Wear of Ni$_3$Al-based materials and its chromium-carbide reinforced composites

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ABSTRACT

A number of laboratory studies have indicated that Ni$_3$Al-based alloys have significant potential in wear-critical applications, especially in sliding wear in a temperature range between 400 and 650 °C. In this study, the wear behavior of an iron-alloyed Ni$_3$Al with composition of Ni–18.8Al–10.7Fe–0.5Mn–0.5Ti–0.2B in atomic percentage and its composites reinforced by 6 vol.% Cr$_3$C$_2$-particles were investigated.

Hot isostatic pressing (HIP) and casting processes were applied for preparing the materials. The wear rate of the tested materials under different loads and their scuffing resistance were measured by means of the pin-on-disc method. Analytical SEM, EDS, and XRD techniques were used to observe the microstructures and identify the phase constitutions of the materials. The tribological performance related to the analytical results revealed that the single-phase Ni$_3$Al-based alloy showed an improved scuffing resistance, compared to a duplex-phase microstructure. Also, the investigation indicated that the added hard Cr-carbide played a positive role for the tribological behavior of the intermetallics, especially in terms of reducing the wear rate.

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1. Introduction

Metal-matrix composites containing a high volume fraction of carbide, nitride, boride, and oxide particles are frequently the materials of choice for applications which require good wear resistance. It is also recognized that for metal-matrix composites containing hard particles, sliding against a metal counterface results in the generation of metal filings due to micro-cutting and their compaction during sliding. Lubrication could help to avoid this problem.

In metal carbides, tungsten- and chromium-carbide are suitable for adding in metal matrix as hard particles for their very high hot hardness and good wetting ability with metal (such as iron, cobalt, and nickel) matrix. Compared with tungsten-carbide, chromium-carbide is more suitable to be used in air for its excellent oxidation resistance [1].

Some intermetallics as high-temperature wear-resistant materials attracted attention due to their intrinsic long-range ordered crystalline structures with strong oriented atomic bonding. In the group, Ni$_3$Al-based intermetallic alloys are especially interesting for certain tribological applications [2–7]. Bonda and Rigney [4] investigated the sliding wear of several Ni$_3$Al-based alloys in both air and vacuum. Materials were sliding against themselves. Sliding tests were done without lubrication at room temperature and at 400 °C. The results indicated that the wear rate in air is reduced at higher temperature after a transition period which occurred after a certain sliding distance and was recognized by decreased friction force. Blau and DeVore [6] have studied sliding friction and wear rate for a series of alloys based on Ni$_3$Al as part of an effort to evaluate the potential of these alloys as bearing materials. Counterface materials included different steels; ceramics; and the Ni$_3$Al-based alloys themselves. The typical findings of this set of experiments were that the wear resistance of Ni$_3$Al-based alloys was improved as temperature increased, and that the friction coefficient tended to decrease slightly as temperature increased. A boron-doped alloying work gave the most obvious improvement in the alloy group. The authors related the results to the microstructures and mechanical properties of the tested alloys, and summarized that the greater the proportional improvement in yield strength with temperature, the greater is the improvement in wear resistance. It was also noticed that finer microstructure of the materials made a positive contribution to the wear resistance.

Other studies [2,7] have involved the abrasive wear and cavitations erosion behavior of Ni$_3$Al-based alloys. In general, the erosion resistance of nickel aluminides is comparable with that of many commercial alloys that are often used for erosion service. There have been many attempts to correlate the erosion resistance of materials to mechanical properties, or to some general features

Table 1
The tested materials

Designation	Composition	Process
Specimen 1[#]	NAC-alloy	HIPing
Specimen 2[#]	NAC-alloy + 6 vol.% coarse Cr_3C_2-particles	HIPing
Specimen 3[#]	NAC-alloy + 6 vol.% fine Cr_3C_2-particles	HIPing
Specimen 4[#]	NAC-alloy	As-cast

of the microstructure. For example, low stacking fault energy of fcc metals that work-harden rapidly tend to have good resistance to erosion [8,9]. The existing results for the nickel aluminides are consistent with the observation. On the contrary, the abrasive wear resistance of the Ni_3Al-based alloys is less than that of 304 type stainless steel. Furthermore, the abrasive wear resistance is reduced significantly by alloying, because of a loss of stability of the ordered structure. From the studies, it was revealed that the Ni_3Al-based alloys are potential candidates to be used as sliding wear-resistant and cavitations erosion-resistant materials under high loads and elevated temperatures. Their improved strength, formability, corrosion resistance and ductility in the temperature range of 400–650 °C may make them competitive with other wearing component materials.

Our earlier work [10], has investigated several different intermetallic alloys with respect to their tribological performance. It was noticed that the Ni_3Al-based alloys are most hopeful as a new kind of high-strength wear-resistant materials at high temperature. In the present study, the wear behavior of an existing Ni_3Al-based alloy and its Cr_3C_2-reinforced composites were studied, and related to their phase constitutions.

2. Experimental results

2.1. Testing materials and preparation

An iron-alloyed Ni_3Al (NAC-alloy) was selected for this study. The composition of the alloy is Ni–18.8Al–10.7Fe–0.5Mn–0.5Ti–0.2B in atomic percentage. The monolithic NAC-alloy and its Cr_3C_2-reinforced composites were studied by wear testing related to their microstructures. The designation of the tested samples is summarized in Table 1.

The powders of NAC-alloy were prepared by using plasma-rotating-electrode-process (PREP) equipment in the Central Iron and Steel Research Institute (CISRI), Beijing. At the starting, the PREP-unit was evacuated up to 0.1 Pa to prevent oxidation of the powders formed. The chamber was then flooded with helium and argon. The electrode rod of the master alloy is accelerated up to the desired speed of rotation, $14,500 \pm 500$ rpm. An argon/helium plasma arc was ignited. The plasma jet melts tip of the rotating rod. A fusion film was formed on the front end of rod, which disintegrated into small liquid metal droplets as a consequence of the centrifugal force. Due to surface tension the droplets are spherical. On their trajectories towards the chamber wall the droplets solidified rapidly in the inert atmosphere and formed spherical powder particles. The cooling rate of powders is around 100 °C/s. The size of NAC-alloy powders used for preparing hot isostatic pressing (HIP) materials is in a range of 45–100 μm.

The tested bulk materials 1[#], 2[#], and 3[#] were produced by means of the hot isostatic pressing process at Bodycote, Surahammar, Sweden. To prepare the composites, the coarse particles of Cr_3C_2 in a range of 45–90 μm and the fine Cr_3C_2-particles less than 45 μm were used. The temperature 1130–1160 °C, pressure 100 MPa and time 3 h are applied during the HIP process.

The as-cast bulk material 4[#] was casted by CISRI using a vacuum (33×10^{-2} Pa) induction melt furnace. The holding temperature of
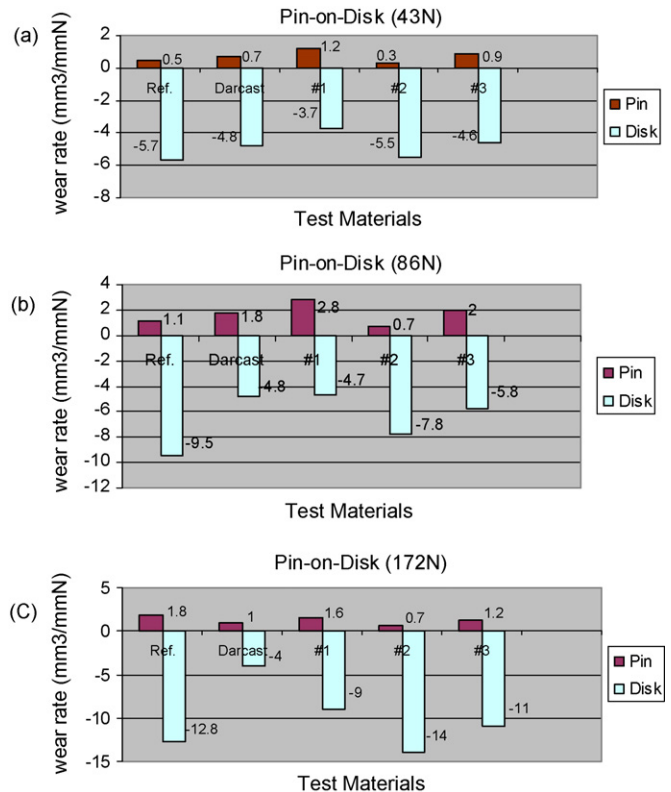

Fig. 1. (a) Specific wear rate (mm^3/mm N) under 43 N for a sliding distance 20,000 m, (b) specific wear rate (mm^3/mm N) under 86 N for a sliding distance 20,000 m, and (c) specific wear rate (mm^3/mm N) under 172 N for a sliding distance 20,000 m.

melt is 1550 °C. The pouring temperature is 1460 °C for the vacuum investment casting into a ceramic shell.

2.2. Friction and wear measurement

The pin-on-disc test was used for the evaluation of friction and wear to the sliding contact surface of bulk materials. In the test a stationary test specimen pin is loaded with normal force against the surface of a rotating disc. The force of friction is measured during the test and wear of the test specimens determined afterward. The dry friction and wear test in a test room where the temperature is 22 ± 1 °C and relative humidity is adjustable between 40 and 60% were carried out. The normal forces were 43, 86, and 172 N, respectively, under the testing. The tested materials were machined into pins with dimensions of Ø8 mm × 25 mm. The disc material is a standard Tarkalloy-C cast iron which is usually used as the material for cylinder liner in internal combustion engines. Three running pins of each listed material were tested under the determined loads. The wear rate of the pins for the sliding distances of 5000 and 20,000 m were measured. The wear results obtained during this work have been presented in terms of specific wear rate which is calculated as follows:

$$\text{specific wear rate} = \frac{V}{F_N S}, \tag{1}$$

where V is the volume worn away in mm^3, F_N is the normal load in N, and S is the sliding distance in mm. Specific wear rate (mm^3/N mm) under three various loads from the specimens 1[#], 2[#], 3[#], and Darcast, a Ni-superalloy, as two reference materials, were carried out and are given in Fig. 1(a–c). The Darcast is a compacted graphite cast iron and widely used as wear-resistant material with reasonable strength level. It can be recognized that the wear rate of Darcast is
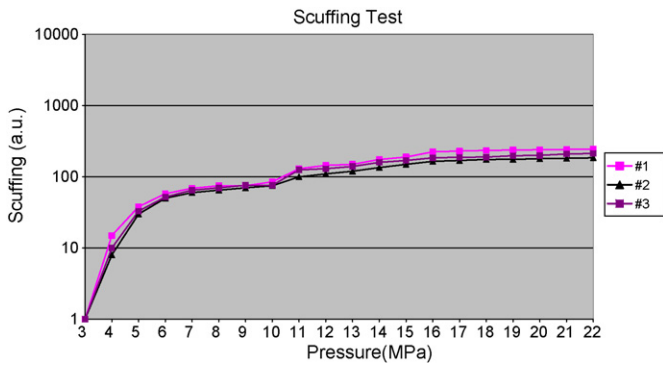
Fig. 2. The scuffing resistance in (a.u.) curves of the specimens 1#, 2#, and 3# against applied pressure in (MPa).

Table 2
Scuffing loads of the tested materials by pin-on-disc

Tested material	Scuffing pressure (MPa)
Specimen 1#	>22
Specimen 2#	>22
Specimen 3#	>22
Specimen 4#	<15
Darcast cast-iron	<10

reasonable small up to a pressure of 3.44 MPa in the test. The tested intermetallic specimens 1#, 2#, and 3# also showed rather good wear resistance, compared to the Darcast material. For the inter-metallic specimens comparatively, the sample 2# with the coarse carbide reinforcement has the best wear resistance in the group under the applied loads. The composite 3# reinforced by the fine Cr_3C_2-particles showed relatively worse wear resistance.

Scuffing phenomenon usually occurs when the material is running on sliding wear under high contact pressure. The scuffing is very complicated and results in a serious wear-off component. In fact, the danger of scuffing depends on the product of rubbing speed, pressure and the friction coefficient. Therefore the scuffing resistances of the tested materials were also investigated by pin-on-disc method in this study. The curves of scuffing resistance in (a.u.) of the specimens 1#, 2#, and 3# against applied pressure are shown in Fig. 2. There was no scuffing effect observed on those specimens even under the highest applied pressure of the testing machine, i.e. 22 MPa. The measured scuffing results of the tested intermetallic materials, including as-cast 4# of NAC-alloy, and Darcast are collected in Table 2. Clearly, all tested Ni_3Al-based materials have much better scuffing resistance than the cast iron.

3. Analytical experiments

In Fig. 3 showed a secondary electron image (SEI) of NAC-alloy powders and a backscattering electron image (BEI) of HIP specimens 1#, respectively, Fig. 3a shows that NAC-alloy powder particles are nearly perfect-spherical and have smooth and suppos-

edly clean surface. Flaky and hollow particles are seldom observed, resulting in a good flow ability of the powders. The powders are mostly distributed in the size range of 45–100 μm. Impurity content of the powders is very low (oxygen less than 0.007 wt.%, nitrogen less than 0.005 wt.%). There are only a few non-metallic inclusions observed in the powders. Fig. 3b reveals that the HIP monolithic NAC-alloy is crack-free and almost no porosity exists. A quantitative microanalysis by means of EDS indicated that the composition of the matrix is very close to the composition of the NAC-alloy. There are also some tiny particles, less than 0.5 μm, distributed along the previous powder particle boundaries. The EDS analysis on these second-phase particles revealed that they have higher Cr-content than the matrix, but lower Fe- and Ni-content, based on a formula of $Ni_3Al_{1.62}Fe_{0.38}Cr_{0.16}$.

Fig. 4a is a BEI image of specimen 2#, a composite reinforced by the so-called coarse Cr_3C_2-particles. It was noticed that the carbide particles have reacted with the matrix around them. An unaffected core still existed in some big Cr_3C_2-particles. Otherwise, the whole particle changed its composition due to the reaction between the particle and matrix. Such situation was observed in the composite 3# which was reinforced by the finer Cr_3C_2-particles. The reacted particle was analyzed by means of EDS. There is only a Cr-peak being detected from the dark core. The C-peak is non-detectable with the EDS equipment used. Still, it is reasonable to conclude that the dark core is non-reacted Cr_3C_2. The grey phase around the core has higher content of Fe and Ni, which come from the matrix. Around the reacted carbides, there are some tiny bright submicron precipitates. It is impossible to solely analyze such tiny precipitates by means of SEM + EDS. A spectrum from the precipitates and the matrix around in an area of $1\,\mu m \times 1\,\mu m$ revealed that they have higher Cr-content compared to the matrix. Most probably, the features result from the dissolution of the added Cr_3C_2-particles during the heating period of HIP processing, and followed by the reprecipitation around the reacted Cr_3C_2-particles during the cooling process. It should also be stressed that metallurgical bonding was formed between the added carbide-particles and the matrix by
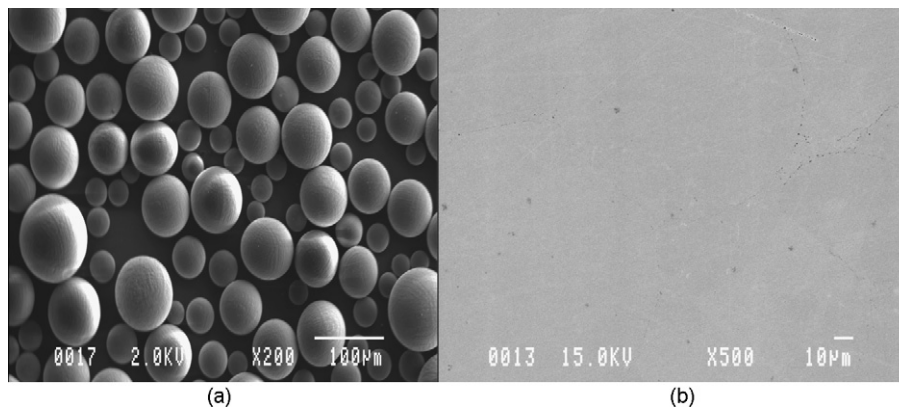

Fig. 3. (a) SEI image of NAC-alloy powder showing that the powder particles are nearly perfect-spherical and has smooth and supposedly clean surfaces. (b) BEI image of HIP 1# sample.
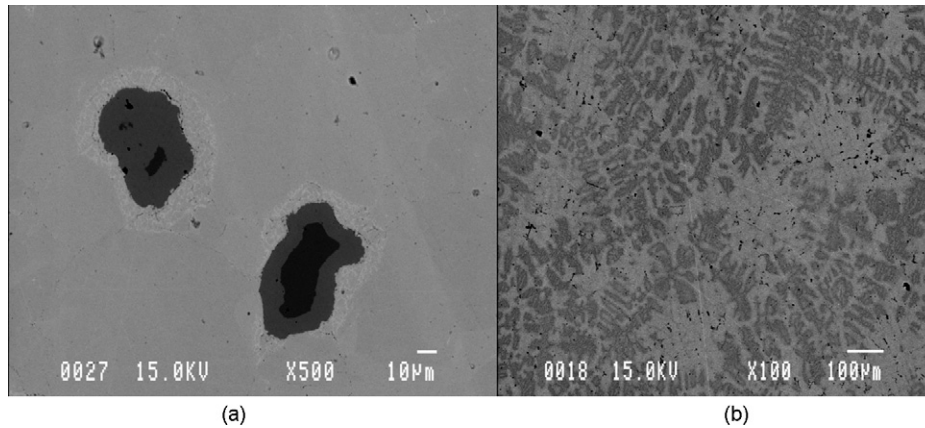
Fig. 4. (a) BEI image of hipped 2# sample reinforced by Cr-carbide particles. (b) BEI image of casted 4# sample with non-equilibrium duplex phases.

the reaction. This observation can be a meaningful fact for improvement on the wear behavior of the composites materials.

Fig. 4b is a backscattering electron image of the as-cast NAC-alloy specimen 4#. A composition contrast of the image indicated that two different phases existed in the material. Twenty-point analyses on each phase were performed by means of EDS. The results are summarized in Table 3. Obviously, the matrix phase has higher Ni-content and lower Al-content, compared to the second phase. The Fe-content in both phases is quite similar, but it is only a little less in the second phase.

For further confirming the phase constitution of the as-cast NAC-alloy, X-ray diffraction spectrometry was performed on the as-cast specimen 4#. For a comparison, the NAC-alloy powders and the HIP specimen 1# were also analyzed. In order to identify the diffraction peaks of NiAl-phase, a NiAl-single-phase alloy with a composition as Ni–46.71Al–1.97Nb–2.01Cr–0.08Zr in atomic percent was used as a reference. The Cr Kα X-ray radiation was used to get the diffraction pattern of the analyzed specimens. The results are collected in Fig. 5. The diffraction spectrum of the specimen 1# (Fig. 5a) indicated that the HIP NAC-alloy is a single-phase material with a Ni$_3$Al-type of crystalline structure. The diffraction spectrum from the specimen 4# (Fig. 5b) clearly revealed that two phases existed in the material. As a major phase, the matrix has a Ni$_3$Al-type of crystalline structure. Also, there is a NiAl-type of phase in co-existence with the Ni$_3$Al-matrix. This is even more clearly seen when the spectra are compared with that from the NiAl-single-phase reference sample (Fig. 5c). This latter spectrum has a $\{1\,1\,0\}$ diffraction peak at the position of $2\theta = 68.66°$, which is coincident with the diffraction peak of the second phase in the cast sample 4#. The different cooling rates of HIP and as-cast NAC-alloy could be the reason for their different microstructures. The cooling rate of the HIP material in the pressure chamber was slower than the as-cast material

prepared by the casting in a ceramic shell. This fact is further proven by the X-ray diffraction analysis of the NAC-alloy powder in Fig. 5d. The $\{1\,1\,0\}$ diffraction pattern peak of NiAl-phase was also shown in the spectrum of the as-cast material.

4. Discussion

The wear-rate measurement by pin-on-disc in this study revealed that the wear rates of the HIP NAC-alloy are rather similar to the traditional wear-resistant cast iron under low loads, i.e. at 43, 86, and 172 N, respectively. However, the wear-resistant cast iron will run into scuffing under a high pressure corresponding to below 10 MPa. Comparatively, the HIP NAC-alloy was even not scuffed under a pressure of 22 MPa; the maximum pressure condition that can be reached with the test-unit. The excellent wear performance of the tested Ni$_3$Al-based alloy for high loads is related to its crystalline structure and mechanical properties.

Adhesion is the consequence of contact which means that the adhesive wear is concerned with a micro-welding and tearing process. Obviously, the materials of a sliding pair with similar crystal structures could be suffered more seriously to this kind of wearing. The intermetallic materials have long-range ordered crystal structures, which are completely different, compared to the metallic wearing counterpart. The difference in crystal structure will be meaningful for itself and its counterpart to reduce wear impact.

Mechanical properties are also very important and related to the wear behavior of materials [11–13]. Especially, the strength of mate-
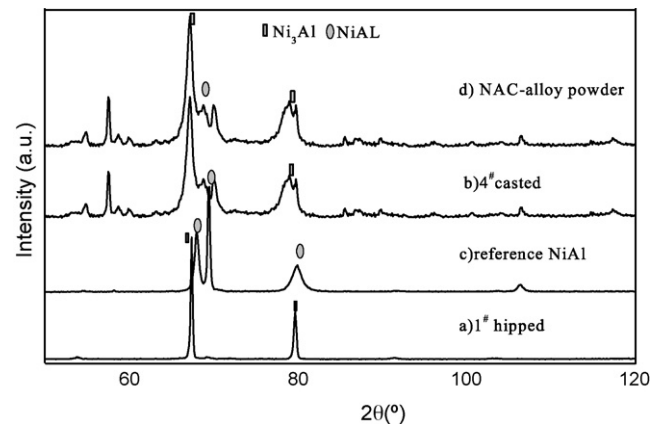
Table 3
Average composition of two phases in as-cast NAC-alloy of 4#, in atomic percent

	Ni	Al	Fe	Cr	Mn	Ti	Mo
Matrix-phase							
Mean	73.98	12.48	12.41	0.01	0.55	0.58	0.00
S.D.	0.859	0.256	0.325	0.300	0.055	0.068	0.050
Maximum	76.39	13.06	12.98	0.06	0.62	0.73	0.10
Minimum	71.54	11.80	11.52	−0.04	0.44	0.50	−0.062
Second phase							
Mean	66.04	22.52	10.29	0.00	1.04	0.09	0.01
S.D.	1.065	0.511	0.256	0.023	0.073	0.029	0.041
Maximum	70.36	24.32	11.12	0.02	1.20	0.14	0.10
Minimum	62.33	21.10	9.69	−0.04	0.91	0.05	−0.05

Fig. 5. X-ray diffraction spectra of (a) HIP NAC-alloy sample of 1#, (b) as-cast sample of 4#, (c) single-phase NiAl sample as a reference, and (d) NAC-alloy powders.

rial and its work-hardening behavior in plastic flow will control the extent of plasticity in the contact region. Certainly, the resistance to brittle fracture, commonly described by the fracture toughness, can lead to completely different mechanisms of wear from those dominated by plastic flow.

It is known that the ordered Ni_3Al-based alloy becomes stronger as temperature increases in a certain range. Also, Ni_3Al-based alloys have high work-hardenability. Thus, the mechanical deformation and frictional heating would create a harder surface region. This character could make Ni_3Al-based alloys resistant to adiabatic shear, and perhaps to shear instability in general. Also, boron doping greatly strengthens grain boundaries of Ni_3Al, improving ductility and fracture toughness. The effect could make the doped material resistant to transfer, and therefore to sliding wear. The studied NAC-alloy also contained Fe. Our earlier work and another study [14] indicated that the addition of iron in the amount not exceeding 11 at.% contributes to the increase of the mechanical properties mentioned above.

The Cr_3C_2-particle reinforced NAC-composites 2# and 3# have even better wear properties. They showed the same level of scuffing resistance over 22 MPa and lower wear rate for the lower loads, compared to the monolithic NAC-alloy. The reason for this is the effect of the added hard particles, keeping the sliding surfaces apart during the wearing process. There is then reduced contribution of adhesion between the sliding surfaces.

In this study, the Ni_3Al-matrix composites were reinforced by Cr_3C_2-particles of two different sizes. The composite with coarse Cr_3C_2-particles showed lower wear rate than the composite with fine Cr_3C_2-particles. The EDS analytical data on a large reacted Cr-carbide particle indicated that the dark core is still non-reacted Cr_3C_2. The grey phase in the reacted zone around the Cr-carbide core contains Fe and Ni due to the diffusion from the matrix to the carbide. Therefore, the chemical bonding between carbide and matrix will assist the matrix to hold the hard particles tightly during the wearing procedure, and results in a low wear rate of the materials. It is also believed that the tiny precipitates formed on the matrix around the reaction zone should strengthen the interfacial region and prevent the generation and propagation of cracks coursed by sliding process. This would also finally delay the wear-off process. Comparatively, the fine carbide particles were completely reacted with the matrix during the HIP process. There were even no "Cr-carbide cores" left in the composite to act against wear. This means that a certain size of the added particles is needed to improve the wear-resistance of the composites.

The as-cast 4#NAC-alloy has worse scuffing resistance than the HIP alloys of 2# and 3# owing to its different phase constitution. There are two phases in the as-cast alloy: Ni_3Al-matrix and NiAl-secondary phase, while there is only one single Ni_3Al-phase in the HIP alloys. Our earlier study [10] showed that NiAl-based alloy has worse wear performance than the Ni_3Al-based alloy. Therefore, the observed phenomenon can be simply understood based on a mixture of these two phases. However, it should be also considered that the fragments of the brittle NiAl-phase as hard particles become embedded in the counterface and cause abrasion.

The reason to form $Ni_3Al + NiAl$ microstructure in the as-cast NAC-alloy is due to the fast cooling rate during the casting process. On the contrary, there is only the Ni_3Al-phase in the HIP alloy, which is related to a slow cooling rate from a temperature over 1100 to 500 °C. Therefore, the microstructure of the as-cast alloy is in non-equilibrium condition. This was further shown by means of the analytical result of XRD on the NAC-alloy powder; there is an even stronger {1 1 0} diffraction peak of the NiAl-phase in the spectrum than the peak from the as-cast alloy.

5. Conclusions

The HIP NAC-alloys show low wear rate, comparing with the reference material, under low pressure (i.e. 0.86, 1.72, and 3.44 MPa) and the HIP NAC-alloy have critical high scuffing resistance under the pressure over 22 MPa.

The coarse Cr_3C_2-particle reinforced of NAC-composite has lower wear rate under the testing condition, comparing to the monolithic NAC-alloy. The added hard particles will keep the sliding surfaces apart during the wearing process and reduce the contribution of adhesion between the sliding surfaces. In fact, a size of the added Cr_3C_2-particles over 45 μm is needed to improve wear resistance of the composites because of the interfacial reaction.

The as-cast NAC-alloy has lower scuffing resistance than the HIP alloys due to the secondary NiAl-phase in microstructure. The fast cooling rate of the casting process is the major reason for the obtained non-equilibrium $Ni_3Al + NiAl$ microstructure.

Corresponding to their wear behaviors and the unique mechanical properties, the Ni_3Al-based materials are considered as potential candidates of the wear-resistant materials for heavy duty applications at elevated temperatures in general.

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