SOLID LUBRICATING, HARD AND FRACTURE RESISTANT COMPOSITES FOR SURFACE ENGINEERING APPLICATIONS

Applicant: University of North Texas, Denton, TX (US)

Inventors: Sundee Gopagoni, Parker, CO (US);
Thomas W. Scharf, Prosper, TX (US);
Rajarshi Banerjee, Denton, TX (US);
Jaimie S. Tiley, Brooksville, OH (US)

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ABSTRACT
A method and composition for producing a monolithic hybrid composite consisting of a composite matrix, a reinforcement phase, and a solid/self-lubrication phase. The composition may comprise a graphite ("C") phase and a titanium carbide ("TiC") phase in a nickel ("Ni") matrix. The process may include the step of blending pure Ni and pure titanium ("Ti") powders with Ni-coated graphite powder using Laser Engineered Net Shaping ("LENS"). The novel composite, when achieved with an optimum chemical and structural phase ratio, exhibits a balance of high hardness, fracture toughness, and low friction/wear.
FIGURE 4

Friction Coefficient

Wear factors

NI-10Ti-10C

NI-3Ti-20C

Distance (m)

Distance (m)

pure Ni

6.1x10^-6

6.8x10^-7

(mm^3/Nm)
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CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims, and is entitled to the, priority to U.S. Provisional Patent Application Ser. No. 61/613, 341, entitled SOLID LUBRICATING, HARD AND FRACTURE RESISTANT COMPOSITES FOR SURFACE ENGINEERING APPLICATIONS, filed on Mar. 20, 2012, the entire content of which is hereby incorporated by reference.

STATEMENT OF GOVERNMENT RIGHTS

[0002] The present invention was partially funded by Federal Grant NSF CMMI-1100648. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates generally to the field of composites having utility as coatings deposited on engineering materials. In some embodiments, the invention relates to monolithic hybrid composites exhibiting solid/self-lubrication, high mechanical hardness, and high fracture toughness.

BACKGROUND

[0004] Coatings deposited on engineering materials frequently experience mechanical wear, delamination, and/or fracture. Thus, composites simultaneously exhibiting the properties of solid/self-lubrication, high mechanical hardness, and high fracture toughness, are needed for coating engineering materials.

[0005] The present invention solves this problem by providing, in certain embodiments, monolithic composites exhibiting solid/self-lubrication, high mechanical hardness, and high fracture toughness. Metal matrix/hybrid composites are highly versatile engineering materials in which a metal is combined with two or more non-metallic phases to yield a novel material that has superior engineering properties such as high hardness, high fracture toughness, and low wear rates. Such materials find utility in many applications ranging from aerospace, drilling, wind energy, and land-based turbines and compressors.

[0006] The process of the present invention may include the use of a Laser Engineered Net Shaping ("LENS") process to make a hybrid monolithic composite that merges solid/self-lubrication, high hardness, and high fracture toughness properties. This process allows the composite to be processed near net shape, and is a flexible process that allows for tailoring of the material phases both chemically and structurally, which cannot be accomplished using conventional laser cladding and hard facing techniques. Near net shape indicates that the initial processing of the composite is very close to its final (net) shape to be used in service, without the use of additional surface finishing operations such as machining or grinding.

SUMMARY

[0007] The present invention relates generally to hybrid monolithic composites exhibiting characteristics of solid/self-lubrication, high hardness, and high fracture toughness, and a method for fabricating hybrid monolithic composites.

[0008] In certain embodiments, the invention comprises a novel, bulk hybrid composite for surface engineering applications comprising a graphite ("C") phase, a titanium carbide ("TiC") phase, in a nickel ("Ni") matrix.

[0009] In certain embodiments, the hybrid monolithic composite of the present invention is produced using a LENS process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

[0011] FIG. 1 shows a ternary phase diagram of Ni, Ti and C. Compositions A and B are Ni-10Ti-10C and Ni-3Ti-20C, respectively, and are shown on the phase diagram.

[0012] FIG. 2 shows X-ray diffraction of the Ni-3Ti-20C composite. The structural phases were determined to be nickel (face-centered cubic crystal structure), titanium carbide (rocksalt crystal structure), and carbon (graphite allotrope).

[0013] FIG. 3 shows a planar surface Auger electron spectroscopy map of the unworn Ni-3Ti-20C composite. The chemical phases were determined to be Ni, TiC and C.

[0014] FIG. 4 shows friction coefficient and wear rates/factors of the Ni-10Ti-10C and Ni-3Ti-20C composites.

[0015] FIG. 5 shows planar surface Auger electron spectroscopy map of the worn Ni-3Ti-20C composite. Tribochemical formation of an in situ, low interfacial shear strength carbon film is determined inside the wear track.

[0016] FIG. 6 shows scanning electron microscope image of the subplanar (subsurface) focused ion beam cross-section of worn Ni-3Ti-20C composite. Sheared graphite that comes to the surface is shown that proves the solid/self-lubrication of the composite.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0017] The present invention relates generally to monolithic hybrid composites exhibiting solid/self-lubrication, high mechanical hardness, and high fracture toughness. In certain embodiments, the invention comprises a novel, monolithic hybrid composite for surface engineering applications comprising: a graphite ("C") phase, and a titanium carbide ("TiC") phase, in a nickel ("Ni") matrix. In some embodiments, LENS is used to make the monolithic hybrid composite. The LENS process allows the composite to be processed at near net shape, while allowing for tailoring of the material phases both chemically and structurally.

[0018] Broadly, metal matrix/hybrid composites are highly versatile engineering materials in which a metal is combined with one or more non-metallic phases to yield a novel material that has desired engineering properties.

[0019] Atomic ratio as used herein is defined as a ratio between the atomic weight percents of the given components.

Composition for Surface Engineering Applications

[0020] In one embodiment, the invention provides a monolithic hybrid composite consisting of a composite matrix, a reinforcement phase, and a solid/self-lubrication phase.
The composite matrix has properties of high fracture toughness (>50 MPa√m), high stiffness (>150 GPa elastic modulus), high yield strength (>150 MPa), high tensile strength (>400 MPa), and high melting point (>1000°C). Examples of the composite matrix include nickel, Ni, and/or titanium (Ti). The composite matrix consists of a pure metal or alloy, which, in general, exhibit high fracture toughness in comparison to intermetallics, ceramics and polymers.

The chemical bonding in this phase should be metallic and not intermetallic (mixed bonding between metallic and ionic/covalent), since ionic/covalent character can lead to brittleness. If additional metallic phases are added to the composite during the LENS process, they should have low chemical reactivity with other phases during solidification, since they may form unwanted chemically-alloyed phases. Thus, intermetallic bonding and high reactivity may result in unwanted chemical phases with detrimental properties.

The reinforcement phase has properties of high melting point (>1000°C), high stiffness (>300 GPa elastic modulus), high tensile strength (>500 MPa), and high hardness (>1000 HV, Vickers hardness number). Examples of the reinforcement phase include titanium carbide (TiC), TiN, and/or titanium nitride, TiN, titanium boride (TiB2), or any other refractory metal carbide, nitride, or boride. The ceramic reinforcement phase consists of a refractory metal carbide, nitride, or boride, which, in general, exhibit high hardness and high stiffness in comparison to metals, intermetallics, and polymers.

The chemical bonding in this phase, e.g. Titanium Carbide ("TiC") should be ionic/covalent mixture with mostly covalent bonding to promote high lattice energy. The chemical reactivity with other phases during solidification to form this compound, or others, should be high.

The self-lubrication phase has properties of high melting point (>1000°C), low steady-state sliding friction coefficient (<0.1) and low wear rates/factors (<10^-7 mm²/Nm) under a variety of loading conditions, low stiffness (<30 GPa elastic modulus along at least one crystallographic direction, which allows for easy mechanical shearing), and low hardness (<20 HV, Vickers hardness number). Examples of the solid/self-lubrication phase include graphite carbon, C, and/or molybdenum disulphide, MoS2. These phases are termed solid lubricants, which, in general, exhibit low friction, low wear, low elastic modulus, and low hardness.

The chemical bonding in this phase should be mixed between weak out-of-plane secondary bonding, like Van der Waals bonding that undergoes easy shear, and strong in-plane primary bonding, like covalent bonding. The chemical reactivity with other phases during solidification should be relatively high, since chemical phase formation with the base metal (Ti or Ni) will result in metal carbide formation, e.g. TiC. In addition, the self-lubricating phase, e.g. graphite ("C"), should not entirely transform into the TiC phase as to retain its self-lubricating properties.

The overall thickness of the composite should be about ±5 mm. The size of the primary graphite ("C") self-lubricating phase in the composite should be about ±1 μm, and the size of the Titanium Carbide ("TiC") reinforcement phase in the composite should be about ±0.5 μm.

The composition of the present invention exhibits a balance of high hardness, fracture toughness, and low friction/wear, and is suitable for many moving mechanical assembly applications including oil-drilling components such as wear bands, stabilizers, drill collars for tunnel boring, and land-based turbines and compressors.

In some embodiments, the raw materials include near spherical, pure Ni (40-150 μm diameter), pure Ti powder (40-150 μm diameter), and Ni-coated graphite powder (40-150 μm diameter) [Crucible Research]. The term near spherical powder refers to a mixed atomized particle that is near-spherical in shape. The purity of the Ni and Ti powders are >98.99.5% pure. In some embodiments, the ratio of Ti to C to Ni is 3 atomic % Ti, 20 atomic % C, and 77 atomic % Ni, referred to as Ni-3Ti-20C. FIG. 1 shows a ternary phase diagram of the Ni, Ti and C phases. Compositions A and B shown on the phase diagram are atomic ratios Ni-10Ti-10C and Ni-3Ti-20C, respectively. The acceptable ranges (in atomic weight percent) for Ni, Ti and C are from 73 to 82, 3 to 5, and 15 to 20, respectively.

Method of Fabricating a Monolithic Composite

In certain embodiments, the present invention provides a method for fabricating a monolithic hybrid composite comprising the step of: blending elemental Ni powder and titanium ("Ti") powder together with nickel-coated graphite powder. In some embodiments, the hybrid monolithic composite is fabricated using pure spherical Ni (40-150 μm), pure Ti (40-150 μm), and Ni-coated graphite powder (about 40-150 μm in diameter).

In one embodiment, the method of the present invention comprises blending Ni and Ti powders with Ni-coated graphite powder. In this embodiment, the components may be in a ratio of 3 atomic % Ti, 20 atomic % C, and 77 atomic % Ni (Ni-3Ti-20C), shown in FIG. 1. The acceptable range, in atomic ratio, of self-lubrication phase ("C") to reinforcement phase ("TiC") is about 3 to 4.

In certain embodiments, monolithic hybrid composites are laser processed via Laser Engineered Net Shaping ("LENS"). These monolithic hybrid composites may be comprised of non-metallic titanium carbide ("TiC") and graphite ("C") reinforcements in a metallic nickel ("Ni") matrix.

In one embodiment, the monolithic hybrid composite of the invention is fabricated using a LENS process, wherein the monolithic hybrid composite is fabricated based on direct laser deposition. Similar to rapid prototyping technologies such as stereolithography, the LENS process begins with a computer-aided design (CAD) design file of a three-dimensional component, which is sliced into series of layers electronically. The LENS system uses nozzles which direct a stream of metal powder at a moveable central point while a high powered laser beam heats that point. The substrate is continuously moved, guided by the data from the CAD model, and layer-by-layer the nozzles and laser work together to build up the three-dimensional part. The detailed mechanism of this process has been reported in references [1-3].

In one embodiment, a nickel plate substrate was used for depositing the Ni-Ti-C composites with atomic ratios shown in FIG. 1. A high powered 500 W Nd:YAG laser, emitting near-infrared laser radiation at a wavelength of 1.064 μm, is focused on the substrate to create a melt pool into which the powder feedstock is delivered through an inert gas flowing through a multi-nozzle assembly. The nozzle is designed such that the powder streams converge at the same point on the focused laser beam. Subsequently the substrate is moved relative to the laser beam on a computer-controlled stage to deposit thin layers of controlled width and thickness. The scan speed of the Nd:YAG laser was about 10 inches/min.
and the hatch width used for the deposition was about 0.018 inch with about 0.01 inch of layer thickness.

The LENS process produces near-net shaped components that do not necessarily require secondary rough machining. Moreover, the LENS process is an industrial scale tool, which works automatically and without constant supervision. Furthermore, LENS parts exhibit close to theoretical bulk density, and have excellent as-fabricated mechanical and tribological (friction and wear) properties.

In some embodiments, the LENS process can be used to apply a surface layer of the hybrid monolithic composite of the present invention to a pre-existing component. In some embodiments, the LENS process can be used to fabricate a near net shape functionally and compositionally-graded component wherein the surface composition has the combined high hardness, fracture toughness, and excellent solid/self-lubrication.

Example 1

Based on the x-ray diffraction structural analysis of the Ni-3Ti-20C atomic ratio composite shown in Fig. 2, the structural phases were determined to be nickel (face-centered cubic crystal structure), titanium carbide (rocksalt crystal structure), and carbon (graphite allotrope). Fig. 3 is an Auger electron spectroscopy chemical map of the unworn Ni-3Ti-20C composite that shows a typical surface distribution of the Ni, TiC and C chemical phases. These chemical phases are in agreement and complement the x-ray diffraction determined structural phases.

The effect of the C/Ti atomic ratio of the powder mixtures shown in Fig. 1 was found to have a dominant influence on the microstructure, microhardness, and tribological properties of the composites. Evolution of monolithic hybrid composites revealed that the volume fraction of the primary titanium carbides (TiC), which form during solidification, versus primary graphite ("C"), changes substantially as a function of the C/Ti ratio. The presence of primary graphitic carbon enhanced the solid/self-lubricating behavior of these composites resulting in an optimum combination of hardness and lubricity while still maintaining the high fracture toughness inherent to the Ni matrix, which is desirable for many surface engineering applications.

To achieve this balance, a composite powder was produced with a composition of 3 atomic % Ti, 20 atomic % C, and 77 atomic % Ni, the Ni-3Ti-20C composite shown in Fig. 1. Fig. 4 shows the improvement in friction coefficient and wear rate/factors of the Ni-3Ti-20C composite in comparison to the Ni-10Ti-10C composite and baseline LENS deposited pure Ni. The sliding wear behavior is evaluated with a pin-on-disk tribometer. The higher C/Ti atomic ratio of the Ni-3Ti-20C composite resulted in significantly lower steady-state friction coefficient (0.12) and wear factor (6.8 x 10^{-7} mm³/Nm) than the Ni-10Ti-10C composite and pure Ni. The corresponding Vickers hardness numbers are 165, 240 and 370 for pure Ni, Ni-3Ti-20C, and Ni-10Ti-10C composite, respectively. While the Ni-10Ti-10C composite has the highest mechanical hardness due to increased amount of TiC phase, the Ni-3Ti-20C composite still retains respectable hardness due to some TiC phase. Thus, the acceptable range C/Ti atomic ratio of self-lubrication phase ("C") to reinforcement phase ("TiC") is about 7 to 4.

The novelty of this Ni-3Ti-20C composite is that it exhibits solid/self-lubricating behavior, forming an in situ, low interfacial shear strength, disordered carbon film during sliding, resulting in a decrease in friction coefficient and wear factor compared to a Ni-10Ti-10C composite (high hardness only) and pure Ni (high fracture toughness only). These chemistry and microstructural phases were examined with advancedelectron microscopy and chemical spectroscopy techniques. Fig. 5 shows an Auger electron spectroscopy chemical map of the worn Ni-3Ti-20C composite. The formation of an in situ, low interfacial shear strength carbon film was confirmed inside the wear track. Fig. 6 shows the complementary subplanar (subsurface) focused ion beam cross-section inside the worn surface. This scanning electron microscopy structural image shows that the sheared primary graphite is led to the surface during the wear process. This microstructural evolution during wear proves the solid/self-lubrication mechanism of the composite. Zone I labeled in Fig. 6 shows that the Ni grains also exhibit strain-induced grain refinement (smaller grains) due to the tribological shearing process. Zone I transitions into the undeformed (non-sheared) Ni, TiC and C phase region.

The LENS deposited titanium carbide/graphite nickel hybrid composite can be processed in near-net shape for direct use in a wide array of engineering operational parts, e.g., oil-drilling components (wear band, stabilizer, and drill collar). LENS has applicability in an industrial setting. It is also a low cost, low maintenance fabrication process. Relatively large shapes/parts (up to cubic foot) can be fabricated with LENS.

REFERENCES CITED

The following references, to the extent that they provide exemplary procedural or other details supplementary to those set forth herein, are specifically incorporated herein by reference.


What is claimed:

1. A monolithic hybrid composite comprising:
   a. a composite matrix;
   b. a reinforcement phase;
   c. a solid/self-lubrication phase.

2. The monolithic hybrid composite of claim 1, wherein the composite matrix is a nickel matrix.

3. The monolithic hybrid composite of claim 2, wherein the nickel matrix is processed using pure nickel powder having a diameter of between about 40-150 μm.

4. The monolithic hybrid composite of claim 1, wherein the solid/self-lubrication phase is graphitic carbon.

5. The monolithic hybrid composite of claim 4, wherein the graphitic carbon is processed using nickel-coated graphite powder having a diameter of between about 40-150 μm.

6. The monolithic hybrid composite of claim 1, wherein the reinforcement phase is titanium carbide.

7. The monolithic hybrid composite of claim 6, wherein the titanium carbide is formed by reacting the pure titanium powder, having a diameter of between about 40-150 μm, with the graphitic carbon powder during the process.
8. The monolithic hybrid composite of claim 1, wherein the ratio of the self-lubrication phase to the reinforcement phase, in atomic ratio, is about 7 to 4.

9. A method of fabricating a monolithic hybrid composite, comprising the step of:
   blending elemental nickel powder and titanium powder together with nickel-coated graphite powder.

10. The method of claim 9, wherein the atomic percent ratio of nickel:titanium:nickel-coated graphite powders are approximately 77:5:20, or Ni-3Ti-20C.

11. The monolithic hybrid composite of claim 10 exhibits optimum fracture toughness, hardness, and solid/self-lubricating properties.