Synthesis and High-Temperature Stability of Titanium Aluminide Matrix *in situ* Composites

Y. Tsunekawa, K. Gotoh, M. Okumiya, and N. Mohri

A premixture of elemental powders of titanium and aluminum was supplied as a spray material for the direct fabrication of titanium aluminide matrix *in situ* composites by means of reactive low-pressure plasma spraying with a nitrogen and hydrogen mixed plasma gas. The aluminum content varied from 10 to 63 wt.% in the premixtures. The matrix of sprayed layers consisted of three kinds of titanium aluminides—Ti_3Al, TiAl, and $TiAl_3$—which begin to form on a low-carbon steel substrate immediately after deposition. The formation of nitrides, which act as a reinforcement, occurs both during the flight of liquid droplets and on the substrate. The nitrogen content is approximately 4 to 5 wt.% in the sprayed intermetallic matrix composites, regardless of the aluminum content of the premixtures. The kinds of titanium aluminides and *in situ* nitrides developed depend on the aluminum content of the premixtures. The homogeneity of the distribution of aluminum and titanium in sprayed intermetallic matrix composites has been improved by vacuum annealing. The predominant TiAl phase that formed in the sprayed intermetallic matrix composites with a Ti-36 wt.% Al premixture increases in quantity through annealing. Although some minor nitrides disappear through annealing, the principal reinforcement, Ti_2AlN, does not decompose, but increases in quantity. The hardness of sprayed intermetallic matrix composites varies with aluminum content of the premixtures, but is always greater than that of sprayed titanium aluminides containing no nitrides. Annealing does not reduce the hardness of sprayed intermetallic matrix composites. Sprayed and annealed intermetallic matrix composites with a Ti-36 wt.% Al premixture maintain their hardness of approximately 500 HV up to 800 K. Hence, reactive low-pressure plasma spraying offers a promising fabrication method for titanium aluminide matrix *in situ* composites, which are expected to excel in wear resistance applications at elevated temperatures.

1. Introduction

LOW-DENSITY titanium aluminides are known to exhibit superior high-temperature strength and antioxidation properties. However, hardness and wear resistance need to be improved for severe environments such as high load-bearing applications requiring wear resistance at elevated temperatures. Development of intermetallic matrix composites (IMC) is one promising approach to overcome these difficulties.

Hot-pressing has been widely used to produce intermetallic matrix composites, although new compound layers appear at the interface between the Ti_3NbAl matrix and the boron fibers coated by SiC or B_4C[1], and between the matrix and the TiC particulates.[2] Application of high-pressure casting, which is a promising production method for metal matrix composites, is inappropriate for intermetallic matrix composites processing, because of the high melting points and reactivity of intermetallics. However, Al_2O_3 fiber/Ni_3Al matrix composites can be fabricated with an appreciable interfacial reaction layer by pressure casting.[3]

The preparation of Al_2O_3 fiber/Ni_3Al composites was also performed by reactive sintering from elemental powders of nickel and aluminum.[4] The reaction synthesis process can be applied to TiAl matrix composites. They were successfully fabricated from elemental powders of titanium and aluminum through the use of SiC[5] or TiB_2 particulates.[6,7] In addition to the above processes, there is a new fabrication method for intermetallic matrix composites, in which *in situ* reinforcement is formed during processing without preparing any fibers or particulates. Addition of boron to TiAl normally produces primary TiB_2 as equiaxed particulates, but if tantalum or niobium is also added, the reinforcement morphology changes to elongated rods with a crystal structure of TiB.[8] Nitrogen ion implantation into TiAl substrates was also used for the formation of *in situ* nitrides as a surface modification.[9,10]

Spray processing is a well-developed technique with high potential that has been used for the application of protective coatings and the fabrication of metal matrix composites.[11] Low-pressure plasma spraying has been successfully applied to produce intermetallic matrix composites containing TiC[12] or TiB_2 particulates,[13] using intermetallic powders as a spray material.

This study is concerned with the direct fabrication of titanium aluminide matrix *in situ* composites by reactive low-pressure plasma spraying (RLPPS) with premixtures of elemental powders of titanium and aluminum. The sprayed layers were heated to 1373 K in vacuum to investigate the high-temperature stability of titanium aluminide matrices and *in situ* nitrides, because the constituents in sprayed intermetallic matrix composites cannot reach their thermodynamical equilibrium states within a short processing time.

Key Words: composites, high-temperature properties, phase stability, reactive spraying, titanium aluminide

Y. Tsunekawa, K. Gotoh, M. Okumiya, and **N. Mohri**, Toyota Technological Institute, Nagoya, Japan.

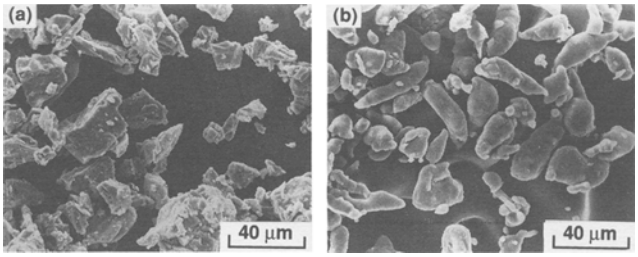

Figure 1 Scanning electron micrographs of (**a**) titanium and (**b**) aluminum powder.

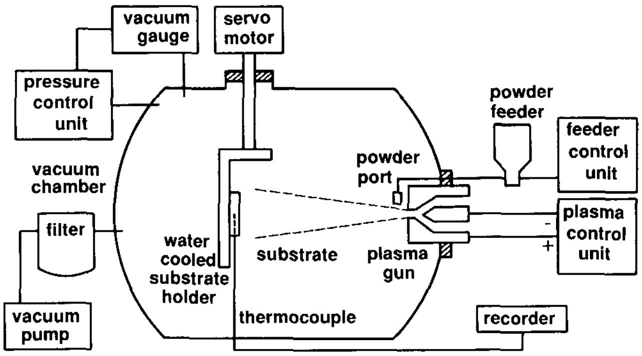

Figure 2 Schematic of reactive low-pressure plasma spraying system for the direct fabrication of intermetallic matrix composites.

2. Experimental Procedure

A premixture of elemental powders of titanium (99.5 wt.%) and aluminum (99.7 wt.%) was supplied as a spray material for the direct fabrication of titanium aluminide matrix composites by reactive low-pressure plasma spraying with a nitrogen and hydrogen mixed plasma gas. The powder sizes of titanium and aluminum were prepared in the range of 20 to 44 μm by sieving, as shown in Fig. 1. The aluminum content of the premixtures was varied from 10 to 63 wt.%.

The spray material of the Ti-Al premixture with a given aluminum content was sprayed by the reactive low-pressure plasma spraying system as shown in Fig. 2, and the spray parameters are listed in Table 1. A nitrogen atmosphere was then maintained in the spray chamber at a given low pressure during spray processing. Low-carbon steel plates 30 mm by 30 mm by 5 mm were used as a substrate. The substrate was preheated by the plasma flame, because the substrate temperature must be higher than 930 K to form titanium aluminides and duplex nitrides, an experimental feature that was confirmed in preliminary experiments. Differential thermal analysis (DTA) was also performed to examine the onset temperature of exothermic reaction on loosely compacted premixtures with various aluminum contents.

To investigate the high-temperature stability of titanium aluminide matrices and *in situ* nitrides, the sprayed intermetallic matrix composite specimens were heated to 1373 K for 86.4 ks (24 h) in a vacuum of 1.5×10^{-3}Pa (1.1×10^{-5} torr). Spectroscopic analyses of the chemical composition of sprayed intermetallic matrix composites, optical and scanning electron microscopy observations of the cross sections, analyses of X-ray diffraction (XRD) with CoKα radiation, and electron probe microanalyses (EPMA) were then performed to characterize the constituents of matrices and nitrides in sprayed intermetallic matrix composites before and after annealing. Vickers microhardness measurements were carried out under a 4.9-N load for 15 s at high temperatures.

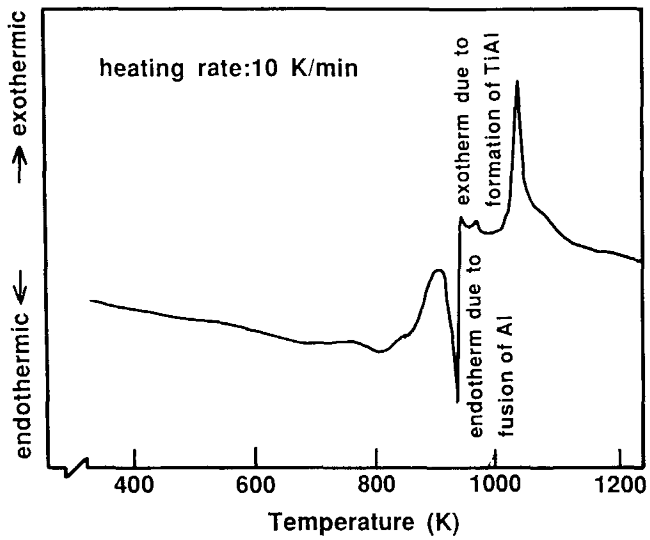

Figure 3 DTA analysis of premixed powder of Ti-36 wt.% Al in argon atmosphere.

Table 1 Spray Parameters Used in Reactive Low-Pressure Plasma Spraying

	Plasma gas	
	Nitrogen	Hydrogen
Plasma gas flow, m^3/s	1.1×10^{-3}	5.5×10^{-5}
Current, A		500
Voltage, V		60 to 61
Spray rate, g/s		0.06 to 0.14
Carrier gas flow, m^3/s..............		N_2; 2.1×10^{-5}
Chamber pressure, kPa............		6.7
Spray distance, mm..................		300

3. Results and Discussion

3.1 *Titanium Aluminide Matrix* in situ *Composites*

The substrate temperature was increased to about 950 K by the plasma flame just before spraying; then it was increased gradually up to 1160 K as spraying proceeded. Nitriding of elemental powders occurred on the droplet surfaces during flight in the plasma flame, as indicated by the fact that the nitrides of titanium and aluminum were formed without preheating of the substrate. However, there appears to be a few elemental powders that collapse or come in contact with each other to form titanium

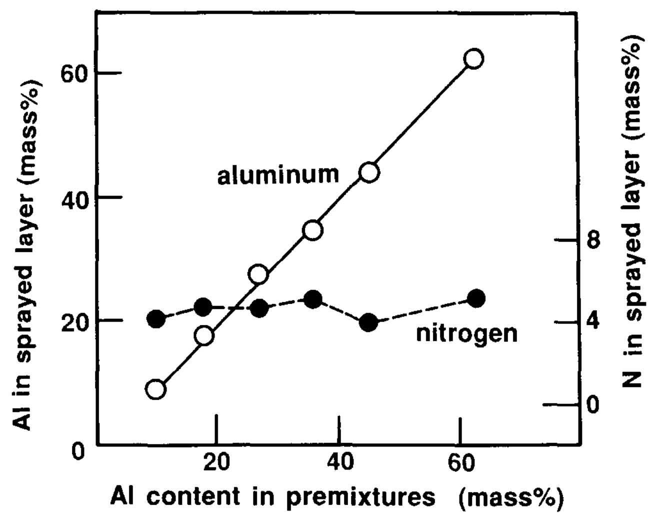

Figure 4 Aluminum and nitrogen content of premixtures and as-sprayed intermetallic matrix composites.

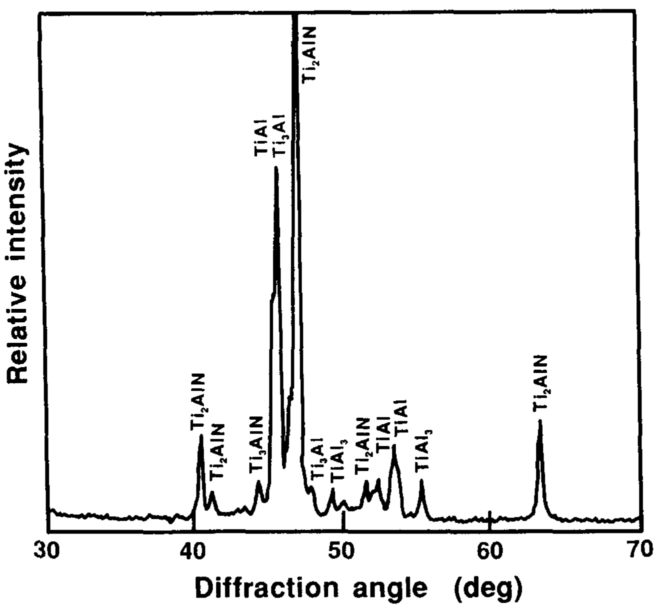

Figure 5 X-ray diffraction pattern of as-sprayed intermetallic matrix composite with Ti-36 wt.% Al premixture.

aluminides and duplex nitrides. They are not formed during flight, but after deposition of the droplets on the substrate.

Heating of titanium and aluminum powder premixtures causes the formation of titanium aluminides to occur with a strong exothermic reaction. This is demonstrated in Fig. 3, which shows a DTA scan performed on the loosely compacted premixture with Ti-36 wt.% Al. A strong exothermic peak is visible at approximately 1000 K; the exotherm occurs shortly after the fusion of aluminum, and the compact undergoes self-heating. The XRD pattern of the powder compact scanned by DTA up to 1273 K consisted of a predominant TiAl phase. The exothermic reaction is also detected on the substrate temperature during the spray process; it reaches 1160 K in reactive low-pressure plasma spraying with a Ti-36 wt.% Al premixture, but 1050 K with a TiAl intermetallic powder.

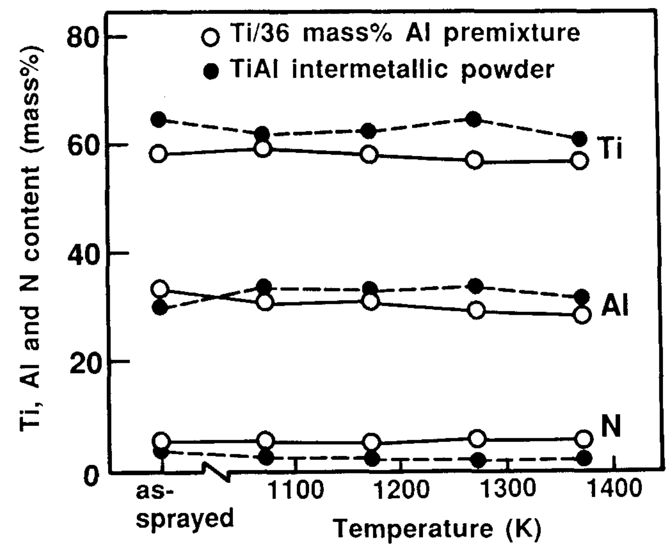

Figure 6 Change in titanium, aluminum, and nitrogen content in sprayed intermetallic matrix composite with Ti-36 wt.% Al premixture.

Table 2 Matrix and Nitride Constituents in As-Sprayed Intermetallic Matrix Composites

Constituent	Al, Wt.% 10	18	27	36	45	63
Matrices						
Ti_3Al	S	S	S	W	W	N
TiAl	N	VW	W	S	S	VW
$TiAl_3$	N	N	VW	W	S	S
Nitrides						
Ti_3AlN	S	S	W	W	VW	N
Ti_2AlN	N	W	W	S	S	W
AlN	N	N	N	VW	VW	W

Note: S,strong; W,weak; VW,very weak; N, nondetectable

When the aluminum content of the premixture varies from 10 to 63 wt.%, then the aluminum content in the sprayed layers almost coincides with that in the premixtures, as shown in Fig. 4. Thus, the constituents in the sprayed layers can be controlled by the premixed aluminum content. The nitrogen content resulting from plasma-assisted nitriding is constant in the range of 4 to 5 wt.% with the fixed spray parameters, regardless of the aluminum content in the premixtures. If necessary, the nitrogen content in the sprayed layers can be controlled by varying the spray parameters. Lowering the degree of vacuum in the spray chamber is particularly successful for nitriding.

The microstructure of the cross sections parallel to the spray direction is not homogeneous, and it exhibits a wavy layered structure similar to conventional metallic sprayed layers. However, because the aluminum content of the premixture and the spray parameters were maintained constant during spray processing, the distribution of each element does not vary along the

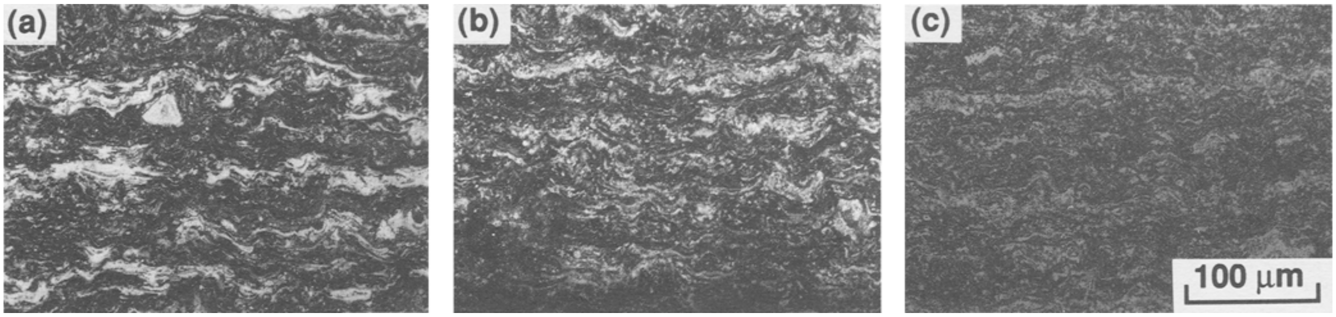

Figure 7 Optical micrographs of cross section of sprayed and annealed intermetallic matrix composite with Ti-36 wt.% Al premixture. (**a**) As sprayed. (**b**) Annealed at 1173 K. (**c**) Annealed at 1373 K.

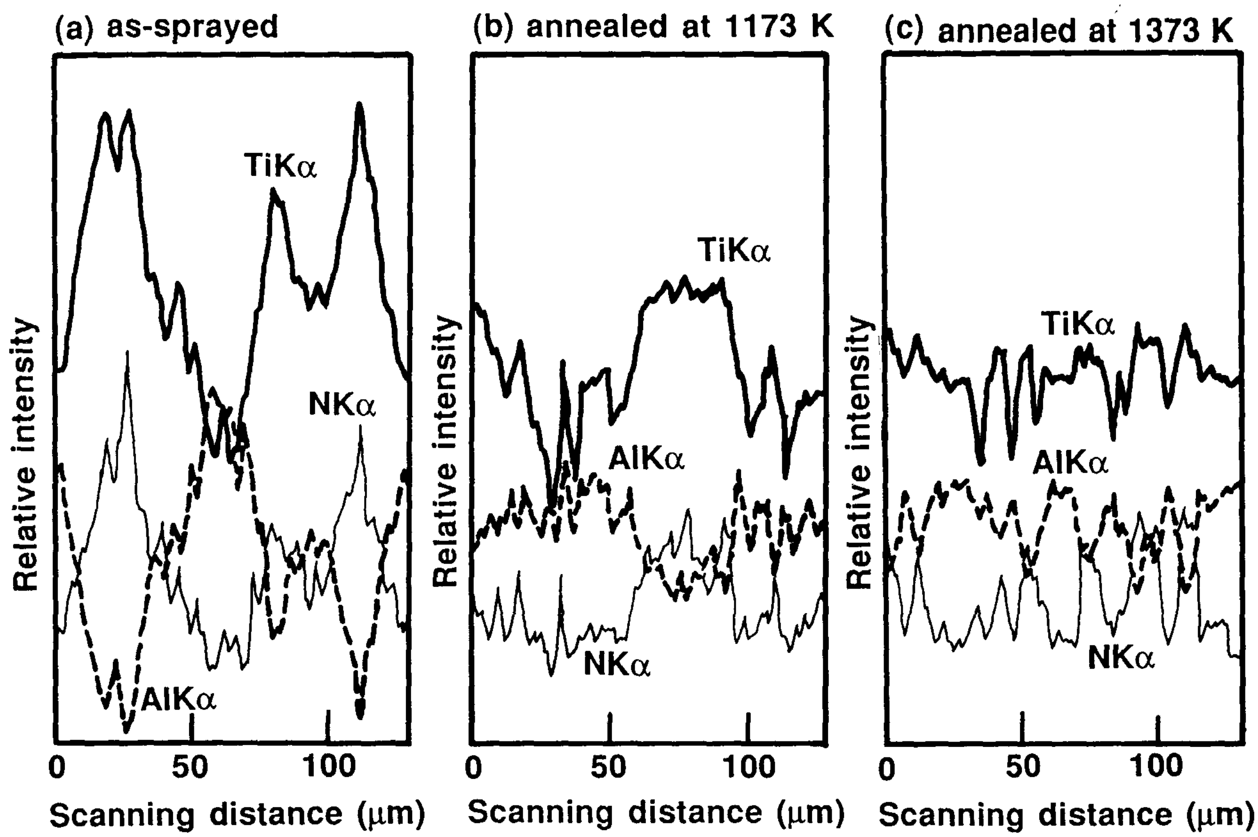

Figure 8 Intensity profiles of characteristic X-ray of cross section of intermetallic matrix composite with Ti-36 wt.% Al premixture. (**a**) As sprayed. (**b**) Annealed at 1173 K. (**c**) Annealed at 1373 K.

spray direction macroscopically. The porosity appears to increase as the aluminum content of the premixtures increases, although it is a very low percentage by volume.

A typical XRD pattern of the sprayed layer with a Ti-36 wt.% Al premixture is shown in Fig. 5. The predominant TiAl phase and small amounts of Ti_3Al and $TiAl_3$ are identified as titanium aluminide, and the principal Ti_2AlN and a small amount of Ti_3AlN are nitrides. The constituents of the matrices and nitrides are listed in Table 2 as a function of the aluminum content of the premixtures. Sprayed intermetallic matrix composites contain a nonreacted titanium phase, or an aluminum phase in extreme cases. The formation of Ti_3Al, TiAl, and $TiAl_3$ as a matrix depends on the aluminum content of the premixtures. The formation of Ti_2AlN, Ti_3AlN, and AlN as a reinforcement also depends on the aluminum content.

3.2 *High-Temperature Stability of Titanium Aluminide Matrix* in situ *Composites*

To investigate the high-temperature stability of sprayed intermetallic matrix composites, the chemical composition was analyzed before and after annealing. The titanium and alumi-

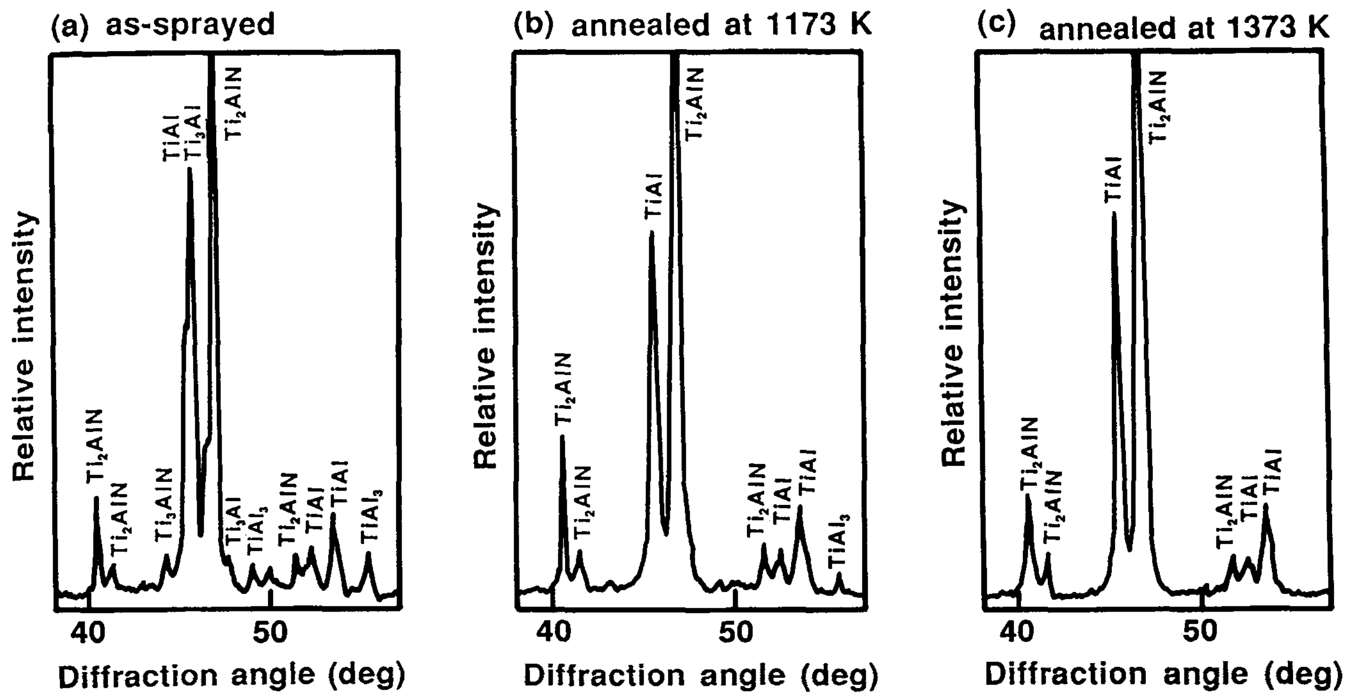

Figure 9 X-ray diffraction patterns of intermetallic matrix composite with Ti-36 wt.% Al premixture. (a) As sprayed. (b) Annealed at 1173 K. (c) Annealed at 1373 K.

Table 3 Matrix and Nitride Constituents of Reactive Low-Pressure Plasma Sprayed Intermetallic Matrix Composites after Annealing at Different Temperatures for 86.4 ks in Vacuum

Constituent	As sprayed	Annealing temperature, K 1073	1173	1273	1373
Matrices					
Ti_3Al	W	N	N	N	N
TiAl	S	S	S	S	S
$TiAl_3$	W	W	VW	N	N
Nitrides					
Ti_3AlN	W	N	N	N	N
Ti_2AlN	S	S	S	S	S
AlN	VW	N	N	N	N

Note: S, strong; W, weak; VW, very weak; N, nondetectable

num content do not change during annealing, and the nitrogen content does not decrease, as shown in Fig. 6. The titanium, aluminum, and nitrogen contents of intermetallic matrix composites sprayed with a TiAl intermetallic powder are also essentially unchanged by annealing; however, the nitrogen content is less than the content in the sprayed intermetallic matrix composites with Ti-36 wt.% Al premixtures. Thus, the nitriding reaction in reactive low-pressure plasma spraying is more likely with Ti-Al premixtures than with a TiAl intermetallic powder. The elemental titanium and aluminum powders form their nitrides more readily because they capture more nitrogen in flight.

Typical optical micrographs of the cross sections of sprayed intermetallic matrix composites with Ti-36 wt.% Al are shown in Fig. 7 in the as-sprayed condition and annealed for 86.4 ks (24 h) at 1173 and 1373 K, respectively. The wavy layered structure becomes indistinct after annealing. The high-temperature anneal causes the constituents to become homogeneous. An iron aluminide intermetallic phase grows at the intermetallic matrix composite-substrate interface, along with an aluminum diffusion layer.

The characteristic X-ray intensity EPMA profiles of the as-sprayed intermetallic matrix composite cross sections are quite different from those of the annealed intermetallic matrix composite, as shown in Fig. 8. The distribution of each element along the spray direction becomes homogeneous after annealing. Hence, the titanium aluminide phases change to the equilibrium

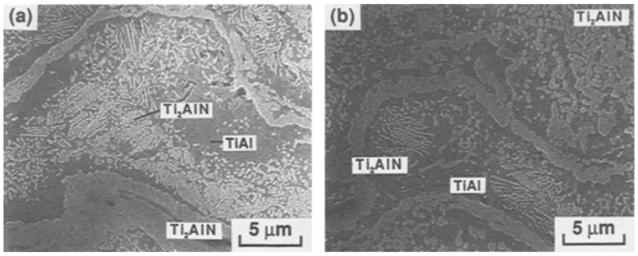

Figure 10 Scanning electron micrographs of cross section of sprayed intermetallic matrix composite with Ti-36 wt.% Al premixture. (**a**) As sprayed. (**b**) Annealed at 1173 K for 86.4 ks.

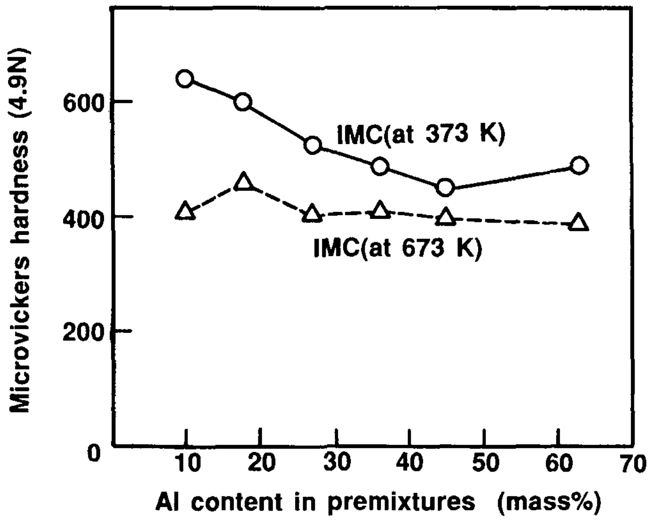

Figure 11 Effect of premixed aluminum content on the microhardness of as-sprayed intermetallic matrix composites at elevated temperatures.

phases, corresponding to each composition, although the total nitrogen content is not decreased by annealing at 1373 K for 86.4 ks (24 h). The sprayed intermetallic matrix composite can be applied at elevated temperatures without decomposing the principal nitride, Ti_2AlN.

The XRD patterns of as-sprayed intermetallic matrix composites and intermetallic matrix composites annealed at 1173 and 1373 K are shown in Fig. 9. Comparison of the patterns shows that the peak intensities from the matrix of TiAl and the nitride Ti_2AlN are increased by annealing. The constituents of matrices and nitrides after annealing at 1173 K for 86.4 ks (24 h) are included in Table 3. According to Tables 2 and 3, Ti_3Al in the intermetallic matrix composite range of Ti-10 to 18 wt.% Al increases after annealing and TiAl in the intermetallic matrix composite range of 36 to 45 wt.% Al also increases. The principal nitride, Ti_2AlN, in the intermetallic matrix composite range of up to 45 wt.% Al increases, as does AlN intermetallic matrix composite of 63 wt.% Al.[14]

Scanning electron microscopy observations were performed to detect any microstructural change in sprayed intermetallic

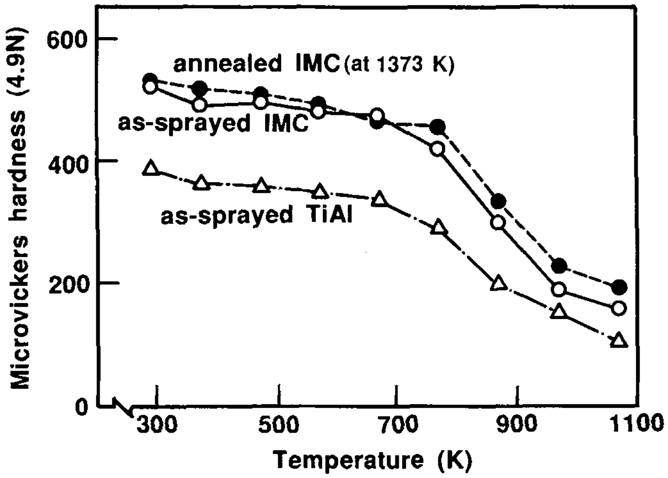

Figure 12 Microhardness of as-sprayed and annealed intermetallic matrix composites with Ti-36 wt.% Al premixture at elevated temperatures.

matrix composites due to annealing, as shown in Fig. 10. Wavy Ti_2AlN bands are observed in the cross section of as-sprayed intermetallic matrix composites from the Ti-36 wt.% Al premixture; fine Ti_2AlN particulates are embedded in the TiAl matrix. The wavy Ti_2AlN bands become thinner and discrete, and the Ti_2AlN particulates seem to grow slightly during the annealing.

3.3 *Hardness of Sprayed Intermetallic Matrix Composites at High Temperatures*

The hardness change in sprayed intermetallic matrix composites at 373 and 673 K is shown in Fig. 11 as a function of the aluminum content of the premixtures. All the intermetallic matrix composite specimens exhibit superior hardness compared to that of titanium aluminides without nitrides, regardless of the aluminum content of the premixtures. Although the hardness at 373 K is the least for the sprayed intermetallic matrix composites, with Ti-45 wt.% Al, intermetallic matrix composite specimens with different aluminum contents do not differ in hardness at 673 K. Hardness differences arise from the combined effects of nonreacted titanium and the differing amounts and kinds of titanium aluminides and nitrides, depending on the aluminum content of the premixtures. However, it is difficult to determine the proportion of each titanium aluminide and the nitride in the sprayed intermetallic matrix composite, because of the wide variety of titanium aluminides and nitrides present.

The hardness of sprayed intermetallic matrix composites with Ti-36 wt.% Al at high temperatures is shown in Fig. 12 for as-sprayed specimens and for those annealed at 1373 K. The hardness change due to annealing is hardly detectable throughout the temperature range. Both of the hardnesses almost maintain the room-temperature value of 500 HV up to 800 K. Comparing the hardness of intermetallic matrix composites, with that of sprayed TiAl intermetallic, the intermetallic matrix composite has a remarkably high hardness resulting from *in situ* nitrides. Hence, the sprayed intermetallic matrix composite is expected to be an advanced material in wear resistance applications at elevated temperatures.

4. Conclusions

Titanium aluminide matrix *in situ* composites were simply and inexpensively fabricated by reactive low-pressure plasma spraying using elemental powders of titanium and aluminum. The sprayed intermetallic matrix composite specimens were then heated up to 1373 K for 86.4 ks (24 h) in vacuum to study the high-temperature stability. The following results were obtained.

The nitriding reaction occurs partially on the surface of titanium and aluminum droplets in flight through the plasma flame, but the formation of titanium aluminides and duplex nitrides occurs on the substrate. A layered structure is observed microscopically on the cross section of sprayed intermetallic matrix composites parallel to the spray direction. The matrix constituents of sprayed layers vary successively from Ti_3Al to TiAl, and $TiAl_3$ as the aluminum content of the premixtures increased. The *in situ* nitrides are analogous to the case of titanium aluminides, progressing from Ti_3AlN to Ti_2AlN, and AlN.

The proportion of Ti_3Al in intermetallic matrix composites with a high titanium content premixture increases during annealing at 1173 K; TiAl increases with a high aluminum premixture. Of the nitrides, Ti_2AlN becomes predominant in the intermetallic matrix composite with up to 45 wt.% Al, AlN in the intermetallic matrix composite with 63 wt.% Al. A small amount of Ti_3Al and $TiAl_3$ in the sprayed intermetallic matrix composite with a Ti-36 wt.% Al premixture decomposes during annealing, as TiAl and Ti_2AlN become predominant. Fine Ti_2AlN particulates embedded in the TiAl matrix, which is surrounded by wavy Ti_2AlN bands, are observed in the cross section of as-sprayed intermetallic matrix composites made with a Ti-36 wt.% Al premixture. The microstructure of Ti_2AlN is changed slightly during annealing.

The hardness of sprayed intermetallic matrix composites is higher than that of sprayed titanium aluminides without nitrides. The hardness at 373 K of the intermetallic matrix composite made with a Ti-45 wt.% Al premixture is the lowest, but all of the intermetallic matrix composite hardnesses were approximately equal at 673 K. The high-temperature hardness of sprayed intermetallic matrix composites is not affected by annealing, because of the superior high-temperature stability of TiAl and Ti_2AlN.

5. Acknowledgments

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