Towards a High Strength Ductile Ni/Ni3Al/Ni Multilayer Composite using Spark Plasma Sintering

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Abstract:
This paper is an attempt to develop an innovative high strength and ductile Ni/Ni3Al/Ni multilayer composite, using spark plasma sintering (SPS). Ni3Al powders were first synthesized by mechanical alloying of elemental pure Ni and Al powders. The synthesized intermetallic powders were then mixed with Ni powders in a way that a Ni/Ni3Al/Ni multilayer composite can be achieved. Scanning electron microscope, optical microscope, energy dispersive X-ray spectroscopy (EDS), microhardness, and shear punch tests were used to characterize microstructure and mechanical properties of the synthesized composite. Results show that a rather sharp interface with a perfect metallurgical bonding has formed at the Ni/Ni3Al joint. The synthesized multilayer composite has a perfect combination of strength and ductility. The maximum shear strength of Ni/Ni3Al/Ni multi-layer composite is significantly higher than that of Ni3Al, while its ductility is comparable to that of pure Ni.

Keywords: Composite; Spark plasma sintering; Ni3Al intermetallic.

1. Introduction

The well-known Ni3Al intermetallic alloy is widely used for high-temperature applications, due to its attractive properties such as high strength and good oxidation resistance at elevated temperatures.

However, this intermetallic is in nature very brittle, making it a difficult option when it comes to forming-based manufacturing techniques. Improving the ductility of Ni3Al alloys is indeed a topic of interest for many research groups [1]. Current strategies in improving ductility of Ni3Al alloys, including changes in the chemistry of the alloy and modifying processing parameters, have reached their limits. Any improvement, using these strategies, will therefore be marginal. An alternative approach would be making a composite from Ni3Al and an alloy which has a higher ductility. Nickel, for instance, is an optimum candidate given that it has comparatively much higher ductility [2, 3]. A variety of different techniques, including magnetron sputtering techniques and electron beam physical vapor deposition (EB-PVD), have been used to synthesize Ni/Ni3Al multi-layer composites [3-5]. However, most of these methodologies are based on synthesizing multi-layer thin films. To our knowledge there is no report on synthesizing bulk Ni/Ni3Al multi-layer composite.

Spark plasma sintering (SPS) is a sintering method in the presence of a direct high energy electric pulse under uniaxial pressure. SPS is known to be a fast powder consolidation technique, currently widely used in production of high dense bulk materials [6].

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Comparatively significantly lower sintering time, associated with this technique, makes this methodology an ideal option when it comes to controlling microstructure during sintering. Short holding and fast heating rate will obviously result in minimal grain growth during sintering and superior properties [6-11]. Some attempts have been made to go beyond sintering in SPS and try to do parallel welding/sintering during high temperature consolidation [7]. Examples are ZrB2-SiC [12], β-SiC [13], C/SiC composites [14] and SiC-graphite [15], dissimilar metals joining (Aluminum to stainless steel) [16], metal/glass joining [17], and Al2O3–ZrO2 [18]. Dong et al. [8] used SPS as a welding methodology to fabricate TiNi5/Al composite. They postulated that there are three welding processes that take place between powders during SPS; micro-arc welding, electrical resistance welding, and diffusion welding.

This study is an attempt to produce an innovative high strength ductile Ni/Ni3Al/Ni hybrid composite, using SPS. This could be the beginning of a new generation of ultra-strong ductile Ni3Al-based composites.

2. Materials and Experimental Procedures

Fig. 1. Schematic diagram of the SPS process for the triple layer Ni/Ni3Al/Ni composite.

Ni (99.9 % purity, 3 µm average size) and Al (99.9 % purity, 22 µm average size) powders were used as initial materials to synthesize Ni3Al alloy, via mechanical alloying method. Mechanical alloying was conducted with ball to powder ratio 10:1 in a steel vial with a rotation speed of 350 rpm under Ar atmosphere. X-Ray diffraction (XRD) method was used to confirm the formation of Ni3Al compound during milling. Synthesized Ni3Al powders were used to produce a composite of triple layers in SPS with two layers of Ni at the bottom and the top and a layer of Ni3Al in the middle, with each layer having thickness of 0.4 mm. SPS was conducted in a 15 mm die under uniaxial pressure 50 MPa and heating/cooling rates of 100 °C/min. To perform sintering samples were held at 970 °C for 10 minutes. Figure 1 shows schematic representation of SPS set-up. Scanning electron microscope (SEM, Philips), energy dispersive X-ray spectroscopy (EDS), optical microscope (OM), Vickers micro-hardness test (0.1 Kg force), and shear punch test (with the punch diameter 3 mm and a rate of 0.1 m/s) were used to characterize the synthesized composite. Shear strength in the shear punch test can be calculated by using applied load (P) and shear area (A) as following equation [19], where d is punch diameter and t is thickness of sample (see Figure 2):
\[ \tau = \frac{P}{A} = \frac{P}{(\pi d)\ell} \]  

Shear punch is not a real standard testing method. The data, obtained from shear punch in this investigation is more used to compare mechanical properties of materials.

![Schematics of shear punch test.](image)

**Fig. 2.** Schematics of shear punch test.

### 3. Results and Discussion

#### 3.1. Synthesis of Ni$_3$Al compound

XRD results, depicted in Fig. 3a, shows that Ni$_3$Al has been formed after 30 h of milling. In order to make sure that the compound is homogeneous, milling was further done up to 40 h. Figure 3b is an example of a Ni$_3$Al particle, after 40 h of milling, showing that synthesized particles are rather rounded with almost no sharp corners. Figs 3c and 3d show elemental mapping of Ni and Al elements in the shown particle, confirming that mechanical alloying has resulted in a perfectly homogeneous distribution of alloying elements in the matrix.

Fig. 4 shows optical microscope and SEM images of the Ni-Ni$_3$Al-Ni triple layer hybrid composite, made by SPS. As it is seen a uniform interface is formed between layers on both sides of the middle Ni$_3$Al layer. In fact, two dissimilar materials, consisting of metal and intermetallic, are clearly perfectly joined with a rather smooth interface without any noticeable macro/micro defects, porosities, interface cracks/delamination, or any other irregularity. As well, there is no indication of existence of any interlayer between metal and intermetallic layers.

Fig. 5 shows EDS line scanning analysis, representing the variation of chemical composition across the interface. To some extent, there is an interdiffusion of aluminum towards the Ni side. However, the change in the chemical composition at the interface Ni/Ni$_3$Al is rather sharp, inferring that no new phase is formed at the interface. The perfect metallurgical bonding, observed at the interface, is obviously due to the diffusion bonding [8].
Fig. 3. Results of mechanical alloying, showing a) XRD spectra of Ni and Al elemental powders with milling time, b) a rounded Ni$_3$Al particle after 40 h of milling, c) elemental mapping of Ni, and, d) elemental mapping of Al.

Fig. 4. a) Optical and b) SEM images of the Ni-Ni$_3$Al-Ni triple layer composites joined by SPS method.
3.2. Mechanical properties

Microhardness test was conducted across the interface. Results are shown in Figure 6a. The hardness varies from 220 HV for nickel layer to almost 600 HV for Ni₃Al layer. Interestingly, the hardness transition at the interface is rather smooth, which possibly has to do with the interdiffusion of aluminum at the interface. This smooth hardness transition has obviously positive implications for the integrity of the joint. Fig. 6b shows the shear strength vs. displacement for the Ni/Ni₃Al/Ni composite. Results for pure Ni₃Al and pure Ni are shown as well for the sake of comparison. Interestingly, Ni/Ni₃Al/Ni composite has a remarkably better ductility and maximum shear strength. It appears that this composite offers a perfect combination of shear strength up to 500 MPa and ductility.

Fig. 6. Mechanical properties of Ni/Ni₃Al/Ni composite; a) variation of microhardness across the interface and b) shear strength vs. displacement.

Fig. 7 is an interesting example of crack growth in Ni/Ni₃Al/Ni composite. In this case, it appears that the crack has been deviated from its original propagation path and is
slightly propagated alongside the interface. Further away the crack is stop at the Ni matrix. One can conclude that Ni/Ni₃Al interface acts as a barrier against crack propagation.

Fig. 7. Crack at the Ni/Ni₃Al interface.

Fig. 8 shows SEM images of the fracture surface of the composite at the interface. Remarkable adhesion between two layers and lack of decohesion or debonding at the interface is noticeable, which has to do with the fact that crystal structure of Ni and Ni₃Al are similar and that diffusion bonding takes place at the interface. There is a clear transition of fracture mode from ductile fracture in Ni side to brittle fracture in Ni₃Al side. The former is characterized with large deformation and formation of dimples, whereas the latter exhibits a minimum of plastic deformation prior to fracture.

Fig. 8. Fracture surface at a) interface, b) at Ni side, and c) at Ni₃Al side.

4. Conclusion

An innovative high strength ductile Ni/Ni₃Al/Ni composite was synthesized using spark plasma sintering. Nanocrystalline Ni₃Al powders were first synthesized by mechanical alloying of Ni and Al powders. Synthesized Ni₃Al powders and Ni powders were then put in a
graphite die in succession and sintered, to achieve a Ni/Ni$_3$Al/Ni multi-layer composite. Following conclusions can be drawn:

- Mechanical alloying of Ni and Al elemental powders after 30 h results in the formation of nanocrystalline Ni$_3$Al compound.
- Spark plasma sintering can be used as a promising method for producing layered composites. A rather sharp interface, with almost no remarkable porosities and defects (i.e. interface decohesion or interface cracking) can be achieved using this technique.
- The Ni$_3$Al/Ni interface showed a perfect adhesion, such a way even after a large deformation, layers of composite do not separate. This sharp interface acts as a barrier against crack propagation. Results showed that when crack tip reaches the interface, it deviates from its original propagation path and will soon stop at the Ni matrix.
- Results of fractography showed a large deformation and ductile fracture at the Ni side, whereas the Ni$_3$Al side exhibits a brittle fracture.
- A significant improvement of mechanical properties is observed in the developed composite. The maximum shear strength of Ni/Ni$_3$Al/Ni multi-layer composite is significantly higher than that of Ni$_3$Al, while its ductility is comparable to that of pure Ni.

5. References

1. Heathcote, J., Odette, G.R., Lucas, G.E., Rowe, R.G., Skelly, D.W., On the micromechanics of low temperature strength and toughness of intermetallic/metallic microlaminate composites, Acta Mater. 44 (11) (1996), pp. 4289-4299.
2. Mohammadnejad, A., Bahrami, A., Sajjadi, M., Karimi, P., Fozveh, H.R., Yazdan Mehr, M., Microstructure and Mechanical Properties of Spark Plasma Sintered Nanocrystalline Ni$_3$Al-xB (0.0< x< 1.5 at%) Alloy, Mater. Today Communications 17 (2018), pp. 161-168.
3. Yang, X., Peng, X. and Wang, F., Size effect of Al particles on the structure and oxidation of Ni/Ni$_3$Al composites transformed from electrodeposited Ni–Al films. Scripta Mater., 56 (6) (2007), pp. 509-512.
4. Meng, X.K., Shen, H., Vehoff, H., Mathur, S. and Ngan, A.H.W., Fractography, elastic modulus and oxidation resistance of novel metal-intermetallic Ni/Ni$_3$Al multilayer films, J. Mater. Research, 17 (4) (2002), p. 790-796.
5. Li, Y., Zhao, J., Zeng, G., Guan, C. and He, X., Ni/Ni$_3$Al microlaminate composite produced by EB-PVD and the mechanical properties. Materials Letters, 58 (10) (2004), pp. 1629-1633.
6. Krishnan, V.K., Sinnaeruvadi, K., Synthesis of Vanadium-Vanadium Carbide in-situ Nanocomposites by High Energy Ball Milling and Spark Plasma Sintering. Science of Sintering, 48 (2016), pp. 325-332.
7. Yang, J., Trapp, J., Guo, Q. and Kieback, B., Joining of 316L stainless steel by using spark plasma sintering method. Mater. & Design (1980-2015), 52 (2013), pp. 179-189.
8. Dong, P., Wang, Z., Wang, W., Chen, S. and Zhou, J., Understanding the spark plasma sintering from the view of materials joining. Scripta Mater., 123 (2016), pp. 118-121.
9. Mansourirad, N., Ardestani, M., Afshar, M.R., Synthesis and Characterization of Ag-8 %wt Cr$_2$O$_3$ Composites Prepared by Different Densification Processes. Science of Sintering, 50 (2018), pp. 323-335.
10. Terzić, A., Obradović, N., Pouchly, V., Stojanović, J., Maca, K., Pavlović, V.B., Microstructure and Phase Composition of Steatite Ceramics Sintered by Traditional and Spark Plasma Sintering. Science of Sintering, 50 (2018), pp. 299-312.
11. Liu, L., Ye, F., Zhou, Y., Zhang, Z. and Hou, Q., Fast bonding α-SiAlON ceramics by spark plasma sintering. Journal of the European Ceramic Society, 30 (12) (2010), pp. 2683-2689.
12. Pinc, W.R., Di Prima, M., Walker, L.S., Wing, Z.N. and Corral, E.L., Spark plasma joining of ZrB2–SiC composites using zirconium–boron reactive filler layers. J. American Ceramic Society, 94 (11) (2011), pp. 3825-3832.
13. Grasso, S., Tatarko, P., Rizzo, S., Porwal, H., Hu, C., Katoh, Y., Salvo, M., Reece, M.J. and Ferraris, M., Joining of β-SiC by spark plasma sintering. J. European Ceramic Society, 34 (7) (2014), pp. 1681-1686.
14. Rizzo, S., Grasso, S., Salvo, M., Casalegno, V., Reece, M.J. and Ferraris, M., Joining of C/SiC composites by spark plasma sintering technique. J. European Ceramic Society, 34 (4) (2014), pp. 903-913.
15. Okuni, T., Miyamoto, Y., Abe, H. and Naito, M., Joining of silicon carbide and graphite by spark plasma sintering. Ceramics Int., 40 (1) (2014), pp. 1359-1363.
16. Matsugi, K., Wang, Y., Hatayama, T., Yanagisawa, O. and Syakagohri, K., Application of electric discharge process in joining aluminum and stainless steel sheets. J. Mater. Proc. Tech., 135 (1) (2003), pp. 75-82.
17. Liu, C.R., Zhao, J.F., Lu, X.Y., Meng, Q.S., Zhao, Y.P. and Munir, Z.A., Field-assisted diffusion bonding and bond characterization of glass to aluminum. J. Mater. Science, 43 (15) (2008), pp. 5076-5082.
18. Bermejo, R., Torres, Y., Sanchez-Herencia, A.J., Baudin, C., Anglada, M. and Llanes, L., Fracture behaviour of an Al2O3–ZrO2 multi-layered ceramic with residual stresses due to phase transformations. Fatigue & Fracture of Eng. Mater. & Structures, 29 (1) (2006), pp. 71-78.
19. Bao, Y.W., Chen, J.X., Wang, X.H. and Zhou, Y.C., Shear strength and shear failure of layered machinable Ti3AlC2 ceramics. J. European Ceramic Society, 24 (5) (2004), pp. 855-860.

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