Communication

The Influence of Ni-Coated TiC on Laser-Deposited IN625 Metal Matrix Composites

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IN625 Ni-based metal matrix composites (MMCs) components were deposited using Laser Engineered Net-Shaping (LENS) with Ni-coated and uncoated TiC reinforcement particles to provide insight into the influence of interfaces on MMCs. The microstructures and spatial distribution of TiC particles in the deposited MMCs were characterized, and the mechanical responses were investigated. The results demonstrate that the flowability of the mixed powders, the integrity of the interface between the matrix and the TiC particles, the interaction between the laser beam and the TiC ceramic particles, and the mechanical properties of the LENS-deposited MMCs were all effectively improved by using Ni-coated TiC particles.

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Particle-reinforced metallic matrix composites (MMCs) are of interest in many applications due to their multifunctionality, which yields combinations of properties, such as high specific strength, stiffness, and toughness, and a low coefficient of thermal expansion, that are unachievable with conventional materials.[1] Ni-based MMCs with ceramic reinforcements are used in a wide range of industrial operations with cutting, rolling, pelletizing, stamping, piercing, drawing, punching, *etc*.[2] Various synthesis methods, including casting and powder metallurgy techniques, have been used for conventional manufacturing of MMCs.[3,4] The presence of undesirable interfacial reactions and particle segregation represents two key issues that have limited the use of casting methods, partially due to an extended contact time between ceramic particles and the molten metal and density differences between ceramic and metals. In contrast, whereas conventional powder metallurgical routes avoid the presence of a liquid phase, these are relatively complex processes frequently limited in terms of product geometry. The LENS* process, incorporating features from stereolithography and laser cladding, is a laser-assisted direct metal manufacturing process that provides a pathway to produce net-shaped components from a three-dimensional (3-D) computer-aided design file.[5] The primary advantages associated with LENS are the following: a small heat affected zone with high cooling rate resulting in fine microstructures; easy gradient deposition of multiple materials within a single component; and fully dense near-net-shape metal components. However, only spherical powders with diameters of 36 to 150 μm are recommended for use in LENS processing.[6] Thus, optimization of the LENS requires fundamental study of the influence of fine and irregular shaped ceramics particles in the case of MMCs.

The strength and stability of the interfacial region between the reinforcement particles and metal matrix govern the mechanical properties of MMCs, and extensive efforts have been devoted to understanding and manipulating the interfacial behavior in MMCs. In the case of metal-ceramic MMCs, it is often desirable to promote wettability while simultaneously avoiding undesirable interfacial reactions. One strategy that has been implemented is to coat the reinforcement particles in order to modify the interfacial structure and to promote wettability.[3] The challenge of achieving wetting at the metal-ceramic interface can be mitigated by encapsulating the ceramic particle with a metal coating.

In the present study, Ni-coated TiC particles (TiC/30 wt pct Ni) were used as a reinforcement phase in Ni-based IN625 (Ni-based superalloy—Ni: balance, Cr: 22 to 23 wt pct, Fe: 5 pct, Mo: 8 to 10 pct, (Nb + Ta): 3.15 to 4.15 pct, Co: 1 pct, Mn: 0.5 pct, Si: 0.5 pct, Al: 0.4 pct, Ti: 0.4 pct, and C: 0.1 pct[7]) MMCs. TiC was used because of its extremely high hardness, 33 pct higher than that of WC at room temperature,[8] and chemical inertness. TiC reinforcement is also thermodynamically stable in Ni matrices and has a low coefficient of friction. The LENS process was employed to fabricate IN625-based MMCs with Ni-coated and uncoated TiC particles as reinforcements. The microstructures of the LENS-deposited MMCs were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques. Efforts were devoted to evaluating the effects of using Ni-coated TiC on the flowability of mixed powder, the interface between the matrix and the TiC particles, the interaction between the laser beam and TiC ceramic particle, and the mechanical properties of the LENS-deposited MMCs in combination with analysis of the LENS process.

*LENS is a trademark of Sandia National Laboratories, Albuquerque, NM.

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The matrix powders used in LENS deposition were gas-atomized IN625 powder, which have a particle size range of 45 to 125 μm. The reinforcements were Ni-coated TiC particles with size up to 45 μm, which were produced with a chemical vapor deposition (CVD) fluid bed reactor.[9] Uncoated TiC particles were also used for comparison purposes. 14 wt pct uncoated TiC particles was added in the mixed powder, which has the same amount of TiC as 20 wt pct Ni-coated TiC. The powders with different weight fraction of reinforcements were mixed and blended using a V-blender for 1 hour.

The LENS experiments were performed with a 750 LENS system (Optomec, Inc. Albuquerque, NM), which consists of a continuous wave (CW) mode Nd:YAG laser operating to 650 W at 1064 nm, a four-nozzle coaxial powder feed system, a controlled environment glove box, and a motion control system.[10] The entire process was carried out in Ar environment to avoid oxidation, and the oxygen level in the glove box was maintained around 5 ppm during deposition. A 316L stainless steel plate was used as the substrate. The processing parameters of laser output power, traverse speed, and powder feed rate are also listed in Table I.

Cubical samples of 10 mm $\times$ 10 mm $\times$ 50.8 mm were fabricated. Successive layers were deposited with the hatch lines of two adjacent layers at an angle of 90 deg. The layer thickness, hatch spacing, and work distance (from end of nozzle to the deposited surface) were set at 0.25, 0.38, and 9.5 mm, respectively.

The cross-sectional microstructure of the fabricated MMC samples was observed with SEM. The TEM samples were first mechanically ground and polished to a thickness of about 80 μm, and then thinned further through mechanical dimpling and ion milling to obtain electron-thin areas for TEM observation. The XRD with Cu K_α radiation was used for microstructure and phase analysis. Mechanical behavior was evaluated using tensile tests at ambient temperatures with an INSTRON** 8801 universal testing machine. The as-deposited MMCs were electrodischarge machined into flat dog-bone tensile specimens along the deposition direction, with a gage length of 12 mm, width of 4 mm, and thickness of 2 mm. The gage sections of the tensile specimens were polished in order to reduce the effect of surface defects. The tensile specimens were tested to failure with an initial strain rate of 10^{-3}/s, with a load cell with an accuracy of less than 0.5 pct of the indicated load and a dual-camera video extensometer with an accuracy of 5 μm for directly measuring the displacement of the tensile gage section.

**INSTRON is a trademark of Instron, Canton, MA.

Figure 1(a) shows the SEM (backscattered electron (BSE)) micrographs of Ni-coated TiC particles (TiC/Ni), indicating that irregularly shaped TiC particles are completely encapsulated by the Ni coating with a thickness of about 2 μm. Some fine TiC particles (1 to 5 μm), which presumably originate from interparticle collisions during the coating processing, were embedded in the Ni coating layer.

The TEM studies, as given in Figure 1(b), showed that the coating is comprised of single-phase, nearly equiaxed grains with a size range from 10 to 100 nm, indicating that the Ni coating is nanocrystalline. Nanostructure in the coating can be rationalized to a rapid quenching during cooling from the vapor state during CVD. As such, it has been argued that rapid displacement of the liquid/solid interface will lead to an equiaxed structure with nanoscale dimensions due to limited growth time during rapid solidification.[11,12] No apparent reaction or defects, such as pores, cracks, or dislocations, were observed at the interface between the nanocrystalline Ni coating and TiC particles. The TiC core and the Ni coating appear to be well bonded, at least from a physical standpoint.

The morphology of coated TiC particles is more spherical and smooth than that of uncoated TiC particles. Spherical particles are beneficial for the delivery system used in LENS processing, given that their flowability is higher. During LENS deposition, feedstock powder is delivered *via* a carrier gas through four nozzles that converge at the same point as the focused laser beam to form a molten pool, and a 3-D part can be generated by scanning the surface depositing layer by layer *via* additive processing. The variation of powder flowability was studied by collecting delivered powder within 2 minutes with different feeder rotational speeds, and the results are shown in Figures 1(c) through (f). The flowability of mixed powder (*e.g.*, including the coated particles) is about 12 pct lower than that corresponding to gas-atomized IN625 powder and is much higher, about 108 pct, than that containing uncoated ceramic powder. Generally, it is difficult to feed fine ceramic particles (<30 μm) into the molten

Table I. Processing Parameters for LENS-Deposited IN625 MMCs

	Mixed Powder			LENS Process Parameters			
		Reinforcement					
Number	Matrix	(Wt Pct)	(Vol. Pct)	Geometry (mm)	LOP (W)	LTS (mm/s)	PFR (rpm)
A	IN625	0	0	10 × 10 × 50	280	14.8	10
B		10 pct TiC/Ni	11 pct TiC/Ni				
C		20 pct TiC/Ni	22 pct TiC/Ni				
D		14 pct TiC	22 pct TiC				

Note: Laser output powder (LOP), laser travel speed (LTS), and powder feeder rate (PFR).

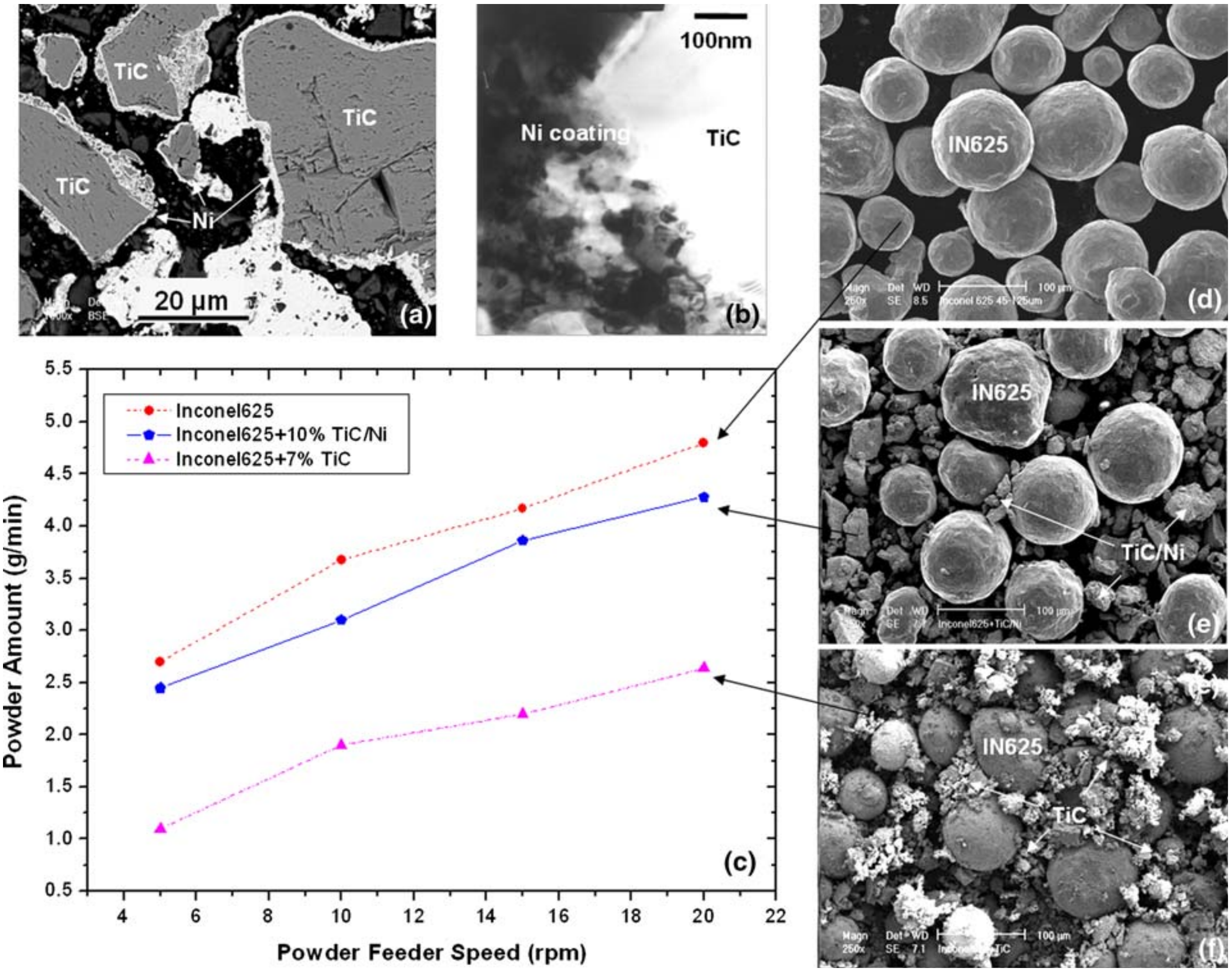

Fig. 1—Variation of powder flowability with different mixed powders: (*a*) SEM and (*b*) TEM morphology of Ni-coated TiC particles; (*c*) curve of powder delivery amount with feeder speed; and feeding powder of (*d*) gas-atomized IN625, (*e*) mixed powder of IN625 + 10 pct TiC/Ni, and (*f*) mixed powder of IN625 + 7 pct TiC.

pool due to the low weight and density of fine ceramic particles (the density of TiC is 4.9 g/cm^3) and low flowability of irregular ceramic particles. Fine ceramic particles are easily carried away by gas flow, and hence fail to attain intimate contact with the molten pool during feeding, partly due to vigorous turbulent gas flow in the region immediately adjacent to the powder nozzles. In principle, metal-coated powder particles should have improved flowability and more effective powder feeding due to increases in ceramic particle mass, more spherical morphology, and a smoother surface.

Figures 2(a) and (b) show the SEM micrographs of the LENS-deposited IN625 MMC with 20 wt pct Ni-coated TiC. The TiC particles are uniformly distributed in the IN625 matrix. A portion of the Ni coating still remained on TiC particles, as shown by the arrow marked in the Figure 2(b) SEM (BSE) micrograph, and the interface between TiC and matrix appeared as continuous and defect free. The Ni coating on the TiC particle surface was also observed to have undergone partial remelting and dissolved into the IN625 matrix during LENS processing. Typical microstructures of LENS-deposited IN625 with uncoated TiC are shown in Figures 2(c) and (d). The fraction of TiC particles shown in Figure 2(c) is evidently lower than that shown in Figure 2(a) due to a loss of uncoated TiC particles during feeding. This is consistent with the flowability analysis shown Figure 1. Porosity was also observed in deposited MMCs with uncoated TiC, as shown with the arrow (P) marked in Figure 2(c). Ceramics are generally harder to process by laser beam than metals due to their poor thermal shock characteristics and high melting points. The metal coating on the ceramic particles may have helped diminish the thermal shock experienced by ceramic particles when exposed to the incident laser beam, thereby reducing porosity formation.

The surface of some uncoated TiC particles was found partially melted and resolidified during LENS processing, as shown in Figure 2(d). The phenomenon of TiC particle melting during exposure to a laser beam has also been noted by another investigator[13] and rationalized by the fact that TiC particles have a much higher capability to absorb laser energy than that of metals. In fact, ceramics absorb energy better than metals only at both ends of the spectrum of wavelength: 0.1 to 10 μm, such as for a CO_2 laser with a wavelength of 10.6 μm, but worse than metals in the case of a Nd:YAG laser,

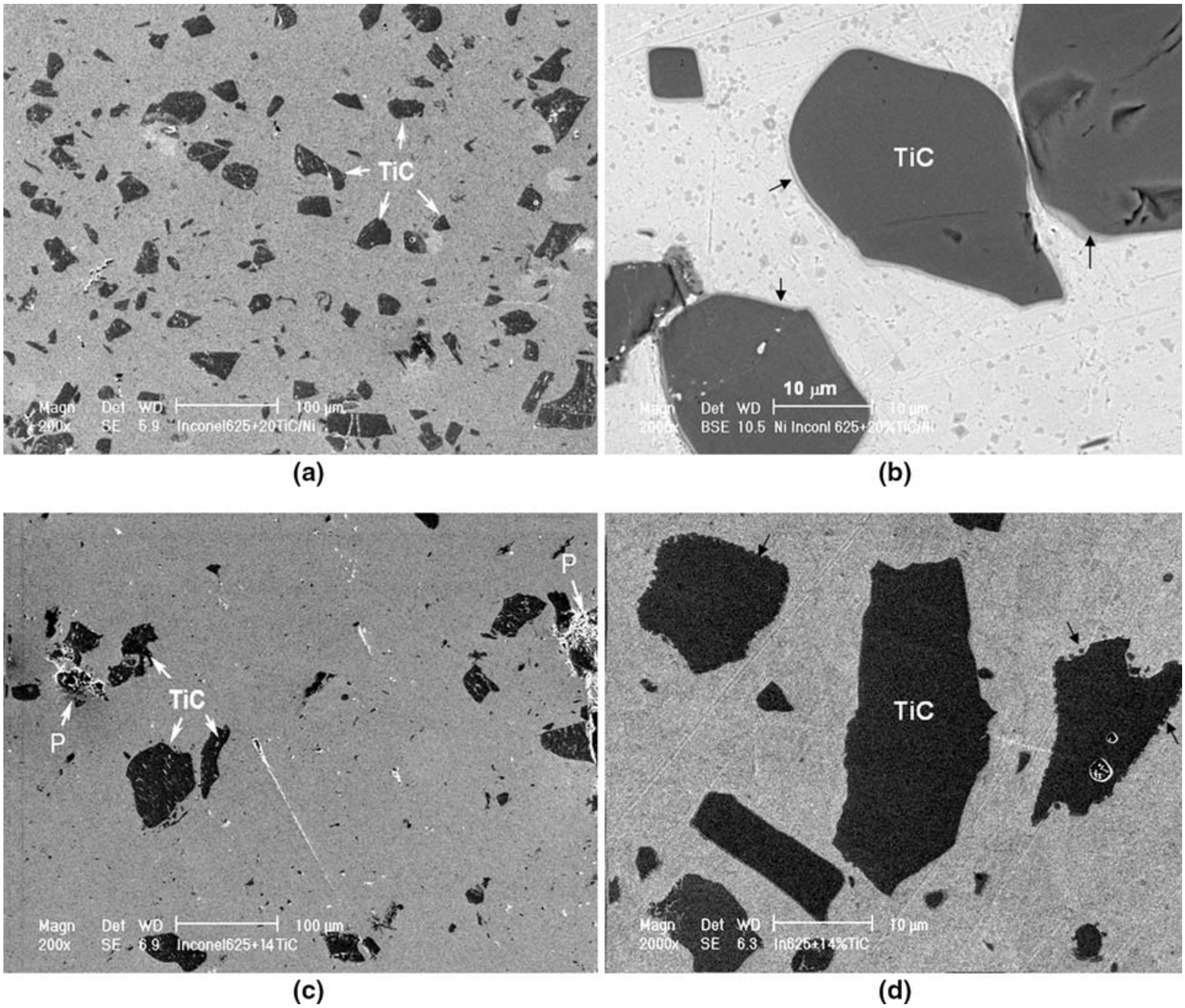

Fig. 2—SEM micrographs of LENS-deposited (*a*) and (*b*) IN625 + 20 wt pct TiC/Ni and (*c*) and (*d*) IN625 + 14 wt pct TiC MMCs.

whose wavelength is 1.064 μm. The CW Nd:YAG laser beam used in LENS processing has a circular cross section with a Gaussian intensity distribution, which can generate a high-temperature gradient in the molten pool. The temperature in the center of the molten pool may be high enough to cause melting of TiC particles, even though the melting temperature of TiC is 3160 °C, which is much higher than that of IN625 (1350 °C). Since the laser processing time is extremely short (about 2.5 ms), melting of coarse TiC may not occur completely. The extent of TiC melting is basically governed by the magnitude and amount of incident laser energy, which depends on the processing parameters used, such as laser power output, laser travel speed, and powder feed rate.[5,14,15]

The uniform distribution of TiC particles observed can be attributed to the stirring effect produced by the high-energy density of the laser beam, in combination with vigorous convection flow in the molten region. The motion of liquid metal is very turbulent in the molten pool, where the convection is a dominant transport mechanism.[16,17] Convection is primarily responsible for mixing in the molten pool and therefore possibly leads to an increase in the randomness of the TiC particle distribution during LENS processing. Meanwhile, it is evident that the Ni coating on the TiC particles surface experienced remelting during deposition, which can be resolved into IN625 matrix liquid due to the convective flow of melt in the molten pool. Evidence for the presence of Ni coating on TiC particle surfaces is shown in Figure 2(b); this figure also provides support for the suggestion of a strong bonding between the Ni-coating and TiC particles. From XRD results, only peaks corresponding to TiC and Ni crystals were found in the LENS-deposited MMCs, suggesting the absence of or limited reaction between the Ni-based matrix and the TiC particles, while the intermetallics and other reagents could not be observed within the resolution of XRD (less than 2 vol pct) techniques.

Figure 3 shows TEM bright-field images of the microstructure of the laser-deposited MMC containing Ni-coated TiC particles. A large amount of dislocations are evident in the matrix and were presumably induced by the residual stress between the reinforcement and matrix, possibly generated by rapid melting and cooling to accommodate the difference in coefficient of thermal

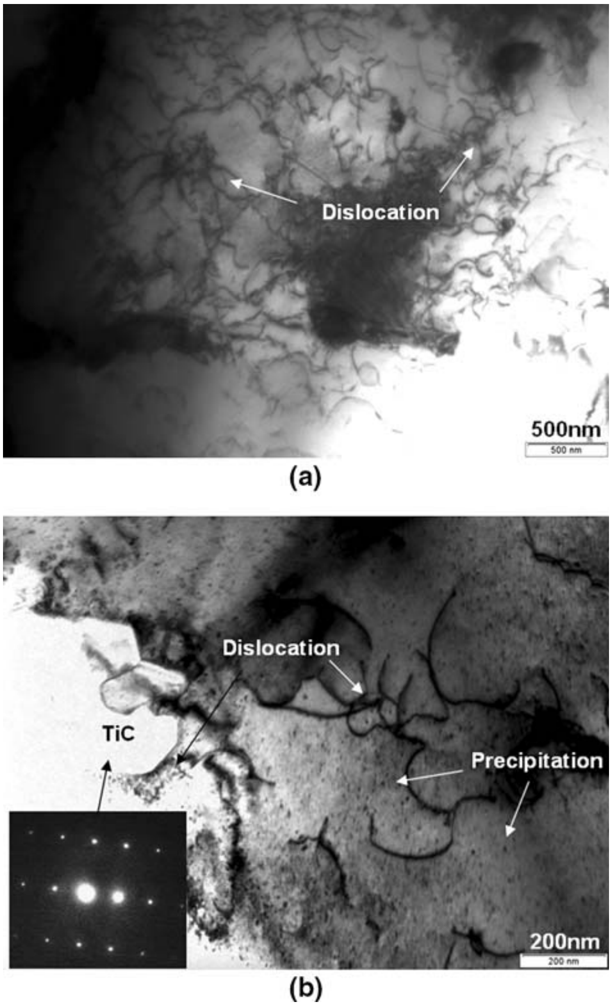

Fig. 3—TEM micrographs of LENS-deposited IN625 + 20 wt pct TiC/Ni MMCs: (*a*) high density of dislocation in matrix and (*b*) large amount of precipitation interacting with dislocations.

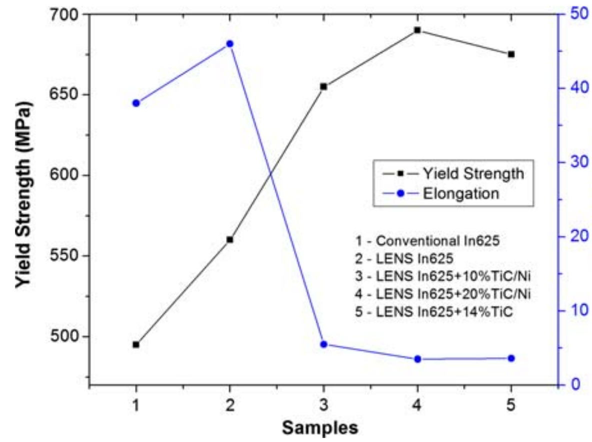

Fig. 4—Tensile test result of LENS-deposited IN625 alloy and composites.

expansion (CTE) between the matrix and TiC reinforcements. The average CTE of TiC is 7.4×10^{-6}/°C,[8] whereas the average CTE of IN625 is 13.1×10^{-6}/°C.[7] Therefore, when cooled to room temperature, the thermal stress around TiC particles could reach over 500 MPa, which is higher than the yield strength of annealed IN625. Furthermore, due to the layer additive nature of LENS processing, the thermal behavior associated with LENS processing involves multiple reheating cycles,[15] leading to thermal stress cycles, which could also cause the generation of dislocations in IN625 matrix. The TiC particles were dispersed in the matrix with a clean interface, and no voids, cracks, inclusions, or other defects were evident at the interface between the TiC and surrounding matrix. This suggestion is supported by the observation that, despite the severe strain applied to the sample during TEM sample preparation, no cracking or debonding was evident. This qualitative observation suggests that a strong interface bond between the hard phase particles and the matrix was achieved. Large amounts of nanosized particles $<$20 nm, possibly of gamma prime, γ', were evident in the matrix. These nanoprecipitates likely evolved during tempering or aging cycles, which is typically imposed by the inherent cyclic thermal environment during LENS deposition, leading to some solid-state transformations.[10]

The mechanical tensile test results of the LENS-deposited IN625 alloy, IN625 + 10 wt pct TiC/Ni MMC, IN625 + 20 wt pct TiC/Ni MMC, and IN625 + 14 wt pct TiC MMC are summarized in Figure 4. Both the yield strength (YS), 560 MPa, and percent elongation (pct EL), 46, of LENS-deposited IN625 alloy are higher than those of conventional wrought IN625 (conventional IN625 at RT: YS is 496 MPa and EL is 38 pct[7]). The YS values of IN625 + 10 pct TiC/Ni and IN625 + 20 pct TiC/Ni are 655 and 690 MPa, respectively, obviously improved as compared to monolithic matrix alloy IN625. The ductility, however, is relatively low, 5.5 pct for IN625 + 10 pct TiC/Ni and 3.5 pct for IN625 + 20 pct TiC/Ni. In comparison with the tensile test results of the LENS-deposited IN625 + TiC MMCs, the strength of LENS-deposited IN625 + 20 pct TiC/Ni MMC is higher. There is, however, no significant difference observed for YS and pct EL between using Ni-coated and uncoated TiC particles. The increased strength of the MMC containing Ni-coated TiC can be rationalized on the basis of an improvement in interfacial behavior between TiC and the matrix and a reduction of porosity. The increase in strength of the LENS-deposited IN625 containing TiC MMCs can be attributed to the reinforcing effect of TiC particles, the grain size refinement of IN625 matrix from the relatively high cooling rate during LENS processing, the presence of precipitated nanosized particles, and an increased dislocation density, as shown in Figure 3.

In summary, the LENS process was successfully used to fabricate IN625 MMC components with Ni-coated and uncoated TiC particles as the reinforcement phases. Analysis of the deposited microstructures reveals that a portion of the Ni coating remains on the TiC particles and that some of the uncoated TiC surfaces remelted during LENS processing. Large amounts of nanosized particles precipitated in the LENS-deposited IN625 MMCs, which showed much higher strength as compared to that of the monolithic matrix IN625 alloy.

The strength of MMC with coated TiC particles is also slightly higher than that of MMC with uncoated TiC particles. The flowability of the mixed powder, the interface between the matrix and the TiC particles, the interaction between the laser beam and TiC particles, and the mechanical properties of the LENS-deposited MMCs were effectively improved by using Ni-coated TiC particles.

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