Development of TiC-reinforced high performance composites for wear-resistance application

R. Liu¹, C. D. Opris¹, M. X. Yao² & D.Y. Li³
¹Department of Mechanical and Aerospace Engineering, Carleton University, Canada
²Deloro Stellite Inc., Canada
³Department of Chemical and Materials Engineering, University of Alberta, Canada

Abstract

Two Stellite alloys, which are co-based superalloys mainly for high-temperature wear/corrosion applications, and on pseudoelastic TiNi alloy are functionally graded with the reinforcement of TiC. The designed composites were fabricated using the powder metallurgy (PM) technique, combined with hot isostatic pressing (HIP). Calorimetric effects of the alloy powders were investigated using the differential scanning calorimetry (DSC) technique, which provided the basis of the sintering cycles designed. The phases present in the microstructures of the specimens were analysed using SEM and X-ray diffraction. The wear test was conducted on a pin-on-disc tribometer. It demonstrated that the wear resistance of these alloys had been increased significantly by the TiC reinforcement and the HIP process had improved the density of the specimens and thus enhanced the wear resistance of the materials. However, the pull-out TiC particles from the worn surface were found under the SEM, which indicated that the interfacial bonding between the alloy matrix and the hard particle needs improving.

Keywords: superalloy, TiNi alloy, TiC reinforcement, pseudoelasticity, composites, powder metallurgy, hot isostatic pressing, microstructure, wear, interfacial bonding.

1 Introduction

Design and fabrication of high-strength, high-temperature, wear/corrosion resistant materials will offer much benefit in aerospace, automotive, chemical
and oil industries to combat the severe service conditions and always offer a challenge to the researchers. Traditionally, superalloys are widely used under these application conditions. Many of the properties of these alloys arise from the crystallographic nature of cobalt, Co (hexagonal crystal form hcp at normal temperature, transforming to cubic form fcc at higher temperatures), the solid-solution-strengthening effects of chromium, Cr, tungsten, W, and molybdenum, Mo, the formation of metal carbides, and the corrosion resistance imparted by chromium [1,2]. The development of cobalt-based alloys is traced from their origin on a cutting tool to their present uses for resistance to wear, heat and corrosion in dentistry and surgery, powder production, chemical and general engineering [3]. Extensive research on these alloys has been conducted in erosion-corrosion behavior [4-6] and wear performance [7-9]. These studies have demonstrated that the microstructure of the alloys is typically comprised of chromium rich carbides, M7C3 and/or M23C6 (M = metal), in a cobalt rich superalloy matrix and the alloys have unique combinations of tribological properties such that they are good in both adhesive and abrasive wear applications and also have super cavitation-erosion resistance.

Near equiatomic TiNi alloy is a well-known shape memory alloy. The shape memory effect of this alloy results from a thermoelastic martensitic transformation occurring around room temperature. The thermoelastic martensitic transformation can be induced either by changing temperature or by applying a stress [10,11]. When the alloy is under an external stress, the martensitic transformation from the parent phase (\(\beta\)) to a martensite phase (\(M\)) may occur, accompanied with a large reversible strain. As a result of the reversibility of the martensitic transformation, TiNi alloy exhibits a special mechanical behavior termed pseudoelasticity. Recently, TiNi alloy has been found to exhibit excellent wear resistance to erosion, cavitation and abrasive wear [12-15]. It is suggested that the high wear resistance of TiNi alloy is mainly owing to its pseudoelasticity. Plastic strain generated in the contact layer during wear predominates the surface damage, thus the material removal. The pseudoelasticity may reduce the accumulated plastic strain in the surface layer thus diminishing the surface damage [13].

An advantage over these alloys may be further gained in functionally graded composites by combining high fracture toughness of alloys with high hardness and wear/corrosion resistance of carbide-based materials. These composites can be coated at the surface of a material to increase its performance and extend its service life. For wear application, especially at high temperature titanium carbide (TiC) with a high melting point (3065°C), high hardness (3200 kg/mm²) and the low density (4.94 g/cm³) is very attractive. In the present research, the Co-based superalloys, Stellite 694 and Stellite 712, and pseudoelastic TiNi alloy were reinforced with TiC to form the composites. The reinforcement has high hardness so that they may sustain external load, while the pseudoelastic or high toughness matrices can accommodate large deformation, absorb impact energy and bind the particles. Superior wear resistance was anticipated from such a combination. The developed composite materials may find application in aerospace, automotive, chemical and oil industries, including (1) metalworking:
deep-drawing tools, calibrating tools, bending and flanging tools, cutting and punching tools, cold extrusion moulding tools; (2) plastics processing: injection moulds and gates, ultrasonic welding sonotrodes, palletizing and crushing tools; (3) chemical plants: valve seats and cones, spray diffusers, scrapers, gear-type pumps; (4) pumps and fittings: plunger for high-pressure pumps, components for valves; (5) special applications: grinding spindles, boring bars, guide rails, gauges and measuring tools, crushing tools, sockets and guide arms, guide and straightening rolls. These materials with superior wear performance because of the combination of strength, hardness, toughness and ductility, and also with low cost will certainly surpass many currently used commercial materials, definitely having benefits to accrue to many industries.

The designed materials were fabricated using powder metallurgy (PM) technique, combined with hot isostatic pressing (HIP). The phases present in the microstructures were examined and analysed using the X-ray diffraction and SEM. The wear tests were conducted on a pin-on-disc tribometer. For comparison, pure alloy samples were also tested. The effects of TiC particle, the pseudoelasticity of TiNi alloy and the HIPing process on the microstructures and wear resistance of the materials were discussed.

2 Experiments

2.1 Sample fabrication

Pre-alloyed Stellite 694 and Stellite 712 powders were provided by Deloro Stellite Inc. with the compositions listed in table 1. Composite samples were created by adding 20% (by weight) of TiC powder to the alloy powders. The particle sizes of the Stellite 694 and Stellite 712 powders were about -325 mesh or 44 micron and TiC was about 10 micron. Prior to sintering, the powders were mixed for at least 45 minutes, with 3.5% organic binder added. The mixture was then poured in a beaker with 7% hot water and mixed on a hot plate until a uniform paste of medium consistency was obtained. The time of mixing varied with the quantity of powder made. The paste was then poured in an alumina mould and left to dry for at least one week in room air. The mould had a ring shape, with an inside diameter of 40 mm, a wall thickness of 2 mm and a height of 8 mm.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Co</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stellite694</td>
<td>Bal.</td>
<td>1.0</td>
<td>28</td>
<td>0</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Stellite712</td>
<td>Bal.</td>
<td>1.8</td>
<td>29</td>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The sintering cycles were determined in terms of the phase transformation temperatures of the alloys; therefore calorimetric effects of the Stellite 694 and Stellite 712 alloy powders were investigated using the differential scanning calorimetry (DSC) technique. The DSC scans were performed using a Netzsch DSC 204 F1 Phoenix instrument, and the phase transformation temperatures were determined using the software provided by the instrument manufacturer. The results showed that the phase transformation temperatures of the Stellite 694 and Stellite 712 powders were significantly lower than those of the pure alloys, indicating that the addition of TiC powder reduced the phase transformation temperatures and improved the sintering properties of the composite materials.

calorimetry (DSC) technique before sintering. The DSC results demonstrate that the starting and ending points of melting for Stellite 694 are around 1211°C and 1321°C respectively, and for Stellite 712 they are around 1123°C and 1240°C respectively. Since liquid phase sintering was adopted, the maximum sintering temperature was selected to be between the starting and ending temperatures of the first phase transformation occurs, that is, 1277°C for Stellite 694 and 1141°C for Stellite 712. Since TiC would not melt during the sintering process and its presence would not influence the sintering temperature much. During the sintering process of Stellite 694 and TiC/Stellite 694, the pressure was kept at 200 mT using argon gas for the first two hours, until debinding was finished at 815°C, then the furnace was vacuumed. Pre-sintering was performed at 1207°C for 30 minutes and sintering was taking place at 1263°C for one hour. For Stellite 712 and TiC/Stellite 712 the only differences were pre-sintering at 1096°C and sintering at 1152°C.

Half of the sintered samples then experienced a HIPing process, in an effort to minimize porosity. Stellite 694 and TiC/Stellite 694 were HIPped at 1120°C under 20 ksi for four hours and Stellite 712 and TiC/Stellite 712 at 1065°C. The temperature used in the HIPing process for each sample was selected as 85% ~ 95% of the corresponding sintering temperature.

For the TiNi alloys, different contents of the particles in the composites and different sintering temperatures were tested in order to find the optimal combination condition of fabrication process, obtaining high wear resistance. Ti, Ni, TiC powders having assize of mesh –325 (5 ~ 44 µm) were mixed in air using a ceramic ball mill apparatus for two hours. The mixed powder was then pressed into pin specimens under a pressure of 787 MPa for thirty seconds. The cylindrical specimens were 8 mm long and 6 mm in diameter. The specimens were sintered at in a vacuum of about 5.0 × 10⁻⁴ torr. The nominal composition of the matrix was Ti-51 at.% Ni (Ti-56 wt.% Ni). A range of sintering temperature up to 1800°C and varying times were tested. The contents of TiC in the composites were selected to be 20%, 40%, 60% and 80% respectively. The sintered samples were then HIPed at 1300°C under a pressure of 207 MPa in argon for two hours.

2.2 Microstructure examination

Microstructure analysis was carried out using backscatter electron imaging and EDX from a Hitachi Model S-570 Scanning Electron Microscope. X-ray diffraction was used to identify the phases present, with Cu $K_\alpha$ radiation.

2.3 Wear test

Wear resistance of the samples was determined on a pin-on-disc tribometer. A ball made of 94% WC and 6% Co, with the hardness of HV 1534, was wearing the sample surface which was spinning with the rotational speed $\omega = 319$ rpm, resulting in a wear track or pit. The wear loss was evaluated by calculating the volume of the wear pit after the sample was worn for 2.8 hrs. The diameters of
the ball and the wear track are 5 mm and 6 mm respectively. The wear load applied was 10 N.

3 Results and discussion

The X-ray results show that the HIPing process did not change the phases present in the materials, that is, the sintered and HIPed samples of each material have identical phases. Fig. 1 shows the microstructures of TiC/Stellite 694 and TiC/Stellite 712 specimens in the SEM backscatter image. The microstructure of the Stellite 694 matrix contains complex combinations of fcc Co₃W₃C, and fcc Cr₂₃C₆ carbides embedded in a Co-Cr-W solid solution matrix, which corresponds to the X-ray results. As shown in fig. 1(a) and fig. 1(b), in the Stellite 694 matrix exist a Co-rich solid solution containing W and Cr as strengthening elements, seen in darker grey, and two types of second phase particles, which are the carbides Co₃W₃C seen in white and Cr₂₃C₆ seen in lighter shade of the background grey. The microstructure of the Stellite 712 matrix contains fcc Co-rich solid solution in grey and two types of chromium carbides, fcc Cr₂₃C₆ in white and Cr₃C in dark shade, as shown in fig. 1(c) and fig. 1(d), in both hcp and orthorhombic forms (X-ray results). Another noteworthy characteristic of this microstructure is the presence of Mo, from the SEM EDX analysis. Mo acts as a strengthening element together with Cr in the Co-rich solid solution.

For the TiC/TiNi composite sample, the X-ray results show that the TiNi matrix has been well alloyed, with a solid TiNi phase in β phase. The microstructure of the TiC/TiNi composite sample is presented in fig. 2, which shows a uniformly distributed TiC phase in the TiNi alloy matrix.

To evaluate the volume loss, the cross-sections at three locations along each wear track were simulated using a surface profiler. The volume of each wear track (or pit) was calculated by taking the average of the cross-sectional areas multiplied by the periphery of the circular wear track (πd), which is the wear loss of the material. Fig. 3 shows the cross-sectional profiles of sintered and HIPed samples of Stellite 694 and TiC/Stellite 694. The depth of the wear track (vertical scale) is measured in the current unit of kA (kilo ampere from the profilometer signal), which can be transferred to the dimensional unit µm, with the relation of 1kA = 0.1 µm. The width of the wear track (horizontal scale) is graduated in µm.

Firstly, comparing the cross-sectional profile of wear track of the sintered Stellite 694 (fig. 3(a)) with that of the sintered TiC/Stellite 694 (fig. 3(b)), it is found that the wear depth of Stellite 694 is above three times more than that of TiC/Stellite 694 and also the wear width is almost two times. However, the differences between the corresponding HIPed samples (fig. 3(c) and fig. 3(d)) are greatly decreased. Secondly, comparing the sintered Stellite 694 with the HIPed one, it is found that both the wear width and depth of the HIPed sample are tremendously less than those of the sintered one. Similar results were obtained for the TiC/Stellite 694 samples, but the reduction of the wear width and depth due to the HIPing process is less than that of the pure Stellite 694 sample.
The similar results were obtained on the Stellite 712 samples and the same conclusions can be reached.

As concerns the TiC/TiNi samples, the wear test results show that the wear resistance of the composites increases with the content of the TiC particle. However, it was also observed during the wear test that the samples became very brittle when the particle content was over 80wt.% in the composites and the wear resistance then decreased greatly. In regard of the sintering temperature, it is
found that 1500°C is the best temperature for the composites obtaining high wear resistance. Furthermore, the wear behaviour of the TiC/TiNi sample which had a particle content of 60wt.% in the composites and was sintered at 1500°C is compared with that of pure TiNi alloy. As illustrated in fig. 4, the wear resistance of the TiNi alloy has been significantly increased (more than one order of magnitude) when reinforced with the TiC particles.

![Microstructure of 60 wt.% TiC/TiNi sample sintered at 1500°C for six hours.](image)

In general, pore structure occurs inevitably in sintering due to the point contacts between particles growing into necks [16]. The measured densities of current fabricated materials indicated that fully dense material was not achieved (about 94%), which may be attributed to the weak bonding between adjacent particles and to internal porosity. Another possible reason causing the porosity was the debinding process in the sintering. The 3.5% organic binder mixture was added to the “green body” of the samples before sintering and there was a debinding process during the sintering process at 815°C and then the furnace was vacuumed. The evaporation of the binder might cause the formation of porosity. Hot isostatic pressing, a manifestation of stress-enhanced densification process, is helpful in reducing porosity and thus securing high-density materials [17]. Comparing the microstructures of the HIPed samples to the sintered ones (fig. 1), it is seen that the porosity has been reduced by the HIP process. The measured densities also confirmed this improvement of the microstructure that the density has been increased at ~ 20% by the HIP process. The HIP process did not change the phases present in the microstructure of the materials, as the temperature during HIPing was below the sintering temperature.
Figure 3: Cross-sectional profiles of the wear tracks: (a) sintered Stellite 694; sintered TiC/Stellite 694; (c) HIPed Stellite 694; (d) HIPed TiC/Stellite 694.

The worn surfaces of the samples were also examined with SEM in order to investigate the damage mechanism of the materials under wear. Cavities were observed the worn surfaces, as shown in fig. 5. These cavities might have resulted from the spalling of TiC particles from the matrix during the wear. In addition, cracks were found in the vicinity of the cavities, which would expedite the damage of the surface, thus the wear of the material.
Figure 4: Comparison of wear resistance between TiNi alloy and TiC/TiNi composite.

Figure 5: Worn surface of 60 wt.% TiC/TiNi sample.

4 Conclusions

Stellite 694 and Stellite 712 alloy matrices were reinforced with TiC particles to enhance the wear resistance of these alloys. The P/M technique was employed to fabricate the samples, in combination with the HIP process. The X-ray and SEM analyses of the microstructures show that the presence of TiC particles in the composites did not change the phase formation of the alloy matrices, so did the HIP process. However, the addition of TiC particles has increased significantly the wear resistance of the alloys. The HIP process has reduced the porosity of the microstructures and improved the density of the materials, thus enhancing their wear resistance.
Two Co-based superalloy composites and pseudoelastic TiNi composite of TiC reinforcement have been developed using powder metallurgy technique, joined with hot isostatic pressing. It was found that the composites had much higher wear resistance than the corresponding pure alloys. The HIP process did not change the phases present in the materials but greatly improved the microstructures by reducing the porosity, thus increasing the wear resistance of the materials. The developed composite materials have potential to achieve superior wear performance to existing wear-resistant materials with improving the manufacturing process and the interface bonding.

References

