JMEPEG (2001) 10:178-185

Influences of Porosity on Mechanical and Wear Performance of Pseudoelastic TiNi-Matrix Composites

H.Z. Ye, D.Y. Li, and R.L. Eadie

(Submitted 22 June 2000)

Pores usually exist in sintered tribo-composites and may strongly affect the performance of the composites. In this work, the influence of pores on the wear behavior of sintered pseudoelastic TiNi-matrix tribo-composites was investigated. In particular, changes in the density of pores and corresponding variations in wear resistance of the composites were studied. It was demonstrated that mechanical properties and the wear resistance of the composites were strongly affected by voids. The wear resistance was enhanced when the density of pores was reduced by using wax to enhance the compaction during pressing. It was also interesting to observe that pores are sealed during the wear process. This results in improving wear resistance during wear, especially under high loads. Some other contributing mechanisms are also discussed.

Keywords composite, porosity, sintering, TiNi, wear

1. Introduction

Recent studies[1–13] have demonstrated that the equiatomic TiNi alloy exhibits high resistance to several different wear modes. Richman *et al.*[7] demonstrated superior cavitation resistance of TiNi alloy, compared to a number of standard wear-resistant materials commonly used for hydraulic machinery. Jin and Wang[8] showed that TiNi alloy is more resistant than commercial wear-resistant Co45 alloy and nitrogenized 38CrMoAlA steel during dry sliding. Singh and Alpas[9] compared Ti50Ni-47Fe3 to SAE 52100 bearing steel and demonstrated that the former has significantly higher wear resistance than the latter. The wear resistance of TiNi alloy greatly benefits from its pseudoelasticity, resulting from a reversible martensitic transformation by twining. This special property makes the alloy exhibit a recoverable strain around 5 to 8%.[3] It was observed that the composition corresponding to the highest wear resistance is in the range of Ti-55 wt.% Ni to Ti-56.5 wt.% Ni, where the alloy behaves pseudoelastically.[10,11] Recent finite element analysis further demonstrates the beneficial effect of pseudoelasticity on wear.[12] It was also observed that the high wear resistance of TiNi alloy is not only attributable to its pseudoelasticity but also to other properties such as the strain-hardening capability. Clayton[13] investigated wear and rolling fatigue of TiNi alloy having a composition beyond the range in which the martensitic transformation can occur. He correlated the good cyclic hardening capability of TiNi alloy to its high resistance to rolling fatigue. Other studies have also confirmed the good fatigue resistance of TiNi alloys.[14] More recent work[15] has demonstrated that the high wear resistance of TiNi alloy is dependent on the balance between the pseudoelasticity and hardness. As a matter of fact, this alloy has a high intrinsic wear resistance even without the pseudoelasticity. Such intrinsic wear resistance makes this material attractive for wear applications under different conditions. In previous studies, TiNi alloy has been shown to be a highly promising matrix material for tribo-composites, especially when used in "open" systems in which temperature remains in the range where the TiNi matrix behaves pseudoelastically. The pseudoelasticity makes the matrix flexible and resistant to wear. Such a combination of flexibility and high wear resistance is greatly beneficial for integrated wear resistance. Recently, the authors explored the possibility of developing such a tribo-composite employing TiNi matrix reinforced by hard TiC particles using a vacuum sintering process.[16] It was demonstrated that such a composite containing 60% TiC (atomic percentage unless noted otherwise) provided a wear resistance that is about three orders of magnitude higher than that of 304 stainless steel and one order of magnitude higher than that of TiNi alloy. Compared to WC/NiCrBSi composite, a hardfacing overlay widely used in the oilsand and mining industries, the TiC/TiNi composite showed superior performance under low loads but the former was better under higher loads. It was believed that this composite could be further improved, since many voids were observed in the composite, which should be very detrimental as stress raisers. It was expected that the wear resistance of the TiNi-matrix composite could be improved if the density of pores were decreased. An attempt was made to decrease the volume fraction of pores by using wax to improve the compaction during pressing of the powder specimens before sintering. Since the density of pores might change during a wear process, research was conducted to investigate the effects of voids on the wear behavior of TiNi-matrix composites and possible variation in wear resistance during wear. This paper reports the results of the research with a discussion on possible mechanisms involved.

2. Experimental Procedure

TiC/TiNi and TiN/TiNi composites were fabricated using a vacuum sintering process. The Ti, Ni, TiC, and TiN powders

---

H.Z. Ye, D.Y. Li, and **R.L. Eadie,** Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB, Canada T6G 2G6. Contact e-mail: ye@ualberta.ca.

having a mesh size of −325 were mixed in hexane, respectively, with and without dissolved wax (1.5 wt.%), using a ceramic ball mill for 2 h. The mixed powders were dried at 50 °C for 3 h to vaporize the hexane and then pressed into pin specimens under a pressure of 787 MPa for 30 s. The cylindrical specimens were 8 mm long with a diameter of 6 mm. The specimens were sintered at 1500 °C in a vacuum of 5.0×10^{-4} torr for 6 h. The waxed specimens were first heated at 350 °C in a vacuum of about 10^{-2} torr for 45 min to bake off the wax before vacuum sintering at 1500 °C. The nominal composition of the matrix was Ti-51% Ni, and the composites contained 60% TiC or TiN particles, respectively. The microstructures of the composites were examined using both scanning electron microscopy (SEM) and optical microscopy. The bulk density of the specimens was measured with a pycnometer. The wear resistance of the specimens was evaluated using a pin-on-disc tribometer by measuring the volume loss after sliding 600 m on a steel disc at a speed of 60 m/min under different loads. The volume loss was obtained by averaging four or five measurements. The disc of the tribometer was made of 304 stainless steel with an attached copper tube through which cooling water passed to reduce the temperature produced by frictional heat. In order to understand changes in the wear resistance during wear, the sintered specimens were analyzed using x-ray diffraction (XRD) before and after wear testing to determine whether there were phase changes. The worn surface of the composites was examined using both optical microscopy and SEM. The pseudoelasticity and hardness of the TiNi matrix were investigated using a Hysitron (Hysitron, Inc., Edina, MN) triboscope—a combination of an atomic force microscope and a nano-mechanical probe.

3. Experimental Results and Discussion

3.1 Composition and Microstructure

The microstructure of the composites was examined using an optical microscope and a JEOL 6301F SEM (Japan Electron Optics Ltd., Tokyo). Figure 1 is an SEM metallograph of a 60% TiC/TiNi specimen. The dark areas are TiC particles and the less dark region is the TiNi matrix. One may see that the TiC particles were distributed homogeneously. However, many pores were observed, especially in the central region of the specimen. The pores formed nets along grain boundaries, as shown in Fig. 2. The composition of the matrix was analyzed using EDX and the result showed that the matrix was not very uniform in composition and the typical measured value was in the range of Ti-Ni 54.6 at.%. Therefore, the sintering process needs to be further improved, although such a specimen has already shown very good wear resistance.[16] Efforts are being made to improve the compositional homogeneity.

Phases in the composites were analyzed using XRD. Figure 3 presents a diffraction pattern of the TiN/TiNi composite, which demonstrates that no separated Ti and Ni powders exist in the composite, that is, the matrix was in a TiNi alloy state. The situation was the same in the case of the TiC/TiNi composite.

3.2 Wear Behavior of the TiNi-Matrix Composites under Various Conditions

Influence of Lubrication during Compaction. As shown, the sintered TiNi composites contained many pores, which were detrimental to the wear resistance of the composites. One task of this work was to reduce porosity using wax during the

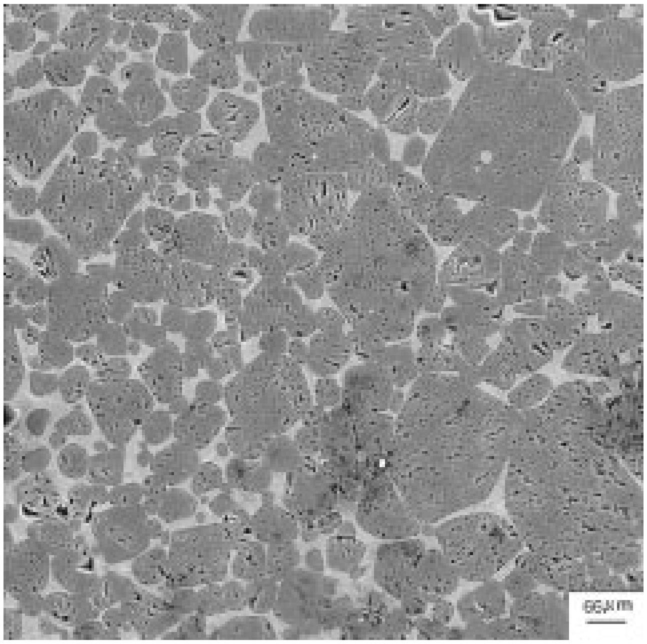


Fig. 1 Microstructure of a TiC/TiNi sample

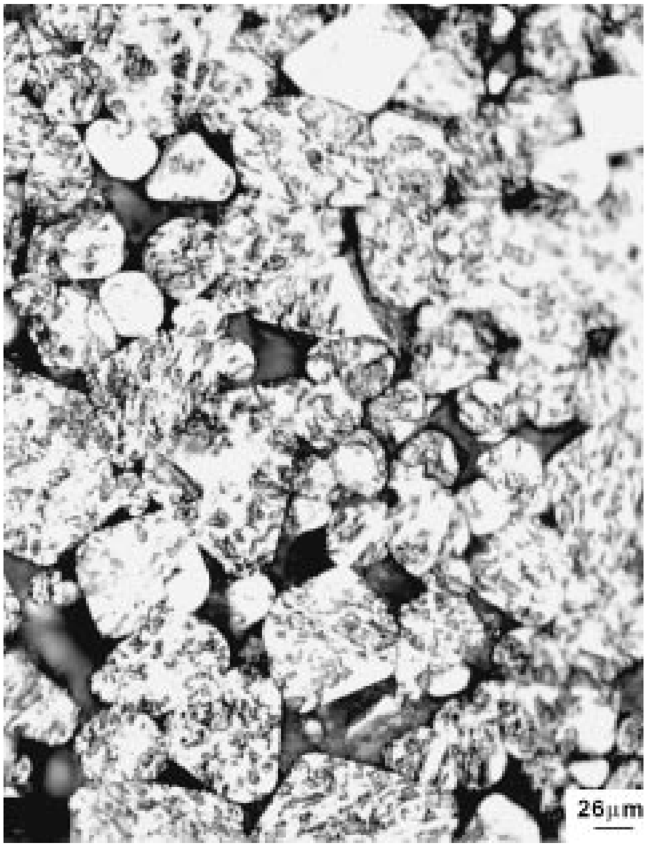


Fig. 2 Voids in the specimen

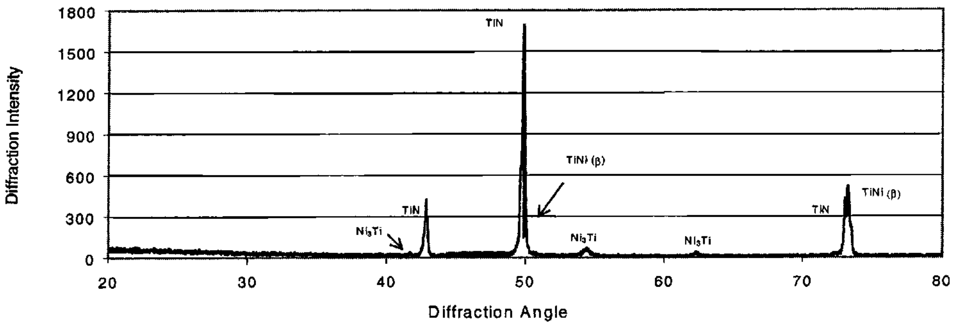


Fig. 3 (Co-α) XRD pattern of a TiN/TiNi sample

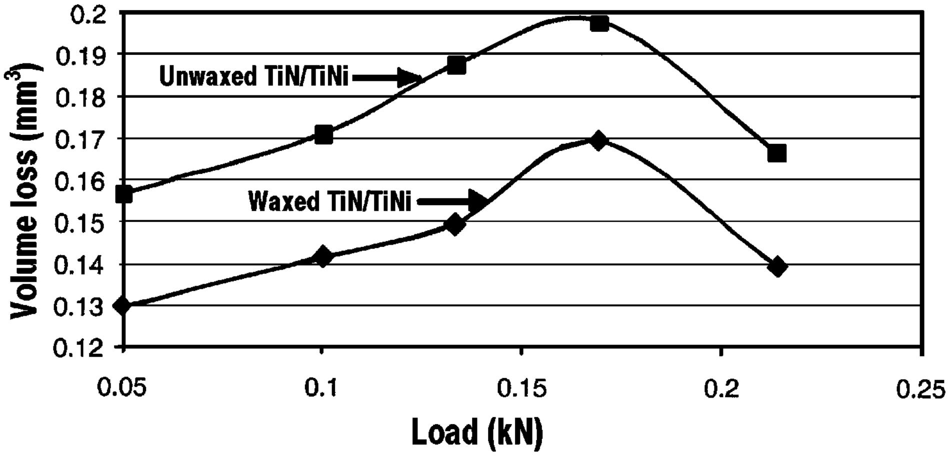


Fig. 4 The wear losses of waxed and unwaxed TiN/TiNi specimens

pressing of the specimens and to evaluate the effect of this porosity reduction on the wear resistance of the specimens. Some TiN/TiNi specimens were prepared with wax and their wear resistance was evaluated and compared to that of the unwaxed specimens. Results of the wear tests are illustrated in Fig. 4. One may see that the volume losses of both the waxed and unwaxed specimens increased as the load was increased. However, when the load exceeded 0.17 kN, the volume losses decreased. The waxed specimens had a wear resistance about 15 to 20% higher than that of the unwaxed specimens in the tested loading range.

Bulk densities of the waxed and unwaxed TiN/TiNi specimens were 5.03×10^3 and 4.80×10^3 kg/m^3, respectively. With the TiN density of 5.22×10^3 kg/m^3 from the provider and the theoretical density of TiNi of 6.45×10^3 kg/m^3,[17] the density of the 60% TiN/TiNi composite is calculated to be 5.81 g/cm^3, which shows that pore volume fractions in waxed and unwaxed specimens are 13.4 and 17.4%, respectively. The density measurement is consistent with SEM surface image analysis of the pore fraction. Figure 5 and 6 illustrate etched surfaces of the unwaxed and waxed specimens under the SEM with measured pore fractions equal to 16% and 11%, respectively. This difference in the pore density should be attributed to the wax, which acted as a lubricant to permit densification of the powder specimens during the pressing process before sintering. Such difference in porosity made the wear resistance of the waxed specimens different from that of the unwaxed ones.

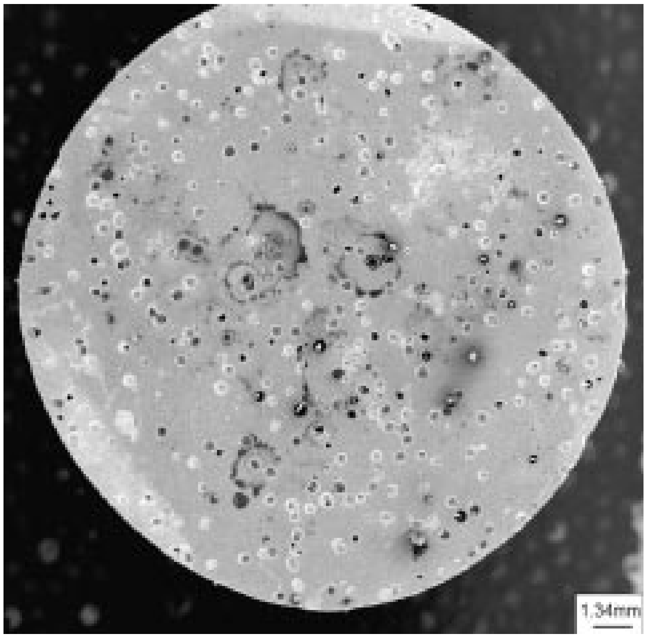


Fig. 5 A new unwaxed TiN/TiNi surface

Enhanced Wear Resistance by Sealing of Pores during Wear. Improvement in the processing conditions to reduce pores is an important step to optimize the material. Since wear is a dynamic surface process, the density of pores may vary during wear and this could result in changes in the wear resistance. In fact, it was observed that the wear rate of the TiNi composites decreased as the sliding distance increased. Such a decrease in the wear rate was remarkable especially under high loads. Fig. 7 illustrates the wear rate of unwaxed TiC/TiNi samples versus the sliding distance under 0.05 and 0.214 kN loads. Under the low load, the wear loss rate did not show significant changes, while under the higher load, a considerable decrease in the wear loss rate was observed. Clearly, the wear resistance of the composites was enhanced during wear.

In order to better understand such a change in wear resistance, we examined new and worn specimens to see possible changes in their density of pores, mechanical properties, and corresponding wear performance. Figure 8 illustrates the volume losses of TiC/TiNi and TiN/TiNi specimens after sliding over 600 m under different loads. Similar to what was illustrated in Fig. 4, as the applied load was increased, the volume losses of the composites increased until the load reached 0.17 kN, followed by decreases in the volume loss. Under higher loads, the performance of the composites was considerably superior. This change was accompanied by changes in the surface morphology displayed in Fig. 9.

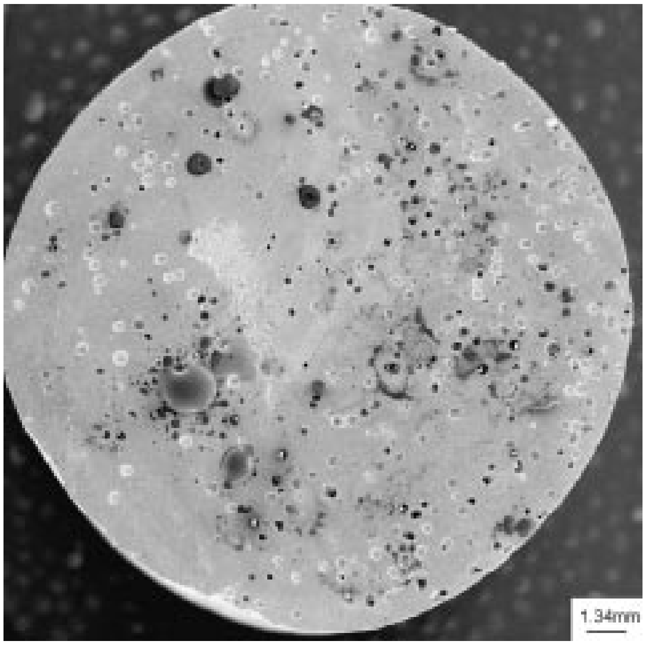


Fig. 6 A new waxed TiN/TiNi surface

In Fig. 8, volume losses of the specimens that experienced pre-wear under a load of 0.243 kN over 4800 m are also presented. The pre-worn specimens showed similar behavior, but their changes in volume loss were much more gradual. In particular, the volume losses of the pre-worn specimens were considerably lower than those of new ones under high loads. However, under lower loads, the new and pre-worn specimens did not show significant differences. The new and pre-worn specimens were examined using XRD to check if there were phase changes caused by the pre-wear treatment. Figure 10 illustrates a diffraction pattern of a pre-worn TiN/TiNi specimen. No structural change in the TiNi composite was detected. During the pre-wear process, material transfer from the steel disc to the composite pin specimen was involved. The additional peaks of $(Cr,Fe)_2O_3$ and Fe_3N may come from the material picked up from the stainless steel disc. The formation of the oxide and Fe_3N implies that the interfacial temperature could be high, even though water cooling was applied inside the disc during the pre-wear treatment.

The XRD result did not show detectable structural changes in the TiNi composite during the pre-wear treatment. However, the density of pores was greatly reduced. Figure 11 is an SEM metallograph of a worn TiN/TiNi specimen, whose surface was lightly polished and etched before examination (Fig 5). Compared to a new specimen (Fig. 5), this pre-worn specimen surface was considerably denser with many fewer pores.

As demonstrated by SEM and XRD, the pre-worn specimens had considerably fewer pores and no detectable second phases were induced. This implies that the improvement in wear resis-

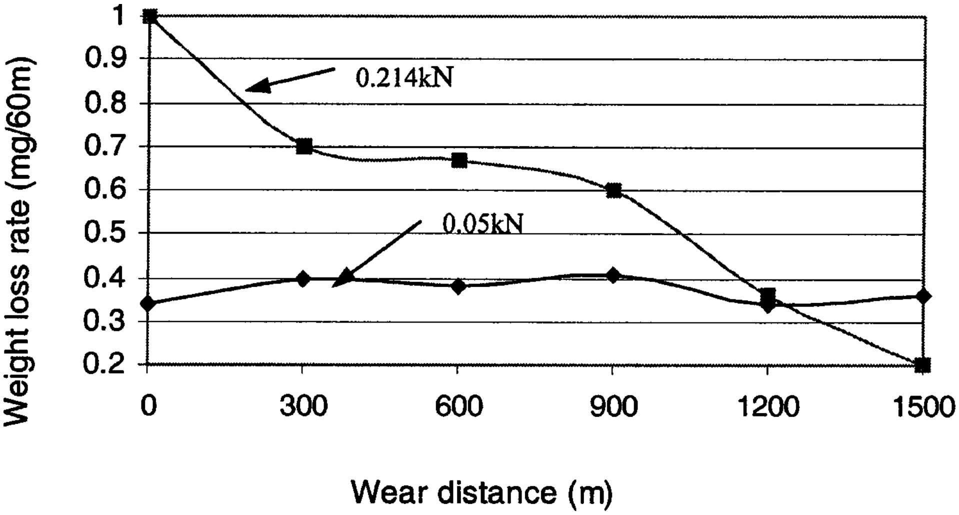


Fig. 7 The wear loss rate of unwaxed TiC/TiNi specimen

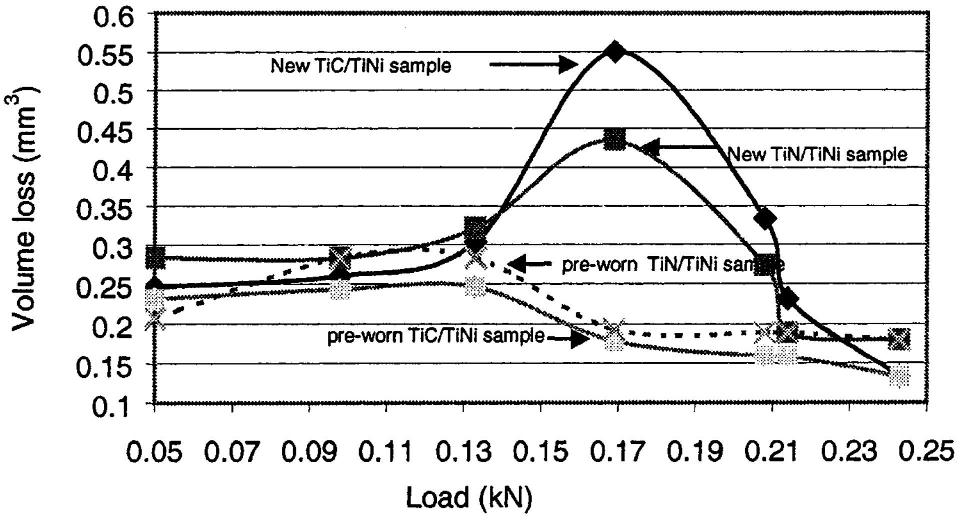
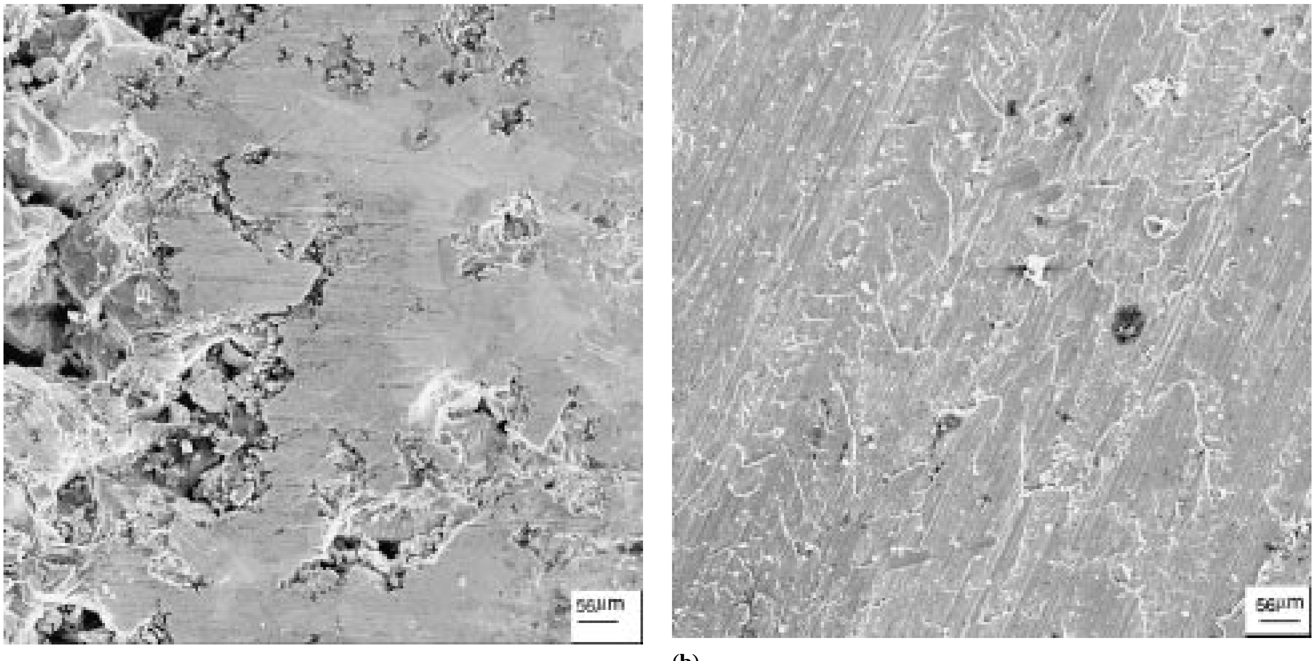


Fig. 8 Wear losses of samples at different loads



(**a**) (**b**)

Fig. 9 Worn surfaces of TiN/TiNi composite: (**a**) worn under a low load of 0.05 kN and (**b**) worn under a high load of 0.243 kN

tance of the pre-worn specimens could be largely attributed to the reduction of pores. However, strain-hardening may also play a role since the density of dislocations would increase during wear, which could influence the hardness and thus the wear resistance.

3.3 Influence of Voids on the Mechanical Behavior of TiNi Composites

In order to better understand the effect of voids on the wear resistance, hardness and pseudoelasticity of the TiNi matrix were investigated using a nano-mechanical probe. Figure 12 illustrates typical load-depth curves of TiN/TiNi composites during nano-indentation. The tested specimens included a new specimen, a worn one under a load of 0.214 kN over a sliding distance of 1200 m, and one with a double-wear treatment (*i.e.*, twice the sliding distance under the same load).

The inverse of the penetration depth d is a measure of the hardness of the specimen; while the ratio (η) of the recoverable deformation energy (*i.e.*, the area enclosed by the unloading curve and maximum penetration depth) to the total deformation energy (*i.e.*, the area enclosed by the loading curve and maximum penetration depth) reflects the degree of pseudoelasticity.[16] The indentation test indicated that the new sample was

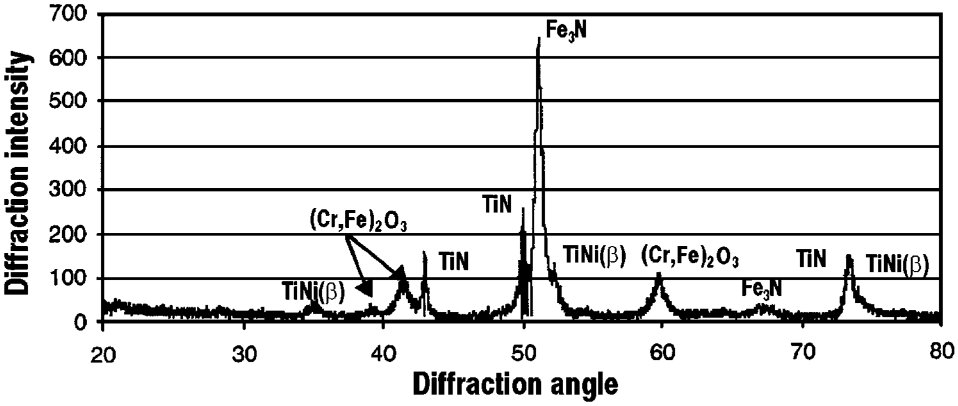


Fig. 10 (Co-α) XRD pattern of a TiN/TiNi sample that was pre-worn at 0.243 kN

the softest, followed by the worn one, and the double-wear treated sample was the hardest. Figure 13 presents *d* values of these samples versus the indentation loads. Regarding the η ratio, the new sample had the highest η value, while the one with double-wear treatment had the lowest η. However, under higher loads, η values of all samples became closer, as Fig. 14 shows. The difference in the matrix's mechanical behavior between the three types of composites could be strongly affected by voids. The sample with double-wear treatment had fewer pores and this diminished the stress concentration and thus the probability of fracture. The increased density of dislocations introduced during wear may also contribute to the enhanced hardness. On the other hand, the compacted structures of the worn (or pre-worn) samples with fewer voids and higher density of dislocations behaved less pseudoelastically. However, the difference in η between the new and worn/pre-worn samples decreased under high indentation loads, since during such an indentation process all samples were heavily deformed with the generation of a high density of dislocations.

4. Further Discussion

The present research shows that the wear resistance is strongly influenced by the density of pores. A decrease in the density of voids results in enhanced wear resistance. This is understandable, since the voids may act as stress raisers and thus increase the probability of cracking or fracture. A reduction in the density of pores should be beneficial, and this has been confirmed by the above wear tests of TiNi composites (Fig. 4 and 8).

Since pores usually exist in composites produced by a sintering process, it is of importance to investigate the effect of pores on wear and the possible changes in porosity during wear, a dynamic surface process. As observed, the density of pores decreased during wear, and this decrease in pore density was significant especially under high wearing loads. Such a decrease could be attributed to the self-sealing of pores during the wear by the compaction effect of the contact force as well as the sealing of surface pores by the material transferred from the stainless steel disc. From the XRD examination, $(Cr,Fe)_2O_3$ and Fe_3N were detected on the worn surface of TiNi composite. This means that the material of the stainless steel disc has reacted with the composite specimen and been transferred to the latter. The self-sealing and material transfer under high load could densify the surface layer of the specimen. It was also observed that the color of the worn surface under high loads turned to yellow. It is therefore expected that the interfacial temperature was high under high wearing loads and this made the compaction effect stronger, similar to a hot pressing process. Indeed, during high-load wear, the wear rate decreased considerably as the sliding distance increased, while such a decrease was negligible under lower loads, as shown in Fig. 7.

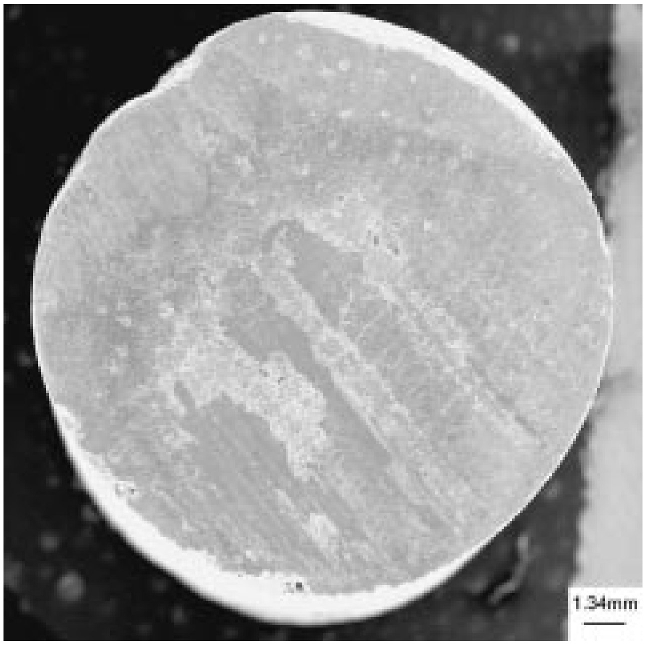


Fig. 11 A worn TiN/TiNi surface

The wear loss of a composite usually increases as the applied load is increased. However, in our study of TiNi composites, it was interesting to observe that there existed a critical load corresponding to the maximum wear loss, after which the wear loss decreased as the load was continuously increased within the loading range of the wear test. Generally, at high temperature, TiNi alloy loses its pseudoelasticity and its yield strength should

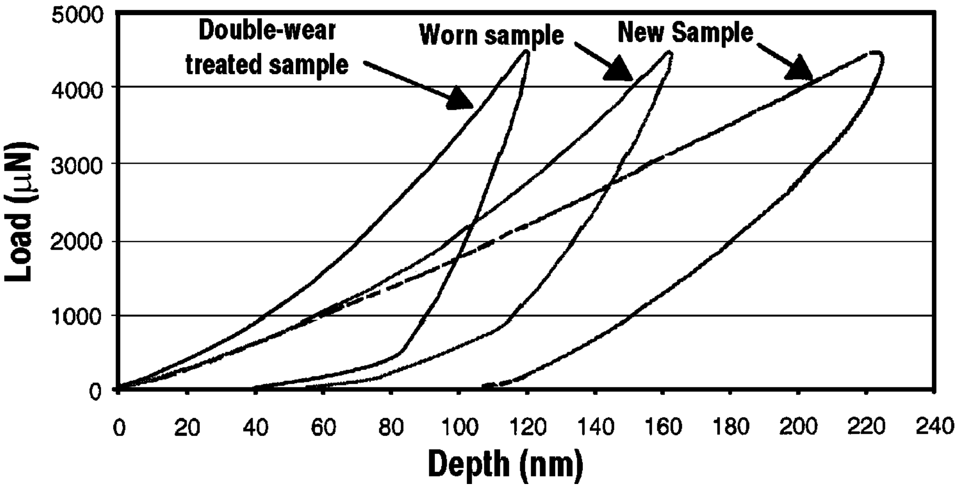


Fig. 12 The load-displacement curves during indentation under 4500 μN

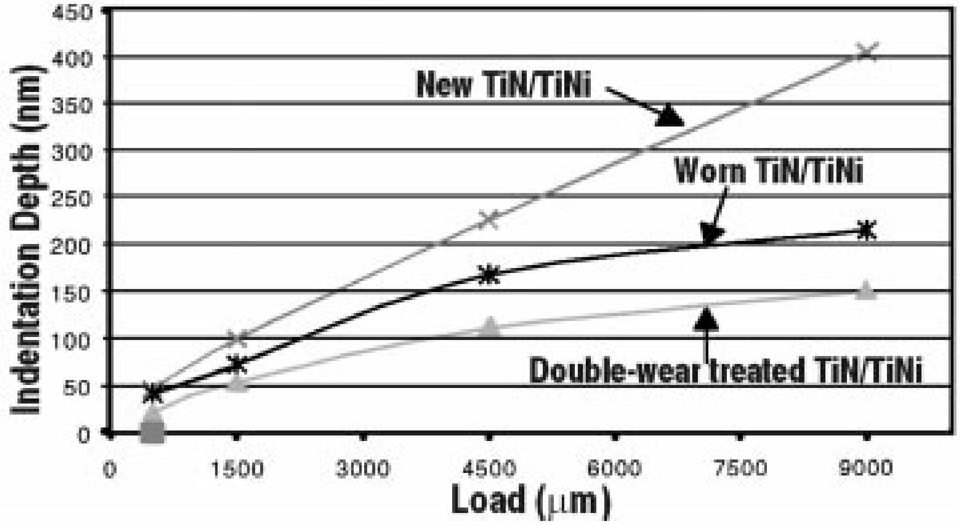


Fig. 13 The maximum depth vs the nano-indentation load

also decrease. This should lead to an increase in the material's wear loss. Therefore, the decrease in wear loss may be attributed to the compaction effect on pores. The higher the applied load, the more effective the compaction effect. As a result, the pores were considerably reduced in the surface layer under higher loads, resulting in a significantly enhanced wear resistance. Although higher wearing loads may increase the wear damage, the effect of load on the enhancement in the wear resistance of TiNi composite could be greater than that on the increase in wear damage, thus leading to a decrease in the wear loss, as Fig. 8 illustrates. The variation in wear loss as a function of load was significantly smaller for the pre-worn specimens (Fig. 8). This is understandable, since in the surface layer of the pre-worn specimens, the density of pores has already been reduced. It should be noted that, during wear, dislocations were introduced and the increased dislocation density (*i.e.,* strain hardening) may also benefit the wear resistance. However, it is believed that the density of pores has a predominant effect on wear, since the failure of a material is more sensitive to pores or microcracks. In addition, the possible twining process existing in the TiNi-based composite[18] may also have some influences.

The nano-indentation test showed that the sample with double-wear treatment exhibited the highest hardness with a lower degree of pseudoelasticity. As indicated earlier, the wear resistance of TiNi alloy does not rely entirely on its pseudoelasticity. Recent studies[15] demonstrate that the wear resistance of TiNi alloy is dependent on the balance between its pseudoelasticity and hardness. Although the pseudoelasticity helps to accommodate large-scale deformation and absorb impact energy with less damage, the TiNi alloy still cannot effectively resist high-stress wear if its hardness is low. On the other hand, if the pseudoelastic TiNi alloy is too hard, its wear resistance is also low. Therefore, an appropriate combination of pseudoelasticity and hardness will result in the optimum wear resistance. In addition, the hardness becomes important during high-load sliding wear, since in this case the TiNi alloy may lose its pseudoelasticity, and intrinsic wear resistance then plays a predominant role under high loads accompanied with larger frictional heat-

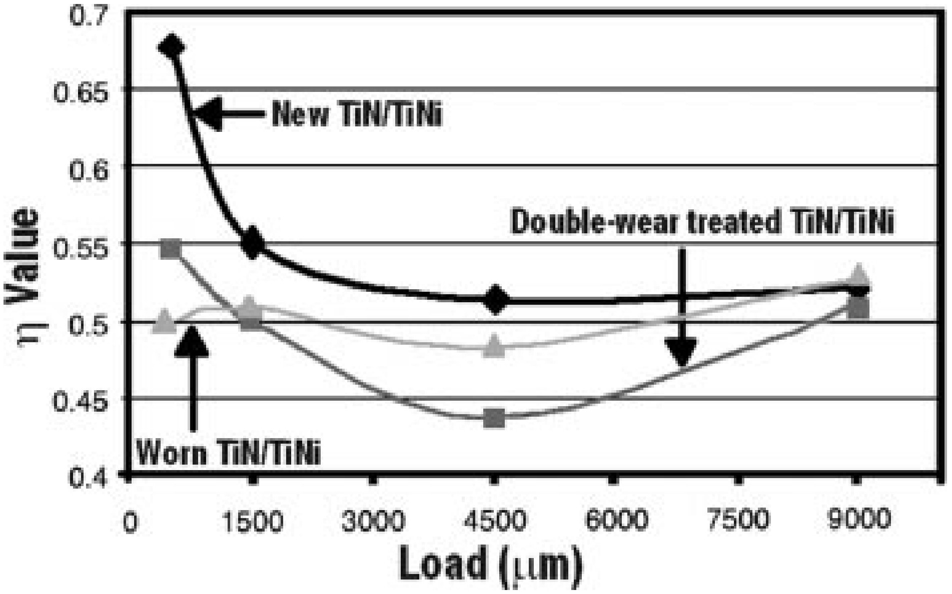


Fig. 14 The η values of a new sample, a worn sample, and a double-wear treated sample

ing. In this case, the hardness becomes particularly important. The measured macrohardness of TiN/TiNi ranges from HRC 50 to 59 and TiC/TiNi from HRC 58 to 62. This high hardness certainly enhances the material's wear resistance.

5. Summary

Since pores typically exist in sintered composites, it is of importance to understand the effects of pores on the wear of composites and variations in porosity during wear. In this work, the effects of pores on the wear resistance of sintered TiC/TiNi and TiN/TiNi tribo-composites were investigated. It was demonstrated that pores or voids in the composites are detrimental to the composites' wear resistance. The voids may act as stress raisers to diminish the wear resistance of the composites. By using wax during pressing powder specimens before sintering, porosity in the composites was reduced, resulting in an improved wear resistance. It was interesting to observe that the voids were sealed during the wear process and the wear resistance of the composites increased continuously under high loads. The obtained information is useful for further improvement of sintered TiNi-based composites and understanding of their performance during wear, a dynamic surface destructive process.

Acknowledgments

The authors are grateful for the financial supports from the Natural Science & Engineering Research Council of Canada (NSERC), Syncrude Canada Ltd., Alberta Oilsand Technology and Research Authorization (AOSTRA), and Alberta Science and Research Authority (ASRA).

References

1. A. Ball: *Wear,* 1983, vol. 91, p. 201.
2. R.H. Richman, A.S. Rao, and D. Kung: *Wear,* 1995, vol. 181–183, p. 80.
3. D.Y. Li: *Wear,* 1998, vol. 221, p. 116.
4. H.C. Lin, H.M. Liao, J.L. He, K.M. Lin, and K.C. Chen: *Surface Coatings Technol.,* 1997, vol. 92, p.178.
5. Y. Suzuki, and T. Kuroyangi: *Titanium Zirconium,* 1979, vol. 27, p. 67.
6. C.A. Zimmerly, T. Inal, and R.H. Richman: *Mater. Sci. Eng.,* 1994, vol. A188, p. 251.
7. R.H. Richman, A.S. Rao, and D.E. Hodgson: *Wear,* 1992, vol. 157, p. 401.
8. J. Jin, and H. Wang: *Acta Metall. Sinica,* 1988, vol. 24, p. A66.
9. J. Singh, and A.T. Alpas: *Wear,* 1995, p. 302.
10. Y. Shida, and Y. Sugimoto: *Wear,* 1991, vol. 146, p. 219.
11. Y.N. Liang, S.Z. Li, Y.B. Jin, W. Jin, and S. Li: *Wear,* 1996, vol. 198, p. 236.
12. R. Liu and D.Y. Li: *Mater. Sci. Eng.,* 2000, vol. A277, pp. 169-75.
13. P. Clayton: *Wear,* 1993, vol. 162-164, p. 202.
14. K.N. Melton and O. Mercier: *Acta Metall.,* 1979, vol. 27, pp. 137-44.
15. D.Y. Li and X. Ma: *J. Mater. Sci. Technol.,* vol. 17, 2000, p. 45.
16. H.Z. Ye, R. Liu, D.Y. Li, and R. Eadie: *Scripta Mater.,* 1999, vol. 41, (10), pp. 1039-1045.
17. C.M. Jackson, H.J. Wagner, and R.J. Wasilewski: NASA-SP 5110, NASA, Washington, DC, 1972, p. 86.
18. D.C. Dunand, D. Mari, M.A.M. Bourke, and J.A. Roberts: *Metall. Mater. Trans. A.,* 1996, vol. 27A, pp. 2820-36.