PAPER • **OPEN ACCESS**

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To cite this article: T Lindner *et al* 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **118** 012009

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IOP Conf. Series: Materials Science and Engineering **118** (2016) 012009 doi:10.1088/1757-899X/118/1/012009

Analytical methods to characterize heterogeneous raw material for thermal spray process: cored wire Inconel 625

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Abstract. In wire arc spraying, the raw material needs to exhibit sufficient formability and ductility in order to be processed. By using an electrically conductive, metallic sheath, it is also possible to handle non-conductive and/or brittle materials such as ceramics. In comparison to massive wire, a cored wire has a heterogeneous material distribution. Due to this fact and the complex thermodynamic processes during wire arc spraying, it is very difficult to predict the resulting chemical composition in the coating with sufficient accuracy. An Inconel 625 cored wire was used to investigate this issue. In a comparative study, the analytical results of the raw material were compared to arc sprayed coatings and droplets, which were remelted in an arc furnace under argon atmosphere. Energy-dispersive X-ray spectroscopy (EDX) and X-ray fluorescence (XRF) analysis were used to determine the chemical composition. The phase determination was performed by X-ray diffraction (XRD). The results were related to the manufacturer specifications and evaluated in respect to differences in the chemical composition. The comparison between the feedstock powder, the remelted droplets and the thermally sprayed coatings allows to evaluate the influence of the processing methods on the resulting chemical and phase composition.

Keywords: Inconel 625; Chemical analyzes; Arc spray; Coating; Cored wire

1. Introduction

In thermal spraying wire-shaped feedstock material is mainly used for arc spray techniques. It is available as massive material or as hollow sheath with pre-processed powder inside. This so-called cored wire material is a special wire type that is predominantly used for processing hard materials as core material in a ductile and electrically conductive sheath to form pseudo-alloys. Generally cored wire material is more expensive than massive wire. However, this applies only for big production quantities, since the production of smaller amounts of massive wire is often unprofitable. Thus for small quantities, cored wires are usually cheaper than massive wires or even the only wire form, which is commercially available. This can be attributed to the fact that most wire manufacturers have a wide selection of powders and thin metal sheets in stock, which allows the on-demand production of cored wires in the customer-requested quantity. Cored wires offer the opportunity to adjust almost any desired material mixture by filling the appropriate powder in the hollow sheath. This allows the production of coatings, that cannot be achieved by other coating processes. However, very often it is difficult to predict the final chemical composition in the coating based on the used sheath and filler material. The reason for that is the complexity of chemical reactions that take place during the processing of the wires. This includes reactions in the sheath and the powder material as well as reactions with each other and with the surrounding atmosphere. By the example of Inconel 625 - a widely used corrosion-resistant Ni-based material - it was intended to investigate the changes in the chemical composition by a comparison of the feedstock cored wire material, arc-sprayed coatings and droplets, which were remelted in an arc furnace under argon atmosphere.


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2. Experimental

2.1. Coating

As stated previously, this study focuses on the Ni-base material Inconel 625 (IN625). Therefore, a cored wire DURMAT® AS-755 provided by DURUM Verschleißschutz GmbH (Willich, Germany) was used. The wire has an outer diameter of 1.6 mm. The nominal composition in weight percentage as stated by the manufacturer is shown in Table 1.

Table 1. Chemical composition of IN625 cored wire as stated by the manufacturer

Element	Ni	Cr	Mo	Nb	Fe	C
wt.-%	balance	20–23	7–10	3–4	< 0.1	< 2

A wire arc spray system VisuArc 350 (Oerlikon Metco, Switzerland) was used to produce the coatings. The spray parameters were adjusted as recommended by the gun manufacturer (Table 2).

Table 2. Spray parameters for wire arc-sprayed Inconel 625

Substrate	S235
$\varnothing_{substrate}$ (mm)	25
Gas pressure (bar)	3.5
Voltage (V)	30
Current (A)	120
Spray distance (mm)	130
Spray velocity ($m \cdot s^{-1}$)	1
Shift z (mm)	5
No. of passages	7
Mean coating thickness	280

The used substrate was mild steel containing about 99 % of iron (S235). Prior to the coating process, the substrate surface was roughened by grit blasting.

2.2. Sample preparation and characterization techniques

In order to produce solid Inconel 625 droplets, the cored wire was molten in a self-constructed electric arc furnace. The furnace was flooded with argon when vacuum reaches (2×10^{-4} mbar). By using argon as inert gas, it was intended to avoid uncontrolled oxidation. After the ignition of the arc with a tungsten electrode, the cored wire was molten in a water-cooled copper crucible to droplets with a diameter of about 20 mm. The parameters are shown in Table 3.

Table 3. Arc furnace parameters

Mean quantity (g)	Droplet size (mm)	Vacuum (mbar)	Argon pressure (bar)	Gas purity (%)	Current (A)
15	20	2×10^{-4}	1.1	99.9999	250

The feedstock cored wire, the arc-sprayed coating as well as the droplet were firstly subjected to XRF analysis in a Fischerscope X-ray XAN device (year 2005) [1–3]. This device does not need any sample preparation and provides direct qualitative measurement in less than one minute. The number of imposed strokes was roughly 3000 $stk \cdot min^{-1}$. An acceleration voltage of 30 kV was applied and the current passing through the anode was 950 µA.

The samples were then analyzed by a scanning electron microscope (SEM) LEO 1455VP (Zeiss, Oberkochen, Germany) equipped with an EDAX Genesis EDX spectroscope. According to the device and the specimen-holder prerequisite, samples were subjected to a special specimen preparation. Metallographic cross-sections of the cored wire, the IN625 coating and the droplet were prepared according to standard metallographic procedures. The resulting samples were mounted into conductive resin, followed by grinding and polishing. Subsequently, the morphology, microstructure and chemical

composition were investigated by means of secondary and backscattered electron imaging in conjunction with EDX measurements [4].

Crystallographic study was performed on all the previous samples by XRD using a D8 DISCOVER device from Bruker Corporation (Billerica, USA). The used X-radiation was a monochromatic wavelength Cu-K_α. A voltage of 40 kV, a current of 40 mA, a scanning rate of 24° h^{-1} and diffraction angles of 20° to 130° were utilized. The used X-rays sensor was a LynxEye-XE detector, the aperture size after the beam gun was 1 mm and a polycap was utilized in order to obtain a better parallel beam emission. The evaluation of the data was done by using Rietveld refinement, requiring knowledge of the theoretical structure which has to be close to the real structure [5].

3. Results and discussion

3.1. Characterization of Inconel 625 cored wire

The analyses of the heterogeneous cored wire were performed on metallographic cross-sections (Fig. 1). Therefore, the wire was mounted in epoxy resin to avoid a trickling out of the powder.

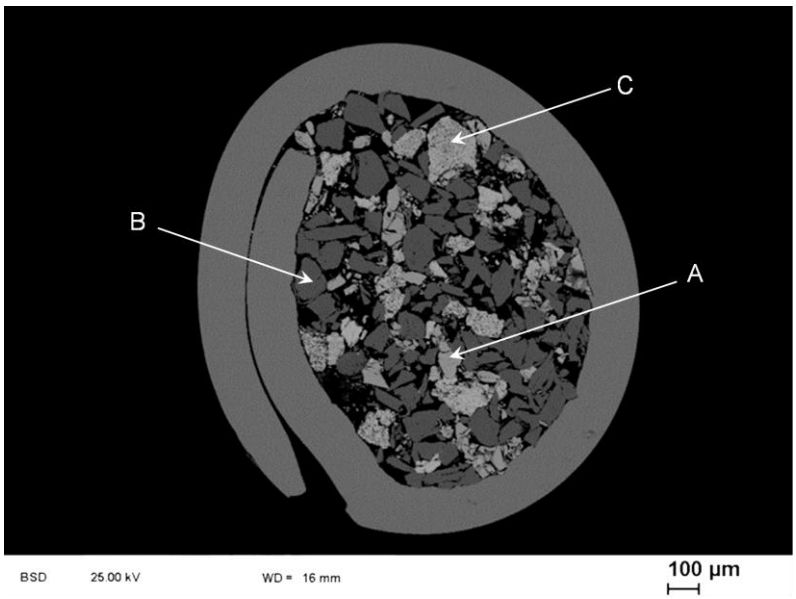


Figure 1. SEM image (BSE mode) of the cross-section of IN625 cored wire

In a first step, global XRF and EDX analyses were carried out. Therefore, the investigated area comprised of the whole cross-section of the cored wire. The back scattered electron image (Fig. 1) shows the atomic number contrast that illustrates clearly the heterogeneous character of the powder and the whole wire, respectively.

Unlike XRF, EDX enables the measurement of the local chemical composition. By this means, it was proven that the sheath consists of pure nickel. The results for the marked grains in Fig. 1 are shown in Table 4.

Table 4. Local concentration in IN625 cored wire as determined by EDX

	EDX (relative wt-%)			
	Sheath	Grain A	Grain B	Grain C
Ni	100	-	-	-
Cr	-	-	100	-
Mo	-	100	-	-
Nb	-	-	-	68.6
Fe	-	-	-	28.2
Si	-	-	-	3.2

The heterogeneity of the cored wire allows the detection of the different phases of the contained components because - in contrast to the remelted droplet and, to a certain extent, the arc-sprayed coating

(see the results below) - the elements are not solved in the nickel matrix. Consequently, the nickel phase of the sheath shows the highest intensity level. Also the characteristic peaks of pure molybdenum and pure chromium can be found in the XRD pattern (Fig. 2). The niobium-rich phase that was previously detected by EDX (Tab. 4) was not stored in the database. However, an undefined phase was found, which most probably can be attributed to the mentioned niobium-rich component.

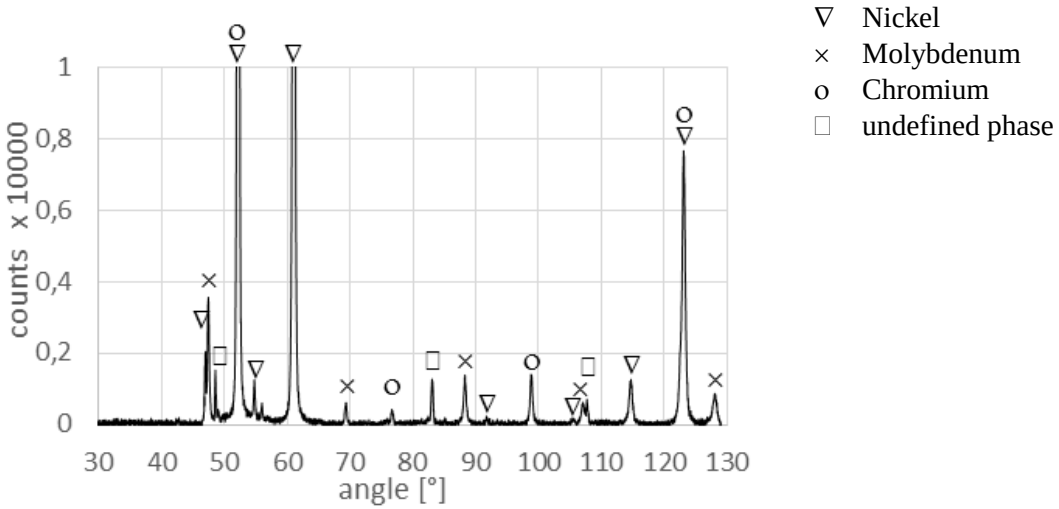
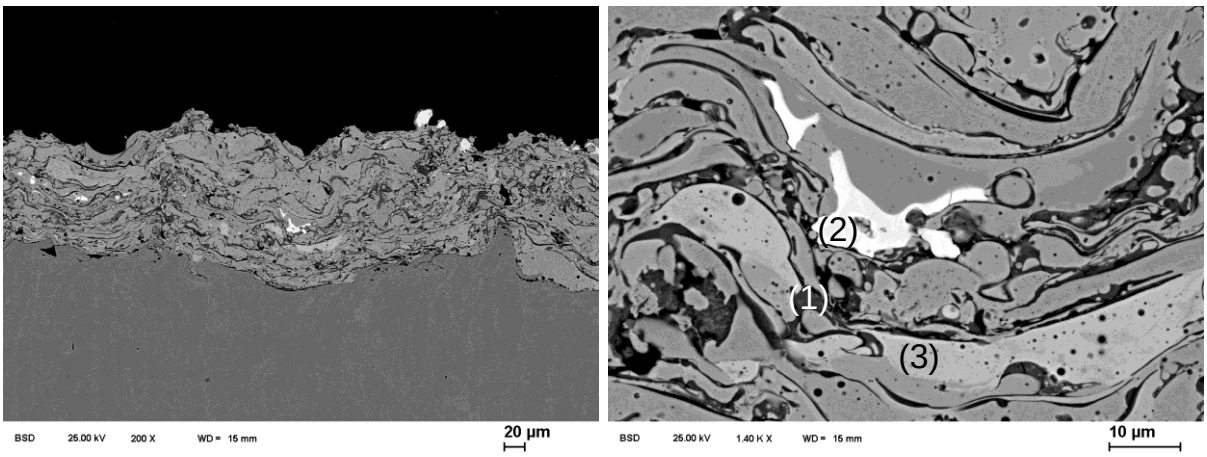


Figure 2. XRD of IN625 cored wire

3.2. Characterization of arc-sprayed Inconel 625 coating

The metallographic cross-section of the Inconel 625 coating shows the typical lamellar structure of arc-sprayed coatings (Fig. 3). The different brightness values in the back scattered electron SEM image indicate an incomplete blending of the different alloying components (Fig. 3). However, since no unmolten powder particles are found in the coating, it can be assumed that the feedstock material was fully molten during the arc spray process. As can be seen in Fig. 3b, an oxide layer may have formed on a few of the molten droplets, preventing them from being flattened upon impact.



a) Overview *b) Detail*

Figure 3. SEM image (BSE mode) of arc-sprayed IN625 coating

It is presumed that the time window, in which the material is in a liquid state, is too short to obtain homogeneous material alloying. This is also connected to the differing solubility time of the materials.

In comparison to the cored wire, the phase composition has changed due to the thermal spray process. The EDX measurements (Table 5) show that the main phase (3), which appears grey in Fig. 3, is nickel-rich. Since no precipitations were observed, it is assumed that all remaining alloy elements are solved in this phase. Furthermore, a chromium-rich phase (1, displayed dark grey in Fig. 3) was detected. Presumably, these are stable chromium oxides, which were formed in the oxidative process atmosphere. The white phase (2) is nearly pure molybdenum, which is known for its slow solubility. A pre-alloyed phase - comprising e.g. iron - could improve the solubility.

Table 5. Local concentration in IN625 coating as determined by EDX

	EDX (relative wt-%)		
	Dark grey phase (1)	White phase (2)	Grey phase (3)
Ni	16.1	9.4	49.9
Cr	50.1	-	14.4
Mo	8.7	90.6	28.6
Nb	20.4	-	4.6
Fe	3.6	-	2.3
Si	1.1	-	0.2

Even though the mainly pure elements from the feedstock cored wire were mixed for the most part due to the thermal spray process, the previously described (Table 1) composition of IN625 was not reached homogeneously across the whole coating. The coating microstructure contains different phases in a heterogeneous distribution. This has to be considered as disadvantageous in terms of corrosion resistance since a heterogeneous microstructure bears the danger of local corrosion damage.

The EDX results were confirmed by XRD measurements by which several phases were detected (Fig. 4). The assumed process-induced oxidation of chromium was proven by the presence of a chromium oxide peak in the XRD pattern.

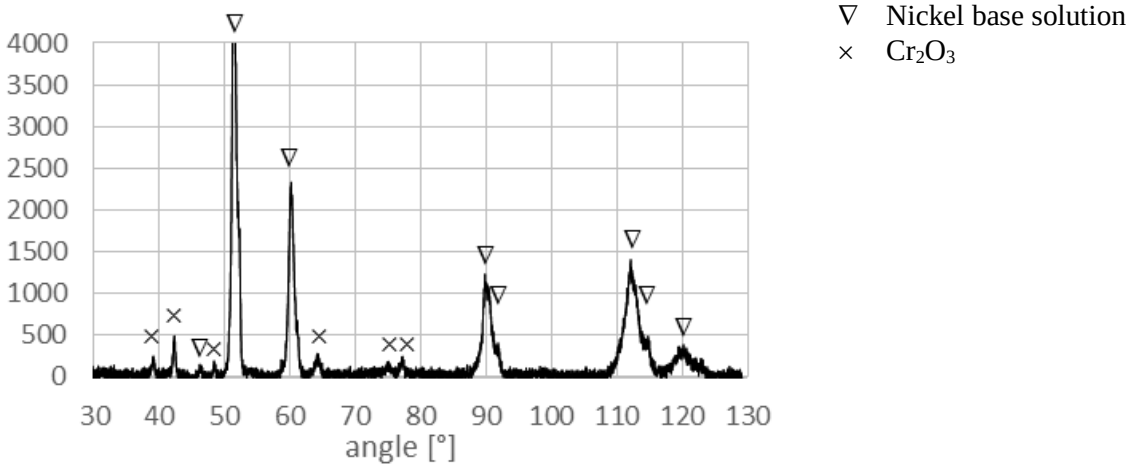


Figure 4. XRD of IN625 coating

3.3. Characterization of Inconel 625 droplet

In order to reach a homogeneous element distribution, the cored wire was remelted to droplets in an electric arc furnace. In contrast to the heterogeneous cored wire, the droplets microstructure exhibit a more homogeneous element distribution, by alloying in process.

A cross-section of the droplet was prepared in order to analyze the microstructure. As can be seen in Fig. 5, a homogeneous microstructure was not achieved completely, even though the droplet was held in molten state for several seconds.

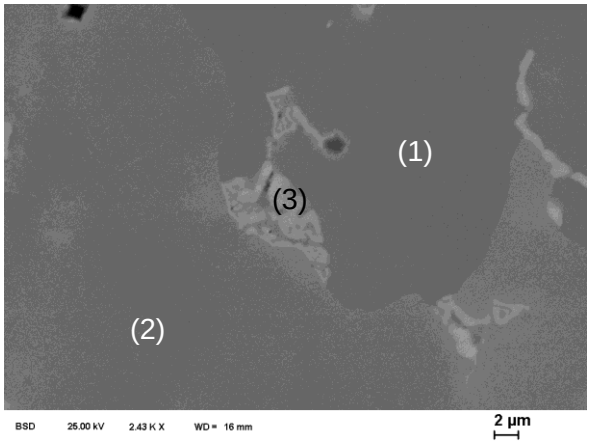


Figure 5. SEM image (BSE mode) of IN625 droplet

Due to the very coarse-grained microstructure (Fig. 5), a quantitative evaluation by means of XRD was not possible. The investigated area covered too few grains, leading to insufficient statistical data. Therefore, no XRD measurements are presented for the droplet.

Table 6. Local concentration in IN625 droplet as determined by EDX

	EDX (relative wt-%)		
	Dark grey zone (1)	Grey zone (2)	White zone (3)
Ni	62.0	61.8	45.9
Cr	22.2	22.0	15.3
Mo	9.0	9.5	16.8
Nb	3.8	3.7	17.4
Fe	2.2	2.4	1.6
Si	0.8	0.6	3.0

Table 6 shows that the chemical compositions of the grey and dark grey areas in Fig. 5 are very similar, whereas the white area represents a molybdenum-rich phase with a different composition. A comparable observation was made for the Inconel 625 arc-sprayed coating (see Table 5). Again it can be assumed that the heterogeneity is attributed to the slow solubility of molybdenum.

3.4. Comparison of XRF and EDX measurements

Table 7 shows the comparison of the results of the XRF and EDX measurements of the feedstock cored wire, the droplet and the arc-sprayed coating.

A special precalibration for the investigated alloy system was not performed. However, this does not have a negative influence on the validity of the measurements, since the comparability of the results of wire, droplet and coating with each other is not affected. Lightweight elements such as oxygen and nitrogen, that are basically detectable with EDX, were not analyzed because of the high error probability. The measured values in Table 7 are relative values summed to 100 %.

Table 7. EDX and XRF analyses presenting the average element concentrations

	XRF (relative wt-%)			EDX (relative wt-%)		
	W*	D†	C‡	W	D	C
Ni	58.0	63.2	63.7	52.3	60.8	60.8
Cr	21.0	21.6	20.2	24.6	21.2	20.7
Mo	11.5	9.5	9.7	12.2	10.0	10.3
Nb	7.5	3.7	4.3	7.5	4.9	4.8
Fe	2.0	2.0	2.1	2.3	2.3	3.0
Si	0	0	0	1.1	0.8	0.4

* Cored wire † Droplet ‡Coating

For both analysis methods, a significant decrease of the element content of several alloy components could be observed when comparing the feedstock cored wire on the one hand with the droplet and the coating on the other. This led to a shift in the chemical composition, which is similar for droplet and coating. The strongest decrease in concentration shows niobium followed by molybdenum. The fact that nickel is the only element that increases in amount leads to the conclusion that the iron and chromium contents also decrease, but the relative amount does not change. This suggests that alloy systems for arc spraying in form of cored wire, which include certain amounts of refractory elements and elements that tend to vanish during the spraying process, need to be composed in consideration of the change in chemical composition by processing.

Silicon was only detected by EDX, but not by XRF. However, the low Si content hardly affects the comparability, so this is not considered to be the main reason for the differing measurement results of XRF and EDX. The highest deviation between the two measurement techniques can be found in the results of the cored wire. Especially the nickel and chromium contents differ significantly (Table 8).

Table 8. Relative differences between the values determined by EDX and XRF (wt-%)

	ΔW	ΔD	ΔC
Ni	5.7	2.4	2.9
Cr	-3.6	0.4	-0.5
Mo	-0.7	-0.5	-0.6
Nb	0	-1.2	-0.5
Fe	-0.3	-0.3	-0.9
Si	-1.1	-0.8	-0.4

Also for the droplet and the coating, the XRF analysis revealed a higher Ni content in comparison to EDX, even though the difference is smaller than for the cored wire. Apart from Ni, the XRF and EDX results showed only small deviations for the elemental concentration in the droplet and the coating. This suggests that the comparability of the results of these two analysis methods increases with an increasing homogeneity of the investigated samples.

4. Conclusion

This paper shows the potential and the limitations of different chemical analysis methods by the example of an Inconel 625 cored wire. Contrary to hard particle-filled cored wires, the main application for Inconel 625 coatings is not wear protection, but corrosion protection, which implicates the requirement for a homogeneous microstructure after the arc spray process. The investigated samples, however, show a heterogeneous phase distribution in the coating and, to a lesser extent, even in the remelted droplet. An approach to solve this problem might be the use of pre-alloyed components that have to be determined in a further study.

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