °C, as well as higher temperatures of 600 and 800 °C. As shown in Figure 15a, at low and moderate temperatures, Sn-Ag-Cu melts and flows into the cracks during sliding friction. Meanwhile, the cracks are gradually filled with the formation of rich oxides, thus promoting self-healing of the NST. As shown in Figure 15b, at higher temperatures of 600 and 800 °C, Ti₃SiC₂ on the subsurface of the wear scar plays a significant role in supporting the solid lubricating film of the NST [11]. The synergistic effects of the enhancement of Ti₃SiC₂, Al₂O₃ and SiO₂ and the lubrication of SnO₂ and TiO₂ are conducive to forming a stable lubricating film [37]. In addition, under high-temperature friction, the cracks are filled by the oxides due to the partial decomposition and oxidation of Ti₃SiC₂, promoting the crack self-healing of NST. Figure 15c shows the evolution of various oxides in the solid lubrication film during the dry sliding friction of NST against the Si₃N₄ ball from 20 to 800 °C. The composition of the oxides varies with temperature, which is related to the Gibbs free energy of the various oxides. The oxides generated on the worn surface of NST mainly include Al₂O₃, SnO₂, Ni₂O₃ and CuO from 20 to 400 °C. As the temperature rises from 400 to 800 °C, the oxide Al₂O₃ forms, together with SnO₂, CuO, TiO₂, SiO₂, NiO and NiAl₂O₄. These rich oxides can enhance the anti-friction and wear resistance of NST [40]. In brief, the synergistic action mechanisms of Sn-Ag-Cu and Ti₃SiC₂ regarding crack self-healing from 20 to 800 °C play a significant role in forming a stable solid lubricating film, improving the anti-friction and wear resistance of NST.
Table 5. Average values of crack widths on the cross-sections of NST and NBA against Si₃N₄ ball from 20 to 800 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>NBA</th>
<th>NST</th>
<th>Recovery ratio relative to NBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>9.1</td>
<td>10.9</td>
<td>70.6%</td>
</tr>
<tr>
<td>400</td>
<td>12.7</td>
<td>3.2</td>
<td>83.4%</td>
</tr>
<tr>
<td>600</td>
<td>2.8</td>
<td>35.6</td>
<td>89.2%</td>
</tr>
<tr>
<td>800</td>
<td>4.5</td>
<td>5.9</td>
<td>88.7%</td>
</tr>
</tbody>
</table>

Figure 15. The schematic diagrams of the crack self-healing of wear scars of NST during sliding friction at low and moderate temperatures (a), as well as high temperatures (b); (c) schematic drawing showing the evolution of the composition of oxides on the worn surface of NST against Si₃N₄ ball from 20 to 800 °C.

4. Conclusions

In this paper, to meet the increasing demand for the metal matrix composites with excellent tribological performance over a wide temperature range, the tribological behavior and self-healing properties of NST were studied from 20 to 800 °C. The main conclusions are as follows:

1. The tribological behaviors of NST are strongly dependent on the testing temperature and self-healing properties. Compared with NBA, NS and NT, NST shows lower friction coefficients (0.22–0.29) and wear rates (0.62–1.25 × 10⁻⁵ mm³N⁻¹m⁻¹) from 20 to 800 °C.

2. At low and moderate temperatures from 20 to 400 °C, as the Sn-Ag-Cu flows into the cracks and is oxidized during sliding friction, the cracks on the worn surfaces are filled with the oxides consisting mainly of Al₂O₃, SnO₂ and CuO, promoting the self-healing of the NST. Compared with other testing temperatures, the recovery ratio relative to NBA of the cracks on the worn surface of NST is the highest at 400 °C, which is about 76.4%.
(3) At higher temperatures of 600 and 800 °C, the cracks are filled by the oxides consisting mainly of Al₂O₃, TiO₂ and SiO₂ due to the partial decomposition and oxidation of Ti₃SiC₂, which will be conducive to the self-healing of the NST during sliding friction.

(4) The synergistic action mechanisms of Sn-Ag-Cu and Ti₃SiC₂ on crack self-healing from 20 to 800 °C play a significant role in forming a stable solid lubricating film on the worn surface, improving the anti-friction and wear resistance of NST.

Author Contributions: Conceptualization, Y.H.; data curation, Y.M.; writing—original draft, Y.H.; writing—review and editing, H.M.; funding acquisition, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Natural Science Foundation of Henan (202300410097), Doctor Cultivation Funds of Henan University of Engineering (DKJ2019023), Open Fund of State Key Laboratory of Solid Lubrication (LSL-2108) and Natural Science Basic Research Program of Shaanxi (2021JQ-652).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Authors were grateful to X. Li and W.W. Xu in Analysis and Testing Center of HAUE for their kind help with XRD and SEM. The authors would like to thank Su TianTian from Shiyanjia Lab (www.shiyanjia.com, accessed on 22 November 2022) for the Raman spectrum analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References
15. Yang, K.; Ma, H.R.; Zhao, W.B.; Li, X.X.; Liu, H. Investigation of the preparation and tribological behavior of a frictional interface covered with sinusoidal microchannels containing SnAgCu and Ti3SiC2. Tribol. Int. 2020, 150, 106368. [CrossRef]
20. Liu, X.Y.; Shi, X.L.; Huang, Y.C.; Deng, X.B.; Yan, Z.; Xue, B. Anti-friction and wear properties of the friction surface of M50-10 wt% (50Sn+40Ag+10Cu) composite. J. Alloys Compd 2018, 765, 7–17. [CrossRef]
33. Taheridoustabad, I.; Khosravi, M.; Yaghoubinezhad, Y. Fabrication of GO/RGO/TiC/TiB2 nanocomposite coating on Ti-6Al-4V alloy using electrical discharge coating and exploring its tribological properties. Tribol. Int. 2021, 156, 106860. [CrossRef]