Original Article

Making iron aluminides out of scrap

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ABSTRACT

The abundance of iron and aluminum raw materials is often quoted as a strategic advantage of iron aluminides against other competing materials (not only stainless steels, but also nickel and titanium aluminides). These raw materials, however, are not only abundant in the form of ores in earth’s crust, but also as scrap produced in the extensive technological activity associated with these base metals. The present work reports results of two prospective experiments designed for obtaining iron aluminides exclusively from readily available scrap (aluminum cans, carbon steel strips and stainless steel sheet metal forming residues, this last as a source of chromium and molybdenum). Two base alloys with nominal composition Fe–30Al–6Cr and different carbon contents were molten in a laboratory induction furnace with no atmosphere protection other than blowing Argon over the melt surface. The produced ingots were characterized concerning their microstructures and final composition, which allows estimating the incorporation efficiency of the alloying elements using this processing route.

Oxidation tests at the temperature range of 800–1100 °C under air were performed to demonstrate that these alloys show similar behavior as the ones obtained using conventional processing routes. The results are discussed concerning the viability of this low-cost processing route for the industrial production of iron aluminides.

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1. Introduction

Iron and aluminum are two of the major components of earth’s crust. Estimated reserves of iron ore and bauxite amount to 180 billion and 28 billion tons, respectively [1,2]. These two base metals also define two large industrial branches, which leads to the extensive processing of these ores into metallic products. As a consequence of this extensive technological activity, metallic residues, known as scrap, are produced. These scraps, produced during the processing of the metal, are known as new (or prompt) scrap and have a higher value than old (or post-consumer) scrap.

Secondary metallurgical techniques, used to recover these metals, are well developed (and, in the case of iron products, more than hundred years old), such that about all aluminum or iron new scrap produced in the iron and aluminum industry are recycled into metal in a second stage processing [3,4].

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A technical iron aluminide, in addition, is not merely a binary Fe–Al alloy. A typical technical composition includes many alloying elements, e.g. Cr, Mo and C, among others [5]. The first two metals are quite expensive in the pure form, but may be, for example, available in stainless steel scrap, since they are added as alloying elements in a larger amount in this class of materials. Carbon on the other hand, although not expensive, may be difficult to incorporate in the melt if graphite is used as additive, mostly due to the large difference in densities between the melt and graphite, surface tension issues, and also due to the excessive melting temperature of the later. Carbon, however, comes as a natural alloying element (already incorporated in the alloy) in carbon steel.

The use of special melt processing techniques (vacuum smelting, ladle degassing) is also an issue. While this is justified in the case of nickel aluminides (due to the high added value of the produced part) and unavoidable in the case of titanium aluminides, prospective applications of iron aluminides in the automotive industry require productivity and cost reduction. Processing of conventional aluminum and iron-based alloys, on the other hand, may be well done under air with little atmosphere protection.

Finally, the quality of the produced alloy: as expected, alloys produced using recycled raw materials are subject to incorporating higher levels of impurities and presenting higher defect densities. Here, however, two apparently paradoxical results support the use of impure alloys in the case of iron aluminides. Alexander et al. [6] investigated the mechanical properties of B2-FeAl produced by casting, ingot metallurgy and powder metallurgy followed by extrusion. These authors observed that the powder-processed samples showed superior tensile elongations and fracture energy on impact testing than the ones produced in the other routes, in spite of possessing a large number of oxide particles in the matrix. They attributed this result to the observation of multiple crack branching events starting at the intersection of the main crack and the oxide particles. Similarly, Matsuura et al. [7] investigated iron aluminides produced using recycled raw materials, comparing with conventionally produced alloys, obtaining slightly better results for the former. The authors attribute this observation to solid solution strengthening, but an explanation in the line of the one described above could well be in place.

The aim of the present work is to investigate the viability of a recycled raw material-based processing route in the production of an iron aluminide. In order to be consistent, the melt was processed in a conventional laboratory induction furnace, with simple means of atmosphere protection.

2. Methodology

2.1. Raw materials

The selected raw materials were AISI 1020 steel strips (as the ones used in steel making), AISI 444 stainless steel sheet metal forming residues and conventional used aluminum cans. The products were cleaned (with a conventional detergent) to remove possible organic contaminants and dried in a muffle furnace at 120 °C. Table 1 presents the analyzed composition of the three materials, the values for the steels are averaged analyzed values and those for the aluminum cans are averaged literature data, considering all components of the cans [8]. Chemical analysis was performed using a calibrated energy dispersive spectroscopy (EDS) sensor, installed in a Scanning Electron Microscope (SEM), for all elements, except carbon, which was analyzed using the usual combustion method.

2.2. Alloy preparation

Based on the values presented in Table 1 two alloys were prepared, targeting a composition close to Fe – 30 at.% Al (17.2 wt.% Al) – 6 at.% Cr (6.6 wt.% Cr). Two 1 kg loads were prepared and their final projected compositions are 16.6 wt.% Al, 7.3 wt.% Cr, 0.76 wt.% Mo and 0.09 wt.% C. With these values we were able to estimate the incorporation efficiency in the smelting process. In addition, alloy A was molten using a graphite crucible, which allowed the alloy to reach carbon content corresponding to the equilibrium with the melt at high temperatures. Alloy B, on the contrary, was molten using an alumina crucible, resulting in much lower carbon content.

The load was placed in the furnace chamber according to the scheme suggested by Deevi and Sikka [9]. According to this sequence, the steel pieces were placed at the bottom and the aluminum cans were placed over them. The reaction of the molten aluminum with the iron in the steel is highly exothermic and helps in the quick melting of the load.

After melting, the alloys were poured into cast iron ingot molds. The first ingot presented extensive cracking during solidification. In the second alloy an attempt to avoid this cracking was made by heating the ingot mold to about 500 °C prior to melt pouring, but the cracking still persisted.

2.3. Sample preparation, characterization and metallography

Samples taken from the ingots were prepared for metallographic observation using standard techniques. Microstructure of the samples was analyzed in a Scanning Electron Microscope (SEM) equipped with EDS accessory; therefore, the samples were observed in the unetched condition.

During this investigation it was observed that both alloys presented profuse precipitation of carbides. In order to investigate the stability of this microstructure, one annealing experiment was performed by subjecting one sample from each alloy to 1200 °C/4 h heat treatment and quenching it in water. These annealed samples were later submitted to an aging treatment at 800 °C/10 min to investigate the possibility of producing a fine carbide distribution in this microstructure.

Vickers hardness testing using 3 N load to obtain a large impression area (including matrix+carbides) and 0.5 N to restrain the impression only to the matrix were performed. Ten measurements were made in each case and the average was computed. Dispersion was found to be negligible, so only the average values will be reported.

Finally, the “as cast” samples were analyzed using X-ray diffraction, using Cu Kα radiation.

Samples for the oxidation experiments were prepared by cutting the original ingot in the form of parallelepipeds with approximate dimensions 15 mm × 10 mm × 2 mm. These
samples were ground using SiC paper up to 600# and a hole of 2 mm diameter was drilled in the upper part, such that this sample could be suspended over an alumina crucible using Kanthal® wires.

2.4. Oxidation experiments

The oxidation samples were carefully weighed and measured such that their initial mass and surface areas were obtained. The whole set (crucible + sample) was placed inside a pre-equilibrated muffle furnace and kept in the furnace for the prescribed times. The sample, with the attached wire, was suspended over an alumina crucible in order to collect eventual fragments of the oxide scale. Treatment temperatures were 800, 900, 1000, 1100 °C and treatment times were 20, 50, 100 and 200 h. After treatment the set was carefully removed from the furnace and left to cool in still air. After that the sample and the eventual residues collected in the alumina crucible were again weighted to calculate the mass surplus. In spite of this care, results showed a large dispersion and prevented the determination of a kinetic model. Therefore the results will be presented and discussed only in a qualitative fashion.

3. Results and discussion

3.1. Ingot production and alloying efficiencies

The comparison of ingot mass with the load mass showed that only about 70% of the load was recovered as metal. The largest part of this mass loss came from a thick slag cover formed over the melt. This slag is reminiscent of the Al2O3 surface layer and of the non-metallic additives in the aluminum cans (e.g., the glaze coverage). Similar efficiencies are observed in conventional aluminum recycling technology and, from this source, it is known that the use of inorganic fluxes lead to a dramatic increase in (metal recovery) efficiency [10,11]. This suggests that the same solution could be used in the production of the iron aluminides. It is interesting to observe that the efficiency is similar in both cases, in spite of the large difference in processing temperature.

Chemical analysis of the produced ingot in the case of alloy A resulted in 13.6 wt.% Al (82% efficiency), 5.4 wt.% Cr (74.5% efficiency) and 0.81 wt.% Mo (107% efficiency). Carbon, as expected was incorporated from the graphite crucible and its content in alloy A was 0.5 wt% C (550% above the projected value).

In the case of alloy B, the obtained composition was 14 wt.% Al (85% efficiency), 8.6 wt.% Cr (117% efficiency) and 0.75 wt.% Mo (98.5% efficiency). It is interesting to observe that the efficiency values for Al and Mo are similar for both alloys, while the one for Cr is completely different. The only difference between both cases lies in the use of a graphite crucible (in alloy A) or of an alumina crucible (alloy B). One hypothesis to explain this difference would be possible that chromium reacted with graphite forming a high melting point chromium carbide in the first case, but this would not explain why this hypothetical carbide does not incorporate Mo in the same way. Carbon slightly increased to 0.15 wt.% (166% efficiency). After close scrutiny of the procedure it became clear that a graphite rod, which was used for solid charge accommodation during heating, briefly and inadvertently entered in contact with the melt, justifying this increase.

3.2. “As cast” microstructures

Fig. 1 shows a transversal section of the alloy A ingot. As can be seen the whole section is dominated by a columnar macrostructure. Two large cracks can be seen and these originated from the central shrinkage void. This shrinkage void was observed in the center of the ingot, almost through its entire length. It is apparent that this large shrinkage void is related to the ease with which the columnar structure is formed, since the columnar solidification is characterized by a plane front, which localizes the last liquid in the center of the ingot. Previous results by one of the present authors suggests that this prominently columnar structure is natural to iron aluminides with similar compositions, rather than a particularity of using recycled raw materials [12]. Common foundry strategies like the use of inoculation, which could break the columnar structure turning it into equiaxed, or the use of an appropriate mold project, could lead to a controlled contraction of the semi-solid aggregate and elimination or at least
control of this foundry defects. The findings in the alloy B ingot were similar showing that the results are unaffected by the carbon content or by the use of a pre-heated ingot mold.

Fig. 2 shows the microstructures obtained in alloys A and B. Alloy A shows eutectic microconstituents at the interdendritic spaces. A possible identification using X-ray diffraction was not possible due to the small volume fractions, but EDS measurements in the larger areas show that these particles are rich in iron and chromium (~54 wt.% Cr); this suggests that they are chromium carbides (probably M7C3). The particles in alloy B are finer and they are distributed over the entire matrix. They are also Cr-rich, but none of the particles is large enough to allow an unbiased estimate of the contents. The matrix in this eutectic is the body centered cubic phase (α); hence the eutectic reaction corresponds, probably to liquid → α + M7C3. This conclusion is consistent with accepted Fe–Al phase diagram [13], assuming that most carbons present in the alloy are combined in the form of Mo and Cr-rich carbides.

X-ray analysis of both “as cast” samples shows D0₃ superlattice spots for alloy A and only B2 superlattice spots for alloy B. A possible explanation for the absence of D0₃ spots in alloy B would be that Cr-content is in excess to 6 wt.%. Chromium is known to slightly reduce the D0₃/B2 critical temperature, while the B2/A2 critical temperature is kept approximately constant. In the case of alloy A Cr is depleted in the matrix due to the presence of the Cr-rich precipitates. A set of weak additional reflections was observed in the case of alloy A, but they are too weak for a positive indexing. They correspond, probably, to the observed carbide precipitates. Table 2 shows the results of individual EDS measurements in the matrix for both alloys. These are consistent with the previous interpretation of the diffraction results, since the measured chromium content is clearly smaller in alloy A, when compared with alloy B.

### 3.3. Heat treated samples

Fig. 3 shows the microstructure of the annealed and aged of the alloy A sample. A profuse precipitation of coarse faceted carbides in the matrix was identified. In comparison, alloy B shows much finer acicular precipitates (Fig. 4). Two additional carbide morphologies are also identified in alloy B. These particles are too small to allow an unbiased EDS measurement, but they are enriched in Ti and Nb [14]. The simultaneous presence of Ti and Nb seems to suggest that they are carbonitrides. The source for both metals probably being the AISI 444 steel, which contains small contents of both elements in its composition, added as carbon getters.

### Table 2 – Results of EDS measurements in the matrix region for the “as cast” samples of Alloys A and B. Primary values given in wt.% are converted to molar fractions, at.%, in the parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>14.14 (24.89)</td>
<td>4.95 (4.52)</td>
<td>0.75 (0.37)</td>
<td>0.66 (2.61)</td>
</tr>
<tr>
<td>Alloy B</td>
<td>14.63 (25.95)</td>
<td>7.82 (7.19)</td>
<td>0.66 (0.33)</td>
<td>0.20 (0.80)</td>
</tr>
</tbody>
</table>

### Table 3 – Vickers microhardness of the alloys in the “as cast”, annealed (1200 °C/4 h) and annealed + aged states (800 °C/10 min). Values in GPa represent averages of 10 measurements and were obtained with a 3 N load. Standard deviation is smaller than 0.01 GPa in all cases.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>“As cast”</th>
<th>Annealed</th>
<th>Annealed + aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.73</td>
<td>3.78</td>
<td>3.58</td>
</tr>
<tr>
<td>B</td>
<td>3.46</td>
<td>3.45</td>
<td>3.11</td>
</tr>
</tbody>
</table>
Table 3 shows the results of Vickers hardness measurements for both samples in the three investigated conditions. As observed, alloy A hardness increases in the annealed condition compared with the “as cast” sample and decreases after aging. In the case of alloy B, hardness of the annealed sample is practically the same as in the “as cast” condition, but decreases dramatically after aging. These observations suggest that solid solution strengthening due to carbon is more effective than particle strengthening due to the newly formed particles. Matrix hardness was obtained only in the aged state and corresponds to HV_{65N} = 2.93 and 2.70 GPa, respectively for alloys A and B. In all states, therefore, matrix is softer than the whole microstructure, showing that the existing carbides have an effect over alloy strength.

Direct comparison with the literature is not possible, since many factors affect hardness (e.g. composition and grain size) and no similar alloy, to the knowledge of the authors, has been reported in the literature. It is interesting, however, to observe that the present values are consistent with the ones reported for conventionally processed iron aluminides [15].

3.4. Oxidation experiments

In spite of all care adopted in the present experiments, mass gain values showed large dispersions. One possible explanation would be that spalling occurs in the oxide layer, eventually projecting the oxide outside the range of the protective crucible. This observation prevented the identification of the kinetic model, but a qualitative analysis of the data can still be performed. The complete set of acquired data can be obtained in Ref. [14]. The largest values are smaller than 1 x 10^{-4} g cm^{-2} even at 1100 °C/200 h. Comparison of Alloys A and B regarding oxidation suggests that the latter is slightly less resistant than the former, since the oxide layer is more fragmented in it. The results show, however, that oxidation resistance is still excellent in both alloys.

EDS measurements in the oxide layer showed that it is Al-rich, suggesting that it is formed predominantly by Al_{2}O_{3}. At some spots in alloy B Cr-rich areas in the oxide layer were identified. These areas seem to be related with spots in which the previous alumina layer fragmented, exposing fresh metal to further oxidation. This result suggests that the formation of the alumina scale depletes the matrix from Al. In this sense, Cr would act as a “back-up” protective element, avoiding catastrophic oxidation even in the situations in which the alumina coverage fragments.

Fig. 5 shows the typical aspect of the oxide layers formed in the present alloys. This case corresponds to alloy A, after oxidation at 800 °C/200 h, but it is also found in the remaining cases, differing only in the thickness of the layers.

The numbers in the image refer to EDS measurements, whose results are given in Table 4, which refer only to Al, Cr and Fe.

Fig. 5 shows a complex layer system, composed at least, of two different oxides. For comparison, an hypothetical mixture of Al_{2}O_{3}:Fe_{2}O_{3}:Cr_{2}O_{3} in the proportion 2:0.5:1 would result in an oxide mixture with 24.5 wt.% Al, 11.6 wt.% Cr, 25.4 wt.% Fe and 38.2 wt.% O. The overestimated amount of iron could be attributed to signal originating from the matrix below the oxide layer, but the result shows that the layer is enriched in Al_{2}O_{3} and Cr_{2}O_{3} in the dark areas and contains somewhat more Cr_{2}O_{3} in the lighter areas, where the previous oxide layer detached.

4. Conclusions

The results obtained in the present work allow to conclude that:

1. It is possible to obtain iron aluminides using exclusively recycled raw materials and a low-cost processing route.
2. Carbon can be added to the alloy simply by using a graphite crucible or by placing the melt in contact with graphite tools, suggesting that adding graphite pellets to the load is unnecessary in processing iron aluminides.

3. In spite of the excessive contents in carbon, the microstructures obtained in both alloys seem to be adequate for use.

4. The oxidation behavior of both alloys was excellent, showing that the produced alloys could, at least, be used in applications where this property is critical.

Conflicts of interest

The authors declare no conflicts of interest.

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