Original Article

Rapid fabrication and characterization of AISI 304 stainless steels modified with Cu additions by additive alloy melting (ADAM)

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\begin{abstract}
Rapid alloy prototyping is quickly emerging as a manufacturing approach to design novel structural alloys since allows producing low volume of high quality castings quickly at low cost. Thus, a large number of alloys can be produced and tested for finding the optimal composition in an alloy system. In this work, a new high throughput method for rapid alloy manufacturing has been developed and employed to cast AISI 304 stainless steel samples modified with an addition of Cu in the range of 1–4 wt.%. The homogeneity of the microstructure and chemical composition of as-cast materials has been characterized at the macro- and micro-scale, using optical and scanning electron microscopy, X-ray fluorescence, X-ray diffraction and electron probe microanalysis. At the macro-scale, no compositional variations have been found, while variations in the distribution of phases in the microstructure were related to variations in the cooling rate and thermal path undergone across the solidifying ingot. At the micro-scale, it has been found that segregation of austenite and ferrite stabilizing elements occurs during solidification, as expected from the phase diagram. Additive alloy melting (ADAM) has been demonstrated to be a suitable, rapid and versatile casting method for manufacturing metallic samples on a laboratory scale with good chemical homogeneity at the macro-scale.

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\end{abstract}
1. Introduction

Nowadays materials science faces the challenge imposed by the industry to develop new advanced materials at minimum cost within a short period of time. Traditionally, steel foundries use almost exclusively electric furnaces for the fabrication and formulating steel, usually under argon atmosphere to prevent oxidation [1]. There are two types of electric furnaces: induction furnaces [2], which require long times of heating, homogenization and cooling, or electric arc furnaces, where the samples are melted several times to ensure homogeneity [3]. Thus, the development of new metallic material is an expensive and time consuming process. In order to speed up the process of design and fabrication of a prototype, several tools have been developed. Computational tools, like ThermoCalc [4] are useful to predict what phases (and its composition) are present in a certain alloy as a function of temperature. However, its real use is still limited as it only predicts microstructures under equilibrium conditions, which are sometimes far from real processing ones and cannot fully replace the experimental work needed to develop a new alloy compositions tailored for advanced applications. In the field of experimental tools, high throughput methods have been introduced during the last years. These methods involve the rapid production and characterization of new materials through the systematic variation of key parameters, like chemical composition or thermomechanical processing route. Rapid prototyping methods are well developed for thin films [5], but these methods present limitations due to the small amount of material produced and the complexity of measuring mechanical properties of thin films. Concerning bulk materials, a few attempts have been made so far for the rapid design of structural alloys. The diffusion multiple (DM) method [6], where different metals blocks are put in close interfacial contact at high temperature to produce the diffusion in the interface with the aim of generating composition variations, has been used for a long time to evaluate diffusion coefficient and phase diagrams. The development of instrumented nanoindentation technology for evaluating the mechanical property of materials at small scale allows to extent the DM approach for mapping the dependency of alloys’ properties on composition and phases present. The main disadvantages of diffusion multiples are the time required and the scale of the diffusion layer.

Recently, Springer et al. [7] have developed a rapid alloy prototyping approach for the accelerated design of new materials. They obtain, in an induction furnace, five different alloys in one operation by installing on a stage five consecutive copper casting moulds, which can be moved step by step and then filled with melt. After casting an alloy, the composition of the remaining melt is modified by adding the amount of alloying elements necessary to obtain the desired composition, and then the new alloy is cast in the next mould. The main limitation of this method falls to the freedom in the possible composition of the produced alloys: as the remaining liquid is always used to produce the next alloy; each alloy is a modification of the previous one.

Within this work, a new method named additive alloy melting (ADAM) has been developed with the aim of reducing the time and cost of producing new alloys at a laboratory scale and overcoming the limitations of the existing technologies. This method consists in melting and casting sequentially several alloys from appropriated amount of the raw material using an arc furnace with a non-consumable tungsten electrode. This approach may be advantageous against many other rapid alloy manufacturing technologies due to the speed of the process and the versatility in terms of composition, as each alloy is produced individually. However, the uncontrolled fast cooling rate during solidification and the impossibility of re-melting the ingots several times on each side to prevent the presence of macrosegregations could give rise to heterogeneous alloys. For AISI 304 stainless steels, it is widely reported that depending on the range of cooling rates, solidification can produce different microstructures characterized by different amount and morphologies of ferrite and austenite [8]. In this work, to determine the limits of this new high throughput method, the microstructural and compositional variations have been studied at micro and macro scales using a commercial AISI 304 stainless steel modified through the addition of Cu in the range of 1–4 wt.% to improve the performance at high temperature [9].

For this reason, the main objective of this work is to study the compositional and microstructural inhomogeneities across each sample layer to study the consequences of the single melting on the homogeneity of the samples.

2. Materials and experimental procedure

Commercial AISI 304 stainless steel of chemical composition given in Table 1 was modified by the addition of 1, 2, 3 and 4 wt.% of 99.99 (wt.%) pure Cu. These samples will be referred henceforth as Base, 1Cu, 2Cu, 3Cu and 4Cu respectively.

The 5 alloys were processed by additive alloy melting (ADAM) under argon atmosphere in an arc furnace ARC 200 from ARCAST Inc. using a non-consumable tungsten electrode. The intensity of the electric arc is controlled by a pedal, and the maximum value can be limited in the power supply, between 0 and 600 A. By the ADAM approach, alloys with the desired composition were prepared by melting the base AISI 304 with pieces of pure Cu and then cast sequentially to form layers inside a special crucible. Fig. 1 shows schematically the experimental process followed. In this figure, a cross section of the water cooled copper crucible is represented in orange. This crucible has a hole in the middle closed by a piston (dark grey) that can be moved up and down. After filling the furnace with the raw materials of the different alloys that are going to be melted in the crucible around the hole, several cycles of vacuum and argon are applied in order to remove the highest amount of oxygen from the interior of the chamber. The process starts melting the first alloy and letting it to

| Table 1 – Composition in wt.% of the base AISI 304 plate with Fe to balance. |
|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| C         | Si     | Mn     | P      | S      | N      | Cu     | Cr     | Ni     | Mo     |
| 0.04      | 0.22   | 1.15   | 0.03   | <0.01  | 0.04   | 0.25   | 18.00  | 8.52   | 0.24   |
pour into the hole. To help mixing all the alloying elements homogeneously, the arc was kept a few seconds after casting in the central hole which subsequently solidified after power was turned off. Before casting the second alloy, the piston is lowered to leave the necessary space to keep the next molten material inside the hole. It is very important to control the size left in the crucible: if this size is too small, the previous alloy could be re-melted and mixed with the new one, but if it is too big, the new alloy could not be completely molten after casting during the time that the arc is homogenizing the alloy.

As a result of the ADAM, it was obtained a bar of approximately 2.5 cm in diameter formed by layers of different alloys, as shown schematically in Fig. 2 (left side). This figure presents in the right side an image of a bar formed by 2 layers. The shape of each layer is a consequence of the molten metal surface tension, which results in the onset of a meniscus curving the interface between layers. It is also important to notice that the different layers are not always fully joined. Beside, different alloying systems can be combined since each layer is independent from the other layers.

The alloys produced following the ADAM approach described previously, were cut and prepared following standard metallographic preparation procedures, which included grinding with SiC grinding sandpapers ranging from very
coarse to very fine sizes, rough polishing with 3 µm diamond paste and finishing with a crystalline colloidal silica suspension. Then the microstructure present in the samples was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM) and electron probe microanalyses (EPMA). It is important to state than not all the samples have been characterized; only the Base, 2Cu and 4Cu, to have representative results of the ends and the mid part of the bar.

X-ray fluorescence measurement were performed using a FISCHERSCOPE X-ray XUV spectrometer (Helmut Fischer GmbH, Germany) equipped with a micro focus rhodium X-ray tube and a Si-Pin semiconductor detector with 180 eV of energy resolution at Mn Kα energy. The instrument is controlled by the WinFTM software, which is also used both for the spectra acquisition and for the spectral data treatment. All spectrometric measurements were carried out at 20 kV, with a 1 mm diameter collimator without filter on the incident radiation path, at 50 s of acquisition time. The current was automatically adjusted by the system to reduce the dead time in the detector. Automatic measurements side by side (12 × 2 spots = 24 spectra) and from top to bottom at the central vertical line (6 spectra), in both cases with steps of 2 mm, were configured with the help of a programmable XY-stage, a high-magnification video camera and a laser pointer. The overall uncertainty of measurements was computed taking into account the uncertainty of the calibration standards, the counting statistics of the calibration measurements, and statistics functions calculated for the measurement itself.

Selected area XRD measurements were performed with a Bruker AXS D8 diffractometer equipped with a cobalt X-ray tube, Goebel mirror optics collimator, an incident beam slit of 200 µm, and a LynxEye linear detector for ultrafast XRD measurements. Four automatic measurements from top to bottom of the arc melted samples were configured with the help of a motorized ¼-Eulerian cradle stage, which allows moving the sample to the desired XY-position. The area of interest on the sample was accurately and precisely located in the X-ray beam by using a laser/video microscope from Bruker AXS. On the other hand, as the cross-point of the laser beam and the optical axis of the zoom video are aligned to the instrument centre, the sample height can be controlled by monitoring the relative positions of the laser spot. A current of 30 mA and a voltage of 40 kV were employed as tube settings. The XRD spectra were collected over a 2θ range of 35–135° with a step size of 0.01°. In this study, the version 4.2 of Rietveld analysis programme TOPAS (Bruker AXS) was used for phase quantification and calculation of structural parameters. Crystallographic information of the different phases for the Rietveld refinement was obtained from Pearson's Crystal Structure Database for Inorganic Compounds [Pearson’s Crystal Structure Database for Inorganic Compounds, Release 2015/2016. Materials Park: ASM International, 2015]. The refinement protocol included also other parameters like, background, zero displacement, the scale factors, the peak breadth and the unit cell parameter. In order to eliminate the instrumental contribution to peak broadening, instrument functions were empirically parameterized from the profile shape analysis of a corundum sample measured under the same conditions. Thus, we calculated the volume weighted mean crystallite size using the double-Voigt approach.

Optical micrographs were obtained after etching with Lichtenegger and Blöch (L-B) reagent for 30 s at 60 °C [10] using a Nikon Epiphoto 200. EPMA analyses have been carried in a JEOL Superprobe JXA-8900M with a WDS microprobe located at the National Centre for Electron Microscopy (CNME, Madrid, Spain).

3. Results and discussion

3.1. Macro-segregations

Inhomogeneous distribution of alloying elements during the ADAM process results from liquid metal flow during the melting process and solute partitioning between solid and liquid phases during solidification. Macro-segregation behaviour of the Base, 2Cu and 4Cu alloys was investigated by X-Ray fluorescence. Axial and radial distribution of the alloying elements was determined following the diagram shown in Fig. 3, being each spot 1 mm in diameter.

XRF analysis showed that the composition is quite homogeneous along most of the samples, as presented in Figs. 4–6 for the Base, 2Cu and 4Cu alloys, respectively. It can be seen

Fig. 3 – Drawing of a test sample showing the position of the measurement points in XRF analysis.
Fig. 4 – Composition of AISI 304 Base measured by XRF at different locations across the sample (see Fig. 3).

Fig. 5 – Composition of AISI 304 2Cu measured by XRF at different locations across the sample (see Fig. 3).
that Cu content is very close to the desired value. Only in one region of 4Cu sample a drop in the Cu content is observed (Fig. 6) that was associated to an insufficient incidence of the arc in that particular area. The results of chemical analysis on the macroscale reveals that one single melting is effective to obtain alloys with a low degree of macro-segregation, but the manual control of the arc should be carefully carried to ensure repetitiveness.

3.2. Solidification-phase balance in the microstructure

The properties and performance of austenitic stainless steels are strongly related to the presence of delta ferrite, which depends on chemical composition and on the cooling rate during solidification. The empirical Schaeffler’s diagram can be a very useful tool for representing the phase balance in the microstructure of stainless steels of a given composition, when rapid cooling processes, like welding and casting, are involved. These diagrams use Ni$_{eq}$ and Cr$_{eq}$ as a measurement of the contribution of the austenite and ferrite stabilizing elements, respectively, and also take into account the influence of Cu [11]. As rapid solidification conditions are made possible by the ADAM approach, the Schaeffler’s diagram was used to predict the constituents for the base and 4Cu alloys from the values of Cr$_{eq}$ and Ni$_{eq}$ given in Table 2. As shown in Fig. 7, it is expected a microstructure formed by austenite and δ-ferrite in both alloys.

As in the ADAM approach process-related factors such as component geometry, heat transfer and solidification kinetics, affect local variations in solidification conditions, the microstructure of the solidified casting displays local variations throughout the thickness of the specimen. Thus, several selected area XRD measurements were performed to determine the solidification-phase balance at different places. In Fig. 8, it is presented the schematic of the scans performed in the vertical direction, where the red rectangles show the area covered by each measurement.

The results of the quantitative phase analysis performed by fitting these XRD measurements with the Rietveld method are shown in Table 3. It can be observed that austenite and δ-ferrite are present in all samples, as expected from the Schaeffler’s diagram of Fig. 7. In addition to these phases, a small amount of ε martensite is present at the upper and lower edge of the AISI 304 base sample. The ε martensite is only observed in the Base alloy, which suggests that Cu hinders the formation of this phase [12]. This phase has been reported to form in AISI 304 by martensitic transformation of the austenite induced by plastic deformation at low temperature [13]. Although in this case no macroscopic deformation was applied to the sample, the rapid cooling rates during ADAM process can introduce significant macroscopic residual stresses and then the strain relaxation after the cutting process could be enough to cause phase transformation. The possibility of being formed during

![Composition of AISI 304 4Cu measured by XRF at different locations across the sample (see Fig. 3).](image-url)
metallographic preparation is discarded since \(\varepsilon\) martensite only appears in the parts of the sample that solidify first. Table 3 shows also the presence of some amount of CuO in the 4Cu alloy, which could be a consequence of some contamination or the oxidation of the copper during melting prior to mixing with the base steel.

Phase variations observed amongst the different samples can be explained based on the Cu content in each alloy. Since Cu stabilizes austenite, the overall \(\delta\)-ferrite content decreases when the Cu content is increased. On the other hand, the variation of solidification-phase balance observed at different places of each sample cannot be attributed to variations in composition, since XRF measurements show that these variations are negligible. Then, they must be a consequence of the fabrication process itself. Each part presents a different cooling rate due to the distance to the surface and the different materials in contact with that surface (Ar on top, Cu crucible on the sides and the cooled piston or other sample in the bottom). Also each part is subjected to different thermal cycles, since the top part supports the molten metal of the next cast sample. All these heating cycles cannot be fully controlled since the process is done manually.

### 3.3. Microstructural characterization

Compositional and microstructural variations at the micro-scale have been studied, since chemical segregation is a characteristic phenomenon of casting processes of AISI 304 stainless steel [14]. Figs. 9 and 10 show optical micrographs...
of AISI 304 Base and 4Cu inner (A and B) and outer part (C and D), respectively. Although the L-B colour reagent used to reveal the microstructure leaves δ-ferrite unetched (white) and colours austenite from orange to blue depending on the composition of this phase [15], it should be highlighted that the etching response obtained highly depends on the temperature of the etchant and the etching time.

Microstructure of the inner and outer part is similar in both samples, and the differences observed inside are a consequence of the variation of the cooling rate through the sample. For the base and 4Cu alloys used, Cr<sub>eq</sub>/Ni<sub>eq</sub> are calculated as 1.66 and 1.50 from the values given in Table 2. As these values are between 1.48 and 1.95, samples present the microstructure characteristic of cast austenitic stainless steels solidified in FA mode (L → L + δ → L + δ + γ → δ + γ). As the solidification starts, dendrites of δ-ferrite will precipitate from liquid parallel to the heat flux, which is perpendicular to the nearest surface. When the temperature decreases to the three phase region, the solidification behaviour will deviate from equilibrium to non-equilibrium due to the high cooling rate developed during the ADAM process, with the formation of a coupled microstructure of δ-ferrite and austenite [16]. First of all, plates of δ-ferrite form in the liquid, rejecting the austenite stabilizing elements to the surrounding liquid. This results in Cr depletion and Ni enrichment at the interface, which enables the formation of austenite layers adjacent to δ-ferrite. Now Cr becomes enriched and Ni becomes depleted at the interface of austenite, and then δ-ferrite is formed again. The alternative formation of δ-ferrite and austenite in the three phase (δ ferrite, austenite and liquid) it is referred very often as the peritectic/eutectic reaction, and it gives rise to a lathy microstructure. This process occurs until the temperature is low enough for the austenite to become the primary phase, and the remaining liquid solidifies in the form of austenite. This solidification sequence produces a microstructure consisting of lathy ferrite and austenite surrounded by austenite. However, some amount of primary dendritic ferrite was also observed in the regions where de solidification velocity is sufficiently low to allow near equilibrium solidification conditions.

The range of colours observed in the austenite (Fig. 10) reveals compositional variations in Cr and austenite stabilizing elements. This chemical segregation has been studied by the comparison between EPMA maps and optical micrographs.

### Table 3 – Phase distribution in vol.% measured by XRD for the base alloy, 2Cu and 4Cu.

<table>
<thead>
<tr>
<th>Area</th>
<th>Phase vol.%</th>
<th>Base</th>
<th>2Cu</th>
<th>4Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Upper edge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>93.3 γ-Fe</td>
<td>96.3 γ-Fe</td>
<td>98.0 γ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1 δ-Fe</td>
<td>3.7 δ-Fe</td>
<td>2.0 δ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6 ε martensite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Int. Up</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87.1 γ-Fe</td>
<td>96.1 γ-Fe</td>
<td>97.8 γ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.7 δ-Fe</td>
<td>3.9 δ-Fe</td>
<td>2.2 δ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Int. low</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76.2 γ-Fe</td>
<td>95.2 γ-Fe</td>
<td>98.1 γ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.8 δ-Fe</td>
<td>4.4 δ-Fe</td>
<td>1.9 δ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lower edge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94.5 γ-Fe</td>
<td>91.8 γ-Fe</td>
<td>95.9 γ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 δ-Fe</td>
<td>8.2 δ-Fe</td>
<td>3.1 δ-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 ε martensite</td>
<td></td>
<td>1.0 CuO</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9 – Optical micrographs of AISI 304 Base etched with L-B at inner part at (a) lower and (b) higher magnification and outer part at (c) lower and (d) higher magnification.
Fig. 10 – Optical micrographs of AISI 304 4Cu etched with L-B at inner part at (a) lower and (b) higher magnification and outer part at (c) lower and (d) higher magnification.

Fig. 11 – (a) Optical micrograph and EPMA maps of (b) Cr, (c) Ni and (d) Cu of AISI 304 4Cu.
of a particular area. Fig. 11 shows an optical micrograph (a) and EMPA maps of Cr (b), Ni (c) and Cu (d) of AISI 304 4Cu. The image “a” shows the area where the EPMA maps were performed enclosed in yellow and the reference indentations performed to locate the selected area. EPMA maps show in yellow the areas where an element is more abundant while in blue where it is less abundant.

This figure shows that Ni and Cu present the same segregation behaviour while Cr shows an opposite tendency. While Cr is segregated mainly in the δ-ferrite and in a lesser degree inside the austenite surrounding the lathy structure, austenite is enriched by Ni and Cu. Concentration of both elements in the austenite included in the lathy microstructure is lower than in the austenite transformed directly from the liquid. This behaviour is similar in all the samples and it agrees with the analysis of the solidification sequence as described before.

Fig. 12 shows a dark field image (SEM-BSE) micrograph of the 4Cu sample. In this image three main areas can be differentiated: (i) Light grey areas surrounding the lathy microstructure that includes, (ii) medium grey austenite, and (iii) black areas of δ-ferrite. This figure also shows the presence of a few Cu- and Mn-rich particles. These Cu-rich particles are probably CuO, as revealed by XRD.

As maps depicted in Fig. 11 are only qualitative, WDX quantitative microanalysis were also performed. Table 4 presents the composition (in wt.%) of the surrounding austenite and lathy δ-ferrite for the 4Cu sample, showing that Cr is segregated in the δ-ferrite while Cu and Ni are segregated to the austenite, as it would have expected for ferrite and austenite stabilizing elements.

4. Conclusions

ADAM has demonstrated to be a suitable and versatile method for the production of AISI 304 stainless steels in the laboratory, reducing the casting time and obtaining compositionally homogeneous samples at the macro-scale in the radial and longitudinal directions, as confirmed by XRF analysis. However, the phase balance determined by XRD displayed local variations throughout the thickness of the specimen associated to differences in cooling rate and thermal cycles at different locations of the samples. At the micro-scale, the comparison between the EPMA maps and the optical micrographs show microstructure consisting of lathy ferrite and austenite surrounded by austenite, where Cr is segregated in the δ-ferrite while Ni and Cu are segregated partially in lathy austenite and mainly in the surrounding austenite.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES

[3] Isheim D, Vojnyan S, Fine ME, Seidman DN. Copper-precipitation hardening in a non-ferromagnetic...


