- **ELSEVIER**

Journal of Materials Processing Technology 135 (2003) 228-234

Journal or **Materials Processing Technology**

www .e **Isevi er .corn!** locate/j **matpro tec**

Structural characterisation and strength evaluation of spray formed ceramic composite near-net shapes

M. v. Gopalakrishnana,*, Kenneth Metzgarb,
Danny Rosettad, R. KrishnamurthyC
aSuperior Shot Peening Inc.. 13930 Luthe Road. Houston, IX 77039, *USA*
bH.E.F. France, France
c *Indian Institute of Technology, Chennai, Tamil Nadu, India*
dControlled Thermal Technology, USA

Abstract

This paper explores the characteristics of spray fonned near-net shaped ceramic composite. Alumina-titania composite (Al2OJ 60 wt. %; TiO2 40 wt.%) was spray fonned using a plasma dyne atmospheric facility. Micrographs of as-sprayed samples are presented, along with micrographs of samples post-heat treated at different temperatures. EPMA profiles were detennined and XRD phase analysis was carried out. Young's modulus, strength and hardness of the samples was detennined.

Keywords: Structural characterisation; Strength evaluation; Near-net shapes

Introduction

Ceramics/ceramic composites can be used either as mono- lithic structural material or as coatings/depositions on rela- tively softer substrates for perfonnance enhancement. For achieving the desired monolithic shape with good perfor- mance characteristics one can make use of plasma/reactive spray forming techniques to advantage compared to tradi- tional powder compaction/slip casting technique. Spray fonn- ing allows the multiple steps of powder production, sieving, degassing and consolidation to be reduced into a single processing step, whilst retaining microstructural characteris- tics associated with consolidation of powders such as: (i) fine scale and low segregation microstructure; (ii) benefits ofrapid solidification such as metastable phases and extended solu- bilities of alloying elements; and (iii) the production of homogeneously distributed particulate composites.

Fabricating components with spray forming technique combines the benefits of rapid solidification processing with near-net shape manufacturing [1]. Thus, one possible solution to the problem of in-homogenities induced during solidifica- tion is the use of powder metallurgy. An alternative and better solution which avoids the need for handling fine powder with the associated risk of contamination by solid or gaseous impurities, is the use of the spray forming technique [2].

-
Drresponding author. Tel.

-281-4770426: fax" **+1-281-4499151**

The first use of thermal spray to produce solid bodies was in 1924 [3]. Experiments by General Electric using a laboratory-scale spray forming unit at the company's cor- porate research and development centre at Schenectady. New York. have shown favourable results for both wrought alloys such as IN718 [4] and powder metallurgy alloys such as Rene95 [5]. **In** a recent study at State University of New York at Stony Brook two compositions of inter-metallics: as LI2-Ni3Al alloy and two phase NiAI-Ni3Al alloy were vacuum plasma sprayed (VPS) to a thickness of 3 mm and extensively investigated for microstructural and strength properties [6]. MMCs that have been fabricated using the low pressure plasma deposition mode include; dispersion strengthened AI-Fe-Ce, Co-Ni-Cr-Al- Y reinforced with A12O3. nickel-based super alloys containing A12O3. and Cr3C2 and zrO2 reinforced nickel and nickel chromium alloys [7]. Schindler and Schultze [8] and Lutz [9] have carried out thermal shock and strength measurements stu- dies on various spray formed ceramics and ceramic compo- sites.

2. **Experimental**

Alumina-titania ceramic composite (A12O3 60 wt. % and TiO2 40 wt. %) was spray formed using plasma dyne atmo- spheric spraying facility. The spray formed rings were

0924-0136102/$ -see front maIler PII: S0924-0136(02)OOQOf)-

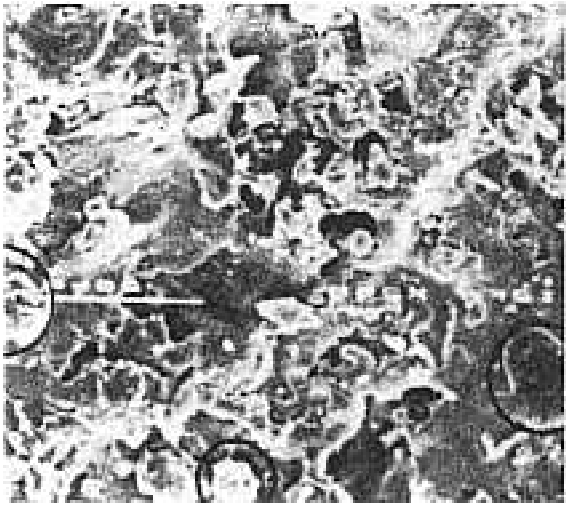
evaluated for the microstructures and strength properties. Details are presented in following sections.

3. Observations

3.1. ***Microstructltres***

The primary objective of spray forming is to achieve a spray deposited product that is, as close to theoretical density as possible while at the same time, maximising the average cooling rate or solidification rate experienced by the deposited material [10]. When the powder with a given size distribution is spray-deposited, the injected par- ticles always form a diverging cone. Some are lead through the cold boundary region of the plasma jet. These particles exhibit a low degree of melting. It is well known that yield efficiency and the microstructure of the final spray formed product are strongly dependant on the over all solid fraction in the spray upon impact with the substrate [II]. The Mandrel will first intercept the particles in the boundary region, collecting a large number of particles with low degree of melting. This entails formation of protrusions and depressions, which leads to the formation of porosity. As the gun penetrates deeper into the spray cone, particles with higher degree of melting are deposited on top forming layers with less porosity. Hence a coating is developed as and when the deposition pattern is scanned over the substrate [12]. As a result, the deposit often exhibited a layered structure (Fig. 1).

The forces (cohesive) holding together the individually solidified splats in the coating are the subjects of intensive investigation. It is certain that successive splats interlock mechanically. In metal coatings, some inter-diffusion may take place dnring deposition and in ceramic coatings, the analogous process of sintering can help to densify the deposit. Ceramic coatings in particular reveal a multitude of flaws. They are riddled with cracks, formed as the ceramic



Fig,

SEM microj(raph of the as-sprayed sample.

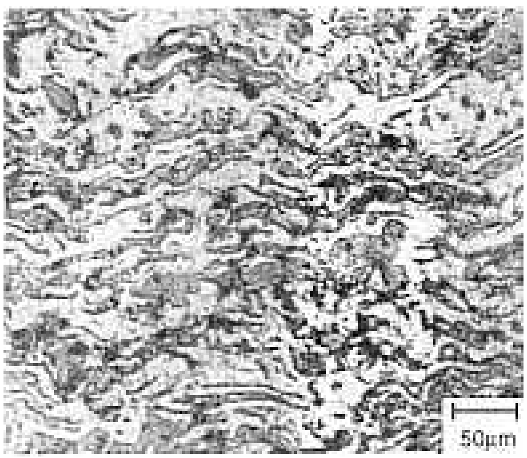


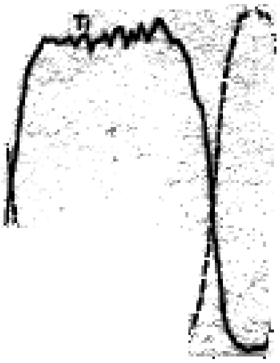
Fig. 2 Optical micrograph of cross-section of **the** as-sprayed sample.

is cooled and honeycombed with \'oids filled with air, trapped in deposit Such flaws, if not minimised can doom a coating when exposed to mechanical stress, At most places, good contact was established between the impacting splat and the underlying lamellae, Due to this good contact, the heat extraction from the impinged splat was rapid; in the neighbourhood of pores, however the heat is slowly removed providing enough time for the grain to grow to a relatively larger size, At some places, poorly molten or already resolidified particles were obser\'ed, These unmolten particles were of round shape. This can also be observed in the optical micrograph of the cross-section of the as-sprayed sample. Fig. 2 shows the optical micrograph of the as- sprayed sample.

The layered structure of the spray deposit with alternate layers of AI_2O_3 and TiO_2 is vel)' e\'idently seen from this figure. Multi-layer coatings in which interfaces are parallel to the substrate can also limit the crack propagation, thus increasing the toughness [13]. Plasma sprayed multi-layered coatings composed of a stack of alternate soft and hard layers can limit crack propagation [13]. The presence of alternate layers of AI_2O_3 and TiO_2 was also confirmed through EPMA analysis (Fig. 3).

;?;- *u;* 0: Q) 5

.'~",A AI .\
,
\
\ I ,



f\

I .'

. *t t I* I r

0

Distance (urn

14.86

Fi~. 3. EPMA profiles for the cross-section of the as-sprayed sample.

:!~()

***M.* ~ *Gopalakrishnan et al.* / *Journal of Materials Processing Technology* 135 (2003) 228-234**

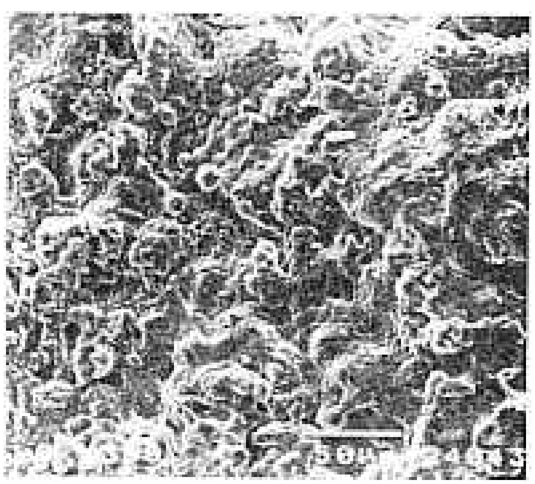


Fig.4. **SEM** morphology of post-heat treated (1200 °C) sample.

It is seen that the profile consists of dominant peaks of AI and Ti. Alternately. with varying thickness. There is a clear indication that there is no diffusion between the layers, except for over-lapping.

3.2. *Inj7l1ence of post-heat treatment*

The spray fonned rings were subjected to post-heat treatments. If however; a sprayed body has to be post-heat treated for strength enhancement. the shrinkage is only between 0.5 and 1.0%. For instance in AI2OlXMgO spinal. only 0.4-0.5% shrinkage was experienced [14].

Fig. 4 shows typical SEM microstructure of the sample heat treated at 1200 "C.

The microstructure exhibits certain changes in the mor- phology. A more densified structure with closing of small open pores is observed. But the layered microstructure is unaffected and the structure is more dense compared to as- sprayed structure. This can again be confirmed by looking at the optical micrograph. Fig. 5 is an optical micrograph of the cross-section of a sample heat treated at 1200 °C.

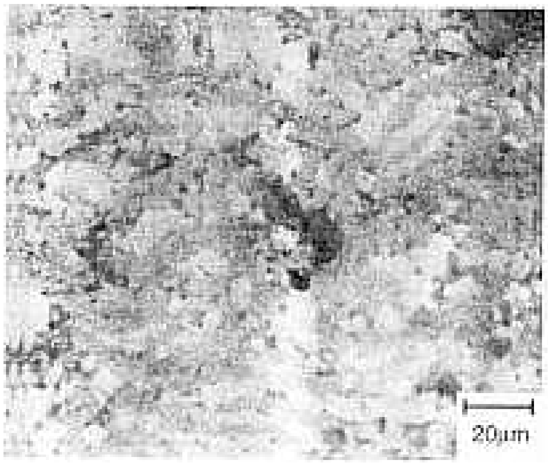


Fig. 5. Optical micrograph of the cross-section of a post-heat treated (12()() C) sample.

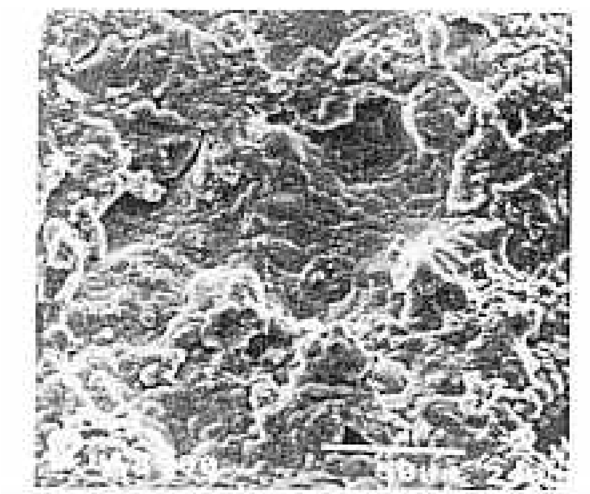


Fig. 6. SEM morphology of a post-heat treated (1400 °C) sample

This can be attributed to the occurrence of homogenisa- tion of the structure, during heat treatment. This has actually imparted the maximum mechanical and tribological proper- ties for this condition, which have been reported in the following sections. With 1400 °C post-heat treatment the structure changes from layered structure to equi-axed one and with increased porosity as shown in Fig. 6.

In this condition the microstructure becomes more porous than the as-sprayed one; this can be attributed to the total structural change from layered texture to equi-axed one. Microstructures of samples, subjected to heat treatments at 1500 and 1600 °C are shown in Figs. 7 and 8, respectively.

The structure for both the heat treatment cases at 1500 and 1600 "C consists of highly porous, and mostly relaxed equi- axed grain morphology.

This may be due to the fact that cracking of dense layers and propagation of microcracks during higher post-heat treatment destroy the structure as a whole and consequently leading to reduction in mechanical properties. Distinct/ appreciable relaxation twins can be seen with higher tem- perature post-heat treatment conditions (Fig. 9).

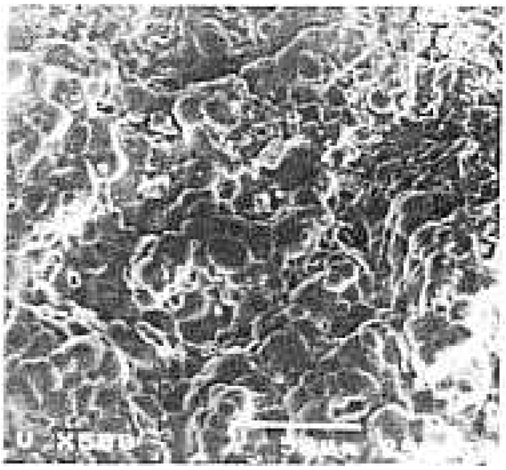


Fig 7. SEM morphology of post-heat treated (1500 C) sample.

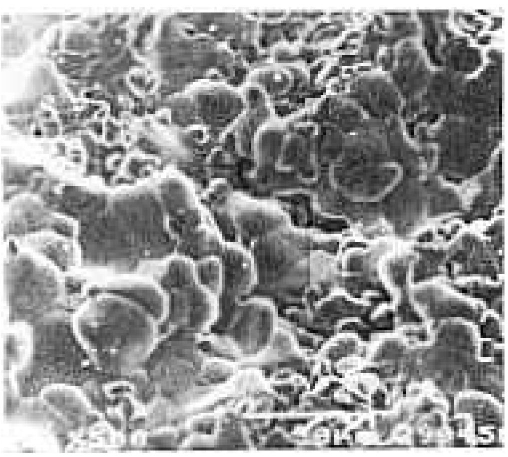


Fig. 8. **SEM** morphology of post-heat treated (1600 °C) sample.

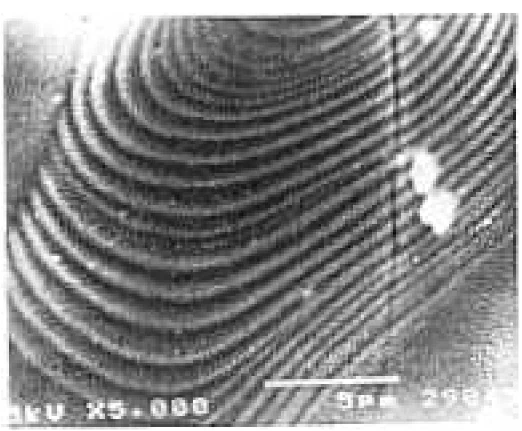


Fig. 9. **Annealing twins on** a **higher post-heat treated sample (SEM).**

With post-heat treatment at 1200 cC. there is an improve- ment in density compared to as-sprayed: However for other higher post-heat treatments there is a reduction in density due to structural changes.

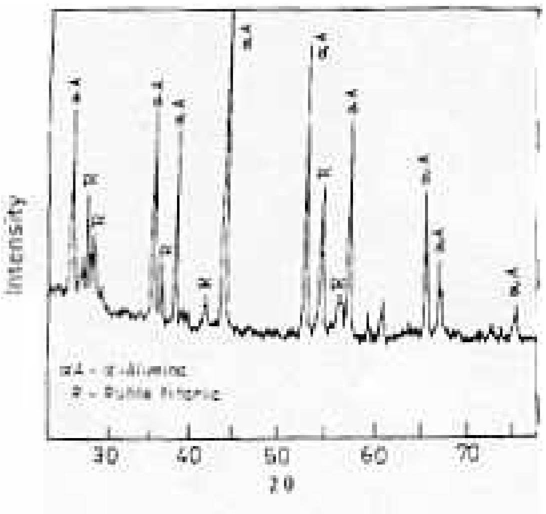
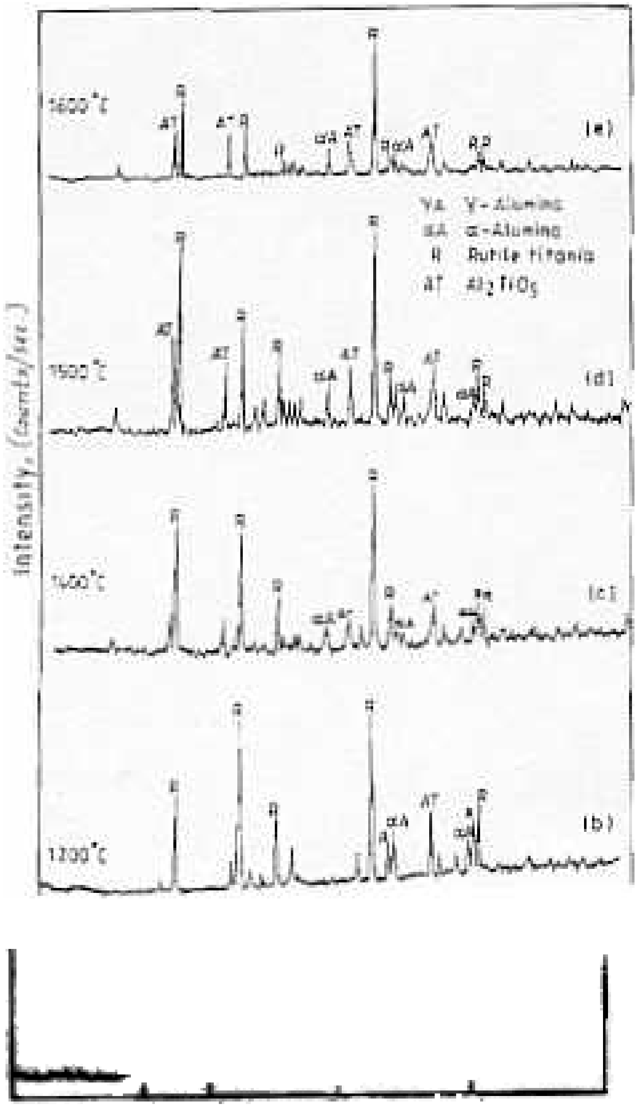


Fig. 10. XRD of the starting powder.

3.3. ***XRD*** *phase analysis of as-sprayed and post-heat treated samples*

Fig. 10 represents the XRD profile of the starting powder. The XRD profiles of the as-sprayed and post-heat treated samples are shown in Fig. 11.

The as-sprayed sample consists of metastable y-A12O3 and rutile TiO2 and traces of o-AI2O3. The occurrence of metastability is anticipated because of rapid cooling of the molten particles of alumina. which limits the ordering of oxyge&and aluminium ion into the stable IX-phase. Posi- tioning of Al in tetrahedral and octahedral voids of oxygen ion. determines the structure of alumina. Rapid cooling results in tetrahedral coordination and the characteristic cubic (y) structure is formed. Further faster cooling. usually occurs with smaller particles and results in y- alumina. McPherson [15] has suggested that with con- siderable undercooling of alumina droplets. homogeneous nucleation results in the formation of y-alumina rather



ASSP

" R **~lJ.J..J.JJ:".~** ~

D

2a

36

5'
28ldQgree)

-72

Fig. II. XRD of as-.prayed and po.t-heat treated sam DIe..

232

than the cx-form, because of the lower critical free energy of nucleation of the former. While the peak intensities are concerned the peak heights are suppressed after spraying. This could be due to preferred orientation of the grains and/or due to the stress induced on the subsequent layers during spraying. On observing the post-heat treated sam- pIes. the peak intensities are found to have significantly increased. The post-heat treated samples showed the pre- sence of cx-alumina, rutile titania and trace of AI2 TiO5 compound. At higher temperatures of heat treatments, more compound formation can be observed. The formation of this compound aluminium titanate (A12 TiO5) which has a pseudo brookite orthorhombic crystal structure is accom- panied by a volume expansion of 10% [16]. Due to this volume expansion, the cracks start developing in the material leading to deterioration in me.~hanical and other tribological properties. Also it can be noticed that to the extent of compound formation, titania peaks are lowered. In the as-sprayed and post-heat treated conditions the titania peaks are more intense than the alumina peaks, which clearly indicates the change in composition between the starting powder and the final product.

3.4. *Observation in strength*

Like any other product functional/performance characteristics of spray formed products are largely dependent on physical properties such as hardness, strength and Young's modulus. They are influenced largely by the composition of the material and the quality of microstructures, porosity and related features. The spray formed composite annular rings (20 mm diameter, 8 mm width and 3 mm thick) were subjected to diametral compression tests [17] for assessing the strength properties.

$$\sigma = P\left(\frac{r-e}{\pi}\right)\frac{h/2-e}{bhe(r-h/2)} \quad (1)$$

h(ln~' *r* ***-h/2***

(2)

3.4.1. *Strength*

The physical str~ngth properties of the plasma spray formed rings were evaluated through diametral compression test. From the result obtained, ultimate strength and Young's modulus were evaluated. Typical observation on parametric influence of strength of the spray formed and post-heat treated parts are illustrated in Fig. 12.

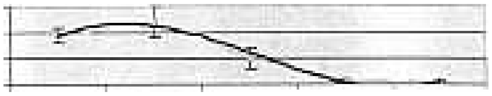
200 0.
~ **150** ~ **100** .c
-a, 50 ~
0~
-50

~

Fig. 12. Effect of heat treatment on strength.

(/) " 3 "8 ~ (/) **-C1** " " 0 >

15 'ii **10** ~ 5 0



30

1200 1400 1500 Temperature (**Deg** C)

1600

Fig. 13. Effect of heat treatment on Young's modulus.

It is seen that compared to the as-sprayed condition the specimens subjected to post-heat treatment (1200 °C) exhib- ited improved properties. This is in order with other observa- tions on microstructure, phase, porosity and related features.

3.4.2. *Young's modulus*

Typical observation on the parametric influence on Young's modulus is presented in Fig. 13.

$$E = \frac{Pr^2}{xbhe}\left\{\frac{\pi}{4} - \frac{2}{\pi}\left(1-\frac{e^2}{r^2}\right) + \frac{2e}{r}\left[\frac{2}{\pi}\left(1-\frac{e}{r}\right) - \frac{\pi}{8}\right]\right.$$

+

e .9(1+11.);

}

(3)

This trend of variation is just similar to the hardness studies. Fig. 14 shows a very typical case of a diametral compression tested spray fonned ring exhibiting resilience effect under wedging action.

3.4.3. *Fractography*

For conforming the structure property correlation, fracto- graphy studies on failed test samples were carried out. Typical observation on the fractured surfaces of as-sprayed section is illustrated in Fig. 15.

The fractured surface shows a quasi-plastic structure. Samples post-heat treated at 1200 °C have exhibited more ductile mode of failures as illustrated in Fig. 16.

This is illustrated by occurrence of relatively larger number of dimples in the fractographs. With higher post- heat treatment temperatures (1400, 1500 and 1600 °C) the samples exhibited distinct brittle mode of fracture as shown in Figs. 17-19.

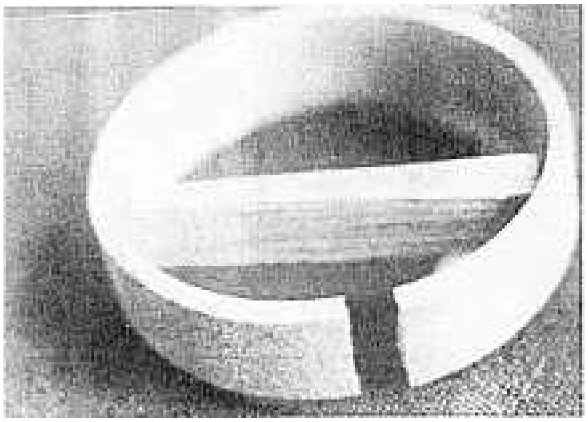


Fig. 14. Wedged spray fonned ring.

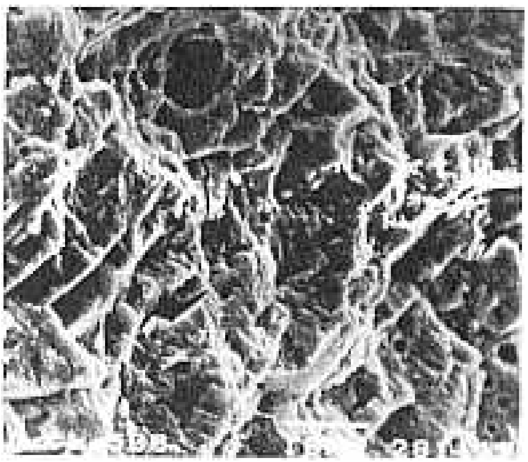


Fig. 15. **SEM** Fractography of as-sprayed sample.

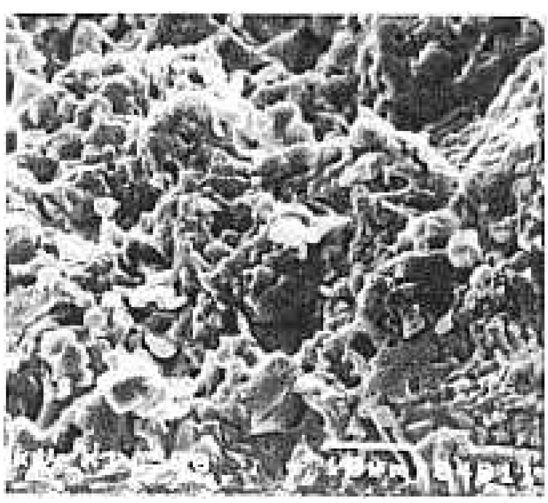


Fig. 16. SEM fractography of heat treated (1200 °C) sample.

3.5. *Hardness*

Typical observation on the parametric influence of post- heat treatment on hardness of spray formed system is illustrated in Fig. 20.

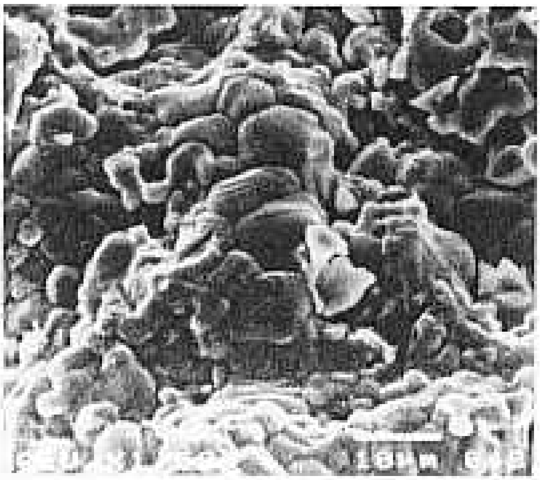


Fig. 17. SEM fractography of heat treated (1400 C) sample

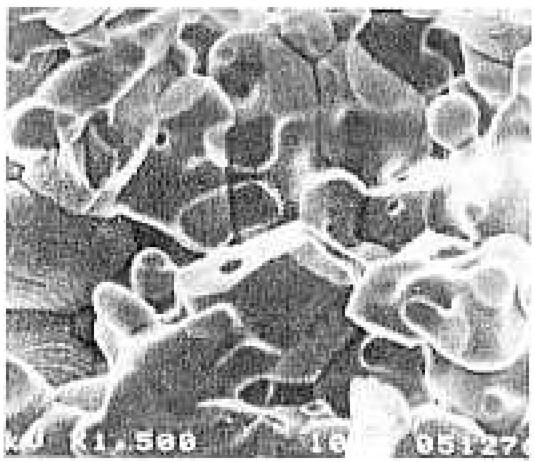


Fig. 18. SEM fractography of heat treated (1500 C) sample.

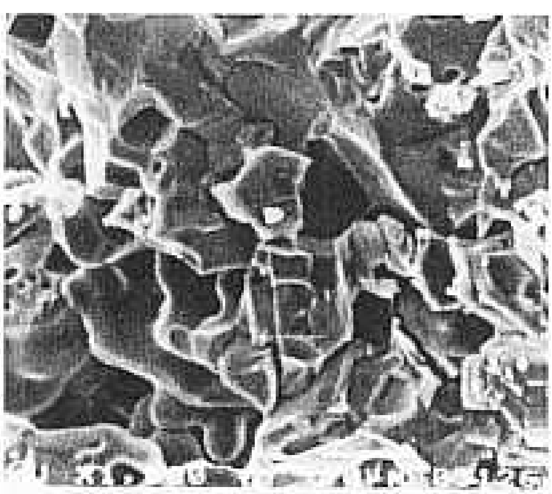


Fig. 19. SEM fractography of heat treated (1600 C) sample

It can be observed that there is a considerable increase in hardness with post-heat treatment at 1200 °C, while with other post-heat treatment temperatures a reduction in hard- ness can be observed. The reduction in hardness can be attributed to occurrence of microcracking due to the volume increase associated with formation of AI_2TiO_5 compound.

One of the indices indicating brittleness is the *E/H* ratio. A reduction in *E/H* means development of a microstructure predominantly brittle in nature (Fig. 21). This has resulted in the observed reduction in the strength (Fig. 12) and also fractographs (Figs. 17-19) associated with brittle failures.

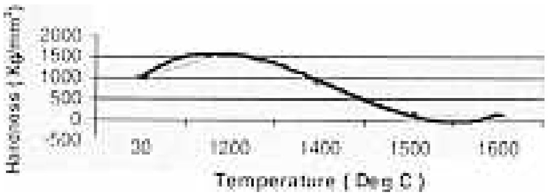


Fig. 20. Effect of heat trl:atml:nt on hardness.

10 8 ;$ ~ 2

30

1200 1400 1500 **Temperature** (**De~ CI**

1600

Fig. 21. Effect of heat treatment on *EIH.*

4. C()ncl"~i()n~

The major advantage of spray forming process is that a near-net shape product with controlled microstructure can be fabricated in a single step operation of rapid solidifica- tion. The layered structure in the as-sprayed condition seems to be most beneficial in the strength point of view. During this condition it behaves like a composite structure with alternate harder alumina and softer titania phases. Post-heat treatment have consequently changed the characteristics of spray fon'ned parts. With post-heat treatment at 1200 °C for this composition of Al_2O_3 60 wt. %, TiO_2 40 wt. % it is possible to achieve the best possible spray formed charac- teristics such as minimum porosity/higher density and mini- mum formation of compound Al_2TiO_5. Post-heat treatments at higher order temperatures have resulted in microstructures containing predominantly equi-axed grains with consequent reduction in density and deterioration in the properties. This is aggravated further by formation of larger amounts of compounds.

Acknowlcd~cments

The Authors wish to thank Ms. Daedra Rosetta, President, Controlled Thermal Technologies Inc., for her support and encouragement throughout the course of this work. We also wish to express our sincere thanks to Mrs. Rosa Metzgar for her valuable suggestions and support.

Reference~

III S. Sampath. H. Hcrn1an. Plasma spray forming of metals. intermetallics and composites. I. Mater. 45 (7) (1993) 42-49.
12] D.G. Morris. M.A. Morris. S. Gunter. M. Lebo. G. Holl Rig. Spray deposition of intermetallics based on AI, Ti and TiAI. Scrip. Metall. Mater. 27 (1992) 1645-1650.
[3] E. Turner. W.E. Ballard. Metal spraying and sprayed metal. I. Inst. Met. 32 (1924) 291-312.
[4] H.C. Fiedler, et al.. The spray forming of super alloys, I. Met. 48 (1987) 28-33.
15] K.M. Chang. H.C. Fiedler. Spray tonned high strength super alloys. in: S. Reichman et al. (Eds.), Superalloys, Metallurgical Society. Warrendale. PA, 1988. pp. 485-493.
[6] S. Sampath. et al., Plasma spray consolidation of Ni-AI inter- metallics. in: T. Bernecki (Ed.). Proceedings of the Third National Thennal Spray Conference. vol. 90. ASM. Materials Park. OH. 1990. pp. 357-361.
[7] R. Tiwari. H. Herman. Incorporation of reinforcements in spray formed MMCS. Scrip. Metall. Mater. 25 (1991) 1103-1107.
[8] S. Schindler. W. Schultze. Plasma generated oxide ceramic components, Int. Ceram. 2 (1988) 39-42.
[9] E.H. Lutz. Plasma ceramics. Powder Metall. Int. (1992).
[10] D. Apelian, Intelligent particulate processing. net shape manufactur- ing and the production of novel powder metallurgy microstructure. 23 (4) (1987) 249-259.
[11] E. Siklee, S. Ahn, Solidification progress and heat transfer analysis of gas atomised alloy droplets during spray forming, Acta Metall. 42 (1994) 3231-3243.
[12] B. Champagne, S. Dallaire. Particle injection in plasma spraying. thermal spray: advances in coatings technology. in: Proceedings of the National Thennal Spray Con!crence. Orlanllo. FL. USA. I')X7. pp. 25-32.
(13] S. Dallaire. G. cliche, The influence of composition and process parameters on the microstructure of TiC-Fe multi-phase and multi- layer coatings. I. Therm. Spray Technol. 50 (1992) 233-239.
[141 Kirner. Plasma spraying of free standing ceramic bodies. in: Pr<JCeellings of the Ninth Intcrnational Conference on Thennal Spraying. Netherlands. 1980. pp. 14-19.
[15] R. McPherson. Thermal spray coatings. I. Thin Solid Films 83 (1981) 297-305.
[16] I.T. Bailey. R. Russel! Ir.. AI2O3-TiO2 system. Trans. Br. Ceram. Soc. 68 (4) (1969) 159-164.
[17] Timoschenko. Strength of Materials. Part I. 2nll ell. Van Nostrand. New York, 1956. DD. 365-388.