Development of CuAlNi Shape Memory Alloy Structures Using Cold Spray Deposition Technique with Laser Remelting



S. Shiva, L. Michaux, A. Cockburn, D. Hopkinson, I. A. Palani, C. P. Paul, and W. O'. Neill

Abstract The current chapter is about the fabricating bulk shape memory allow (SMA) structures using solid-state deposition of nitrogen gas based cold spray deposition. Parallelly the alloying process is carried out by high power continuous wave and pulsed wave laser. The effects of laser energy density are studied in detail. It is found that the laser energy density plays a crucial role in homogeneous alloying of the cold sprayed structure. The deposition gas temperature played a crucial role in a homogeneous deposition, as the temperature is higher the powder gets blocking in the path of the D-Laval nozzle. The critical temperature level is determined to block free deposition. The laser diffusion depth and the dwell time plays a crucial role. Also, the high laser energy density ablates the surface of the sample leading to complete distortion of the sample. Hence the perfect laser energy density has opted for an efficient alloying process. Once the alloy formation is done, the fabricated samples are subjected to several characterizations in the aspect of surface morphology, crystallization, mechanical properties and shape memory effect. The scanning electron microscopy (SEM) revealed the deposition to be highly dense and high porosity free. The mechanical property reveals the fabricated alloy to have good

S. Shiva (🖂)

S. Shiva · I. A. Palani Department of Mechanical Engineering, Indian Institute of Technology Indore, India

L. Michaux · A. Cockburn · D. Hopkinson · W. O'. Neill Institute for Manufacturing, Department of Engineering, University of Cambridge, Cambridge, UK

I. A. Palani

Department of Metallurgy Engineering and Material Science, Indian Institute of Technology Indore, India

C. P. Paul

Laser Development Industrial Applications Division, Raja Ramanna Centre for Advanced Technology, Indore, India

HomiBhabha National Institute, BARC Training School Complex, Anushakti Nagar, Mumbai, India

© Springer Nature Switzerland AG 2020 S. Pathak and G. C. Saha (eds.), *Cold Spray in the Realm of Additive Manufacturing*, Materials Forming, Machining and Tribology, https://doi.org/10.1007/978-3-030-42756-6_7

Department of Mechanical Engineering, Indian Institute of Technology Jammu, Jammu, India e-mail: sshivabemech@gmail.com

strength when alloyed with both pulsed and continuous-wave lasers. The crystalline nature of the alloys was studied using X-Ray diffraction (XRD). The crystallized nature of the alloy is the primary requirement to attain the shape memory effect in SMA. Hence this chapter will give the researchers in beginning stage a clear idea about the evolution of cold spray deposition techniques that can be used by their research works in developing novel research ideas. Also, the nature of laser surface processing techniques is discussed in detail. The idea of laser surface processing can be utilized by budding researchers to deal with any sophisticated or micro-level machining applications.

Keywords Cold spray deposition · Laser · Additive manufacturing · Shape memory alloy

1 Introduction

Additive Manufacturing (AM) has proved itself to be a promising option by overcoming several unsolved problems by other unconventional manufacturing processes, specifically in the stream of powder metallurgy. The technology is equipped with a variety of features that makes the process highly versatile, allowing the users to perform or experiment with tailored complex structure development in the stream of design and manufacture. AM was initially deployed as a process suitable only for concept modelling and rapid prototyping, but over the years the evolution of layer by layer AM gradually took over the position of directly manufacturing netshaped metallic components almost ready to use [1-4]. Though the technology is well-established problems like porosity and lack of fusion defects are yet to address. Researchers have countered the existing issue with specific precautionary techniques with immense heed to ensure defect-free deposition. In that hunt, several spraying technologies are now deployed in developing thick films and structures. The advantage in spraying technology is the alloying happens in almost porosity free nature and with high density. But the limitation of using spraying technique to manufacture bulk component is, only standard shapes can be developed, and even that thoroughly relies on complete post-processing techniques. Also, if a tailored composition is to be used for fabrication, the process of maintaining homogeneity in composition becomes immensely tough. One more consideration to be taken is the powder particles, which are very small in nature. Hence the time taken for deposition of bulk or thick film is always high. Among the several spraying technologies, cold spray deposition has a unique advantage of maximum coating thickness efficiency, which is always of higher advantage. The segment of new generation AM processes by cold spray technology is capable of delivering complete porosity free deposition with good density without any voids in the middle. Metallic parts of tailored composition with high closely packed density, used in various fields, like thermal, aeronautical, etc. possess more significant challenges in their development are now easily addressed using cold spray based deposition technique. Layer by layer deposition technique can fabricate

the entire structure from the base by stacking the tightly bonded powders to beget the desired output of good quality in the very first attempt.

In the cold spray technique, the powders are deposited and later by the assistance of heat treatment techniques, the alloy formation is successfully done. But homogeneously engineering the microstructure is not possible in the conventional technique. In that accord to control the microstructure evolution, a laser-based melting process is carried out to melt the cold spray alloys successfully. As lasers are embedded with several advantages like the control of efficient heat supply, the ability to adapt into several closed environments causing no harm, the possibility of transferring the laser beam from one station to the other without significant loss of intensity and also the superior surface finish of the products developed. Banking on the nature of continuous-wave and pulsed lasers the alloying process can be carried out in an attempt to fabricate samples with microstructures in good homogeneity. Among the two types of lasers, the continuous wave has lesser penetration depth than the pulsed lasers. But the span of a pulsed laser is very small that complete-time is not provided for the metal to melt entirely and evolve the microstructure [5–10].

The current chapter will provide an overview of the history of cold spray based deposition techniques and the role of laser in efficiently developing homogeneous shape memory alloy samples. The compilation of continuous and pulsed wave lasers in the role of melting the alloy will give the readers a vivid picture of the process going on. Laser melting process of cold spray deposited alloy, will give a new dimension in manufacturing and applications in the field of involving SMA. Also, the discussion includes the various desirable parameters and other characteristics features of the chosen three process in brief. In the end, the future prospects and recent research trends in the chosen technologies will be deliberated. This chapter will help the researchers who are at the beginning stage of their research career in an idea to pursue their research work in the field of cold spray in developing bulk net-shaped products.

2 Evolution of Spraying Techniques

The process of coating incepted in an attempt to alter the surface of components, to increase the strength and resistance of the components in the real-time application. Thermal spray techniques are deployed to counter the failures occurring on the surface of the components, eventually increasing their life. The versatile nature of the thermal spray technique provided the option of using them on any type of materials, which makes them maverick in the line of surface engineering. The thermal spray techniques improve the resistance of the components against common surface defects like wear, corrosion, and high temperature. Also, the same spraying technique can repair any surface errors on the components which attracts industries as the overhead exponentially falls down. As the evolution spraying techniques are probed, it's apparent that researchers had initially used the process of metallizing to coat low melting point temperature metals (less than 300 $^{\circ}$ C) on the substrate

by heating the metal powders with an oxygen flame. Sequentially the next stage of thermal spraying was introduced with high-velocity oxygen fuel (HVOF) technique when metal wires were heated by oxygen flame, and the molten metal was atomized by compressed gas that also assisted a homogeneous coating on the surface of the substrate. Similar to HVOF technique D Gun based spraying technique got good attention in the spraying applications as for its very low porosity, strong adhesion to substrates, high cohesive strength and high hardness [11]. As an upgrading in the existing technology, in the place of oxygen flame, the electric arc was introduced. This improvised approach assisted good corrosion resistance coating of high melting temperature metals. The arc spraying process is a good choice for the on plant application due to the low cost of equipment and materials, the simplicity of operation on-site, and highest deposition rate, which is important for onsite manufacturing and repairing [12]. With similar working principle, atmospheric thermal plasma spray (APS) process the coating deposition is at a high rate, and most importantly the entire spraying can be conducted by simple equipment without any controlled atmosphere glove boxes, low-cost film deposition with short duration time can be carried out [13]. The vacuum plasma spraying (VPS) process is another type of spraying technique using electric arc under a controlled atmosphere with low pressure of inert gas, with reduced time of interaction between the plasma jet and the oxidative environment. Hence, VPS technology can be deployed in places where oxidation free deposition is the primary objective. Using VPS more controlled homogeneous coating can be achieved with less contamination [14]. In the LPPS method, the controlled atmosphere gas itself acts as a carrier gas that gushes the powder particles into the plasma jet ignited by a DC plasma torch. The gas used for the process is generally argon plus secondary gases like hydrogen, nitrogen or helium. The powder used for deposition is pre-melted and are accelerated in the plasma jet to coat them over the substrate in the form of splats, that results in the uniform coating. The entire process is carried out in a controlled argon atmosphere inside a vacuum chamber to prevent oxygen contamination. Despite all measures, the oxidation is not thoroughly inevitable as the flame used for melting is oxygen fuel. The exact adjustment of reproducible processing conditions as well as process monitoring is required to ensure fully pronounced pseudoelasticity at operating temperature. The biggest advantage of LPPS technique is to have complete control over the coatings with thickness in the range of nano to microscale and is, therefore, a promising method aiming at a compromise to keep material costs at an acceptably low level while achieving sufficient resistance against cavitation [15]. The third and latest upgrade of spraying techniques is currently using cold spray technique. In this technique, the powders are used as raw material and are deposited using solid-state deposition. The powders are compressed with preheated air and made to pass through a type of convergent and divergent nozzle in a sonic speed to get deposited on the substrate. As shown in Fig. 1, similar to cold spray technique with some mild pre-melting of powders, two more techniques are used for depositing the powders in solid-state deposition.

HVAF is mostly an assembled set up where the deposition process is not entirely reliable in the speed of gas flow. The most critical parameters in tuning the HVAF process are (1) hardware configuration such as the size of the combustion chamber,

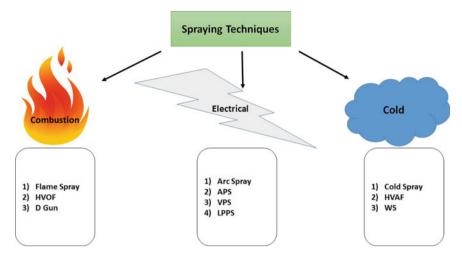


Fig. 1 Evolution of spraying techniques

nozzle, and powder injector and (2) process variables such as standoff distance and powder feed rate [16]. Regardless of the preliminary development of spray conditions specific to given powder chemistry, systematic optimization of HVAF process itself has been scarcely performed. Indeed, in order to spray coatings with required corrosion performance, systematic process parameter analysis must be applied to relate the applied parameters with the produced coating structure and properties [17]. The process-microstructure-properties-performance relationship assessment is a capable tool for process optimization and able to provide precise information on the whole process from the powder to coating performance [18]. In warm spray (WS) the temperature of a supersonic gas flow generated by the combustion of fuel and oxygen is controlled by injecting nitrogen into the mixing chamber placed between the combustion chamber and the powder feed ports. Various powder materials [19] can be deposited in the thermally softened state at high impact velocity, which allows the formation of dense coatings with limited oxidation of the particles what is extremely important in case of the anticorrosion coating.

Among the various discussed techniques, as shown in Fig. 1, cold spray technology is suited high-velocity solid-state deposition of powders. Also, there are certain advantages that keep cold spray technique ahead of the remaining spraying techniques. The advantages are as follows:

(1) CS is an apt technique to carry out the deposition of materials that are temperature-sensitive in nature such as nanocrystalline (NC) and noncrystalline materials, oxygen-sensitive materials such as copper (Cu), titanium (Ti) and aluminum (Al), and also carbide composites which are phase-sensitive materials as the deposition temperature is low [20].

- (2) CS of metals, in general, induces high compressive residual stresses in the deposition due to the micro "shot peening" effect, which enhances fatigue resistance of the deposits [21].
- (3) Metal CS deposits contain microstructures with high degrees of consolidation similar to wrought alloys due to the intrinsic high energy-low temperature features [22].
- (4) CS deposits induce higher chances of thermal and electrical conductivities as the deposition is of high density, completely porosity free and absence of oxide layer [23].
- (5) CS is a good option in the aspect of green machining as the wastage of the powders during deposition is highly negligible [24].
- (6) CS is a primary choice for joining dissimilar metals due to the absence of heat input during deposition. Also, the substrate does not play a crucial role due to the absence of heat [25].
- (7) CS doesn't need for any external masking as the deposition is more precise and controlled over the spraying area on the substrate. In general, the spray beam is very small and less standoff distance [26].

The CS technique can be further divided into two different types like high-pressure CS (HPCS) and low-pressure CS (LPCS). The pressure indicates the pressure of heating gas that is deployed for the deposition. The variation of high and low pressure is architected by a small design variation in the deposition nozzle. The powder injection orifice is placed at two different points, as shown in Fig. 2.

The details about the above mentioned two techniques are as discussed below.

(a) In HPCS the to be deposited powder particles are premixed with the carrier gas before entering the deposition nozzle and are injected into the nozzle that is

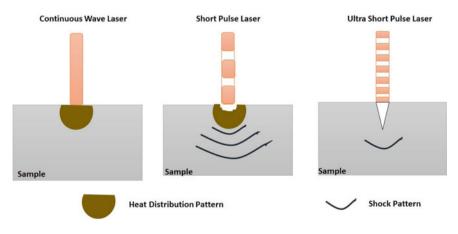


Fig. 2 Nature of heat distribution in various types of laser

Table 1 Parameters used for fabrication of CuAlNi SMA	Parameter	Unit	Values
	Gas pressure	bar	15–20
	Stand of distance	mm	40
	Powder feed rate	g/min	30
	Deposition rate	mm/min	16
	Gas temperature	°C	470
	Powder particles size	μm	10–30

positioned perpendicular to the substrate, preferably downstream type deposition is done. The deposition gets along the gravitational force direction is also an added advantage in the system.

- (b) In LPCS the heating of carrier gas is done at the spray gun, unlike the HPCS system which preheats the gas well before entering the deposition nozzle.
- (c) As the powder feed rate entirely relies on the carrier gas discharge speed, the HPCS is expected to have a higher deposition rate comparing to LPCS [27]. A detailed comparison between the two spray processes is, as quoted in Table 1.
- (d) As the HPCS deals with excess pressure, the entire set up is a bit expensive compared to LPCS. Also, the LPCS has an advantage of low-cost equipment as the process compromises with low Mach speed deposition with low pressure just sufficient to supply powders to the nozzle leading to their deposition.
- (e) Nozzle clogging is a significant issue to deal with in both techniques as the powder gets accumulated when exposed to heat and pressure in the sidewalls of the nozzle, hindering further homogeneous deposition. To counter this issue researchers have used premixtures that prevent powders from clogging and nozzles made of materials that prevent powder clogging on the inner surface [28].
- (f) Deposition of hard particles is yet a challenge for both techniques as the particles erode the nozzle throat during the deposition process. Sequentially erosion wear in the nozzle is expected to harm the homogeneity in the deposition [29].
- (g) Overall the HPCS has specific abilities better than LPCS as the process is equipped with expensive feeders and pressure managing systems that assist the HPCS to have a clear edge over LPCS by more substantial deposition efficiency [30].

3 Role of Particle Deformation in Bonding Properties

In general, the powder particles used for cold spray techniques are subjected to high strain due to the velocity generated during the high-speed deposition process [31]. The high strain-induced powders to assist porosity free deposition. The reason behind the success of cold spray in depositing hard metals and dissimilar metals is possible

with the help of the powder deformation. The ability of the HPCS is to engineer the microstructure using the high speed of the powder particles during deposition. Precisely at the interface region between the coating and the substrate [32, 33]. The nature of the microstructure formed in the deposits can directly reflect on the properties like ultra-fine grain microstructure [34], recovery and recrystallization [35], cold spray precipitation [21], residual stress [36], localized amorphization [37] and phase transformation [38]. Along with the mentioned changes, also the microstructure will have a significant impact on the mechanical properties of the developed specimens in the micron to nano level. Hence before depositing the particular material a thorough knowledge about the nature of microstructure for each parameter is essential to prevent any adverse effects on the developed samples that may induce abnormality in the material property.

4 Deformation of the Powder Particles

The role of powder particle deformation has several other roles apart from the earlier discussed issues like powder substrate bonding and mechanical properties of the deposits. Also, the work hardening induced in the samples during deposition is expected to play a vital role in determining the mechanical properties of the deposition. The nature of particle deformation in a deposition is widely depending on two essential parameters of deposition temperature and particle velocity [39, 40]. The mentioned two properties are governed by three different parameters of powder characteristics, geometric effects and process parameters. The three parameters are detail discussed as follows.

4.1 Powder Characteristics

4.1.1 Particle Size

The powders opted for cold spray deposition are in general of size $20-50 \mu$. The particles opted are to be very small in nature as the deposition rate is maximum when the heat gets quickly dissipated from the particles after deposition. Hence with smaller powder particle, the heat dissipation is quicker. Also, as the powder particles are very smaller in nature, the porosity free deposition is also easily attainable comparative to the bigger powder particle size. Adding to more advantages the shear instability in the deposition can be halted by small powder particles as the environment is entire with higher heat radiation [41]. The heat quenching is smooth when the powder particles are also meagre in smaller powder particles as the surface to volume ratio is higher. Mathematically Eq. (1) is used to determine the critical powder particle size which will be efficient enough for an efficient deposition [42-Schidt].

Development of CuAlNi Shape Memory Alloy ...

$$D_{\rm crit} = 36 \frac{\lambda_p}{C_p \rho_p V_p} \tag{1}$$

where is the λ_p thermal conductivity, C_p is the specific heat of the particle, ρ_p is the density of particle material, and V_p is particle velocity. The properties mentioned in the equation vary for each material and hence accordingly the particle size can be determined prior to deposition. When particles used for deposition exceeds the calculated value, the heat quenching lasts long as the deformation of the powder particles is delayed, eventually leading to a delay in the powder particle bonding.

4.1.2 Powder State and Shape

The powders used for deposition are manufactured using gas atomization or cryomilling. Irrespective of the manufacturing technique, the powder particles are expected to be spherical in nature for an efficient cold spray deposition as irregular powders generate an irregularity in the deformation process that eventually reflects in the quality of the deposition. In the case of spherical powders of smaller size, the powder particle impact velocity can be achieved in cold spray deposition. Irregular shape powders generally generate a drag coefficient in the deposition that leads to irregularity in powder feed during the deposition process and the deformation time variation among the quantity of powder also leads to improper deposition [43]. The increase in powder size and irregular shape leads to poorer flowability and lower powder packing factor.

4.1.3 Surface Oxide Layer

Surface oxide layer plays a crucial role in the deposition process like oxide layer's impact reflects on deposition efficiency and particle deformation [44]. As the powder jet meets the substrate, the oxide layer on the powder surface, in general, tends to create disruption in the interface layer. Reported results claim the higher the thickness of oxide layer present in the powder surface requires higher energy to deposit the powder and lowers the rate of powder deformation [45]. The continuous deposition of the powder with surface oxide layer is deposited the mounting pressure generates cracking oxide layer which ejects out from the surrounding layer of the powder particle's perimeter. The partial ejection of the oxide layer will trap a certain amount of oxides within the deposition that reduces the bond strength between the powders [46].

4.2 Geometric Effects

The following aspects are to be addressed to satisfy the geometrical effects in the cold spray deposition.

4.2.1 Spraying Stand-Off Distance

The distance between the spraying nozzle and the substrate surface is the stand-off distance in the cold spray techniques. The higher stand-off distance decreases the deposition efficiency and deteriorates the deposition's nature. Hence the stand-off distance varies with the chosen particle size for the deposition.

4.2.2 Spraying Angle

To determine the spray angle of the deposition, a small wipe test was conducted by the researchers in the past [47]. The substrate is moved in very high-speed in front of the spraying gun. The deposition thickness is then analysed. The particular angle in which the highest deposition of powder is done. The test results reveal that when the perpendicular direction of deposition has changed the deformation of the deposited particles also change. Also, when the temperature of deposition is varied, the angular impact in the interface varies due to frictional heating leading to high instability.

4.2.3 Position in Particles Jet

The powder particles exiting from the nozzle takes a divergent flow nature before reaching the surface of the substrate. In the mentioned flow, the powder particles remain under the influence of a different velocity due to the bow shock effect [48].

4.2.4 Nozzle Geometry

The nozzle used for deposition is called de laval nozzle, which is convergent and divergent by nature. The Mach number plays a crucial role in the deposition efficiency of the powders by the carrier gas. To enhance the Mach number of the nozzle, usually, the divergent part of the nozzle is extended to achieve the required speed for the powder to get deposited. But the expansion of the nozzle is not be done randomly. The expansion plays a crucial role in the types of nozzles like under expanded, correctly expanded and over-expanded as reported by researchers in the past. Among the three types of nozzles, the correctly expanded nozzle, in general, produces no shock during deposition. The over-expanded nozzle has the ability to produce maximum outlet speed. After extensive research in the nozzle geometry,

the final results concluded that the ambient air around intrudes exit of the nozzle as a result of low static and stagnation pressure. As a result, over-expansion induces unwanted shock within the nozzle that disrupts the powder flow through the nozzle.

4.3 Processing Parameters

4.3.1 Carrier Gas Type, Temperature and Pressure

The carrier gas is a vital processing parameter that assists the preheating of the powder which plays a crucial role in the bonding of the powders on the substrate. There are several types of carrier gasses like nitrogen, helium, oxygen, argon etc. Also, the deformation of powder particles on the surface of the substrate and also based upon the nature of the carrier gas been deployed for the process.

4.3.2 Substrate Hardness, Temperature, and Surface Roughness

Specific mechanical properties of the substrate material play a crucial in the deposition of the powder particles. The properties like hardness, surface roughness and surface temperature. When powder particles of soft materials are deposited on the substrate which is soft in nature, the deformation is considerably high, and when materials of highly hard nature are deposited on the hard substrate, the deformation rate is considerably low. In both cases, the material's strength plays a crucial role in the observations. In the other way around, when soft and hard the deformation rate remains highly distinct [49].

5 Laser Remelting

A laser is a tool that is used primarily for various types of surface processing techniques in modern advanced surface treatment techniques. Similar to surface processing remelting is one among the process widely used to engineer the microstructure and nature of various materials. Hence the concept of laser interaction with metal is to be analyzed in detail to extract the desired output from the process. Laser remelting is possible when the absorption of laser power is high by the material on which the laser is incident, and the laser irradiation is continuous on the material's surface. In general, laser interaction with materials can be classified into two types of resonant and non-resonant interactions. A process like localized heating and photons ionization fall under the first type of resonant type of interactions and melting and plasma generation process falls under non-resonant process. In the case of laserbased remelting, the entire process is accompanied by vaporization. It is inevitable to proceed with laser remelting without vapourization in case of metals. Latent heat of fusion plays a crucial role in the entire laser-based melting process. The required amount of heat to preserve the material in the melting point temperature depends on the nature of the material and the volume of the material to be melted.

Surface remelting is executed by passing multiple tracks of laser on the surface of the material, and subsequentially the melting of the material on the surface takes place followed by rapid solidification. This technique is highly useful in case of bulk alloying as the composition of the material can be easily varied and the process of engineering the microstructure is also quickly done. In fact multiple behaviours of the soft material are utterly unique while comparing to the conventional process. Once the surface melting process is done the solidification of the melted surface initiates when the nucleation of the solid material takes place depending upon the nature of heat flow generated by laser remelting. The liquid phase solidifies in different forms and homogeneity can be obtained in the process by entrapping heat in the material for a longer time. In case if there is undercooling mostly brittle phases are induced which is very much harmful to the materials. Also choosing the type of laser to proceed with the melting process is very important. Researchers have widely used pulsed and continuous-wave lasers. The advantages to be availed using pulsed laser is the diffusion depth is higher than continuous wave laser. Similarly the melting efficiency of the continuous wave laser is higher than the pulsed laser. The nature of pulsed and continuous-wave laser are discussed as follows.

5.1 Pulsed Wave Laser

The pulsed laser can be of two types as short pulse and ultra-short pulse lasers. The nanosecond lasers are termed as short pulse lasers whereas picosecond and femtosecond lasers come under the ultrashort laser. Widely for surface processing purposes short-pulse laser and for ablation types of work ultrashort pulse is deployed. When it comes to short-pulsed laser widely Nd:Yag nanosecond green laser is preferred for its high pulse energy and good output efficiency. As the energy of the source is stored and released in short time the generation of high intensity is possible and also the dwell time is sufficient enough to generate changes on the material in which the laser is impinged. Due to broad bandwidth, the laser pulses are very short. Among several types of pulsed lasers like a nanosecond, microsecond, picosecond and femtosecond laser, the nanosecond lasers have proved themselves much efficient when it comes to the melting of bulk materials with sufficient dwell time on the samples. The pulsed lasers apart from surface melting are widely deployed for surface processing operations like laser annealing and laser shock peening. Also in pulsed lasers an extra option of changing wavelength with various modes are possible. Hence this adjustment facility provides an extra advantage to users to achieve the requirement more precisely.

5.2 Continuous-Wave Laser

In continuous-wave lasers, there is no classification based on laser pulses because here the output is continuous without any break. The power of the laser depends upon the parameters like wavelength and frequency. The continuous-wave lasers are of from several sources and among them fiber optics-based continuous-wave lasers are widely used for their high power performance and cost-effective maintenance. The usage is widely deployed in all higher-end applications like cutting, drilling and other modern machining processes. Similarly they are deployed in applications where melting of powders are also done to form alloys and also in processes like laser cussing where melting of material's surface to mend them. The continuous-wave lasers in general possess very lean bandwidth comparing to pulsed lased lasers which are of broader bandwidth. In case pulsed or continuous the nature of beam chosen for various applications are TEM_{00} for their ability to transfer higher intensity from the center and distributing the intensity homogeneously in all directions comparing to other nature of beams available. The nature of the continuous and pulsed wave interaction with material is as shown in Fig. 2. Hence as discussed above the higher end applications are widely done with continuous-wave laser, in the current chapter the laser surface melting of cold sprayed powders are also to be carried out using the same type.

6 Shape Memory Alloys

Among the several smart alloys used in various scientific applications, shape memory alloys (SMA) have secured a special place for possessing a maverick property of phase transformation on the application of external load in the form of temperature. Also, the broad application of SMA is in the form of thin films in micro-electromechanical systems (MEMS) is used in the form of diaphragms for micropumps. The mechanism behind the functioning of SMA included process like twinning and detwinning by varying the thermal load application in the alloy where the phase transformation from austenite to martensite and vice versa takes place. The functioning of the SMA is as shown in Fig. 3. Among the various SMAs like NiTi, TiNiCu, CuAlNi is also a primary choice for applications. CuAlNi SMA is widely used in applications where vibration damping is of high priority. The Ni in the alloy has enough strength in alloy and Cu provides good ductility in the alloy. Al provides excellent damping efficiency when alloying with Ni specifically. When it comes to bulk CuAlNi SMA fabrication methods like selective laser melting (SLM) is the only method reported to be successful. Also, the report proves that using additive manufacturing technique CuAlNi can be fabricated with good ductile nature which is a unique achievement as fabricating materials of high ductile nature is not an easy achievement using Additive manufacturing technique [50-simmone].

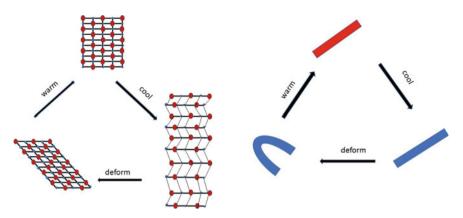


Fig. 3 Mechanism of SMA functioning

7 Experimental Approach

The powders play a crucial role in the deposition efficiency of the cold spray process. Hence the powder particles were assured to be in a size of $10-30 \ \mu\text{m}$. The powder particles size were maintained within the mentioned range because the size bigger than $30 \ \mu\text{m}$ can lead to un uniformity in deposition and the size of powders lesser than $10 \ \mu\text{m}$ tends to fly away in the speed generated by the nozzle. Also, much importance was given to the shape of the powders to be in spherical shape as the deposition efficiency is high when the powders are in a spherical shape. The shape of the powders other than spherical like irregular or flakes shape powders cannot have an efficient deposition as the deformation is not expected to happen uniform throughout. Eventually, the deposition efficiency drastically decreases and also it is expected to induce porosity within the sample. The surface morphologies of the various powders used in the process are as shown in Fig. 4. The powders were mildly preheated before the deposition to get rid of the surface oxidation. Also, the powders were carefully stored in a control atmosphere to prevent any sought of reaction with open room atmosphere, which may eventually deteriorate the property of the powders.

Figure 5 shows the schematic diagram of the indigenously developed cold spray set up used for the fabrication of the CuAlNi samples. The premixed powders of the desired composition were used for the deposition process. The deposition system was designed in such a way that the powders will be fed inside the upper end of the nozzle where the preheated nitrogen air mixes get along. The nitrogen gas plays a crucial role in compressing the powders into the convergent section of the nozzle. The Mach number of De Laval-type nozzle used for the current experiment is 2.9, which assists in accelerating the pre-mixed powders to flow in the supersonic speed. As shown in Fig. 5 the powders pass through the throat of the nozzles a high speed is obtained by expansion assisted by the preheated nitrogen gas, as per the theory of gas dynamics [50]. The drag force exerted by the preheated nitrogen gas in a supersonic stream on the powders accelerates the powders to attain high speeds that

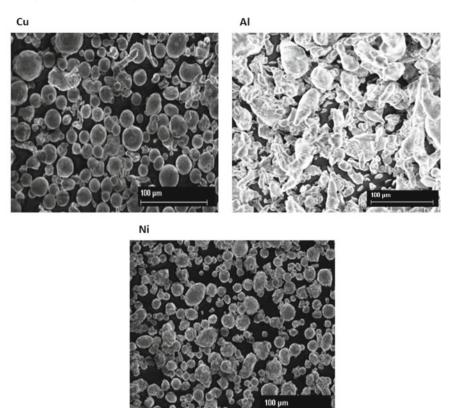


Fig. 4 Surface morphologies of the powders

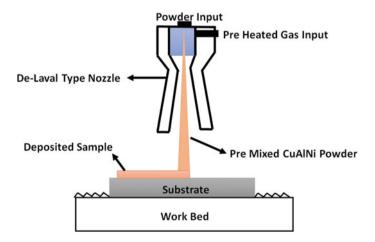


Fig. 5 Schematic diagram of cold spray setup

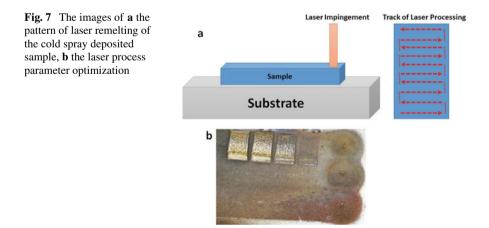
assist efficient deposition of the powders on the substrate in tightly packed nature. An efficient deposition can be assured once the powders travel above a high threshold value after absorbing enough drag force provided by the carrier gas (Nitrogen).

The deposition parameters deployed for the above-mentioned process are as quoted in Table 1.

The samples were successfully deposited on mild steel substrate, and the deposition is as shown in Fig. 6. The deposition was so closely bonded without any sought of porosity, and the bonding between the deposition and the substrate was visibly strong without any cracks in the interface. Once the deposition is done the deposition is done the samples were subjected to laser remelting carried out by two different types of lasers (i.e. pulsed and continuous) to form the perfect alloy formation. The laser power was maintained the same for both laser and the processing time was also uniform. The nature of laser processing and the pattern of processing are as shown in Fig. 7a. Once the sample is deposited to finalize the perfect power for melting sev-



Fig. 6 CuAlNi SMA fabricated by cold spray deposition



eral trials were conducted with various laser powers as shown Fig. 7b. The analyses were carefully done to avoid ablation of the samples during the interaction with the laser. Also, the cross-section analyses were carried out to determine the efficiency of alloying by both the type of lasers. The nature of the samples was analyzed in detail post laser processing.

In a motive to analyze the nature of the samples alloyed by pulsed and continuouswave laser, the surface morphological analyses, the mechanical properties and the phase transformation properties were analyzed. The surface morphological analyses are to study the nature of laser interaction with the sample and the alloying efficiency of the lasers. The mechanical properties of the sample are expected to analyze and to predict the sample's deployment in real-time application. Finally, the phase transformation ability of the sample is directly related to the shape memory effect in the sample. The details about the characterization results are discussed in detail in the sessions coming henceforth. The samples processed with pulsed laser is termed as CuAlNi PL and the sample processed with continuous-wave laser is termed as CuAlNi CW in the chapter ahead. The scanning electron microscopy (Make: Zeiss, Model: Supra55) attached with energy dispersive spectrograph (Make: Oxford Instruments, Model: X-mas), was used for the surface morphological analyses. The micro-hardness (Make: UHL, Model: VMH 002), was used to analyze the mechanical properties of the samples.

8 Results and Discussion

Once after the premixed powders were deposited the cross-section analyses were initiated for the deposits in order to confirm porosity free deposition. As shown in Fig. 8, the cross-section revealed a dense-packed deposition. The bonding at the intermediate layer is observed to be porous free, and the nature powder deposition is homogeneous by the assistance of powder deformation. Also, no pores were observed in the intermediate region, which indicates not much bowing effect has taken place as the standoff distance between the nozzle and substrate is good enough for high efficiency of deposition. Very less dark spots are seen in the image which may be attributed to the removal of powders during the polishing process. To alloy, the deposits two types of lasers opted pulsed and continuous-wave laser. The optimised range of power was opted for both pulsed and continuous-wave laser, to initiate the alloys of the powders. As the wave nature of both lasers is different, it is vivid that the alloying nature is not expected to be similar in nature. To investigate the nature of alloying a scanning electron microscopy (SEM) analyses were carried out. The results of the alloying process using pulsed laser are as shown in Fig. 9. The comparison of before and after laser processing is as shown in Fig. 9a. The impact of pulsed laser processing was visible to be highly efficient. Once when the alloyed surface was brought to a closer look, some sought of mild porosity of slanting pattern was observed on the surface as shown in Fig. 9b. The presence these patterns might

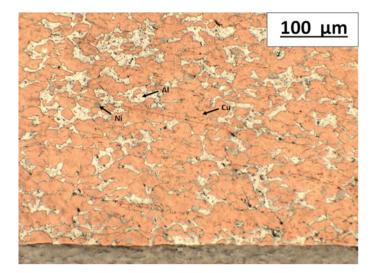


Fig. 8 The deposition of CuAlNi powders using cold spray process

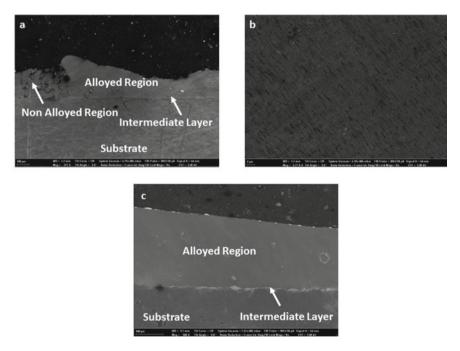
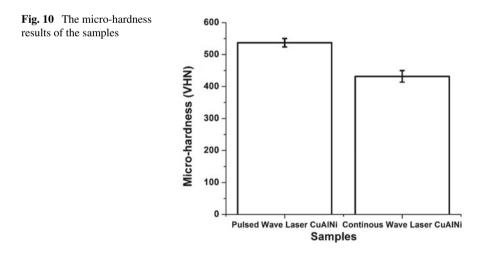


Fig. 9 SEM images of **a** pulsed laser processed sample, **b** the magnified image of pulsed laser processed samples, **c** continuous-wave laser processed sample

be due to the short life span of each pulse generated by the pulsed laser. The nonavailability of enough dwell time to remelt and cover up the formed porosity for the alloys is observed.

But when it comes to continuous-wave laser melting the alloys seem to be having a homogeneous melting throughout the deposits as shown in Fig. 9c. The presence of any form of porosity is not observed, and this may be possible by the continuous wave pattern of the laser. Also, there are not many precipitates observed on the surface of the alloy. The alloying density is observed to be very high for continuous wave laser processed CuAlNi sample and the mechanical properties are expected to be useful as well.

To investigate the mechanical property of the alloys a preliminary micro-hardness test was conducted for the samples. The samples were bisected and prepared following the standard metallographic techniques. After the samples were finely polished, the samples were mounted in Vicker's hardness tester. The readings were noted at a distance of 25 mm at a load of 500 g. The impingement was carefully done ensuring to cover the entire surface area, without any overlap. The results presented in Fig. 10 reveal the micro-hardness test reveal pulsed laser processed samples have the highest value of 536 VHN comparing to continuous wave laser processed sample whose value to be 431 VHN. The nature of the pulsed laser processed sample indicates to be of much more of brittle nature. But the results of continuous-wave laser processed sample indicates the proper alloying that had taken place during the processing.



9 Conclusion

Cold spray deposition technique is an extremely versatile technique in the aspect of coatings. Deploying the same technique to build three-dimensional bulk structures. The novel approach of engineering the cold sprayed deposits using modern tools like lasers, where enough opportunities are availed to alloy the powders. The current chapter plays a crucial role in giving exposure to deploying two different types of lasers to obtain a common objective. Hence depending upon the application and requirement, the users have enough options. The CuAlNi shape memory alloy which is widely used for vibration damping applications. Hence the results reveal when continuous-wave lasers are deployed for the application they tend to have better alloying possibility which is much needed for the robust applications.

Acknowledgements The authors would like to thank Royal Academy of Engineering (RAE), London for assisting the cold spray deposition experimentations carried out at Institute For Manufacturing (IFM), University of Cambridge, UK, under the Newton Bhabha Project (Project No.: HEPI\1516\10). Thanks are also due to Sophisticated Instrument Centre (SIC) at Indian Institute of Technology Indore, India, for providing us with the required characterization facility.

References

- Zavala-Arredondo, M., Boone, N., Willmott, J., Childs, D. T. D., Ivanov, P., Groom, K. M., et al. (2017). Laser diode area melting for high speed additive manufacturing of metallic components. *Materials and Design*, 117, 305–315.
- Harun, W. S. W., Kamariah, M. S. I. N., Muhamad, N., Ghani, S. A. C., Ahmad, F., & Mohamed, Z. (2018). A review of powder additive manufacturing processes for metallic biomaterials. *Powder Technology*, 327, 128–151.
- Zhou, Y. H., Zhang, Z. H., Wang, Y. P., Liu, G., Zhou, S. Y., Li, Y. L., et al. (2019). Selective laser melting of typical metallic materials: An effective process prediction model developed by energy absorption and consumption analysis. *Additive Manufacturing*, 25, 204–217.
- 4. Wei, X., Liu, Y0, Zhao, D., Mao, X., Jiang, W., & Ge, S. S. (2020). Net-shaped barium and strontium ferrites by 3D printing with enhanced magnetic performance from milled powders. *Journal of Magnetism and Magnetic Materials*, 493, 165664.
- Kang, A. S., Grewal, J. S., & Cheema, G. S. (2017). Effect of thermal spray coatings on wear behavior of high tensile steel applicable for tiller blades. *Materials Today: Proceedings*, 4, 95–103.
- López-Ortega, A., Arana, J. L, Rodríguez, E., & Bayón, R. (2018). Corrosion, wear and tribocorrosion performance of a thermally sprayed aluminum coating modified by plasma electrolytic oxidation technique for offshore submerged components protection. *Corrosion Science*, 143, 258–280.
- Lashmi, P. G., Majithia, S., Shwetha, V., Balaji, N., & Aruna, S. T. (2019). Improved hot corrosion resistance of plasma sprayed YSZ/Gd2Zr2O7 thermal barrier coating over single layer YSZ. *Materials Characterization*, 147, 199–206.
- Huang, C. J., Wu, H. J., Xie, Y. C., Li, W. Y., Verdy, C., Planche, M.-P., et al. (2019). Advanced brass-based composites via cold-spray additive-manufacturing and its potential in component repairing. *Surface & Coatings Technology*, 371, 211–223.

- Tan, J.C., & Hashmi, M. S. J. (1995). High velocity oxygen fuel (HVOF) thermal spray: Prospect and limitation for engineering application. In *Current advances in mechanical design and production* (vol. VI, pp. 27–33).
- Liu, M., Yu, Z., Zhang, Y., Wu, H., Liao, H., Deng, S. (2019). Prediction and analysis of high velocity oxy fuel (HVOF) sprayed coating using artificial neural network. In *Surface and coatings technology* (p. 124988).
- Shukla, N., Trivedi, Harshit, Kumar, Hemant, & Yadav, Anant. (2017). Surface engineering analysis of D-Gun sprayed cermet coating in aggressive environment. *Materials Today: Proceedings*, 4, 10212–10215.
- 12. Davis, J. R. (2004). Handbook of thermal spray technology. Cleveland, OH: ASM International.
- Ando, Y., Kindole, D., Noda, Y., Mbiu, R. N., Kosgey, B. K., Maranga, S. M., et al. (2017). Alumina and titania films deposition by APS/ASPPS dual mode thermal spray equipment using Ar added N₂ working gas. *Vacuum*, *136*, 203–208.
- Salhi, Z., Klein, D., Gougeon, P., & Coddet, C. (2005). Development of coating by thermal plasma spraying under very low-pressure condition. *Vacuum*, 77, 145–150.
- Bitzer, M., Rauhut, N., Mauer, G., Bram, M., Vaßen, R., Buchkremer, H. P., et al. (2015). Cavitation-resistant NiTi coatings produced by low-pressure plasma spraying (LPPS). *Wear*, 328, 369–377.
- Wang, Q., Zhang, S., Cheng, Y., Xiang, J., Zhao, X., & Yang, G. (2013). Wear and corrosion performance of WC-10Co4Cr coatings deposited by different HVOF and HVAF spraying processes. *Surface & Coatings Technology*, 218, 127–136.
- 17. Pawlowski, L. (2008). The science and engineering of thermal spray coatings. Chichester: Wiley.
- Li, C.-J., & Yang, G.-J. (2013). Relationships between feedstock structure, particle parameter, coating deposition, microstructure and properties for thermally sprayed conventional and nanostructured WC–Co. *International Journal of Refractory Metals and Hard Materials*, 39, 2–17.
- 19. Molak, R. M., Araki, H., Watanabe, M., Katanoda, H., Ohno, N., & Kuroda, S. (2014). Warm spray forming of Ti-6Al-4 V. *Journal of Thermal Spray Technology*, 23, 197–212.
- 20. Villafuerte, J. (2015). *Modern cold spray: Materials, process, and applications*. Berlin: Springer.
- Shayegan, G., Mahmoudi, H., Ghelichi, R., Villafuerte, J., Wang, J., Guagliano, M., et al. (2014). Residual stress induced by cold spray coating of magnesium AZ31B extrusion. *Materials and Design*, 60, 72–84.
- Chavan, N. M., Kiran, B., Jyothirmayi, A., Phani, P. S., & Sundararajan, G. (2013). The corrosion behavior of cold sprayed zinc coatings on mild steel substrate. *Journal of Thermal Spray Technology*, 22, 463–470.
- Champagne, V. K. (Ed.). (2007). *The CS materials deposition process*. Cambridge, England: Woodhead Publishing Ltd.
- Schmidt, T., Assadi, H., Gartner, F., Richter, H., Stoltenhoff, T., Kreye, H., et al. (2009). From particle acceleration to impact and bonding in cold spraying. *Journal of Thermal Spray Technology*, 18, 794–809.
- Pathak, S., & Saha, G. C. (2017). Sustainable development of cold spray coatings and 3D additive manufacturing components for repair/manufacturing applications: A critical review. *Coatings*, 7(8), 122–149.
- Tang, J., Saha, G. C., Richter, P., Kondás, J., Colella, A., & Matteazzi, P. (2018). Effects of post-spray heat treatment on hardness and wear properties of Ti-WC high-pressure cold spray coatings. *Journal of Thermal Spray Technology*, 27(7), 1153–1164.
- 27. Cui, L., Gerber, A. G., & Saha, G. C. (2019). Cold gas dynamic spray technology: The simulation of aerodynamics of flow. *Key Engineering Materials*, 813, 7–12.
- Barati, H., Wu, M., Kharicha, A., & Ludwig, A. (2018). A transient model for nozzle clogging. *Powder Technology*, 329, 181–198.
- Smith, M. F. (2007). Comparing cold spray with thermal spray coating technologies. In V. K. Champagne (Ed.), *The cold spray materials deposition process: Fundamentals and applications* (1st ed.). Cambridge: Woodhead.

- Karthikeyan, J. (2007). The advantages and disadvantages of cold spray coating process. In V. K. Champagne (Ed.), *The cold spray materials deposition process: Fundamentals and applications* (1st ed.). Cambridge: Woodhead.
- Rokni, M. R., Widener, C. A., Champagne, V. K., & Crawford, G. A. (2015). Microstructure and mechanical properties of cold sprayed 7075 deposition during non-isothermal annealing. *Surface & Coatings Technology*, 276, 305–315.
- Rokni, M. R., Widener, C. A., Crawford, G. A., & West, M. K. (2015). An investigation into microstructure and mechanical properties of cold sprayed 7075 Al deposition. *Materials Science and Engineering A*, 625, 19–27.
- Vlcek, J., Gimeno, L., Huber, H., & Lugscheider, E. (2005). A systematic approach to material eligibility for the cold-spray process. *Journal of Thermal Spray Technology*, 14, 125–133.
- 34. Kim, K., Watanabe, M., Kawakita, J., & Kuroda, S. (2008). Grain refinement in a single titanium powder particle impacted at high velocity. *Scripta Materialia*, *59*, 768–771.
- Coddet, P., Verdy, C., Coddet, C., & Debray, F. (2015). Effect of cold work, second phase precipitation and heat treatments on the mechanical properties of copper–silver alloys manufactured by cold spray. *Materials Science and Engineering: A, 637, 40–47.*
- Luo, X. T., Yang, G. J., Li, C.-J., & Kondoh, K. (2011). High strain rate induced localized amorphization in cubic BN/NiCrAl nanocomposite through high velocity impact. *Scripta Materialia*, 65, 581–584.
- Richer, P., Zúñiga, A., Yandouzi, M., & Jodoin, B. (2008). CoNiCrAlY microstructural changes induced during cold gas dynamic spraying. *Surface & Coatings Technology*, 203, 364–371.
- Bae, G., Kumar, S., Yoon, S., Kang, K., Na, H., Kim, H. J., et al. (2009). Bonding features and associated mechanisms in kinetic sprayed titanium coatings. *Acta Materialia*, 57, 5654–5666.
- Choi, W. B., Li, L., Luzin, V., Neiser, R., Gnaupel-Herold, T., Prask, H. J., et al. (2007). Integrated characterization of cold sprayed aluminum coatings. *Acta Materialia*, 55, 857–866.
- 40. Lange, F. F. (1989). Powder processing science and technology for increased reliability. *Journal* of the American Ceramic Society, 72, 3–15.
- Gartner, F., Stoltenhoff, T., Schmidt, T., & Kreye, H. (2006). The cold spray process and its potential for industrial applications. *Journal of Thermal Spray Technology*, 15, 223–232.
- 42. Wong, W., Rezaeian, A., Irissou, E., Legoux, J. G., & Yue, S. (2010). Cold spray characteristics of commercially pure Ti and Ti-6Al-4V. *Advanced Materials Research*, *89*, 639–644.
- Zhang, Q., Li, C. J., Li, C. X., Yang, G. J., & Lui, S. C. (2008). Study of oxidation behavior of nanostructured NiCrAIY bond coatings deposited by cold spraying. *Surface & Coatings Technology*, 202, 3378–3384.
- Kang, K., Yoon, S., Ji, Y., & Lee, C. H. (2008). Oxidation dependency of critical velocity for aluminum feedstock deposition in kinetic spraying process. *Materials Science and Engineering A*, 486, 300–307.
- 45. Yin, S., Wang, X., Li, W., Liao, H., & Jie, H. (2012). Deformation behavior of the oxide film on the surface of cold sprayed powder particle. *Applied Surface Science*, *259*, 294–300.
- Binder, K., Gottschalk, J., Kollenda, M., Gartner, F., & Klassen, T. (2011). Influence of impact angle and gas temperature on mechanical properties of titanium cold spray deposits. *Journal* of Thermal Spray Technology, 20, 234–242.
- Pattison, J., Celotto, S., Khan, A., & O'Neill, W. (2008). Standoff distance and bow shock phenomena in the Cold Spray process. *Surface & Coatings Technology*, 202, 1443–1454.
- Bae, G., Xiong, Y., Kumar, S., Kang, K., & Lee, C. (2008). General aspects of interface bonding in kinetic sprayed coatings. *Acta Materialia*, 56, 4858–4868.
- Pauly, S., PeiWang, U. K., & Kosiba, K. (2018). Experimental determination of cooling rates in selectively laser-melted eutectic Al-33Cu. *Additive Manufacturing*, 22, 753–757.
- Yandouzi, M., Richer, P., & Jodoin, B. (2009). SiC particulate reinforced Al–12Si alloy composite coatings produced by the pulsed gas dynamic spray process: Microstructure and properties. *Surface & Coatings Technology*, 203, 3260–3270.