MICROSTRUCTURE AND PROPERTIES OF MULTIPHASE AND FUNCTIONALLY GRADED MATERIALS PREPARED BY CHEMICAL VAPOR DEPOSITION

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Chemical vapor deposition (CVD) offers an unique avenue for creating multiphase and functionally graded materials with tailorable composition, microstructure, and properties. The motivation for producing this type of multiphase materials is that their material properties can be favorably tailored by controlling phase composition and microstructure. As an atomistic growth technique, CVD provides versatility in terms of engineering the structure of multiphase materials at a nano-scale level. The size, shape, orientation, and distribution of dispersoids can be tailored, as these characteristics are strongly governed by deposition kinetics and nucleation and growth behavior. The shape of dispersoids can range anywhere from randomly oriented and uniformly distributed equiaxed particles, to columnar grains, to whiskers growing perpendicular to the substrate surface. In principle, deposit composition and microstructure can be tailored by controlling process variables such as temperature, pressure, and reagent concentration. However, in practice, most multiphase CVD processes are often chemically complex, and therefore, are not sufficiently understood or developed to allow such a sophisticated level of proactive compositional or microstructural control. Another critical issue is that, in general, the performance of multiphase CVD materials has not been systematically studied while aiming at practical applications. This paper describes two CVD systems to illustrate the technical issues and challenges associated with the development of multiphase materials for realistic use; a self-lubricating system (TiN+MoS$_2$) for tribological applications and a functionally graded metal-ceramic interface (NiAl+Al$_2$O$_3$) for protective coating applications.

It is envisioned that self-lubricating multiphase coatings containing a solid lubricating phase and a hard ceramic matrix phase can be prepared to achieve the desired combination of lubricity and structural integrity for highly demanding tribological applications. For the lubricating phase, MoS$_2$ was chosen because it is an excellent solid lubricating material with a lamellar crystal structure. TiN was selected for the matrix phase since TiN is a ceramic material whose success as a wear-resistant coating material for wear applications is well-established. A hot-wall CVD reactor was used to co-deposit MoS$_2$ and TiN from MoF$_6$-Ti((CH$_3$)$_2$N)$_4$-H$_2$S-NH$_3$ reagent mixtures. At a deposition temperature of 820°C, TiN and MoS$_2$ were segregated as discretely distinct crystalline phases, thus resulting in the formation of a dispersed multiphase microstructure. Characterization results suggested that it was possible to influence the relative composition of the MoS$_2$ and TiN phases in the multiphase coating by controlling the MoF$_6$ concentration in the reagent mixture. The friction and wear behavior of the MoS$_2$+TiN multiphase coating could also be tailored by adjusting the MoS$_2$ content. These experimental results demonstrated that the multiphase concept could be used to design and engineer a new class of self-lubricating coating materials.

Improving the adhesion between two dissimilar materials such as a metal and a ceramic under thermochemically and thermomechanically severe environments is a major technical challenge. The possibility of improving the adhesion between NiAl and Al$_2$O$_3$ was considered by gradually grading their interface. A graded Al$_2$O$_3$+NiAl interface was created by reacting AlCl$_3$ with a Ni substrate in the presence of H$_2$ to form β-NiAl. At the same time, the control of the CO$_2$ partial pressure by pulsing was used as a means of nucleating and growing small Al$_2$O$_3$ particles in the NiAl coating matrix. Using this method, very fine Al$_2$O$_3$ particles could be dispersed in a NiAl coating matrix. The oxide particles were randomly and isotropically dispersed. The hardness and elastic modulus along the metal-ceramic interface were measured by nanoindentation. Initial results indicated that both hardness and elastic modulus values were somewhere between those of pure NiAl and Al$_2$O$_3$ coatings made in the same CVD reactor. The distribution of residual stress in an idealized NiAl+Al$_2$O$_3$ interface structure formed on a disc-shaped Ni-based superalloy substrate after a uniform temperature drop of 1000°C was modeled using a finite element method. The benefit of the graded layer was pronounced at the corner locations where the Al$_2$O$_3$ and bond coat layers intersect. For example, the out-of-plane stress along the sharp Al$_2$O$_3$-NiAl interface reaches a stress singularity at the corner location, i.e., infinite stress in the tensile direction. But, the stress at the same location with the graded interface was in compression, and much smaller in absolute magnitude (-100 MPa). These results indicated that, from the point of view of managing residual stress, this graded interface may provide a mechanism to reduce crack initiation at these crack-sensitive locations. Optimum graded interface microstructure and compositional grading are being designed by considering various processing, microstructure, oxidation, and fracture mechanics issues.

The experimental results obtained for the above multiphase systems are preliminary, but yet encouraging. These examples demonstrate that it is certainly possible to tailor material properties and performance using a multiphase concept. In future, interdisciplinary investigations are needed to study various aspects of producing highly sophisticated multiphase materials and characterizing, measuring, and optimizing their relevant properties. More fundamentally, a scientific methodology needs to be developed for understanding kinetic mechanisms and nucleation and growth characteristics of chemically complex multiphase CVD systems.

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The synthesis of multiphase and functionally graded materials by chemical vapor deposition is discussed from a perspective of controlling their composition and microstructure at a nano-scale level, and ultimately, tailoring their material properties. Prior research is briefly reviewed to address the current state of this novel material concept. Recent experimental results relating to controlling the selected properties of two multiphase systems, $TiN+MoS_2$ and $NiAl+Al_2O_3$, are described to illustrate this concept's potential merits and challenges for use in realistic applications.

THE CONCEPT

Chemical vapor deposition (CVD) offers an unique avenue for creating multiphase and functionally graded materials with tailorable composition, microstructure, and properties. As previously reviewed by Hirai and Goto (1) and Lackey et al. (2), multiphase deposits have been produced, intentionally or unintentionally, by CVD for several decades. Multiphase materials are formed when a certain combination of reagents allows the simultaneous growth of two or more chemical phases that are immiscible with respect to each other in the deposition environment. The motivation for producing this type of multiphase materials is that their material properties can be favorably tailored by controlling phase composition and microstructure. For example, the fracture toughness of a multiphase CVD coating containing small $TiSi_2$ dispersoids in a SiC matrix is reported to be twice that of a single phase SiC coating (3). This type of toughened coatings may be useful in structural applications where the traditional brittleness of ceramic coatings leads to not only coating failures, but also to catastrophic damage of underlying substrates by crack propagation into the substrate materials. In another example, the property mismatch between coating and substrate materials, which is responsible for many coating failures, can be tailored by gradually grading the substrate-coating interface. Hirai (4,5) recently showed that the thermal shock and thermal fatigue characteristics of a compositionally graded SiC+C coating were superior to a single phase SiC coating for protecting carbon-carbon composites from high temperature environments.

As an atomistic growth technique, CVD provides versatility in terms of engineering the structure of multiphase materials at a nano-scale level. The size, shape, orientation, and distribution of dispersoids can be tailored, as these characteristics are strongly governed by deposition kinetics and nucleation and growth behavior. The shape of dispersoids can range anywhere from randomly oriented and uniformly distributed equiaxed particles, to columnar grains, to whiskers growing perpendicular to the substrate surface. Hirai (4) observed that SiC+C coatings usually contained equiaxed SiC particles of 10 to 100 nm in size, which were dispersed in the carbon matrix of 3 to

5 nm grain size. Stinton and Lackey (3) reported that the shape of $TiSi_2$ dispersoids in a SiC matrix could be changed to be either columnar or equiaxed. Lee et al. (6) prepared multiphase materials containing 20 nm AlN whiskers in a turbostratic BN matrix of 2 nm grains. Hirai and Hayashi (7) prepared a Si_3N_4+TiN multiphase coating which contained finely dispersed, small TiN fibers of 10 nm in length and 3 nm in diameter.

In principle, deposit composition and microstructure can be tailored by controlling process variables such as temperature, pressure, and reagent concentration. However, in practice, most multiphase CVD processes are often chemically complex, and therefore, are not sufficiently understood or developed to allow such a sophisticated level of proactive compositional or microstructural control. This point was addressed by Lee et al. (6,8,9) who studied the co-deposition of BN and AlN (BN+AlN-CVD) as well as single phase deposition of BN (BN-CVD) and AlN (AlN-CVD) in order to compare how the co-deposition process was different from the single phase processes. It appeared that the BN+AlN-CVD process could not be simply described by superimposing the deposition mechanisms derived from the BN-CVD and AlN-CVD processes. The chemical kinetics in the co-deposition environment were drastically altered, presumably due to the surface inhomogeneity created by the co-existence of the BN and AlN surfaces during deposition. Also, the growth characteristics of BN and AlN in the co-deposition environment deviated from those expected from their single phase deposition processes. An example of this behavior was that the growth of AlN whiskers was observed to be much more accentuated in the co-deposition process than in the AlN-CVD process. This work by Lee et al. provided some qualitative insights for examining a multiphase CVD system, but there are still other more fundamental and intriguing questions to be addressed. More basic research is needed to understand, for example, how a multiple number of chemical phases nucleate and grow, causing the evolution of certain multiphase microstructures.

Another critical issue is that, in general, the performance of multiphase CVD materials has not been systematically studied in efforts to obtain practical applications, with the exception of Hirai's work (4,5). It seems that, in order for the multiphase CVD concept to be transformed from a laboratory curiosity to technological reality, the feasibility of the concept must be demonstrated, not just from a synthesis perspective, but from an application view point as well. In the remainder of this paper, two binary systems are considered to illustrate the technical issues and challenges associated with the development of multiphase materials for realistic use; a self-lubricating system (TiN+MoS_2) for tribological applications and a functionally graded metal-ceramic interface (NiAl+Al_2O_3) for protective coating applications.

SELF-LUBRICATING MULTIPHASE MATERIALS

Synthesis and Characterization

It is envisioned that self-lubricating multiphase coatings containing a solid lubricating phase and a hard ceramic matrix phase can be prepared to achieve the desired combination of lubricity and structural integrity for highly demanding tribological applications. For the lubricating phase, MoS_2 was chosen because it is an excellent solid lubricating material with a lamellar crystal structure (10). TiN was selected for the matrix phase since TiN is a ceramic material whose success as a wear-resistant coating material for wear applications is well-established (11). Crystalline MoS_2 can be

prepared as a single phase coating by CVD using MoF_6 and H_2S at temperatures of 330 to 535°C (12,13). MoS_2 deposited by this method was soft and easily scratched. An organometallic precursor, $Ti((CH_3)_2N)_4$, along with NH_3, can be used to deposit TiN as a single phase material at a temperature of 350°C (14). The TiN coating produced by this procedure was stochiometric and nanocrystalline with a hardness value of about 12.7±0.6 GPa. A hot-wall CVD reactor was used to co-deposit MoS_2 and TiN from the MoF_6-$Ti((CH_3)_2N)_4$-H_2S-NH_3 mixture as described elsewhere [15]. At a deposition temperature of 820°C, TiN and MoS_2 were segregated as discretely distinct crystalline phases, thus resulting in the formation of dispersed, multiphase microstructures.

The X-ray diffraction (XRD) patterns in Fig. 1 show that the crystallinity of the constituent phases is strongly influenced by the inlet MoF_6 partial pressure. At the lowest MoF_6 partial pressure (2.8 Pa), the appearance of diffraction peaks attributable to TiN was observed (Fig. 1a). No MoS_2 peaks were observed at this partial pressure. As the MoF_6 partial pressure was increased to 6.9 Pa and subsequently to 9.6 Pa, the XRD patterns (Figs. 1b and 1c) indicated that crystalline MoS_2 and TiN phases were co-deposited. With a further increase in the MoF_6 partial pressure to 13.6 Pa, the TiN peaks disappeared while the MoS_2 peaks became more intense. An Auger electron spectroscopy (AES) analysis on the TiN+MoS_2 coating deposited at the MoF_6 partial pressure of 9.6 Pa indicated that the Mo/Ti atomic ratio decreased from 2.4 to 0.81 to 0.54 with sputtering. This observation suggested that the MoS_2 content was high near the coating surface, but sharply decreased through coating thickness. Although this compositional grading was not initially intended, the formation of the graded structure was thought be beneficial by making the coating surface more lubricious while providing the structural integrity needed at the substrate-coating interface. The reason for the observed compositional grading was not clear since all process parameters were kept constant during deposition. The XRD and AES results were confirmed by electron-diffraction and transmission electron microscopy analyses performed along the transverse direction of the graded MoS_2-rich surface coating. The coating surface was primarily crystalline MoS_2 while the TiN content substantially increased near the substrate interface. The grain size of the TiN phase was ~40 nm. These characterization results suggested that it was possible to influence the relative composition of the MoS_2 and TiN phases in the multiphase coating by controlling the MoF_6 concentration in the reagent mixture.

Friction and Wear Behavior

Fig. 2 shows the friction behavior of the MoS_2+TiN multiphase coatings measured using a pin-on-disc apparatus. The friction measurements were performed using a 9.53 mm Si_3N_4 sphere as a counter surface with an applied force of 16.4 N, a sliding oscillation frequency of 40 cycles/min, and a wear track diameter of 20 mm. The friction coefficient values measured for several specimens having a MoS_2-rich composition (~80% at coating surface) were relatively low, in the range of 0.1 to 0.3 for the test duration of 12.5 min. For longer durations, the coating specimen apparently had worn through as indicated by increases in friction coefficient with time. A wear groove of ~10 μm depth was measured after 80 min. In contrast, a TiN-rich coating specimen (with less than 10% MoS_2) when tested under the same conditions showed higher friction coefficients. The friction coefficient was initially 0.5, increased to 0.7 in the first 2 min of sliding, and eventually increased to 0.8 after 5 min. In this case, the only evidence of wear was the flattening of the coating surface in the wear path caused by the removal of prominent summits that existed on the coating surface.

The general trend from the wear tests was that the friction coefficient tended to increase with run time. The formation of the graded structure probably contributed to the increase in friction as the coatings wore. Other types of frictional variations were also observed, reinforcing the idea that the composition and microstructure of the coatings varied through coating depth and that the surface of some coatings was somewhat compositionally and microstructurally inhomogenous. Nevertheless, the friction and wear behavior observed for the MoS_2+TiN coatings demonstrated that the multiphase concept could be used to design and engineer a new class of self-lubricating coating materials.

GRADED METAL-CERAMIC INTERFACES

Synthesis and Characterization

Improving the adhesion between two dissimilar materials such as a metal and a ceramic under thermochemically and thermomechanically severe environments is a major technical challenge. One may find such an example in trying to protect Ni-based superalloys from oxidative environments. The protection has been traditionally achieved by applying metallic coatings such as diffusion pack NiAl and plasma sprayed NiCrAlY coatings. These coatings typically form an adherent, thin Al_2O_3 scale upon oxidation. Since Al_2O_3 is stable and relatively resistant to rapid oxygen diffusion, further oxidation is retarded once the scale is formed. However, with subsequent thermal cycles, the protective scale tends to microcrack and eventually spall off. From a mechanical point of view, the principal driving force for scale spallation is the development of stresses at the interface between the oxide scale and the metal surface, because of the large differences in coefficient of thermal expansion and Young's modulus. The possibility of improving scale adherence by gradually grading the interface between the metallic surface and Al_2O_3 scale has been explored.

A graded Al_2O_3+NiAl interface can be created by CVD (16). In this method, $AlCl_3$ vapor reacts with Ni atoms from the Ni-based superalloys to form β-NiAl in the presence of H_2 at temperatures of about 1000°C. At the same time, the control of the CO_2 partial pressure during aluminizing by pulsing is used as a means of nucleating and growing small Al_2O_3 particles in the NiAl coating matrix:
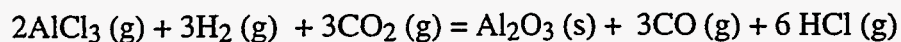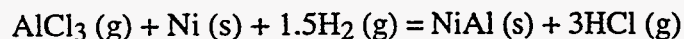
$$AlCl_3 \text{ (g)} + Ni \text{ (s)} + 1.5H_2 \text{ (g)} = NiAl \text{ (s)} + 3HCl \text{ (g)}$$

$$2AlCl_3 \text{ (g)} + 3H_2 \text{ (g)} + 3CO_2 \text{ (g)} = Al_2O_3 \text{ (s)} + 3CO \text{ (g)} + 6 HCl \text{ (g)}$$

Fig. 3 shows that very fine Al_2O_3 particles could be dispersed in a NiAl coating matrix by periodically pulsing a controlled amount of CO_2 during aluminizing (16). The oxide particles were randomly and isotropically dispersed. But, near the coating surface, the shape of the Al_2O_3 particles became more columnar. Fig. 4 shows that the size of the Al_2O_3 particles as well as the amount of the α-Al_2O_3 phase increased with coating thickness, although the dosing sequence and CO_2 concentration were kept constant throughout the deposition experiment. The formation of this somewhat graded structure is attributed to the fact that the NiAl growth process slows with coating thickness since it is controlled by solid-state diffusion (17), whereas the Al_2O_3 formation continues at a constant rate. It was also observed that, if the formation of Al_2O_3 becomes too dominant

so as to form a continuous layer on the deposition surface at high CO_2 concentration or long CO_2 dosing situations, the NiAl growth becomes inhibited since Ni atoms cannot easily diffuse through the oxide layer. The NiAl coating matrix, which was identified to be β-NiAl by electron diffraction, consisted of relatively large grains on the order of several hundred micrometers. The oxide particles were identified as α-Al_2O_3 single crystal grains by electron diffraction.

Mechanical Properties

The hardness and elastic modulus along the metal-ceramic interface have been measured by nanoindentation. Initial results indicate that both hardness and elastic modulus values are somewhere between those of pure NiAl and Al_2O_3 coatings made in the same CVD reactor (18). But, the nanoindentation measurements were found to be rather sensitive to specimen preparation and particularly to the exact location of indents, requiring a detailed microscopic evaluation after the nanoindentation measurements. The distribution of residual stress in an idealized NiAl+Al_2O_3 bond coat structure on a disc-shaped superalloy substrate after a uniform temperature drop of 1000°C was modeled using a finite element method. The calculated benefit of the graded layer was pronounced at the corner locations where the Al_2O_3 and bond coat layers intersect (18). The out-of-plane stress along the sharp Al_2O_3-NiAl interface reaches a stress singularity at the corner location, i.e., infinite stress in the tensile direction. But, the stress at the same location with the graded interface was in compression, and much smaller in absolute magnitude (-100 MPa). Similarly, the graded interface was expected to be useful in managing shear stress at the corner locations. Therefore, these results indicate that, from a point of view of managing residual stress, the functionally graded interface may provide a mechanism to reduce crack initiation at these crack-sensitive locations. Optimum coating microstructure and compositional grading are being designed by considering various processing, microstructure, oxidation, and fracture mechanics issues.

FUTURE DIRECTION

To a large extent, the experimental results obtained for the above multiphase systems are preliminary, but yet encouraging. These examples demonstrate that it is certainly possible to tailor material properties and performance using a multiphase concept. However, as also evident from these illustrations, more interdisciplinary investigations are needed to study various aspects of producing highly sophisticated multiphase materials and characterizing, measuring, and optimizing their relevant properties. From an application point of view, a critical issue is to assess the possibility of preparing multiphase materials with homogenous microstructure and composition over relatively large surface areas, as these deposit characteristics could be significantly affected by process factors such as preferential depletion of particular reagents, non-uniform temperature distribution, flow instabilities, etc. Also, the sensitivity of these microstructural and compositional variations in dictating ultimate material performance should be addressed. More fundamentally, a scientific methodology needs to be developed for understanding kinetic mechanisms and nucleation and growth characteristics of chemically complex multiphase CVD systems. Another important issue is that it currently requires time-consuming and costly iterations between deposition experiments and ex-situ characterization steps before meaningful processing-microstructure relationships can be developed. The concept of integrating in-situ

microstructural sensors with CVD reactors, at least in principle, may allow rapid microstructure optimization.

. ACKNOWLEDGMENTS

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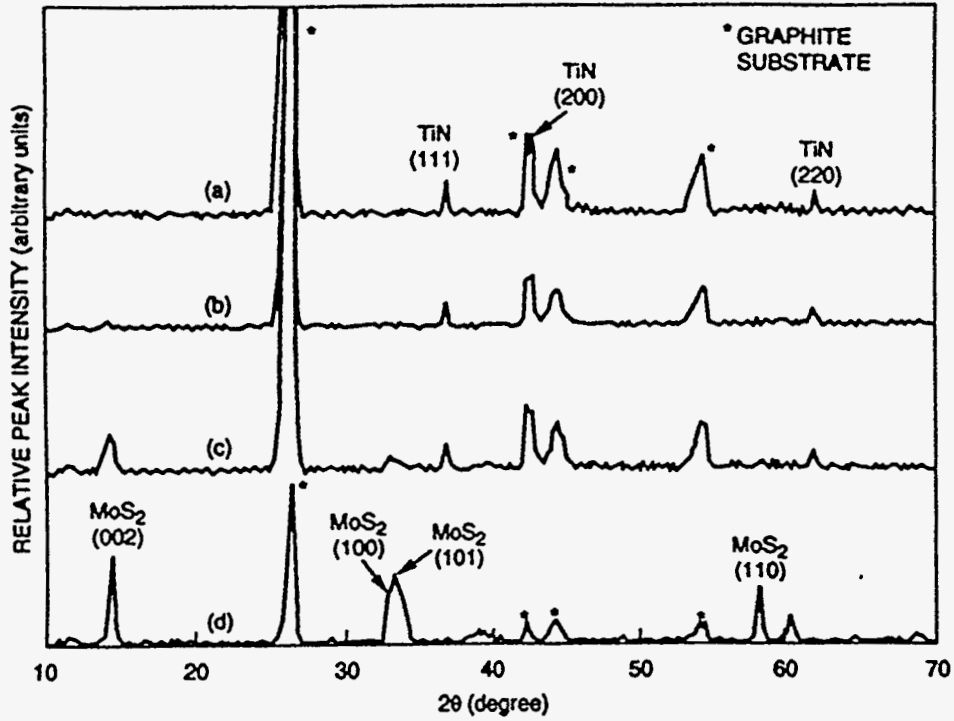18. Manuscript in preparation.

Fig. 1. XRD patterns of multiphase coatings deposited at 820°C and inlet MoF_6 partial pressures of: (a) 2.8 Pa, (b) 6.9 Pa, (c) 9.6 Pa, and (d) 13.6 Pa. All other process parameters were kept constant for the deposition experiments. From Ref. (15).
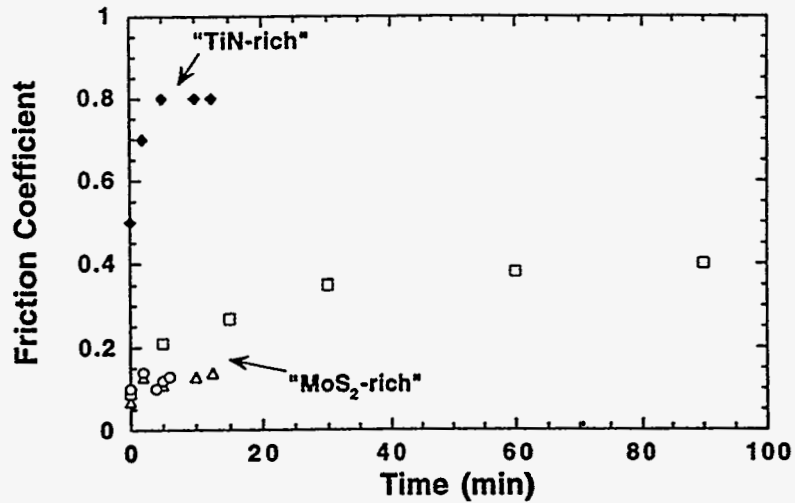
Fig. 2. Friction curves of "TiN-rich" and "MoS_2-rich" coatings deposited on Ti-6Al-4V alloy substrates.
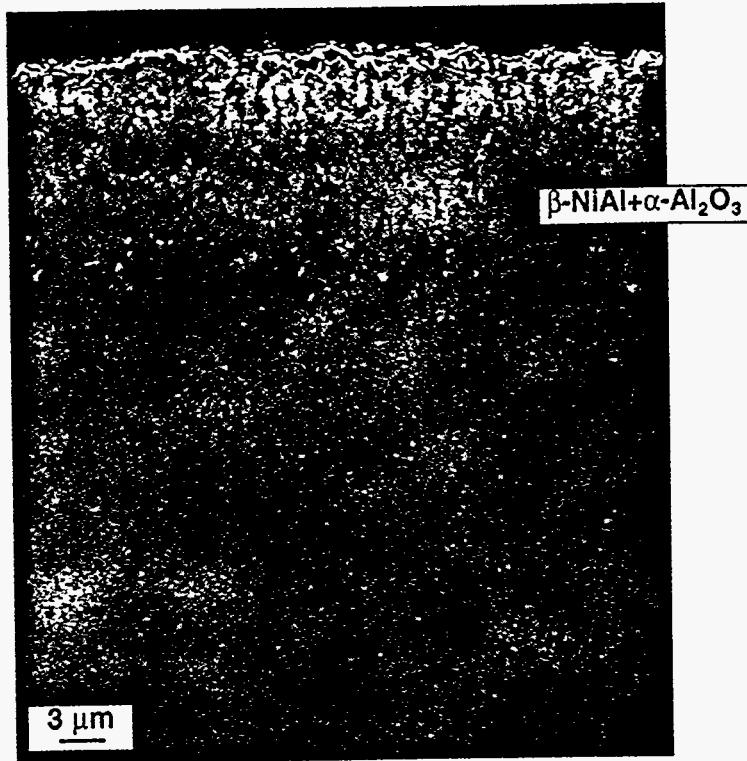
β-NiAl+α-Al$_2$O$_3$

3 μm

Fig. 3. A cross-sectional scanning electron microscopy (SEM) image showing the dispersion of α-Al$_2$O$_3$ particles (dark particles) in a β-NiAl coating matrix. This dispersion was achieved by pulsing a controlled amount of CO$_2$ for 10 s after every 1 min for a 4-hour period (i.e., 205 pulses) while other process parameters remained constant.
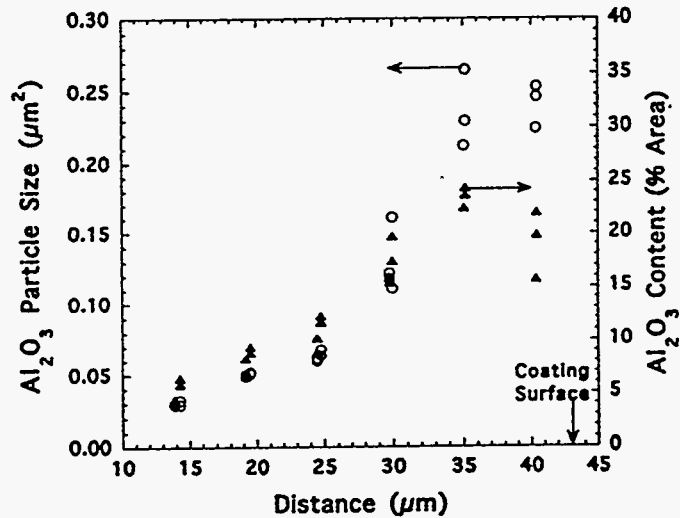
Fig. 4. The particle size and the amount of the Al$_2$O$_3$ phase increased with coating thickness. The SEM image in Fig. 3 was digitally analyzed at three different horizontal locations for each thickness interval.

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