Chapter 3

Glassy Metal: Principles, Processing Routes and Laser Surface Treatment

“That’s not evolutionary, it’s revolutionary” – Bill Johnson, on the future of metallic glasses

This Chapter focuses on the principles and fabrication of amorphous metallic alloys. Alloys are chosen with a view to surface deposition by high-power laser, and the parameters concerned with the production of such layers are explored.

3.1 Introduction

Metallic glass; it sounds like an oxymoron. They have an amorphous structure, and have been around for almost 50 years already, but functional metallic glasses have only come to be realised in the last 15-20 years. The term “amorphous” comes from Greek language (αμορφήνουσ) and means “without regular form” [α = not, μορφή = form]. The atoms in an amorphous metal are therefore considered to be arranged without long range ‘order’. A schematic diagram of the disparity between the crystalline and amorphous ‘systems’ is shown in Figure 3.1.
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Figure 3.1: Schematic comparison of crystalline (left) and amorphous (right) structures

The year 1960 found the first metallic glass, developed by Klement and Duwez [1], with the discovery of the Au-Si metallic glass. In the ensuing years, amorphous alloys have been developed progressively, with one of the driving forces behind the development of metallic glasses being to lower their critical cooling rate, and thus facilitate their fabrication (and determine their size), as shown in the Figure 3.2 [2]. It is common to cast bulk metallic glasses (BMGs) into copper moulds. If the cooling rate during this process is considered, i.e., if a molten sample of dimension, \( R \), is cooled from temperature, \( T_m \) (melting temperature) to a temperature known as the glass transition temperature (\( T_g \)), the time, \( \tau \), required for this to occur is \( \tau \sim R^2/\kappa \). \( \kappa \) represents the thermal diffusivity of the alloy; equal to \( K/C \), where \( K \) is the thermal conductivity and \( C \) is the heat capacity per constant volume. The cooling rate, \( \dot{T} \), is therefore proportional to the dimension of the cast piece (equation 3.1).

\[
\dot{T} = \frac{dT}{dt} = \frac{(T_m - T_g)}{\tau} = \frac{K(T_m - T_g)}{CR^2}
\]  

(3.1)

Figure 3.2: Graph revealing the increase in critical casting thickness for various glass forming alloys over the last 50 years. [2]
It may be appropriate to now outline what is already known about processing and properties of the class of amorphous metals and why they are considered so desirable. Several crystalline materials are inherently vulnerable to failure by corrosion due to their in-built defects – grain boundaries. Grain boundaries represent weak regions of less than optimal packing, and therefore contain numerous small defects due to misaligned planes of atoms. Under sufficient stress (at higher temperature), they may slip, allowing grain-boundary dislocations to move. The resulting deformation is plastic and permanent.

In the tightly-packed glassy structure, the displacement of atoms at room temperature is obstructed. A metallic glass, therefore, absorbs less energy upon stress-induced deformation. With no lattice dislocations present, mechanical properties combine to produce an exceptionally strong material (Figure 3.3) [2]. With great strength (normally) comes exceptional hardness, \( H \sim 3\sigma_y \) where \( \sigma_y \) is the yield strength of a material. Hardness is not an intrinsic material property but it is highly desirable for structural applications. When in the form of bulk materials, this lack of long-range order gives rise to other remarkable properties as well. Because there is no crystalline structure to keep intact, amorphous metals do not need to be machined to create a desired shape or part. The material can be heated and injected into a shaped mould, much like some plastics. It can also be turned into foam. That is, it can be readily mixed with air to create a permanent, lightweight, strong (but brittle) material suitable for insulation, soundproofing, fireproofing, or a host of other applications. For these reasons, much of recent metallurgical research has been conducted on a nano-scale and, as such, has surrounded the development of (metallic) Glass Forming Alloys (GFAs) or Bulk Metallic Glasses (BMGs) since they possess unique and interesting properties compared to many other available materials (Figure 3.3).

![Figure 3.3: Strength - elastic limit relationship of various alloys and materials [2]](image-url)
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As can be seen in Figure 3.2, the range of alloying elements in a ‘standard’ BMG is extremely broad and extensive work has been conducted on glass-forming systems. The complexities surrounding the formation of glassy metals has been the driving force for significant attention within the last two decades, not least from A. Inoue, whose three empirical rules for their production are often quoted, as outlined by Inoue [3]:

1. Three or more elements should be present within the alloy system. The presence of several elements was found to cause a significant extension of the supercooled liquid region before crystallisation.
2. There should be a significant difference in atomic size ratios, above 12% amongst the three main constituent elements. Atomic size differences lead to highly dense random packed structure in amorphous phases, which enables the achievement of a large liquid/solid interfacial energy and makes the redistribution of atoms on a large scale difficult.
3. There should be negative heats of mixing amongst these three main constituent elements. Highly attractive bonding nature in atomic pairs is shown by large negative heats of mixing (H_m). These characteristics suppress nucleation and growth of the crystalline phase in the supercooled liquid phase. This rule reflects the experimental observation that glass formation composition ranges coincide with eutectic and low melting points.

These rules have, however, been challenged, for example by Wang et al [4], who recently proved that, despite rule 1 stipulating multi-component systems and that rule 3 coincides with eutectic points; in many systems, the better glass formers are found to be at off-eutectic compositions. They show that glass forming alloys (suction cast up to 2 mm) can be found in binary systems close to (but not at) a eutectic point which is asymmetric with respect to its liquidus lines; furthermore, the glass forming ability will be higher on the side with the steeper liquidus line. They chose the Cu-Zr system for investigation, as have others who have also presented similar results. [5]

Glass forming metallic alloys have been grouped into two general categories, as cited by Perepezko and Herbert [6]. In the first case, large, bulk volumes may be slowly cooled to the glassy state, which signifies a nucleation controlled synthesis. The other class is represented by metallic glasses that can be synthesised upon rapid solidification processes such as melt-spinning. These glasses are referred to by Perepezko and Herbert as marginal glass formers that are synthesised under growth controlled kinetic conditions.

Most bulk amorphous alloys also have a characteristic dependence of atomic concentrations on their atomic radius, [7] thus, the concentration of solvent atoms > smallest atoms > intermediate atoms, with the scale being concentration, starting with the highest. This produces an upward concave shape of atomic size distribution plot (ASDP), and is said to be
indicative of ‘bulk glass forming alloys’, which is completely different from the concave downward ASDP, characteristic of, what Senkov and Miracle [8] term, marginal amorphous alloys where the solvent element has the intermediate size. The ASDP’s correlate with the low molar volume and high packing efficiency of atoms in bulk metallic glasses. Senkov and Miracle show that the Cu_{47}Ti_{33}Zr_{11}Ni_{8}Si_{1} BMG alloy, whose critical cooling rates is \( \sim 10^2–10^3 \) K/s [3] have an upwardly concave ASDP, while (more expensive) Pd-based metallic glasses with critical cooling rates of \( \sim 10–500 \) K/s has a downward concave ASDP. They also conclude that the concave upward distributions provide for more efficient atomic packing, which is understandable from atomic size differences relative to alloys with concave downward distributions.

Nanocrystalline materials (materials containing crystals of nanometer size) are also producible, and many nanocrystalline alloys produced in recent years have strengths (in tension) up to an order of magnitude higher than their coarse-grained counterparts. These strengths are a direct result of the large population of grain boundaries, which delay yielding by grain-boundary dislocations [9]. Like amorphous materials, their drawback is their lack of plasticity, often induced through thin, sheet-like volumes in which very large strains can be concentrated, leading to the formation of ‘shear bands’. However, He et al. [10] (for example) have successfully applied an idea previously proposed for BMGs to combat such catastrophic shear banding in titanium-based nanocrystalline alloys by creating an ‘in-situ composite microstructure’ of cast alloys.

An entire workpiece should rarely need to be formed wholly from one material, since most manufactured articles gain their main functionality from their surface. Surface engineering has been coined an ‘enabling technology’ or, as defined by Rickerby and Matthews [11], ‘the design of a composite system (i.e. a coating plus substrate) which has a performance which cannot be achieved by either the coating of substrate alone’. By harnessing the properties of selected BMGs in the surfaces of tribologically poor materials, (such as titanium and aluminium) these materials can be exploited in a more diverse range of applications than they currently find. High power lasers have become increasingly accepted as tools for many applications from cutting to welding to surface modification [3]. The high power laser has been proven to be capable of producing adherent, hard, wear- corrosion- fatigue- and fracture- resistant coatings on a wide range of materials [4,5,6].

It is therefore hoped that with advanced, controlled processing by high power lasers, beneficial results may be attainable for surface engineering applications. This is a highly attractive area in which to focus, since in very broad terms, the surface engineering industry in the UK alone (sales value of coatings and treatments produced) was about £7 billion in 2005 - and they critically affect products with a value of about £120 billion. That is coatings for engineering applications (i.e. wear, corrosion and friction control). It does not include coatings for thin film devices (electronics, semi-conductors, sensors, optics, etc), which adds a further
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£14.3 billion in coatings value, and about £26.5 billion in the functional thin films products values [12]. As Greer [13] states, the lack of work hardening (in amorphous alloys) and consequent shear instability in amorphous alloys may make them more attractive as coatings than as bulk materials, with a particular emphasis on the engineering sector.

The work in this thesis is thus driven by a desire to form surface layers of glass forming alloys, it is therefore important that any alloy system should not form (potentially) dangerous by-products during fabrication, nor contain expensive elements. Many of the extremely good bulk glass-formers pose problems for laser cladding (a technique which will be described more fully in section 3.2.1.2) in this respect. Most of these bulk amorphous alloys contain very expensive elements of platinum and/or lanthanum groups, limiting their applications, and only Zr-based alloys that do not contain these elements have found successful use for sporting goods [14].

Many of the BMG compositions published containing Zr often use this element in tandem with Be, as this element considerably improves the glass forming ability of Zr-containing alloys [10,11] by strong bonding between Zr-Be atomic pairs which suppress the formation of competing crystalline phases during solidification. For example, if one of the most famous glass forming alloys, VIT1, with a composition of Zr$_{41.8}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$, and a critical cooling rate of a few 10’s of K/s is considered [15], the fact that it contains beryllium is most disadvantageous for laser processing. If processed in air, this element may form cancerous BeO, for example, and therefore may be deemed too dangerous to public safety for fabrication. An interesting alloy system, however, is as the Cu-Ti-Zr-Ni based system first purported by Lin et al. [16]. One variation on this system is the marginal glass forming alloy Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$Si$_{1}$. Park et al. [17] found that the partial substitution of Ni with Sn addition in the form Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8-x}$Sn$_{x}$Si$_{1}$ improved the glass forming ability of the system, with an increasing critical casting diameter from 4 mm to 6 mm when processing by injection casting for the composition Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{6}$Sn$_{2}$Si$_{1}$. This improved critical casting result implies that the critical cooling rate required to achieve amorpicity is reduced, which as stated already, is one of the most important parameters when considering metallic glass formation since reduced cooling rates facilitate a wider range of processing options.

If we consider the selection of this alloy for processing by high power laser, the process begins by selecting suitable BMG compositions from published works for alloys containing Ti, Al or Fe, which are the proposed substrate materials, which may benefit from surface modifications. All chosen substrates have previously been treated successfully by the laser surface treatment processes [18]. As an example, the Cu-Ti-Zr-Ni system shall be explained in terms of the empirical rules outlined by Inoue. The first rule is satisfied since the alloy system here is quaternary. The second rule is satisfied by the fact that the elements of this BMG have atomic radii of Cu = 128 pm, Ti = 145 pm, Zr = 159 pm and Ni = 125 pm, which gives a percentage difference between the three main constituent elements greater than
12% (Ti is 13.3% larger than Cu, and Zr is 24.2% larger than Cu). These values are for first-order comparisons only, as the actual atom radii depend upon the structure and local chemical environment, and significantly smaller or larger radii may result, depending upon the neighbour with which a bond is formed. For example, significant bond shortening is observed in the ordered Fe–Al compound [19]. Nonetheless, the data provides a consistent basis for comparison and discussion.

The final rule requires that the elements have a strong affinity for one another. When Lin and Johnson [16] first investigated the Cu-Ti-Zr-Ni system, they did so based on the component element binary phase diagrams since Ti-Cu, Ti-Ni, Zr-Ni and Zr-Cu are all reasonable glass formers themselves with deep eutectics. This is because these atomic pairs have a highly attractive bonding nature. With reference to Miedema’s semi-empirical model for the enthalpies in alloys, [20] these elements are indeed compliant to rule 3.

Figure 3.4: Two bulk glass formation regions in the pseudoternary phase diagram. The dots represent the alloys which can be cast to amorphous strips of at least 1 mm thickness. Generally for the titanium-rich region the nickel concentration is about 4 - 12 at. %. The glass forming region is largest when nickel concentration is about 8 at %. For the zirconium-rich region, copper and nickel are roughly interchangeable when at least 4 at. % of either copper or nickel is used. The region moves downward with increasing nickel concentration. In the centre of the diagram the quaternary Laves phase field is shown.

Figure taken from Lin and Johnson [16]

Figure 3.4 shows the Cu-Ti-Zr-Ni system as a pseudo-ternary phase diagram. It contains two broad regions where amorphous casting of bulk samples is possible, the dots in both regions showing the tested compositions. The Ni concentration is about 8 at.% for the Ti-rich region on the left of the diagram. For the Zr-rich region, Cu and Ni were found to be
roughly interchangeable as long as at least 4 at.% of each was present. The centre of the phase diagram shows a MgZn₂-type Laves phase. Despite the number of elements involved, the alloy forms a simpler crystal structure at these compositions, which greatly hinders the formation of amorphous samples. The composition with the best glass forming ability that was found is Cu₄₇Ti₃₄Zr₁₁Ni₈. This particular alloy can be cast in rods of up to 4 mm diameter, which corresponds to a critical cooling rate of about 250 K/s. This, combined with the rather large amount of Titanium in the alloy, makes it very suitable for laser cladding purposes. In addition, the composition is found near the middle of one of the BMG regions, which means that deviations in composition still give an alloy with reasonably good glass forming ability.

Figure 3.5 Phase diagram for the Cu-Ti-Zr-Ni system, showing the compositions where the maximum number of five phases can be in equilibrium. These points are an excellent indicator for good glass forming ability, as demonstrated by their proximity to the compositions that result in a BMG experimentally. Figure taken from Yan et al. [21], experimental values from Lin and Johnson [6].

The experimental diagram from Figure 3.5 has been reproduced on theoretical grounds by Yan et al. [21]. Using thermodynamic descriptions of all six binary systems involved and some available information on the ternaries, they extrapolated a full phase diagram for the quaternary Cu-Ti-Zr-Ni system. From this, they have also calculated the compositions for which the maximum number of phases is in equilibrium, which is five for quaternary systems. These points are similar to eutectic points in binary phase diagrams, where the maximum of three phases is at equilibrium. For the current system 18 such points were found, which are shown in Figure 3.5. The diagram shows that the points are again grouped in two regions of good glass-formers. Also shown in the figure, for comparison, are the experimental results by Lin and Johnson. The similarity between them is quite remarkable,
and gives a firm basis for the experimental work done. The calculations from a thermodynamical perspective give a very good estimation of the compositions where good GFA’s are to be expected, and can become a valuable substitute for the currently used ‘educated guess’.

3.2 Experimental Procedures
3.2.1 Sample Preparation
3.2.1.1 Arc-Melting, Melt-spinning and Arc-Casting

Alloys are prepared by weighing the component elements, such that an approximately 1 cm³ ‘button’ may be produced by arc melting (Figure 3.6). The materials are of at least 99.99 wt.% purity and in sheet, plate, pellet or powder form prior to fabrication. The melting process is conducted in a Ti-gettered, high purity argon atmosphere. To ensure chemical and microstructural homogeneity, the buttons are turned and remelted 3-5 times within the furnace.

Figure 3.6: Schematic representation of the arc-casting procedure. A tungsten tip creates the arc with the sample to be melted. Upon creation of the alloyed button, this may be remelted and ‘sucked’ into the copper mould

The resultant buttons are then weighed and analyzed by optical and secondary electron microscopy (SEM Philips XL30 FEG with EDS). Ribbons of 2-8 mm width, with thicknesses in the region 20-50 µm, are produced from the pre-alloyed buttons by the melt-spinning process. The buttons are reheated above their melting point in an argon or helium atmosphere by induction heating and injected by an overpressure of 500 mbar onto a rotating (1800 rpm) copper wheel (Ø = 50 cm). The buttons may also be cut to appropriate shapes and sizes for arc casting into water-cooled copper moulds (Figure 3.6), to fabricate cylinders 1 mm, 2 mm or 6 mm in diameter and 25 mm in length, or 0.5 mm, 0.75 mm or 1 mm thick plates 5 mm wide and 35 mm in length.
3.2.1.2 Laser Processing

In 1917 Einstein formulated the basic concepts of stimulated emission [22], based on Plank and Boltzmann statistics that evolved into the introduction of the laser, an acronym which stands for “Light Amplification by Stimulated Emission of Radiation”. The principle of a laser is to excite atoms to a high energy level and to have an inversion in population with respect to an intermediate level. When radiation interacts with the excited atom with the frequency that corresponds to the energy difference between the higher energy state of the atom and the intermediate state, produces a radiation with the same phase as the incident radiation. This radiation is amplified with a resonance cavity to obtain a coherent beam. Laser beams are unique in that it is possible to achieve a high degree of monochromaticity which allows efficient focusing. Less than one month prior to Duwez’s publication on the discovery of the first metallic glass, (1960), the first operational, stable, laser was also reported in *Nature*, by Maiman [23], built at the Hughes Research Laboratories in California. High power lasers have since found many diverse and important uses. One of those is for laser surface treatment. The most common laser surface treatments are laser surface remelting, glazing, laser cladding, surface alloying and laser melt injection, which may herald different microstructural changes/properties [18]. They are generally used to improve hardness, wear and/or corrosion resistance. Figure 3.7A shows a schematic diagram of a typical laser surface treatment process, while the laser cladding set-up in our group is shown in Figure 3.7B. In this figure, the treated substrate is a cylindrical bar which is clamped and rotated as a cantilever.

![Figure 3.7: (A) Schematic diagram illustrating the laser-remelting process and the important parameters of laser surface treatment: Power, P; Scanning Speed, S; Defocus, D; and for laser side-cladding/LMI, powder feeding rate, F, shown in (B)](image)

The laser equipment used in this thesis is a 2 kW Rofin-Sinar Nd:YAG laser (wavelength, \( \lambda = 1064 \text{ nm} \)). In this set-up, the laser beam is CNC controlled and may either move with a scanning speed relative to the treated surface itself, or may remain stationary (in
while the treated surface is rotated. The laser has a defined power distribution which strikes the surface of a light absorbing material and a part of the energy is absorbed. If the power and speed parameters are correct, a thin melt pool forms on the surface due to laser heating. It is also possible to simultaneously inject a powder of a different material into the melt pool, which mixes with the molten substrate by convection and diffusion. As the laser source moves away from a location, the melted zone is resolidified, leading to a final microstructure of the alloyed surface. During laser surface alloying, as the heat source interacts with the molten substrate, several complex phenomena such as melting, Marangoni convection, mixing of the powder feed, alloy solidification, and resulting microstructural evolution occur.

The buttons have been prepared for laser remelting (Figure 3.7A) by cutting them into 15 mm diameter hemispheres, followed by grinding and fine polishing to produce a flat surface. Since, during laser treatments, some of the applied energy may be reflected, the surface is fine sand-blasted to improve the absorptiveness, thereby improving the efficiency of the laser processing.

The laser cladding (and subsequent remelting) processes were conducted over a range of processing parameters which will be specified later. An argon shielding of 10 l/min is always applied. Powders for the cladding process will also be discussed where relevant. Dilution, $D$, is a simple but important factor in laser clad coating deposition, as is the clad angle, $\alpha$, both shown in Figure 3.8.

![Figure 3.8: Cross-sectional light micrograph of a laser clad single track with high dilution, $D$, where $A_m$ is the area below the solid black line, bounded by the dotted black line, $A_c$ is the area above the solid black line. The clad is of width, $W$, height, $H$ and $\alpha$ denotes the clad angle.](image)
3.2.1.3 Grinding and Polishing

Before light-, confocal light- or scanning electron- microscopy, or hardness and wear analysis may be performed on the resultant fabrications, it is necessary to prepare the relevant surface of the sample. In the case of the rods, plates, laser-remelted and laser-clad coatings, this is done by mounting the samples in Bakelite, grinding and polishing according to the following sequence. All samples are ground for 30 s on waterproofs papers in the following grit paper size order: 180, 220, 320, 500, 800, 1200, 2400, 4000. In between paper changes, the samples are rinsed in water and ethanol. After this series of grinding papers, the samples are polished on satin fabric disks with 6, 3 1 and ¼ μm diamond sprays (all from Struers™); again the samples are rinsed between each polishing stage. The final polishing stage involves a one hour slow speed polish in silica suspensions of either OPS or OPU, followed by a long rinse in water, and cleansing with acetone and finally ethanol before hot-air drying. The etchant used for the Ti-containing alloys is: 0.5 vol.% HF, 0.3 vol.% HNO3, 99.2 vol.% H2O and the etchant used for the Fe-based alloys is: 10 vol.% HCl acid, 5 vol. % Nitric Acid, 85 vol.% H2O.

3.2.2 Analytical Techniques

3.2.2.1 X-Ray Diffraction and Synchrotron Diffraction

In addition to the analytical techniques outlined in Chapter 2, X-ray and synchrotron diffraction analysis are implemented in order to ascertain the microscopic state of (some of) the produced materials.

As discussed in Chapter 2, section 2.1.2, diffraction from an electron source can provide crystallographic and textural information of a given material. For the typical electron case, Bragg angles must be very small for considerable diffraction to take place. This is not the case for X-ray and neutron diffraction; as well as both techniques permitting valuable crystallographic or textural information to be gathered, they may (for example) even be used to garner knowledge of the stress state in a coating [18]. X-ray diffraction analysis was performed using a Philips PW1710 system.

When an amorphous material is exposed to electrons, the characteristic diffraction pattern is one of a broad band, due to dense random packing, as described in Zernike (of the University of Groningen) and Prins [24]. An English translation of this 1-D model is included as Appendix 3.1 to this chapter, provided by the generous and assiduous Paul Bronsveld.

Synchrotron radiation is a source of high energy radiation which may be considered in much the same way as a XRD, only the X-rays are generated with much higher power [25]. This tool provides benefits in two ways. Due to the very high intensity and penetration depth of a synchrotron beam, relatively thick samples may be characterised, even in transmission. Typical synchrotron results can be seen in standard ‘2θ’ or 2-D powder diffraction patterns. The synchrotron beam used was produced with 80.4 keV photons, giving a working
wavelength of 0.15422 Å, administered with a ‘spot’ area of 30 µm x 20 µm. A more in-depth analysis of the technique and additional possibilities, such as stress analysis, can be found elsewhere [25,26].

3.3 Results and Discussions

3.3.1 Processing by melt-spinning and arc-casting

As stated previously, one of the most important factors in metallic glass production is the cooling rate at which the melt is solidified. In the case of melt-spinning, small masses of glass forming alloys are injected onto very large masses of highly conductive material at high speed and therefore the heat-sink away from the melt (and thus the cooling rate) is huge. Cooling rates of $10^6$ Ks$^{-1}$ are easily attainable by this method. As a result, ribbons from the melt-spinning process can be examined by XRD and a typical scans are shown in Figure 3.9. Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$Si$_{1}$ ribbon is represented in Figure 3.9A and is seen to be fully X-ray amorphous, with the ‘amorphous halo’ [Appendix 3.1] seen around 2theta = 40°. Figure 3.9B shows a Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_{8}$ ribbon, which shows a small diffraction peak (highlighted by the rectangular block) alongside the expected amorphous halo. Such features may signify a nanocrystalline phase, and provide interest for TEM analysis. This result also highlights the effect of the addition of silicon (in quantities < 2 at.%.) on this system’s glass forming ability.

Likewise, the fabrication of amorphous rods has been widely publicised as an appropriate method for BMG production, equation 3.1 signifying the link between rod thickness and cooling rate. If typical numbers for the Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$Si$_{1}$ alloy are put into the equation, such that $T_m - T_g ~ 400$ K, $K ~ 0.1$ W/cm.s$^{-1}$K$^{-1}$ and $C ~ 4$ J.cm$^{-3}$, the following relationship applies ($R$ in cm):

Figure 3.9: XRD scans for (A) Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$Si$_{1}$ and (B) Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_{8}$ melt spun ribbons (Cu-Kα radiation). The box in (B) highlights a small secondary hump, centred at 2theta = 23°, additional to the amorphous halos around 2theta = 45°, which signifies a (possible) nanocrystalline presence.
Conventional arc-casting uses an induction heating source, and an injection method of firing the melt into the mould. This has significant benefits over the suction casting set-up in our group, where the heat source and the mould are not mutually exclusive. This disadvantage has been used to good effect however in manufacturing alloys, not of fully amorphous structure by arc-casting, but also alloys with an amorphous matrix. One example of a GFA fabricated as plates in this way is the Cu\textsubscript{50}Zr\textsubscript{30}Ti\textsubscript{10} alloy, which when cast to 0.5 mm plates, and examined by XRD revealed an amorphous halo overlain with several crystalline peaks (Figure 3.10A). When TEM investigation is implemented, a large portion of the sample was found to be amorphous. Other areas revealed homogeneous, although, spatially limited, dispersions of 50-100 nm sized crystals embedded within the amorphous matrix (Figure 3.10A, (including the accompanying diffraction ring inset from the amorphous matrix)).

![Figure 3.10](image)

\textit{Figure 3.10: (A) reveals the structure found at the base of an arc-cast half mm plate with the matrix amorphicity confirmed by the inserted diffraction ring in (A), (B) an XRD scan revealing the presence of Cu10Zr7 crystals overlain on an amorphous halo.}

In-situ EDS examination showed these crystals to be of average composition: Cu\textsubscript{49}Zr\textsubscript{38}Ti\textsubscript{12}. This relates very well to the crystalline phase found in the XRD examination (Figure 3.10B), whose peaks correlate as those of Cu10Zr7 as published by J. Rawers (1991). The difference in microstructure is the result of differing cooling rates within the copper mould. The ‘bottom’ of the plate (i.e. from the base of the mould, away from the arc heat source) is subjected to rapid and ‘instantaneous’ cooling, which leads to an amorphous structure. If the heat source is held briefly above the mould after suction, the top of the plate is subject to some ‘residual’ heating and, therefore, the plate in this area has enough time to nucleate and grow crystals of the size shown in Figure 3.10A. For the comparative wear experiments, shown in Chapter 5, Cu\textsubscript{47}Ti\textsubscript{12}Zr\textsubscript{11}Ni\textsubscript{6}Sn\textsubscript{2}Si\textsubscript{1} alloy was used without the residual
heating effect and has been investigated to reveal a fully amorphous structure up to 1 mm in thickness.

3.3.2 Processing by High Power Laser

3.3.2.1 Laser remelting

The concepts of amorphous materials may be explored as above; however their practical use and indeed mechanical testing possibilities are limited. Typical ribbon thicknesses are less than 100 µm (those prepared for this investigation ~ 30 µm) and widths are a few mm. As has already been noted, the rate at which a melt can be solidified is very important to metallic glass production. The reported cooling rates afforded by high power lasers [27,28,29] in local areas are certainly in the bounds of the quench rates necessary for “amorphisation”. In laser processing, the physics of laser surface melting is highly complex, which leads to heat flow models involving complex mathematics or computing [30,31,32]. Nevertheless, an estimation of the cooling rates, \( \frac{\partial T}{\partial t} \), obtained during laser surface melting at high scanning speeds can be made using the Rosenthal solution for a moving heat point source, as proposed by Steen [33], in which a proportional relationship between cooling rate \( \frac{dT}{dt} \) and laser scanning speed \( V \) is assumed, as shown in equation 3.3.

\[
\frac{dT}{dt} = -2\pi K \left( \frac{V}{P_d A} \right) \Delta T^2
\]  

(3.3)

Here, \( K \) is thermal conductivity, \( P_d \) is the power density, \( A \) is the area of the laser spot and \( \Delta T \) is the range of temperature variation during cooling. For the calculations, it was assumed that the maximum temperature in the melt pool is the melting temperature of the alloy since we are concerned only with the formation of glass; \( \Delta T \) is given as \( T_m - T_g \), which are explained fully in Chapter 4. A few assumptions are made in this analysis, this being the first, the second assumption is that since the piece is embedded in a large copper block, \( K \) may be considered large (200 Wm\(^{-1}\)K\(^{-1}\)). For the Cu\(_{47}\)Ti\(_{33}\)Zr\(_{11}\)Ni\(_6\)Sn\(_2\)Si\(_1\) alloy, this dependence of cooling rate on scanning speed is shown in Figure 3.11. The curve shown only pays attention to the cooling to \( T_g \), and assumes a constant beam diameter of 1.3 mm. These conditions show that in order to achieve a fully amorphous layer (i.e. in order to achieve \( dT/dt > 1000 \text{ K.s}^{-1} \)), the laser scanning speed should be greater than ~ 0.01 m.s\(^{-1}\).

A range of processing parameters was investigated and a good agreement with equation 3.3 is found experimentally. When these layers are remelted at appropriate speeds (i.e. over 0.01 m.s\(^{-1}\)), laser remelted tracks have been fabricated with amorphous properties [34]. The results here will focus on tracks produced by laser remelting of a Cu\(_{47}\)Ti\(_{33}\)Zr\(_{11}\)Ni\(_6\)Sn\(_2\)Si\(_1\) alloy. The results shown are concerned with both single and overlain tracks with the same parameters with laser head displacements of 1.0 and 1.1 mm.
Generally, in as-cast form, a microstructure consisting of a fine eutectic matrix, which surrounds Ti rich dendrites and Zr-Sn based crystals, was found, as can be seen in Figure 3.12. By remelting this in single tracks (1.3 mm wide) produced at power = 1750 W, table speed = 133 mm/s, beam defocus = -6 mm, amorphous layers up to 250 µm in depth can be produced. A heat affected zone thereafter exists (Figures 3.12A and B), which (in this example) consists of Ti rich dendrites (dark areas) and Zr-Sn rich needles retained within a chemically homogeneous amorphous matrix (Figures 3.12B and 3.12C). These compositions of the needles and dendrites were confirmed as such by in-situ EDS to be Zr$_{31}$Sn$_{20}$Cu$_{18}$Ti$_{24}$Ni$_{4}$Si$_{3}$ and Ti$_{57}$Cu$_{22}$Zr$_{7}$Ni$_{11.5}$Si$_{2}$Sn$_{0.5}$ respectively. This shows that despite the temperature in this area not being sufficient to melt the associated crystalline phases, the cooling rate is high enough to form an amorphous matrix, which initially shows a fine eutectic form. This is a very important observation in terms of creating an amorphous matrix, which can be reinforced by particle injections. Confirmation of structure and chemistry of the laser melted track, along with the retained dendrites, was achieved by TEM (with EDS) investigations (see Figure 3.12C and D).

As stated in the experimental procedures, it is also possible to conclusively determine whether the layers are fully amorphous by synchrotron diffraction. The results in Figures 3.13A and 3.13B show data for one full track and (portions of) two adjacent tracks, divided by the as-cast crystalline material. The test method is so powerful and selective that it is in fact possible to map the area in and around the tracks to determine the transition from amorphous, to amorphous matrix ‘mushy zone’, to crystalline material, and this is shown in the 2θ scans, (Figures 3.13A and B). Given that the wavelength of the synchrotron radiation is approximately ten times shorter than a standard laboratory X-ray diffraction test (XRD)
method (Cu-Kα wavelength = 1.540563 Å), a value of 4° on the X-axis in Figures 3.13A and 3.13B corresponds to a 20 value of around 45° in a standard laboratory Cu-Kα XRD test given that \( n\lambda = 2d\sin\theta \). Therefore, the hump in this region may be considered to be related to an amorphous halo. It is clearly noticeable that this broad peak becomes sharper in the crystalline area, which becomes larger and more pronounced as the depth is increased and relates to an area such as the ‘as-cast crystalline origin’ area shown in Figure 3.13C, which, in turn, relates to the area outlined by a dotted box in Figure 3.13A. The diffused diffraction ring, attained through the centre of the track (Figure 3.13D), confirms that the laser tracks are amorphous. The sample – detector distance was 217.84 mm and the detector size was 10 cm x 10 cm. The image shown (Figure 3.13D) has been cropped to aid clarity, but the centre of the broad band corresponds to the broad peak in Figures 3.13A and 3.13B, which equates to a d-spacing of 1.104 Å, (\( \theta = 4.01° \)).

**Figure 3.13:** (A) SEM image highlighting the laser remelted Cu_{47}Ti_{33}Zr_{11}Ni_{6}Sn_{2}Si_{1} alloy track – the free surface can be seen on the right on the figure and (B) the as-cast microstructure adjacent to the HAZ, exhibiting Ti rich dendrites (dark areas) and Zr-Sn rich needles (white areas) in an amorphous matrix and (C) a TEM image reveal a Ti-rich dendrite in the amorphous matrix from the amorphous matrix interlayer
3.3.2.2 Laser cladding

When powder is introduced to the laser beam, as is the case in laser cladding of a precursor mix of powders, processing becomes a more complicated task than the case of laser remelting. In coaxial laser cladding, powder mixtures often vary in particle size, density and thermal properties. As a result, the different powders behave differently during the cladding experiment. Because there is often a narrow window for the operating parameters (for example Figure 3.14), it is important to know how these change with different powder properties. This can be done to a certain extent by modeling the effects of these differences on the cladding process.

The model presented is based on calculations proposed originally by Jouvard et al. [35] and also used and adapted by de Oliveira et al. [36]. These calculations model the transfer
of energy from the laser beam to the powder and the substrate. They provide an estimate for
the laser powers needed to melt the substrate and the particles, dependent on a given
combination of input parameters. Among these input parameters are the main cladding
parameters of scanning speed, feeding rate and particle speed. The model by Jouvard et al. has
been expanded to incorporate the presence of multiple powders during laser cladding, with
more information and derivations found in Appendix 3.2.

As the laser beam travels from the nozzle to the substrate, it encounters a mass of
powder particles. These particles partially shield the substrate from the laser beam, absorbing
a part of the incoming energy. This attenuation of the laser beam occurs throughout the
interaction zone. When the attenuated beam hits the substrate, part of the light is reflected by
the surface and the rest is absorbed and used directly for heating the substrate. Each powder
particle will absorb light from the moment it enters the interaction zone until it hits the
substrate. The amount of laser light it absorbs per unit time is dependent on the strength of the
attenuated laser beam at the particle’s position, and on the apparent surface area of the particle
relative to the total beam area. These contributions can be summed over the total time the
particle spends in the interaction zone to find the total energy absorbed by the particle. From
this total energy and the thermal properties of a given powder (n), the laser power, \( P \), needed
to reach the melting temperature of the powders can be calculated.

\[
P_{m,n} = \frac{m_n C_n (T_{m,n} - T_{i,n})}{\gamma_n}
\]

where \( m \) denotes the particle mass, \( C \) is the thermal heat capacity of the powder, \( T_m \) and \( T_i \) are
the particle melting temperatures and start temperatures, respectively. \( \gamma \) is a constant described
in Appendix 3.2.

As the heated powder particles reach the substrate, some of them will leave the
system. Others will stay on the surface and will deposit their accumulated energy to the
substrate. These contributions can be added to the energy absorbed directly from the laser
beam to find the total energy used in heating the substrate. From the thermodynamic
properties of the substrate material, we can then calculate the power needed to reach the
substrate melting temperature.

\[
P_{m,s} = \frac{(T_m - T_i) K \pi^{1/2}}{2 \beta \kappa t_{in}^{1/2}}
\]

where subscript, \( s \), denotes the substrate, \( K \) is the substrate thermal conductivity, \( \kappa \) is the
substrate thermal diffusivity, \( t_{in} \) is the laser beam/substrate interaction time and \( \beta \) is a constant
described in Appendix 3.2.

The maps can be plotted for any given cladding combination to gain insight into the
cladding procedure before deposition is necessary. If these results are plotted for the
composition Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{6}$Sn$_{2}$Si$_{1}$, and we assume power, $P = 1800$W, powder feeding rate, $F = 3$ g/min, defocus, $D = 15$ mm, scan speed, $S = 500$ mm/min as in Figure 3.15, it is clear to see that the processing window, denoted as the striped area triangle, is small. Following this model, a laser track of the composition Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{6}$Sn$_{2}$Si$_{1}$ was again chosen for investigation and was clad at the prescribed parameters [37]. In a separate step, the layer was remelted at the speed found to be sufficient for amorphisation in section 3.3.2.1. In this instance the resultant layer is shown in Figures 3.15 A and B. The layer forms featureless regions, indicating that rapid cooling is achieved; the cooling rate is too low, however, to form a fully amorphous layer at the prescribed treatment conditions. This is due to the reduced thermal conductivity of Ti. The flipside of this is that a thicker layer may be attained, and the mechanical properties between the layer and the substrate may be more evenly graded. Upon remelting, however, the faster cooling also leads to higher stresses being developed within the layer, and these are often released by cracking, which may propagate to the as-clad region (Figure 3.15A). Figure 3.15B shows that the bonding is good, while the composition was confirmed by EDS, to be that of Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{6}$Sn$_{2}$Si$_{1}$, at the track centre, in accordance with that expected. It should be noted that the entire Ti-portion of the layer was derived from the substrate by dilution.

![Figure 3.14: Graph showing the power required to melt several component powders (see key) in the laser cladding of a Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{6}$Sn$_{2}$Si$_{1}$ coating deposited on a Ti-substrate (thick line, TiSubs) at 500 mm/min. The striped area highlights the narrow processing window in which all constituent parts of the coating are molten, assuming no evaporation occurs.](image)
Figure 3.15 (A) SEM micrograph revealing the zones of a clad and remelted metallic glass forming layer on a Ti-alloy substrate in cross-section, with (B) revealing more detail from the interfacial area.

TEM observations from the remelted area (an example is shown in Figure 3.16) show that some areas are amorphous in nature. There is a greater proportion of crystalline content than amorphous with the crystals being of the order of 5 – 200 nm (signifying nucleated grains during the laser processing). However, the formation of an amorphous matrix layer has been proven viable even though this procedure involves the deposition of a 5-element powder mix.

Figure 3.16: (A) A 200 nm Ti-rich crystal from a laser clad and remelted layer, retained within an amorphous matrix (confirmed by the diffraction insert taken at the white ring) (B) shows a HRTEM image of a 5 nm size Ti-rich crystal bound in an amorphous matrix

3.3.2.3 NanoSteel Glass Forming Alloys

With the development of glass forming alloys, comes the desire to process them for commercial applications. As is seen in section 3.3.2.2, it is possible to produce thick amorphous matrix/nanocrystalline layers on Ti-substrates even from multi-element powder
mixes; however this is not so convenient for industrial applications. The NanoSteel company is an American organisation who have worked on harnessing the properties of nanocrystalline materials through the development of iron-based glass forming alloys in the form of gas atomised powders with the goal of depositing thermal spray coatings [38]. These powders are, however, also interesting in the scheme of this research since they pose the possibility of being able to form thick, nano-crystalline layers on iron/steel substrates. Of course, the possibility for producing fully amorphous layers with these powders is diminished due to dilution from a substrate, which shifts the composition from a fully glass forming one to a “diluted” variant.

Initial production was somewhat limited since, although the shape and size of the powders is ‘optimal’ for laser processing (spheroids of Ø ~ 50-100 µm) (Figure 3.17A), initial cladding experiments revealed high porosity, which was found to be induced from the powder itself. In order to exhibit this clearly, the powder was set in Bakelite and polished to reveal an assortment of the powders at various cross sections (Figure 3.17B). This does not complicate the thermal spray process too much, for which the powders were originally developed, since, firstly, a degree of porosity is expected in spray processing and secondly, splat formation opens the powder particles and allows the gas to escape. One of the advantages in laser-clad coatings is that they may form with dense, pore-free microstructures and therefore potentially offer greater benefits for tribological or corrosive-environment applications.

Figure 3.17: NanoSteel SHS7574 powder for laser cladding (A) SEM overview of a random sample of the powder and (B) cross-sections of the particles (light areas) which were mounted in Bakelite and polished to reveal significant inherent porosity (dark areas within the white areas (powder)).
In order to combat this problem, a number of variations on the processing were investigated including varying the carrier gas and substrate and/or powder pre-heating, but it was found that an extremely high percentage dilution provides the best solution (for example Figure 3.18A, B, C). This is explained due to the fact that the glass forming alloy compositions are close to eutectic, which implies a (relative) low melting point. The interaction time between the powder and the laser beam is not sufficient to fully melt the impinging particles, and therefore many of the particles only experience melting of the outer shell. If the particles are however deposited into a molten pool which is at a higher temperature than the melting temperature of the particles themselves, an opportunity is present for the particles to become fully liquid and the gasses in the particles may escape from, not only the particles themselves, but also the solidifying melt pool. In the results upcoming, the substrate is A36 steel (a US standard structural mild steel, melting point = 1643 K) and NanoSteel SHS7574 powder (melting point = 1388 K) with a given composition in atomic percent of Fe\textsubscript{balance}Cr\textsubscript{<25}Mo\textsubscript{<15}W\textsubscript{<10}C\textsubscript{<5}Mn\textsubscript{<5}Si\textsubscript{<2}B\textsubscript{<5}. In order to analyse the microstructural evolution of these coatings, here we address the deposition of single track coatings. A plethora of coatings are attainable by simply varying a few cladding parameters.

<table>
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<tr>
<th>Coating Name</th>
<th>Power (W)</th>
<th>Scan Speed (m/s)</th>
<th>Powder Feeding Rate (g/s)</th>
<th>Defocus (mm)</th>
<th>Carrier Gas (Ar) (l/min)</th>
<th>Shielding Gas (Ar) (l/min)</th>
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</thead>
<tbody>
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<td>STA</td>
<td>600</td>
<td>0.01</td>
<td>0.0667</td>
<td>+6</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>STD</td>
<td>1000</td>
<td>0.015</td>
<td>0.1</td>
<td>+6</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>MTA</td>
<td>1000</td>
<td>0.02</td>
<td>0.1</td>
<td>+6</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>MTD</td>
<td>800</td>
<td>0.02</td>
<td>0.1</td>
<td>+6</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>MTE</td>
<td>800</td>
<td>0.02</td>
<td>0.1</td>
<td>+6</td>
<td>3</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 3.19: (A) BSE micrograph of the microstructure of coating ‘STA’ and (B) SE micrograph of the microstructure of coating ‘STD’. (C) and (D) are BSE micrographs revealing excellent interfacial bonding for coatings STA and STD respectively.

Figure 3.20: TEM analysis of Nanosteel single track coatings. In (A) and (C), coating STD is shown to reveal a ~ 100 nm interdendritic phase surrounding a multiphase dendritic phase. In (B), coating STA is shown to reveal a smaller dendritic phase and a similar sized interdendritic phase where (D1, D2) are EDS spectra analyses for the dendritic and interdendritic regions, respectively shown in (B).
Figure 3.21: OIM analysis of coating STD revealing SEM, Image Quality (IQ), austenite, martensite and ferrite as well as the orientation analysis of coating with an accompanying inverse pole figure key (IPF). The ferrite and martensite are seen to be present in the dendritic phase, while the austenite is present only in the interdendritic phase, which is complimentary to the TEM observations in Fig. 3.20.

In Chapter 6 we focus on two single laser tracks with differing microstructures for analysis of scratch hardness (STA and STD). We present those coatings here, with the
processing parameters for the layers shown in Table 3.1 and overviews of the coatings shown in Figures 3.18 B and C respectively. If we view the coatings by SEM, we see that despite the higher scanning speed for coating STD (Figure 3.19B), the dendrite size is larger than for STA (Figure 3.19A), due to the higher laser power which induces a higher dilution. This high dilution is easily recognised in the images of Figures 3.18 B and C. One of the most attractive aspects of laser cladding over other coating deposition techniques is the excellent coating adhesion resulting from metallurgical bonding. This is seen macroscopically in Figures 3.18A, B, C, but also microscopically in Figure 3.19C, D. While the STA coatings exhibit excellent interfacial bonding which can be seen in Figure 3.19C between a well-defined 50 µm band of large dendrites comparative to the ‘bulk’ coating and the substrate. The high dilution in coating STD, Figure 3.19D, is evident through the low contrast in BSE mode. Nonetheless, the interfacial bonding is again excellent and in the design of functionally graded coatings, this is an important observation.

Using X-ray diffraction, orientation imaging microscopy, energy dispersive spectroscopy mapping and/or transmission electron microscopy, we are able to discern the phases and/or elements present in the coatings. XRD is a powerful tool; however, in the analysis of (~1 mm wide) single tracks, the results there-from may contain information from the substrate area surrounding the laser track, and therefore this technique will only be presented for the overlapping tracks shown later in this chapter.

The microstructure appears to be made up of a dendritic phase and an interdendritic phase in both coatings. Rather strikingly, while Figures 3.18B and C reveal that a few macro-pores exist for STA, no macro-pores exist for STD. Both coatings, however exhibit nano-pores, which are only present in the interdendritic phase due to shrinkage during solidification. The reason for the reduced amount of nano-pores in the STD coating, compared to the STA coating, is explained because of the higher dilution in the STD coating.

The microstructures actually appear rather simple, but closer inspection reveals that this is not the case. TEM shows us that indeed the interdendritic phase is ‘small’ – less than one or two hundred nanometres in thickness in both cases (Figures 3.20A, B and C). From the same figures, it is also clear that the dendrites themselves are multiphase. Phase identification by OIM analysis of the microstructure characteristic of higher dilution (coating STD) reveals that the interdendritic phase is made up of austenitic iron, while in the dendritic phase, no austenite is present, but instead a mixture of ferritic iron and untempered martensite iron exists. This martensitic content supports the observation of the ~ 100 nm plate-like volumes seen in TEM analysis of the same dendrites [39].

While many single track layers have been produced, in an industrial application, the contact area of an engineered part can be much larger than the width of a single laser track would permit. It is also possible to deposit overlapping tracks and multi-layer coatings. With a
focus on the results upcoming in Chapter 4, a few of the coatings are exhibited here – MTA, MTD and MTE in Table 3.1 and Figure 3.22.

Figure 3.22: Optical micrographs revealing cross-sectional overviews of coatings MTA, MTD and MTE, with reference to Table 3.1. The first clad track is on the left of each image.

Figure 3.23A shows an area along the longitudinal direction (relative to the cladding direction) within coating MTA, which has two differing microstructures adjacent to one another due to cooling rate differences from the melt. XRD analysis (Figure 3.24B) allows us to gain an insight into the phases which may be present; however, the resolution in standard “lab” XRD is not sufficient to pinpoint such a small region. If this area is viewed using OIM and EDS, however, we can address both the chemical compositions and the phases present in the coatings and confront the microstructural evolution.

Figure 3.23: (A) BSE image of coating MTA taken in the longitudinal direction (parallel to the cladding direction) revealing two adjacent microstructures. Area 2 exemplifies good powder/substrate mixing, while area 1 exemplifies poor powder/substrate mixing. (B) is a $2\theta$ XRD scan from MTA coating and the original powder.
EDS analysis (Figure 3.24) shows that the principal alloying elements of the NanoSteel powder under investigation form the interdendritic phase, while the dendrites have a higher iron content. Since the (nominal) composition of A36 steel is 0.29C max, 0.80–1.2Mn, 0.04P, 0.05S, 0.15–0.3Si bal Fe, it is insufficient to say whether the Mn and Si really show a greater affinity for Fe, or whether their ‘stronger’ appearance in the dendrites of these elements is due to the substrate dilution. Certainly, when viewed in conjunction with the TEM/EDS results in Figure 3.20, it would appear that the latter is the case, and thus area one can be considered as an area where the mixing of the NanoSteel powder and the Fe does not take place.

![Figure 3.24: BSE images of Figure 3.23A overlain with EDS maps for the elements Si (green), Cr (yellow), Fe (light blue), Mn (magenta) and Mo (royal blue). The principle alloying elements of the administered powder mainly lay in the interdendritic phase, while the dendritic phase is made up of the substrate elements.](image)

With reference to the fact that the dendrites appear to be multi-phase in both STA, MTA and MTD, OIM analysis was performed on MTA in order to assess this. The additional OIM analysis shows that in area 1 (Figure 3.25), the dendrites do not form martensite, which is indicative of a reduced cooling rate in this fraction of the coating, compared to the “macroscopic” microstructural evolution in the coatings which consists of uniform ferrite/martensite dendrites and an interdendritic austenitic phase, made-up of the principle alloying elements of the NanoSteel powder. The texture of the interdendritic phase is quite remarkable, with the austenitic phase appearing here in longitudinal cross-section close to (101) (Figure 3.25, right).
Figure 3.25: OIM micrographs for 2 adjacent areas: left micrographs are image quality maps; centre images are phase maps featuring [TOP] alpha (red) and gamma (green) iron and [BOTTOM] alpha (red) and gamma (green) iron as well as martensite (yellow). The right images relay textural information according to the key insert. It is seen that the interdendritic phase is textured in the (101).

When the microstructure is refined, by double layer coatings, the distribution of the elements of the NanoSteel powder form a homogeneous, almost needle-like microstructure, which will be shown together with the specific microstructures for MTA and MTD in Chapter 5 and the effects of these various microstructures on mechanical properties and performance are also investigated in Chapters 5 and 6.
3.4 Conclusions

Metallic glasses have been successfully synthesised by a range of processing routes with the production of amorphous layers by high power lasers being proven viable. The thickness of the layers provides excellent opportunities to fabricate layers on material such as titanium which may be functionally graded, since laser cladding readily facilitates well-adhered layers up to 1 mm in thickness, and the cooling conditions may be tailored simply by processing speed variations. This layer may then be remelted as shown to provide 300 µm layers bonded to the ‘precursor layer’ by an amorphous matrix interlayer. This reduces the ‘egg-shell’ effect often found when depositing high hardness layers directly onto soft substrates, and opens possibilities for commercial applications.

Laser cladding of pore-free layers from porous glass forming alloy powder precursors has been achieved, with the parameter offering the largest influence being high dilution (> 65%). The resultant layers are therefore reduced in glass forming ability, but nonetheless, thick (up to 1 mm) uniform coatings with excellent interfacial bonding may be produced.

These coating evolve with an interdendritic phase of austenitic steel and a dendritic phase of ferrite and martensite. Higher dilution leads to higher ferrite/martensite content since the austenitic phase relates to the NanoSteel powder. In both cases the interdendritic phase ‘thickness’ is found to be 100-200 nm.
References

Chapter 3

[22] A. Einstein, Physikalische Zeitschrift, 18 p.121 (1917)
[38] http://www.nanosteelco.com/
APPENDIX 3.1

The Zernike-Prins one-dimensional model of X-ray scattering from arbitrarily ordered “molecules”

[Die Beugung von Röntgenstrahlen in Flüssigkeiten als Effekt der Molekülanordnung
F. Zernike und J.A. Prins
Zeitschrift für Physik , 41 (1927)184-194]

The distribution function g(x)

N “molecules” each of length $a$ are distributed over a distance $L$ in an arbitrary way. Each “molecule” is identified by its midpoint. Take $x$ as being a certain distance away from one such a midpoint. The question then is what is the probability that between $x$ and $x + dx$ another midpoint can be found. This probability is written as $g(x) \, dx$. Only positive $x$ are taken into account as $g(-x) = g(x)$. Furthermore, $g(x) = 0$ for $x < a$. For $a < x < 2a$ no other “molecule” lies on $x$ in case both end positions are occupied. In general, for $ka < x < (k+1) \, a$ the number of “molecules” on length $x$ can only be $k-1$ at the most. We now introduce the expression $g_k(x) \, dx$ for the probability of “molecule” $k$ lying in between $x$ and $x + dx$ from another “molecule”, consequently,

$$g(x) = \sum g_k(x) \quad \text{(A3.1.1)}$$

with a finite $k$ for each value of $x$.

We may change here to the distribution of the unoccupied pieces of length between the “molecules”, or how we can distribute in a completely arbitrary way $N$ “molecules” over a length of $(L-Na)$. This problem is similar to the calculation of the free path between collisions in the Gas theory and leads to the expression for the distribution of a length $x'$

$$\frac{1}{l} e^{-x'/l} \quad \text{(A3.1.2)}$$

when $L$ and $N$ go to infinity in such a way that $(L-Na)/N = \text{const} = l$. The probability that the sum of $k$ length units lie between $x'$ and $x' + dx'$ is

$$dx' \cdot \frac{x'^{k-1}}{l^k (k-1)!} e^{x'/l} \quad \text{(A3.1.3)}$$

To get back the original distribution we have to replace each point by a “molecular” length $a$ and find for $g_k$ with $x = x' + ka$

$$g_k(x) = \frac{(x - ka)^{k-1}}{l^k (k-1)!} e^{x - ka} \quad \text{for } x > ka \quad \text{(A3.1.4)}$$

$$g_k(x) = 0 \quad \text{for } x < ka$$
Finally, equation (A3.1.1) can be written as

$$g(x) = \frac{1}{l} \left[ e^{\frac{(x-a)}{l}} + \frac{(x-2a)}{l} e^{\frac{(x-2a)}{l}} + \frac{(x-3a)^2}{l^2} e^{\frac{(x-3a)}{l}} + \ldots \right]$$ (A3.1.5)

with the series expansion extended as long as the exponents stay negative. \(l\) is the mean distance between “molecules” and \(l+a\) the mean distance between the midpoints of neighboring “molecules”.

In Figure A3.1 we have plotted formula (A3.1.5) for the values of \(l\) being 0.5, 0.25, 0.1, respectively, while \(l+a=1\).

When we take \(x\) so large that the influence of the starter molecule can be neglected then \(g(x)\) will be constant and equal to \(1/(l+a)\), because on the mean \(1/(l+a)\) “molecules” lie on the unit of length. For larger values of \(l\), that means when the “molecules” have a lot of space in between them, the approach to this constant value goes much more rapidly than for smaller values of \(l\) when the “molecules” have a big influence onto each other due to the limited space between them.

![Graphs showing linear distribution function g(x) vs length x, according to expression (5), the packing parameter l being 0.5, 0.25 and 0.1, respectively.](image)

*Figure A3.1 a: Linear distribution function \(g(x)\) vs length \(x\), according to expression (5), the packing parameter \(l\) being 0.5, 0.25 and 0.1, respectively.*
The intensity function $I(\phi)$

We consider the 1D-distribution of “molecules” as a grating which scatters a beam of X-rays, say $\cos(2\pi vt)$, hitting the grating perpendicularly. The scattering amplitude of a “molecule” under an angle $\phi$ can be written as $A(\phi)$ and for all “molecules” as the sum

$$\sum A \cos 2\pi \left( vt - \frac{d_k}{\lambda} \right)$$

with $d_k$ the specific distance from “molecule” $k$ to the scattered wavefront.

The intensity can be determined by the amplitude squared averaged over one period.

$$I(\phi) = \frac{A^2}{2} \left( \sum \cos 2\pi \frac{d_k}{\lambda} \right)^2 + \frac{A^2}{2} \left( \sum \sin 2\pi \frac{d_k}{\lambda} \right)^2$$

(A3.1.6)

$$= \frac{A^2}{2} \sum_k \sum_l \cos 2\pi (d_k - d_l)$$

In order to determine the mean of this double sum over all configurations we first determine the mean for one $k$ value

$$\sum_l \cos \frac{2\pi}{\lambda} (d_l - d_k) = 1 + 2 \sum_{l > k} \cos \frac{2\pi}{\lambda} (d_l - d_k)$$

(A3.1.7)

When $x$ is the distance between “molecule” $l$ and “molecule” $k$, then for $l-k = m$

$$d_l - d_k = x_m \sin \phi$$

and

$$\cos \frac{2\pi}{\lambda} (d_l - d_k) = \cos \frac{2\pi x_m \sin \phi}{\lambda} = \int_0^\infty dx g_m(x) \cos \frac{2\pi x \sin \phi}{\lambda}$$

With expression (A3.1.4) we may write

$$\int_0^\infty dx g_m(x) \cos \frac{2\pi x \sin \phi}{\lambda} = \int_{ma}^{\infty} dx \frac{(x-ma)^{m-1}}{l^m (m-1)!} e^{\frac{x-ma}{l}} \cos \frac{2\pi x \sin \phi}{\lambda}$$

$$= \Re \left\{ e^{i\alpha y + \gamma} \right\}$$

where $\alpha = a/l$, $y = 2\pi l \sin \phi / \lambda$ and $\Re$ means that the real part of the expression should be taken.

Expression (A3.1.7) can now be rewritten
\[ 1 + 2 \sum_{m=1}^{\infty} \Re \left( \frac{e^{mi}}{(1-iy)^m} \right) = \Re \left( \frac{1 - yi + e^{\alpha iy}}{1 - yi - e^{\alpha iy}} \right) \]

Since \( k \) is not part of the expression, a factor \( N \) is added as result of the summation. Finally, expression (A3.1.7) is in real terms only

\[ I(\phi) = \frac{1}{2} \frac{N A^2}{N^2} \frac{1}{\cos \alpha y + y \sin \alpha y + \frac{1}{2} y^2} \]  \hspace{1cm} (A3.1.8)

In Fig. A3.2 we have plotted \( I(\phi) \) as function of \((l+a)\sin\phi/\lambda\), with \( \frac{1}{2} N A^2 \) and \( l+a \) taken unity while for \( l \) the same values as in Fig. A3.1 were taken 0.5, 0.25, 0.1, respectively. From the curves it is clear that for smaller \( l \) or increase in correlation the maxima become sharper and shift to lower values. For large scattering angles the intensity equals the constant value of \( \frac{1}{2} N A^2 \), which is the value one should expect when all “molecules” are independent. For small scattering angles the intensity approaches the value \( \frac{1}{2} N A^2 l^2/(l+a)^2 \) which value becomes smaller the smaller the value for \( l \) is, which means a denser packing.

\textbf{Figure A3.1 b: Intensity} \( I(\phi) \) \textit{vs} scattering angle \( \sin\phi/\lambda \) according to expression (8), the packing parameter \( l \) being 0.5, 0.25 and 0.1, respectively.
APPENDIX 3.2:  
Modelling the laser power required to melt component parts of a clad layer

To elaborate a little more on the model results discussed in section 3.3.2.2, we require knowledge of the laser-powder interaction area. Two constants in particular are important. The first is the height above the substrate where the powder first interacts with the laser beam, $P_d$. The second one is the radius of the laser beam at this point, $R_n$. From the point of first interaction, we assume the particles to be dispersed homogeneously through the entire interaction area. The values for $P_d$ and $R_n$ can be calculated from the nozzle geometry, laser defocus and powder focus. For our experiments, using an Nd:YAG laser, the following values hold: laser defocus, $L_d = 1 \text{ mm}$. The distance between the nozzle and the substrate, also the point of powder focus, $N_d = 12 \text{ mm}$. The nozzle diameter is 9.5 mm, which sets the angle between the powder flow and the nozzle, $\theta$ at 70°. The half-angle of the defocused laser beam, $\varphi = 6.85°$. From these, we can calculate the required constants through the following equations.

\[
\begin{align*}
c &= L_d \cdot \tan \varphi \\
\beta &= \frac{\pi}{2} - \varphi \\
\gamma &= \pi - \theta - \beta \\
b &= c \frac{\sin \beta}{\sin \gamma} \\
P_d &= b \cdot \sin \theta \\
R_n &= (L_d - P_d) \cdot \tan \varphi
\end{align*}
\]

As was described above, part of the laser beam strikes powder particles instead of the substrate. As a result, the power of the laser beam decreases closer to the substrate. We use the Lambert-Beer law to describe this attenuation.

\[
\frac{dP}{P} = -\varepsilon \cdot c(z) \cdot dz
\]

$\varepsilon$ is an optical factor and $c$ is the particle concentration. The variable $z$ is the perpendicular distance that the particles travel through the interaction zone. For spherical particles that are large compared to the wavelength of the laser light ($2\pi r / \lambda > 100$), we can use geometrical optical laws [1] to describe the light absorption. In that case, we can write
\[ \varepsilon = \frac{2(1 - A_p)}{2 \rho p r_p} \]  \hspace{1cm} (A3.2.8)

where \( A_p \) is the absorption coefficient of the powder particles, \( \rho_p \) the density and \( r_p \) is their radius. The powder concentration varies with \( z \) due to the diverging nature of the laser beam.

\[ c(z) = \frac{F}{v_p \pi (r_n + \tan \phi z)^2} \]  \hspace{1cm} (A3.2.9)

where \( F \) is the powder feeding rate and \( v_p \) is the speed of the particles. To find the power of the attenuated beam after a certain length of interaction with the powder, we integrate equation A3.2.7. The integration runs from \( z = 0 \) (the top of the zone of interaction) to \( z \), which has a maximum value of \( P_d \) at the substrate surface.

\[ \frac{P_i(z)}{P_0} = \exp \left[ \frac{-z \sum \varepsilon_n F_n}{v_p \pi (r_n^2 + r_n \tan \phi z)} \right] \]  \hspace{1cm} (A3.2.10)

where the subscript \( n \) denotes the different powders. Each powder can have its own material properties and feeding rate, but the equation assumes that all powder particles have the same speed.

**Particle Heating**

We can now calculate the total energy stored in each powder particles during its flight through the interaction zone. Equation A3.2.10 gives the total laser power present at a specific height. The amount of energy that will be received be a particle is scaled by the ratio between its surface area and the total area of the laser beam. Furthermore, it is also scaled by the absorption coefficient \( A_n \), because part of the laser light will be reflected off of the particle, leaving the system. The amount of energy absorbed by a particle of material \( n \) during a short section \( dz \) of its flight path \( dz \) is given by

\[ dQ_n = \frac{S_n}{S_i(z)} P_i(z) dt \]  \hspace{1cm} (A3.2.11)

where \( S_n \) is the surface area of the particle and \( S_i \) the area of the laser beam at height \( z \). We substitute equation A3.2.10 into this and use laser geometry to give an expression for \( S_i \). We also substitute \( dt = dz / v_p \), which is allowed for constant particle speed. This yields

\[ \frac{dQ_n}{P_0} = \frac{A_n \pi r_n^2}{v_p \pi (r_n + z \tan \phi)^2} \cdot \exp \left[ \frac{-z \sum \varepsilon_n F_n}{v_p \pi (r_n^2 + r_n \tan \phi z)} \right] dz \]  \hspace{1cm} (A3.2.12)

Integrating this for the entire interaction zone, we find the total energy stored in a particle as a function of the initial laser power.
\[
\frac{Q_n}{P_0} = \int_0^{P_d} \frac{A_n \pi r_n^2}{v_p \pi (r_n + z \tan \phi)^2} \exp \left[ \frac{-z \sum \epsilon_n F_n}{v_p \pi (r_n^2 + r_n \tan \phi z)} \right] dz \tag{A3.2.13}
\]

The integral is solved numerically. For the energy needed to heat the particle to the melting temperature, we know
\[
Q_{\text{melt},n} = m_n C_n (T_{n,m} - T_{n,i}) \tag{A3.2.14}
\]
where \( m \) the mass of the particle, \( C \) the specific heat of the powder, \( T_m \) the melting temperature and \( T_i \) the initial temperature. If we rewrite equation A3.2.13 as \( Q_n = \gamma_n P_0 \) and ignore latent heat of melting, then we find for the laser power to melt the powder
\[
P_{m,n} = \frac{m_n C_n (T_{m,n} - T_{i,n})}{\gamma_n} \tag{A3.2.15}
\]

Substrate Heating

As stated earlier, the substrate is heated through two distinct mechanisms. Part of the laser light is transmitted through the powder cloud and hits the substrate directly. Part of the light is first transmitted to the powder particles, which release their energy to the substrate when they reach it. The total amount of energy that reaches unit area of surface in a unit period of time is
\[
Q = \frac{Q_l + Q_p}{S_{\text{int}} t_{\text{int}}} \tag{A3.2.16}
\]

Here, \( S_{\text{int}} \) is the surface of interaction between the laser and the substrate. The interaction time, \( t_{\text{int}} \), defines how long any particular point of the substrate is under influence of the laser beam. \( Q_l \) is the energy provided by direct irradiation, while \( Q_p \) is the total effect of heating via the powders.
\[
S_{\text{int}} = \pi c^2 \tag{A3.2.17}
\]
\[
T_{\text{int}} = \frac{2c}{S} \tag{A3.2.18}
\]

\( S \) is the scanning speed of the substrate, \( c \) is the radius of the laser spot on the substrate. For the strength of the laser beam at the substrate, we have equation A3.2.10 with \( P_d \) substituted for \( z \).
\[
\frac{P_l}{P_0} = \exp \left[ \frac{-P_d \sum \epsilon_n F_n}{v_p \pi (r_n^2 + r_n \tan \phi P_d)} \right] \tag{A3.2.19}
\]
This laser power is partially reflected away from the surface. \( A_s \), the absorption coefficient of the substrate, gives the fraction of the laser light that is absorbed and transferred to heat. Concentrating our calculations on the center of the laser track, we find that every point on the substrate is located under the laser beam for the same time, called \( t_{\text{int}} \). For the total amount of energy that is delivered directly to a part of the substrate, we write

\[
Q_l = A_s \cdot P_t \cdot t_{\text{int}} \quad \text{(A3.2.20)}
\]

In order to calculate \( Q_p \), we use equation A3.2.13 as a basis. \( Q_n \), which gives the energy stored in one particle. This is multiplied by the amount of particles that reach the surface. For the amount of particles from one powder that reach the surface during the interaction, we can write

\[
N_n = \frac{F_n}{\frac{4}{3} \pi r_n^3 \rho_n} \quad \text{(A3.2.21)}
\]

Of these particles, not all will stick to the surface to transmit their energy to the substrate. The part of the powder that actually enters into the clad is given by the powder efficiency, \( P_e \). We add the contributions from all powders together to find the total amount of energy transferred to the substrate by the powders.

\[
Q_p = \sum_n P_{e,n} \cdot N_n \cdot Q_n \quad \text{(A3.2.22)}
\]

From equations A3.2.19, A3.2.20 and A3.2.13, A3.2.22 we find that both \( Q_l \) and \( Q_n \) are linearly dependent on \( P_0 \). Knowing this, we can rewrite equation A3.2.16 as

\[
Q = \frac{Q_l + Q_p}{S_{\text{int}} t_{\text{int}}} = \beta P_0 \quad \text{(A3.2.23)}
\]

where

\[
\beta = \frac{A_s}{S_{\text{int}}} \cdot \exp \left[ -\frac{P_d}{v_p \cdot \pi r_n^2} \cdot \frac{\sum \varepsilon_n F_n}{r_n \tan \phi \cdot P_d} \right] + \frac{1}{S_{\text{int}} \cdot t_{\text{int}}} \sum_n P_{e,n} \cdot N_n \cdot \frac{F_n}{v_p \cdot \pi (r_n + z \tan \phi)^2} \cdot \exp \left[ -\frac{z}{v_p \cdot \pi (r_n^2 + r_n \tan \phi \cdot z)} \right] \cdot dz \quad \text{(A3.2.24)}
\]

We consider the effects of the heat on the substrate by using the heat conduction equation. For the one-dimensional semi-infinite wall solution, we find from [Jouvard, Reference list Chapter 3, number 34], that

\[
T(x,t) - T(x,0) = \frac{2Q_0 (at)^{1/2}}{k} \text{erfc} \left( \frac{x}{2(\alpha t)^{1/2}} \right) \quad \text{(A3.2.25)}
\]
where $T$ is the temperature of the substrate, $\alpha$ is the thermal diffusivity and $k$ is the thermal conductivity. $x$ is the depth within the substrate. For the temperature at the surface, we substitute $x = 0$. The interaction between the beam and the substrate lasts $t_{\text{int}}$, which we substitute for $t$. We then find

$$T(t_{\text{int}}) = T_i + \frac{2Q(\alpha t_{\text{int}})^{1/2}}{k\pi^{1/2}}$$ \hspace{1cm} (A3.2.26)$$

with $T_i$ the initial temperature of the substrate. By combining equations 4.23 and 4.26 and requiring that $T(t_{\text{int}}) = T_m$, the melting temperature of the substrate material, we find $P_{\text{ms}}$, the laser power needed to heat the surface to the melting temperature.

$$P_{\text{ms}} = \frac{(T_m - T_i)k\pi^{1/2}}{2\beta(\alpha t_{\text{int}})^{1/2}}$$ \hspace{1cm} (A3.2.27)$$

Reference
