MODIFIED T-T-T BEHAVIOUR OF IN625® COLD SPRAYED COATINGS

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Keywords : Inconel 625, Precipitation, T-T-T diagram, Gamma double prime (γ''), Delta (δ), Cold spray coatings

Abstract

Inconel® [Trademark of Special Metals Corporation] 625 (IN625), a well-known nickel based superalloy used for corrosion resistant applications, was cold sprayed on to 4130 steel substrates. The alloy microstructure, typically strengthened by metastable γ'' ($\text{Ni}_3(\text{Nb}, \text{Al}, \text{Ti})$) precipitates, was found to be devoid of any precipitates in the as sprayed coating. The coating process, involving severe plastic deformation of the alloy powder particles, resulted in transforming the IN625 alloy to comprise a complete solid solution. A suppression in the precipitation of both the metastable (γ'') as well as the stable (δ) precipitates, is seen, even up to a temperature 800°C, 100 h. The thermal relaxation of the alloy was evaluated and a modified Time-Temperature-Transformation behavior is proposed, for this alloy when subject to severe cold work.

Introduction

Ni based superalloy Inconel 625® is an excellent choice for applications involving sea water corrosion and is popularly used for other oxidation and corrosion resistant applications, over a wide range of temperatures, up to nearly 982°C [1]. Alloying elements such as niobium and molybdenum, impart the superior corrosion properties to the alloy, as well as serve to strengthen the alloy matrix, via predominantly a solid solution strengthening. However, beyond 650°C, hardening is found to take place by the precipitation of a metastable γ'' ($\text{Ni}_3(\text{Nb}, \text{Al})$) phase, having a DO_{22} (ordered fcc) structure [2-7]. This phase eventually transforms to the equilibrium δ -(Ni_3Nb) orthorhombic phase, upon prolonged aging. This study comprises the phase evolution in IN625 coatings obtained by the cold spray coating process. In recent times, the cold spray coatings technology has attracted a lot of attention for several applications, by virtue of its ability to produce pore-free dense metallic coatings, up to thicknesses as much as 5-6 mm, for various metallic materials [8-12]. Thus the cold spray technology has resulted in being very effective in resulting in surface enhancements over a wide range of industrial sectors, including in enabling cost effective solutions to the equivalent bulk forms. The process is also attractive for various surface engineering applications, including additive manufacturing, since it does not expose the parent or base material to high temperatures, and there is no melting of the powders, thereby avoiding the undesirable effects of oxidation and other associated reactions, normally associated with thermally sprayed coatings. The coating process involves a ballistic impingement of the metal powder particles (at velocities ranging between 800-1000 m/s), upon the substrates (at strain rates ranging between 10^5 - $10^7/\text{s}$), to result in the thick (up to several mm) coatings. Despite the vast numbers of studies on the cold spray technology, there is a scarcity of data when it comes to detailed microstructural understanding of these coatings subject to severe plastic

deformation. Several reports are in agreement as to the severely deformed structure of the cold sprayed coatings, in the as sprayed condition for relatively soft metals such as Cu, Al, Ti, Mg, however, most of these reports focus on obtaining dense coatings and there are not too many reports that record details of the coating microstructure, with particular reference to the coating thermal stability and relaxation of the microstructure.

In the present study, the IN625 coatings sprayed using the cold spray process, have been studied in detail, both in the as sprayed condition as well as upon isothermal heat treatment. The present report will focus on the on coating response to heat treatment, in the as coated condition, as well as upon conventional solution treatment and subsequent aging. Via these studies, this paper brings out a modified T-T-T diagram for Inconel 625 alloy when applied as a cold sprayed coating.

Experimental Details

IN625 commercial powders (5-22 μm) size, obtained from H.C. Starck, were deposited on to low alloy steel, AISI 4130 substrates of 200 x 50 x 6 mm (L*w*t), powders were cold sprayed, using Cold Gas Technology's (CGT) Kinetiks 4000/47 spraying system, using a gas pressure of ~30 bars, with a gas temperature of ~500°C. Table 1 lists the nominal composition of the IN625 powders, along with the measured values, using ICP-OES (inductively couple plasma optical emission spectroscopy). The process gas used was Helium, using ~ 30 bar pressure, to deposit three nominal coating thicknesses, of 0.5, 2 and 3 mm. The substrate was grit blasted prior to depositing the powders, and measured a roughness of ~1 μm R_a , while the coated samples measured between 4-5 μm R_a , after deposition. In order to establish the thermal stability of the cold sprayed coatings, a series of heat treatments between 350°– 800°C were carried using a Lindberg box-type furnace, in air, for various lengths of time. For comparison a bulk IN625, cold rolled alloy solution treated at 1100°C, for 1.5 h, furnace cooled, and aged at 650°C, 100 h, was studied in order to monitor the precipitation kinetics. The typical furnace heating rate used was 10°C/minute and the furnace cooling rate was at 5-8°C/minute. Table 2 lists the range of heat treatments and times, carried out for the cold sprayed IN625 coatings as well as the bulk sample.

Table 1 : Compositions (wt%) of IN625 powders and the 4130 low alloy steel substrate
(*Measured using ICP-OES, NR –Not recorded)

Alloy	Ni	Cr	Mo	Fe	Nb	Ti	Al
Nominal IN625 Bulk	58 (min)	20-23	8-10	5 (max)	3.15- 4.15	0.4	0.4
Measured IN625 Bulk*	59.83	22.29	9.43	4.35	3.30	NR	NR
Measured IN625 powders*	60.25	22.94	9.68	3.66	3.35	NR	NR

Table 2: Heat treatment details with the times and temperatures
(All temperatures are in °C and time in hours)

Solutionizing	1100°C, 1.5 h, Furnace Cool
Annealing Temperature	350, 450, 550, 650, 700, 800
Annealing Time	2, 10, 100, 500, 1000

Preliminary coating characteristics were studied using X-ray diffraction (XRD-XPRT, $\text{CuK}\alpha$ radiation). The coating thickness and porosity was determined using the optical microscope (Nikon-MA200) using a Clemex image analyser. At all the time-temperature combinations, hardness measurements were carried out using a Vickers microhardness tester (Shimadzu), at a load of 300g, on polished surfaces of the aged specimens. An average of 10 readings was calculated for each condition. The coating microstructural evolution was monitored using a transmission electron microscope (TEM) JEOL 2000FX2 as well as a JEOL 2011, FASTEM, operated at 200 KV. Electron transparent samples were electrolytically thinned from ground 100 μm thick discs that were 3 mm in diameter. The polishing solution for TEM samples comprised, methanol and perchloric acid, in the ratio 80:20, 228-238K (-45 to -35°C) 4-5 V and 25 milliamps current. Coating chemistry was assessed using Energy Dispersive X-ray Analysis (EDAX), using an Oxford Link system attached to the TEM.

Results

Three coating with thicknesses of 0.5, 2 and 3 mm were deposited using Helium as the process gas. However since the coating microstructure did not vary as a function of thickness, all the detailed microstructural studies were carried out on the 3 mm thick coating, using the transmission electron microscope. A minimum of 3 foils taken from different locations were studied for each condition.

As Sprayed Coating Microstructure

The coatings showed a dense, well adhered structure, for all the three coating thicknesses, 0.5, 2 and 3 mm, respectively, as shown in Figs. 1 (a-f). Figure.1 (a-c) are optical micrographs taken at 200 X to indicate a nearly 100% dense coating, with the legends indicating the average coating thickness, as well as the corresponding microhardness (in Hv). Figure. 1d is a representative SEM micrograph showing the corresponding coating substrate interface, with the Inset in Fig. 1d, showing a higher magnification of the interface. Figs. 1d and 1e reveal EDAX spectra taken from the IN625 coating and the 4130 steel, respectively. Preliminary phase identification of the coatings, using X-ray diffraction, reveals a single phase solid solution (Fig. 2), with peak broadening as well as a shift in the peaks, as compared to free standing IN625 powders, indicative of micro as well as macro strain in the coatings. There was no indication of any texture from the diffraction pattern, which corresponded to that of a face centered cubic (fcc) structure, with no additional superlattice reflections corresponding to any other phase. The peak broadening was symptomatic of a heavily deformed structure corresponding to non-uniform strain and the peak shift, calculated from the XRD pattern, revealed a lattice parameter of about 10% greater than that for pure Ni. Fig. 3(a-f) shows transmission electron micrographs of the as sprayed coating. The microstructure comprises two distinct regions, as shown in the low magnification TEM images in Fig. 3(a-b), Region I comprises large grains > 1 μm with a heavily deformed structure (Fig. 3c), and Region II, with shear bands and twins, measuring between 300-500 nm, as shown in Fig. 3d, are always present adjacent to each other in all the locations. Selected area diffraction patterns (SADP's) from Region I (Fig. 3e) shows a single crystal orientation of the grain with each reflection showing a somewhat pronounced streaking. Whereas, region II predominantly comprises twins, as seen from the occurrence of twin reflections next to the matrix ones, in the SADP (Fig. 3f). Both the SADP's in Figs. 3e and 3f,

show the beam along the [011] direction. Inserts in Fig. 3(3c and 3d) show dark field micrographs to illustrate the deformed grains and twins, respectively. However, at no instance was there any γ'' precipitate that could be seen, by way of the appearance of extra superlattice reflections in the selected area diffraction patterns (SADP) taken from both regions.

Fig. 1 : (a-c) Optical micrographs of the as sprayed IN625 showing a dense coating, (a) 0.5 mm, (b) 2 mm and (c) 3 mm, thickness, along with the average coating hardness. (d) SEM micrograph of the 3mm thick IN625 coating, along with (Inserts revealing the coating-substrate interface at a higher magnification). (e-f) the corresponding EDAX spectra from IN625 coating and (f) 4130 steel substrate.

Fig. 2 : XRD pattern comparing the cold sprayed coating to the free standing powders and the heat treated coating (after 650°C, 2.5 h).

Heat Treated Coating Microstructure

On annealing the coating, for 2.5 h at 650°C, the onset of recovery of the severe plastically deformed structure is seen, as shown in Figs. 4(a-b), corresponding to both regions, I and II. Region I is seen to have undergone some recrystallization in selective pockets within the grain, as shown in Fig. 4b, at a higher magnification. Insert in Fig. 4b shows the corresponding dark field (DF) image (020), with the SADP (Fig. 4c) now tending to show polycrystalline rings from this location. In a similar manner Region II, comprising twins, is also seen to undergo some relaxation of the deformed microstructure, in Figs. 4(c-d), at low and high magnification, respectively. Upon annealing for a longer time (100 h) at 650°C (Figs. 5(a-b)), as well as higher temperatures, of 700°C (Fig. 5(c-d)) and 800°C (Fig. 6(e-f)), for 100 h, the coating is seen to undergo a continuous recovery process, to result in a strain free grains. At 650°C, after 100 h, there is still the presence of two regions, however, at 700°C and 800°C, there is no longer any distinction in the microstructure with respect to the original two regions, and the overall coating reveals a uniform grain size between (800-1200 nm), with large angle boundaries demarcating the different grains. Inserts show selected area diffraction patterns corresponding to each temperature. Here again, there is no precipitation of γ'' phase even after 100 h at 800°C, with the absence of any super lattice reflections in the diffraction patterns, as well as the absence of any strain contrast with the grains (now presenting a more clean structure with limited deformation).

Fig. 3 : Bright field TEM micrographs showing representative microstructures of the as sprayed IN625 coating, (a-b) at low magnification, revealing two distinct regions adjacent to each other. Region I with $> 1\mu\text{m}$ grains having a highly deformed grain structure, Region II $< 1\mu\text{m}$ displaying deformation twins. (c and d) reveal regions I and II at higher magnification, and (e and f) SADP's from regions I and II, respectively. Inserts: Dark field TEM images from the representative regions.

Solution Treated and Aged Coating and Bulk IN625 Microstructure

In order to understand the phase evolution in the cold sprayed IN625 coating, the as sprayed coating was subjected to a solution heat treatment (1100°C, 1.5 h, furnace cool) and aging, akin to that of a bulk IN625 alloy. Figure 6 (a-c) shows the microstructure of the bulk alloy, after being aged at 650°C for 100 h. The bulk alloy clearly shows the precipitation of 10-20 nm γ'' ($\text{Ni}_3\text{Nb}(\text{Al,Ti})$) within the grains (5-20 μm), as seen from the DF TEM image (Fig. 6b) as well as the occurrence of distinct superlattice reflections, of (1,1/2,0) and (1/2,1,0) along with the matrix reflection of (010) and (100), with the beam along the [001] direction (Fig. 6c). In comparison, the cold sprayed coating, after solution heat treatment and aging, shows a very limited precipitation of the γ'' phase as seen in Fig. 6(d-f). Fig. 6c is a BF TEM micrograph where some faint strain contrast is visible in the γ (Ni-solid solution) matrix. With the aid of weak beam imaging, sporadic occurrence of elliptical lobes of the γ'' precipitates could be observed (Fig. 6d), along with faint superlattice reflections (Fig. 6f), circled. In addition to the fine γ'' precipitates, the bulk alloy also shows the occurrence blocky phase, comprising MC of the type NbC, as shown in Fig. 6a (marked with arrow).

Fig. 4 : TEM micrographs of the IN625 coating after 650°C, 2.5 h heat treatment, representing, (a-b) Region I, (c-d) Regions II, corresponding to the as sprayed coating. Inserts : SADP's from respective regions.

Fig. 5 : TEM micrographs showing the recovery of the recovery taking place in the severely deformed structure of the IN625 coating after, 100 h at, (a-b) 650°C, Region I and Region II, (c-d) 700° C and (e-f) 800°C.

Fig.6 : TEM micrographs of solution treated (1100°C, 1.5 h, FC), and aged (650°C, 100h), (a-c) Cold spray IN625 coating, (d-f) Bulk IN625.

Fig. 7 : IN625 coating phase evolution superimposed on the, (a) T-T-T diagram for bulk IN625 [5], (b-f) cold spray coating microstructure after different heat treatments, with no precipitates, (g) solution treated and aged coating microstructure., showing faint strain contrast indicative of γ'' precipitates.

Discussion

Time temperature transformation curves for γ'' precipitation reveals that the strengthening phase starts to precipitate from 593°C onwards (> 5000 h), and is abundant at 650°C [12-13]. The latest published diagram by Floreen et. al. [4] shows the occurrence of these precipitates as early as 2.5 h at 750°C. In the present study, the cold sprayed IN625 coating does not show any precipitation even after 1000 h at 650°C, as well as after 100 h at a higher temperature of 700°C and 800°C. In addition, at no instance were any of the other phases such as Laves, M_6C , MC, or the δ phase seen. Upon superimposing the coating phase evolution upon heat treatment, upon the existing T-T-T diagram (4), as shown in Fig. 7, it can be seen that in the as sprayed condition, there is no overlap between the existing T-T-T diagram in terms of complete absence of γ'' or any of the other phases. However, on solutionizing and annealing, after 650°C, 100 h, a very sluggish precipitation is seen to occur, as compared to the bulk IN625 alloy that has been taken through a similar heat treatment. The bulk alloy also shows the occurrence of blocky MC (Nb rich carbides), after the solutionizing and aging treatment. In this case it can be seen with a clear precipitate denuded zone around the Nb carbide, caused by the depletion of Nb in the localized region. It is clear that the prior processing history has a dominant role in the γ'' precipitation kinetics and as a result on the mechanical properties of the alloy. In this case, the heavy deformation of the alloy powders during processing, could lead to a much higher solid solubility of the different elements, somewhat akin to high entropy alloys (HEA) that are being studied in recent times [13,14]. In this case, there is a high probability for solid solution strengthening in preference to precipitation or intermetallic compound formation. Although the exact mechanism for the phase evolution (or the lack of it) in the cold sprayed coating is not clear at this point, it can be seen that there is a definite propensity for the cold sprayed coating to remain as a solid solution alloy even after very high temperature annealing treatment and the sluggish precipitation kinetics even after solution treatment at 1100°C and aging.

Conclusions

1. The cold sprayed IN625 coatings were devoid of any strengthening precipitates and were seen as a complete solid solution with a severe deformed structure in the as sprayed condition.
2. Two distinct regions lying adjacent to each other demarcated the coating microstructure, in the as sprayed condition. Region I comprising fairly large grains with a severely deformed structure, and Region II between 0.5–1 μm , comprising mainly twins.
3. The as sprayed coating hardness ranged between 500-550 H_v .
4. Upon heat treatment the severe deformed structure undergoes recovery, recrystallization and grain growth, to lead to strain free grains (between 800-1200 nm).
5. However, at no instance the cold sprayed IN625 coating seen with the γ'' - ($\text{Ni}_3\text{Nb}(\text{Al},\text{Ti})$) precipitate and was found to be devoid of the strengthening precipitate γ'' upon heat treatment, up to 800°C, 100 h. There was also no occurrence of the equilibrium δ - Ni_3Nb phase upon heat treatment and the coating remained a solid solution up to 800°C, 100 h.
6. The severe plastic deformation combined with the instantaneous adiabatic heating and quenching, resulted in a much higher solid solubility of the solutes Nb, Mo, Al and Ti, in the Ni matrix.

7. On superimposing the observed coating phase sequence, on to the T-T-T diagram, it can be seen that there is suppression of γ'' precipitation via the cold spray coating processing.
8. Upon solution heat treatment the coating and aging, the γ'' starts to precipitate out of the matrix, in very low volume fractions as compared to the bulk IN625 alloy that is subject to the same heat treatment.
9. The T-T-T diagram for the IN625 cold sprayed coating shows no precipitation up to 800°C, 100 h.
10. The structure and stability limits of the cold sprayed IN625 coating indicates that this will be well suited for applications up to 700°C.

Acknowledgements

This work was performed under funding from GE Oil and Gas, Adam Drufke, the program manager is gratefully acknowledged. The authors thank Y.C. Lau, GE Power and Water, Schenectady for spraying the coatings, Vighnesh Chandrasekhar, A.S.S. Balan, Priyanka Saxena, GE Power and Water, Bangalore, for helping with the heat treatments and T. Vishwanath, GE, Global Research, Bangalore, for the TEM sample preparation. The authors would also like to acknowledge Surendra Makineni, Indian Institute of Science, Bangalore, for help with some of the TEM characterization.

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