Studies on the Preparation of Nb-Al System Metal Matrix Composites by Mechanical Alloying and Spark Plasma Sintering Method

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学位論文題目	Studies on the Preparation of Nb-Al System Metal Matrix Composites by Mechanical Alloying and Spark Plasma Sintering Method (MA-SPS 法による Nb-Al 系焼結複合材料の作製と特性評価に関する研究)
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Chapter 1: Introduction

Structural materials are generally strong and able to support or withhold the desired load. However there exist micro-cracks and pores whereby stresses are concentrated. Upon shock loading or fatigue, the stress at the pores exceeds the critical value forming cracks that propagates until fracture occurs and fails the material. A concept of crack propagation resistant intelligent material to avoid brittle fracture in case of shock loading or fatigue by channelling the heat energy produced from the stress of crack propagation into forming a new hard material is being focused. There exist promising candidates such as hard intermetallics phase that can act as resistant to the crack propagation. Some good examples are NbAl intermetallics, which have high yield stress with high melting temperature. However, these intermetallics are not being utilized as structural material due to their brittleness and poor workability.

The crack propagation resistant intelligent material promises a new structural material, which have its potential needs or applications in various fields. They include fields such as the nuclear power plants, aircraft structures, space structures, anti heat leak, etc. In this research, the application of crack propagation resistant intelligent material is focused on developing an effective shield against space debris.

Unnecessary artificial object in the outer space called space debris has been accumulating. They consists of all artificial objects orbiting our earth such as decommissioned satellites, spent upper stages, and mission related objects, launch adapters, lens covers, paint flakes, etc. There is about 8000 known space debris[1,2] and increasing each year.

Space debris can be divided into three types. Large objects larger than 10cm in diameter, which are routinely detected, tracked and catalogued. Objects between 1 and 10cm are the risk objects as they cannot be tracked and catalogued. Objects smaller than 1cm in diameter are referred as small debris or micro debris[1,3,4].

Current Anti-debris Shield

Most of the shield are based on Whipple shield (although some variation exists), whereby the principle is to add protective bumper shields in front of the major pressure wall so that hypervelocity incoming debris melts at the shield impact with the sacrificial bumper[3,5,6,7]. The impacting mass is distributed into a larger area and the multiple collisions with the main wall stop the space debris.

However, this system has its disadvantages. The Whipple shield is space consuming, bulky and has a heavy overall shield weight. Moreover, due to the variety of spacecrafts, structures and subsystems such as observed in the International Space Station; this shield couldn't possibly cover the whole fuselage. This increases the possibility of being hit with undetectable space debris (<10 cm) that can cause critical damage.

A new concept is introduced for anti space debris structural material. As per Fig. 1, upon collision of the space debris with the metal mixture, the space debris is fragmented and vaporized instantaneously[8]. The hypervelocity collision generates very high heat energy with high temperature as the kinetic energy of the space debris is transformed into heat energy. This local high heat energy turns the metal mixture into intermetallics instantaneously at the local part hit[9,10,11,12,13]. The intermetallics formed have high yield stress, which blocks, deflects and halts the crack propagation from penetrating deep into the material. In order for the crack to propagate, the stress at the edge of the crack has to overcome a critical value, but this critical value is increased with the formation of intermetallics instantaneously. As such, the crack propagation is stopped because it cannot overcome the critical value and this protects the material from fracture or failure.

Analytical simulation of hypervelocity impact done by Kambe[14] with Al34%-Ni33%-Ti33% composite showed that the hypervelocity collision had enough energy to simulate the growth of intermetallics.

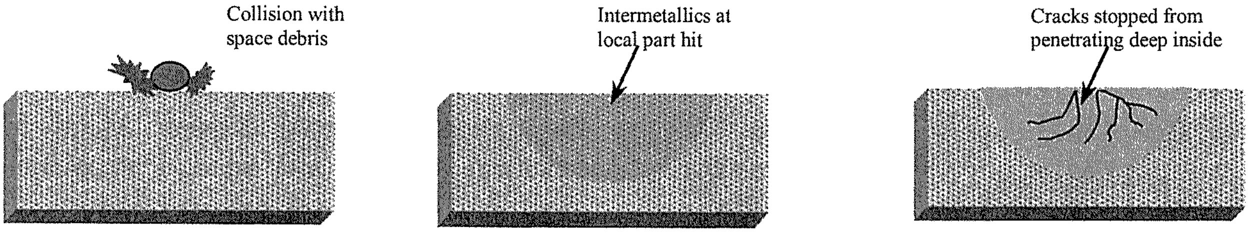

Figure 1: Concept of new shield.

Qualities of New Shield

This new anti-debris shield should be structural material used for fuselage. The structural material should be ductile with qualities such as lightweight, high strength, high workability, and high toughness.

Before collision with the space debris, the material should be in intermetallics-free condition. Intermetallics-free condition before collision is essential because as discussed previously in shield's concept, intermetallics are being pursued upon collision. The material then should be able to produce intermetallics instantaneously upon space debris attack. In addition to that, intermetallics-free condition is advantageous as high workability of the material is anticipated.

Other qualities are that it should also have microstructure of fine (sub-micron) second metal phase dispersion in the matrix, which should be in intermetallics-free condition. The fine dispersion of second metal in the matrix is vital because of two reasons. As instantaneous reaction between the metals is required, the diffusion distance between the metals should be sufficiently short. The second metal phase should be minutely (nanostructured) dispersed in the matrix. When the diffusion distance between the metal phases is decreased, the activation energy is reduced. This can be proved using Arrhenius equation of $t = C\exp\left(\frac{-Q}{RT}\right)$. Whereby, t is particle size, C is rate constant, Q is activation energy, R is molar gas constant and T is temperature. With finer microstructure, less activation energy is needed[15,16,17,18,19].

The second reason, is that fine sub-micron sized dispersion in the matrix increases the material strength. When solute atom is mixed in the solid state of solvent or the matrix, stress field are created around each solute atom. Stress field interact with dislocations (crystal lattice distortion) and make their movement more difficult and thus the mixture becomes stronger. These fine sub-micron dispersion acts as barriers to dislocation movement. The dislocation is forced to either cut through the dispersion or go around them which requires more energy and this causes the increase in material strength[20,21,22].

Material system Selection

In this research, Al is chosen as the matrix because Al alloys exhibits the traits needed for the fuselage material. High strength aluminium alloys are widely used in high-performance automobiles, railway cars, aircraft and spacecraft, light ships, etc. This is mainly due to excellent mechanical strength, low specific weight and good formability with relatively low cost. Al based alloys such as Al-2024 and Al-7075[23] are widely used for aerospace applications. This is because these alloys have the ability to maintain long fatigue strength at finite life and environmental temperatures. The other advantages include lightweight, corrosion resistance, non-toxic, high workability and ductility.

For the dispersion material, considering high fusion point metal aluminates, V, Nb, Mo, W, Ni systems can be potential candidates. Combination in example Al-Ti, Al-Nb, and Al-Ni, which are being widely researched are potential candidates. The combination of Al-Ti composite can produce intermetallics of Al_3Ti with a melting temperature of less than 1400°C. However, since Nb has superior thermal quality with melting temperature at 2469°C and high strength, plus the fact that Al-Nb composite have a much higher melting temperature than other combinations, Nb is chosen in this research. By combining, the merits of the two metal a MMC that have the mechanical and physical properties needed for the structural material can be formed. This combination of MMC can form intermetallics of $NbAl_3$, Nb_3Al, Nb_2Al which have high melting temperatures of 1680±5°C, 1940±10°C and 2060±10°C respectively. $NbAl_3$ with a melting point of 1680±5°C is targeted as from molecular weight calculation, $NbAl_3$ is the lightest compared to Nb_3Al and Nb_2Al. Due to this reason, Al-30vol.%Nb of mixture is utilized in order to promote and target the formation of $NbAl_3$ intermetallics upon collision with space debris.

The objective of this research is to prepare a structural material for fuselage that has fine dispersion of sub-micron sized Nb phase in Al matrix microstructure with intermetallics-free condition through MA and SPS method which is able to produce intermetallics phase instantaneously upon collision with space debris.

Chapter 2

The purpose of this chapter is to produce intermetallics-free powders with fine sub-micron Nb dispersion distributed in Al matrix. In order to achieve this, Nb-Al mechanical alloying (MA) is carried out until it reaches the steady state right before the formation of intermetallics using agate and zirconia media respectively. MA method is being utilized to target the production of intermetallics-free critical MA powders with fine sub-micron Nb dispersion in Al matrix.

Results and Conclusion

Even without NbH, zirconia media is unusable because it produces hollow structure with coarse microstructure. With agate media, NbH formation is observed, however, optimum MA condition is defined. The agate critical MA powder milled at 200rpm for 132hours produced fine sub-micron sized Nb and nano-sized NbH dispersion in Al matrix with an intermetallics-free condition as shown in Fig. 2. Moisture trapped in the micro pores of agate media caused the formation of NbH in the agate media and enhanced the MA mechanism to become brittle-ductile which caused nano-sized dispersion. The formation of NbH also suppressed the intermetallics formation up to the dehydrogenation point. This powder is confirmed to have intelligent properties or $NbAl_3$ intermetallics produced at a temperature above 300°C. This is followed by dehydrogenation at 500°C, which enhances more formation of $NbAl_3$. This critical MA powder is utilized as the starting material in the consolidation part.

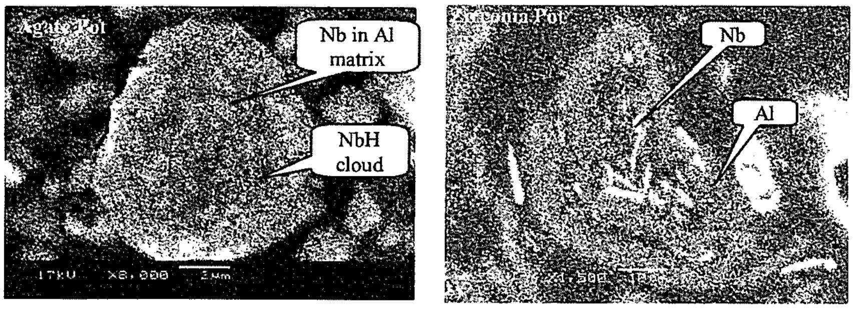

Figure 2: Optimum MA powder using agate and zirconia media.

Chapter 3

The purpose of spark plasma sintering is to achieve densification of optimum MA powders of 200rpm 132 hours. The targeted densified compact is a sintered compact in intermetallics-free condition with the microstructure of fine micron sized Nb and nanostructured NbH dispersion in Al matrix produced at powder level being retained.

Results and Conclusion

Consolidation were achieved with Spark Plasma Sintering. MA powder of 200rpm 132hours were densified up to 96.2% (at the centre part with a diameter of 2mm) with a sintering conditions of 1.5GPa, 280°C which retains the microstructure of fine sub-micron Nb and nano-sized NbH dispersion in Al matrix with intermetallics-free condition.

Relative density of sintered compacts decreases with increase in sintering temperature. The formation of 60.4% of $NbAl_3$ intermetallics causes the relative density to decrease down to 86.1 %. This is because the hard $NbAl_3$ formation hinders the plastic flow and plastic deformation of the MA powder that prevents the densification of the MA powders.

Chapter 4

In chapter 4, the mechanical properties and collision simulation is carried out.

Vickers Hardness

The compositional change with sintering temperature reveals the mechanism of $NbAl_3$ intermetallics formation. The stable NbH suppresses the formation of $NbAl_3$ intermetallics until it is dehydrogenated. Upon dehydrogenation, it is followed by the formation of $NbAl_3$ intermetallics. This increase in $NbAl_3$ intermetallics plays an important role in increasing the Vickers hardness of the sintered samples. The high Vickers hardness of the sintered sample at 280°C compared to pure starting powders is caused by the nanostructured NbH dispersion in the Al matrix. At 400°C, the Vickers hardness increased slightly due to the formation of some nanostructured $NbAl_3$ intermetallics. The huge increase of Vickers hardness at 500°C is caused by the formation of 60.4% of $NbAl_3$ intermetallics dispersed in the Al matrix. The fine dispersion in the matrix, which acts as barrier to dislocation movements is probably the cause that increases the Vickers hardness.

Fracture Toughness

Even though the fracture was brittle, the intermetallics-free sintered compact of 280°C 1.5GPa had a fracture stress of 530.27MPa, which is comparable to Al alloys used for aerospace applications such as Al-2024 and Al-7075.

Space Debris Collision Simulation

$NbAl_3$ formation is observed in intermetallics-free sintered sample irradiated with laser simulating the space debris collision. The intermetallics-free sintered compacts are able to transfer itself into intermetallics instantaneously upon collision with space debris.

Conclusion

A structural material for fuselage consisting of Nb-Al system that has fine dispersion of sub-micron sized Nb phase in Al matrix microstructure with intermetallics-free condition were successfully produced using MA and SPS method. It revealed intelligent properties (was able formed intermetallics phase instantaneously) upon irradiation with fibber laser simulating space debris collision. However, the ductility needs further improvement. A balance between formation of NbH and ductility has to be researched. Hypervelocity impact test also have to be carried out upon availability of bigger samples, which will rule out any other hidden factors or parameters not exerted by the laser simulation.

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論文審査結果の要旨

最近インテリジェント材料の研究が盛んに行われ、各種機能を有する材料が提案されているが、中でもき裂進展抑止型インテリジェント材料は宇宙構造用材料や原子炉構造用材料の信頼性を高める上で注目されている。現在地球周回軌道上では微小なデブリの量が増加し、それらの衝突による宇宙船への致命的損傷が懸念されており、これに対応できる機能性材料の研究が必要になっている。本論文は耐スペースデブリ用のき裂進展抑止型インテリジェント材料に関する研究であり、機体構造用のアルミニウム基複合材料であるが、微小な高速飛翔体が衝突したときに局所的な熱エネルギーによって極短時間に高融点高強度な金属間化合物に反応変化することにより局所的強化や材料内部へのき裂進展を抑え、損傷を最小限にくいとめるような機能を造り込むことを目的としている。

第１章は、序論であり論文の背景および目的を述べている。

第２章では、サブミクロンサイズの微細なNbがAlマトリックスに分散した複合粉末をメカニカルアロイング法で作製する方法を述べている。メカニカルアロイング法は一般に微細混合の後合金化する目的で用いられるが、この研究では合金化がおこる臨界MA条件を明らかにし、これにより合金化が生じる直前に止める、すなわち$NbAl_3$が生じない超微細混合組織の粉末が作製できることを示している。水素化ニオブ（NbH）を生成することでより微細な混合が可能となり、ナノサイズのNbHが分散した組織が得られた。DSCにより$NbAl_3$の生成が約３００℃、NbHの分解温度が約５００℃であることを明らかにし、外部からの熱エネルギーの注入により容易に反応し金属間化合物になること、すなわちインテリジェント性を有することを示した。

第３章では、臨界MA条件直前、すなわち$NbAl_3$の生成をおさえて作製した微細混合粉末を放電プラズマ焼結によりそのままの組織状態で焼結固化する方法を述べている。$NbAl_3$の生成無しに固化するには３００℃以下で緻密化することが必要で、そのためには1.5GPaの超高圧負荷焼結が必要であることを示した。この条件では相対密度は９６％となり、微細混合粉末の組織が維持されることを明らかにした。

第４章では、微細組織のNb/Al複合焼結体の機械的性質およびデブリの衝突模擬試験を行った結果について述べている。破壊強度は530Mpaであり、従来使用されているアルミニウム合金の破壊強度と同程度である。しかし、延性は乏しく脆性的な破壊であることから今後じん性の改善は必要である。本研究ではデブリの衝突を外部からの熱エネルギーの入射に置き換えて模擬し、実験を行っている。その結果、マイクロ秒のオーダーで$NbAl_3$の生成が確認され、最終的には高速衝突試験は必要ではあるが、インテリジェント性の発現の可能性が示されたと考えられる。

第５章は本研究をまとめた総括である。

以上要するにようするに本論文は、サブミクロンサイズの微細なNbがAlマトリックスに分散した複合粉末をメカニカルアロイング法で作製するとともに放電プラズマ焼結によりそのままの組織状態で焼結固化する方法を明らかにし、その機能性を評価することによりき裂進展抑止型インテリジェント材料への可能性を示したもので基礎的研究ばかりでなく工学的応用についても言及しており、材料加工プロセス学の発展に寄与することが少なくない。

よって、本論文は（工学）の学位論文として合格と認める。