Nanocrystalline Al-based alloys - lightweight materials with attractive mechanical properties

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Abstract. In this study, several ways of bulk nanocrystalline Al-based alloys’ production by high-pressure compaction of powders were explored. The effect of chemical composition and compaction parameters on the structure, quality and mechanical properties of the bulk samples was studied. Bulk nanocrystalline Al-Mm-Ni-(Fe,Co) alloys were prepared by ball-milling of amorphous ribbons followed by consolidation. The maximum microhardness (540 HV0.1) was achieved for the samples compacted at 275 °C under 7.7 GPa (which resulted in an amorphous bulk) and nanocrystallised at 235 °C for 20 min. Another group of the produced materials were bulk nanocrystalline Al-Si-(Ni,Fe)-Mm alloys obtained by ball-milling of nanocrystalline ribbons and consolidation. The hardness of these samples achieved the value five times higher (350HV) than that of commercial 4xxx series Al alloys. Nanocrystalline Al-based alloys were also prepared by mechanical alloying followed by hot-pressing. In this group of materials, there were Al-Fe alloys containing 50-85 at.% of Al and ternary or quaternary Al-Fe-(Ti, Si, Ni, Mg, B) alloys. Microhardness of these alloys was in the range of 613 – 1235 HV0.2, depending on the composition.

1. Introduction

Amorphous Al-based alloys are interesting for their excellent mechanical properties, superior to those of the commercial crystalline Al-based alloys, e.g. tensile strength in amorphous alloys is twice higher compared to commercial crystalline ones [1]. However, mechanical properties can still be improved for some alloys exhibiting primary crystallization, in which microstructure consisting of dispersed nano-sized crystals embedded in an amorphous matrix is developed. [2]. The convenient way for achieving this microstructure is the controlled crystallisation of amorphous alloy. Another method to obtain nanocrystalline or amorphous Al-based alloys is mechanical alloying. Although the main interest of Al-based alloys applicability is as bulk samples, the typical procedures for obtaining amorphous or nanocrystalline Al-based alloys yield thin ribbons (melt-spinning) or powders (mechanical alloying or atomisation). Therefore, much effort has been devoted to powder consolidation by different procedures, such as hot-extrusion [3], hot-pressing [4] and cold consolidation using severe plastic deformation [5]. A promising method that retains nanocrystalline structure by careful control of temperature, pressure and processing time is high-pressure hot-pressing [6-9]. Recently, we demonstrated that application of a high pressure hinders grain growth at elevated temperature [6-8].

The aim of this study was to produce bulk nanocrystalline Al-based alloys by high-pressure consolidation of ribbons (powdered by ball-milling) or mechanically alloyed powders. Different ways
of bulk amorphous-nanocrystalline samples’ production were explored and the relationship between hardness and microstructure was studied.

2. Experimental

Ingots of Al-Mm-Ni-(Fe,Co) alloys prepared from pure elements (the composition listed in table 1) and of Al-Si-(Ni,Fe)-Mm alloys prepared from pure elements and from 4xxx series alloy (the composition listed in table 2) were obtained by arc melting in argon atmosphere. Composition of Mischmetal (Mm) was: Ce-50.3, La-43.5, Pr-5.9 and Nd-0.3 and of 4xxx commercial Al alloy was: Si-9.6; Fe-0.54; Zn-0.07; Mn-0.26; Cu-0.27; Mg-0.27; Ti-0.04 (in at. %). The ribbons were made by melt-spinning technique. Subsequently the ribbons were ball milled in a Fritsch P5 planetary mill for 50-90 min under argon atmosphere.

Al-Fe powder alloys containing 50-85 at.% of Al and ternary or quaternary Al-Fe-(Ti, Si, Ni, Mg, B) powder alloys (the composition listed in table 3) were prepared by mechanical alloying using SPEX 8000D mill.

A high-pressure toroidal-cell press was used for powders’ compacting at various temperature. The applied pressure was from 2 to 7.7 GPa. Samples were held at maximum pressure for 3-5 min. Resulting bulk samples are limited to cylinders of 5 mm diameter and a maximum of 5 mm high.

Phase composition determination and structural analysis of the produced materials were performed using X-ray diffraction technique (XRD) operated with Cu Kα wavelength. Crystalline volume fraction \( V_{cr} \) was calculated using the procedure described elsewhere [10]. The mean crystallite size was estimated from the XRD data by the Williamson-Hall method.

Differential scanning calorimetry (Perkin-Elmer DSC7) was used for characterising the crystallisation behaviour of amorphous ribbons and bulk samples with heating rate was 40 °C/min.

Compaction quality of the bulk samples was checked by scanning electron microscopy (SEM) in a Hitachi S-3500N equipment. Philips EM300 transmission electron microscope was used for observations of consolidated sample’s microstructure. Vickers microhardness measurements were performed with a load of 100 or 200 g, while Vickers hardness (HV) with a load of 1kg. Density of compacted bulk samples was determined by Archimedes method using a Gibertini E154 balance with a set for density of solids measurement.

3. Results and discussion

Since three kinds of Al-based alloys have been investigated in this study, the results and discussion were divided into three subsections.

3.1. Bulk nanocrystalline Al-Mm-Ni-(Fe,Co) alloys

All the Al-Mm-Ni-(Fe,Co) ribbons were amorphous in as-cast state. Figure 1 shows the DSC scans obtained at 40 °C/min for the four alloys studied. Crystallisation takes place in two or three different stages. It should be noted that substitution of Mm by Al decreases thermal stability of the amorphous phase, but increases the difference between the crystallisation temperatures, resulting in clearly separated first peak on the DSC traces. The first transformation in Al\(_{88}\)Mm\(_{5}\)Ni\(_{5}\)(Fe,Co)\(_{2}\) alloys is accompanied by a very broad DSC peak, typically found for nanocrystallisation processes [2]. Bulk materials were produced by high-pressure compaction at temperature between the first and the second stage of crystallisation. For all the compacted samples, microhardness was measured and the results are shown in table 1. For all the alloys, the compacted samples have higher hardness, compared to the initial amorphous ribbons. As a reference, Al\(_{88}\)Y\(_{3}\)Ni\(_{5}\)Fe\(_{2}\) alloy was used. The alloys containing Mm have similar hardness in the as cast form, as well as after compaction, in comparison to Y-containing ones. Mm can successfully substitute Y in quaternary amorphous and nanocrystalline Al-based alloys. For optimisation of the consolidation process, the Al\(_{88}\)Mm\(_{5}\)Ni\(_{5}\)Fe\(_{2}\) alloy was chosen. This alloy is characterised by one of the largest temperature differences between the first and the other crystallisation stages, has relatively high hardness and contains Fe, which is cheaper than Co.
Table 1. Microhardness of amorphous ribbons and nanocrystalline compacted samples.

| Alloy            | Vickers microhardness amorphous ribbons | Vickers microhardness nanocrystalline bulk samples |
|------------------|-----------------------------------------|-----------------------------------------------|
| Al_{88}Mm_{5}Ni_{5}Co_{2} | 293                                     | 346                                           |
| Al_{88}Mm_{5}Ni_{5}Fe_{2}  | 259                                     | 364                                           |
| Al_{87}Mm_{5}Ni_{5}Co_{2}  | 287                                     | 351                                           |
| Al_{87}Mm_{5}Ni_{5}Fe_{2}  | 288                                     | 414                                           |
| Al_{88}Mm_{5}Ni_{5}Co_{2}  | 239                                     | 365                                           |
| Al_{88}Mm_{5}Ni_{5}Fe_{2}  | 283                                     | 383                                           |
| Al_{88}Y_{5}Ni_{5}Fe_{2}   | 252                                     | 358                                           |

Three ways of production of bulk amorphous-nanocrystalline material were proposed, each of them starting from amorphous ribbons powdered by milling: (i) cold compaction, which yielded amorphous material, followed by annealing in the calorimeter, (ii) hot compaction and (iii) cold compaction of powder nanocrystallised by annealing. (i): figure 2 shows the SEM micrographs of the bulk samples obtained by cold compaction of amorphous powder. Density is also indicated. Some individual smashed particles could be observed in the sample pressed at 2 GPa, whereas, for the sample compacted at 7.7 GPa, homogeneous flat surface, indicating a good quality of compaction was observed. Density is also lower in the sample compacted at 2 GPa than in the sample compacted at 7.7 GPa (3.06 and 3.18 g cm\(^{-3}\), respectively). From these results, it can be concluded that pressure has a big impact on the quality of compaction at room temperature. (ii): the bulk samples obtained by hot compaction of amorphous powder showed high density (~3.2 g cm\(^{-3}\)) and a flat surface in which the individual particles of the former powder were visible. For the same temperature of pressing, the sample pressed at 7.7 GPa presented a fully amorphous microstructure, whereas the sample pressed at 2 GPa exhibited nanocrystalline microstructure. The increase of the applied pressure shifts the onset of crystallisation to higher temperature. (iii): the bulk samples obtained by cold compaction of nanocrystalline powder presented low quality of compaction and it was possible to distinguish the individual particles of the nanocrystalline powder [10].
In the case of amorphous-nanocrystalline materials, crystalline volume fraction has the influence on their mechanical properties. In order to study the relationship between \( V_{cr} \) and microhardness, annealing of three as-pressed amorphous Al\(_{88}\)Mm\(_{5}\)Ni\(_{5}\)Fe\(_{2}\) bulk samples was performed. Figure 3 shows the evolution of \( V_{cr} \) (figure 3a) and microhardness (figure 3b) with the annealing time. The saturation behaviour is observed for both plots, reflecting the close relationship between \( V_{cr} \) and microhardness. Microhardness increases with the increase of crystalline volume fraction of \( \alpha \)-Al phase, reaching a maximum for \( V_{cr}=0.25-0.3 \). The maximum microhardness (540 HV) was achieved for the samples compacted at 275 °C under 7.7 GPa and subsequently nanocrystallised at 235 °C for 20 min. This value is comparable to the best found in other bulk Al-based alloys. However, in other works, these values are achieved for alloys containing not only amorphous matrix and nanocrystals of \( \alpha \)-Al phase, but also other crystalline phases [4,11].

**Figure 3:** (a) Vickers microhardness of Al\(_{88}\)Mm\(_{5}\)Ni\(_{5}\)Fe\(_{2}\) bulk alloy versus annealing time at 235 °C, (b) crystalline volume fraction in bulk alloy versus the annealing time at 235 °C.

### 3.2. Bulk nanocrystalline Al-Si-(Ni,Fe)-Mm alloys

Figure 4 illustrates the sequence of XRD patterns taken from the: (a) melt-spun ribbons, (b) milled ribbon and (c) bulk sample of Al\(_{73}\)Si\(_{19}\)Ni\(_{7}\)Mm\(_{1}\) alloy. In all the cases not only crystalline peaks corresponding to the \( \alpha \)-Al phase, but also “halo” related to the amorphous phase is visible. The microstructure consists of randomly distributed fcc-Al crystals, of about 10-50 nm in size.

**Figure 4.** XRD patterns taken from the (a) melt-spun ribbons, (b) milled ribbon, (c) bulk sample.

Figure 5 shows SEM images of the bulk nanocrystalline samples of Al\(_{73}\)Si\(_{19}\)Ni\(_{7}\)Mm\(_{1}\) alloy after compaction. One can observe that the quality of compaction increases with increasing of pressure from 2 GPa to 7.7 GPa. The sample compacted applying 2 GPa (figure 5a) is not homogeneous. Pores and particles of the powder are visible. Bulk material pressed at 4 GPa (figure 5b) also exhibits some pores. On the surface of the sample compacted at 6 GPa (figure 5c), residual pores still exist. The sample pressed at 7.7 GPa (figure 5d) is well compacted without pores.
**Figure 5.** SEM micrographs of the surface of the bulk sample (Al$_{73}$Si$_{19}$Ni$_{7}$Mm$_{1}$) compacted at: (a) 2 GPa, (b) 4 GPa, (c) 6 GPa and (d) 7.7 GPa.

Table 2 summarizes consolidation temperature, the hardness values, grain size and the temperature up to which the nanostructure is preserved ($T_{\text{max}}$). The highest value of 330 HV measured for Al$_{81.4}$Si$_{9.6}$Fe$_{7}$Ni$_{3}$Mm$_{2}$ alloy is comparable to the best hardness found for bulk Al-Si-Ni-Ce alloys produced by hot extrusion [12]. However, in our work, high microhardness values were achieved for bulk Al-alloys produced not from pure elements, but from cheaper 4xxx series Al alloy. The highest value of $T_{\text{max}}$ (340 ºC) is attributed to Al$_{81.4}$Si$_{9.6}$Fe$_{7}$Mm$_{2}$ bulk sample made from 4xxx series alloy.

| Alloy composition | Consolidation temperature [ºC] | Hardness HV [1kG] | $T_{\text{max}}$ [ºC] | Grain size [nm] |
|-------------------|--------------------------------|-------------------|----------------------|----------------|
| Al$_{73}$Si$_{19}$Ni$_{7}$Mm$_{1}$ | 250 | 281 | 130 | 10-30 |
| Al$_{72}$Si$_{19}$Ni$_{7}$Mm$_{2}$ | 250 | 314 | 135 | 10-30 |
| Al$_{78}$Si$_{13}$Ni$_{7}$Mm$_{2}$ | 300 | 297 | 245 | 10-30 |
| Al$_{79.4}$Si$_{11.6}$Ni$_{7}$Mm$_{2}$ | 370 | 243 | 255 | 10-30 |
| Al$_{81}$Si$_{10}$Ni$_{7}$Mm$_{2}$ | 320 | 317 | 255 | 30-50 |
| Al$_{80}$Si$_{9.6}$Ni$_{7}$Mm$_{2}$ ($\ldots$)1.4 | 400 | 329 | 270 | 10-30 |
| Al$_{80}$Si$_{9.6}$Fe$_{4}$Ni$_{3}$Mm$_{2}$ ($\ldots$)1.4 | 400 | 330 | 290 | 10-30 |
| Al$_{80}$Si$_{9.6}$Fe$_{7}$Mm$_{2}$ ($\ldots$)1.4 | 400 | 325 | 340 | 10-30 |
| Crystalline 4xxx series alloy | - | 60 | - | - |

3.3. Bulk nanocrystalline Al-Fe and ternary or quaternary Al-Fe-(Ti, Si, Ni, Mg, B) alloys

The XRD patterns of mechanically alloyed Al-Fe powders before and after consolidation are shown in figure 6. One can see that the MA process yielded three kinds of structures: (i) for the alloys containing less than 70% Al, a nanocrystalline supersaturated Fe(Al) solid solution, (ii) for the Al content 70-80%, nanocrystalline Al$_5$Fe$_2$ intermetallic (at least partially ordered), (iii) for the Al content of 83% and 85%, amorphous alloys. Comparing the XRD patterns of bulk samples with those of the powders before hot-pressing, one can notice that phase changes in nanocrystalline alloys and crystallisation of the amorphous ones took place upon thermal stimulus during consolidation. For the group (i) the ordering of the Fe(Al) solid solution, which is the transformation into an FeAl intermetallic compound, has been observed. In the case of Al$_{65}$Fe$_{35}$ alloy, the peaks corresponding to Al$_5$Fe$_2$ phase appeared in the XRD patterns of the bulk material beside the FeAl reflections. In the group (ii), for the Al$_{80}$Fe$_{20}$ alloy, an Al$_{13}$Fe$_{2}$ phase appeared beside Al$_5$Fe$_2$. In the case of Al$_{65}$Fe$_{17}$ and Al$_{65}$Fe$_{15}$ alloys (group (iii)), the diffraction peaks in figure 6b can not be assigned to any equilibrium phase in Al-Fe system, hence products of the crystallisation under high pressure of the amorphous alloys are metastable phases. However, some of the peaks in the patterns can be indexed in cubic system and
attributed to a phase with bcc structure and unit cell parameter of 2.975 Å and 2.964 Å for the Al$_{83}$Fe$_{17}$ and Al$_{85}$Fe$_{15}$ alloy respectively. Another feature in figure 6b is that all the peaks became a little sharper than those in the patterns of the milled powders before consolidation (figure 6a). This reduction in peaks’ width is due to the increase of the mean crystallite size and the decrease of the mean lattice strain. The estimated mean crystallite sizes for the phases in the compacted samples are given in table 3.

Figure 6. XRD patterns of the Al-Fe alloys: (a) after MA, (b) after consolidation.

Figure 7 shows XRD patterns of mechanically alloyed Al-Fe-(Ti, Si, Ni, Mg, B) powders before and after consolidation. Except for Al$_{60}$Fe$_{15}$Si$_{15}$Ti$_{10}$ alloy, where nanocrystalline $\tau_2$ phase was identified, the MA process yielded amorphous alloys. All of them crystallised upon heating during consolidation, while the phase composition of the nanocrystalline alloy was unchanged.

The phases identified as crystallisation products and the estimated mean crystallite sizes (where it was reasonable) are given in table 3. The data listed in table 3 show that in the case of all the nanocrystalline powders, a very limited growth of grains took place during hot-pressing, and the nanoscale grain size has been retained after the applied consolidation, and that amorphous phases’ crystallisation products are nanocrystalline.
The nanocrystalline structure of the Al_{50}Fe_{50} alloy observed in TEM is shown in figure 8 as an example. One can see that the grain size of FeAl phase is between 10 and 35 nm, thus the mean crystallite size estimated using XRD method and observed in TEM are consistent with each other.

![Figure 8. TEM micrograph of consolidated Al_{50}Fe_{50} alloy. Dark field image was obtained using a part of the (110) FeAl diffraction ring](image)

The average values of Vickers microhardness of the consolidated samples are listed in table 3. For comparison, the microhardness of the nanocrystalline FeAl intermetallic prepared by mechanical alloying and hot forging has been found to be 680 HV0.3 [13], the microhardness of nanocrystalline FeAl alloy produced by mechanical milling of intermetallic compound followed by explosive shock wave consolidation was 683 HV0.5 [14], the Vickers microhardness of the Fe-40Al alloy with 1 wt.% of Y_2O_3 particles prepared by mechanical alloying and subsequent hot-extrusion was ~ 4.1 GPa (10 N load) (~420 HV1) [15], and in the case of the Al_{48}Y_{18}Ni_{12}Zr_{12}+3%SiC alloy, the hardness value for the sample consolidated by severe plastic torsion was 467 HV0.3 [16]. On the basis of the quoted results, we can assume that the microhardness of the Al-based alloys obtained in this work is relatively high. In table 3, it is also visible that with the increase of Al content in the alloys, their microhardness decreases, and that for the alloy containing 60% of Al, the microhardness increases with the increase of the number of elements in the alloy, which influences the phase composition of the alloys.

The density values of the bulk samples are given in table 3.

**Table 3.** Phase composition, estimated mean grain size, microhardness and density of bulk samples produced by hot-pressing of mechanically alloyed powders.

| Alloy composition | Phase composition | Mean grain size [nm] | Microhardness [HV0.2] | Density [g/cm³] |
|-------------------|-------------------|----------------------|------------------------|----------------|
| Al_{50}Fe_{50}    | FeAl              | 23                   | 1235                   | 5.54           |
| Al_{50}Fe_{15}Ti_{15}Mg_{5}B_{5} | Al_{3}Fe + ?      | 24                   | 1093                   | 3.951          |
| Al_{50}Fe_{15}Si_{15}Ti_{10}  | τ2 + ?           | 34                   | 1013                   | 3.948          |
| Al_{70}Fe_{30}    | Al_{3}Fe + FeAl   | 26 & 33              | 986                    | 4.34           |
| Al_{80}Fe_{20}    | Al_{3}Fe+ Al_{13}Fe4   | 978                  | 3.668                  |                |
| Al_{60}Fe_{20}    | FeAl              | 37                   | 972                    | 4.989          |
| Al_{60}Fe_{35}    | FeAl + Al_{13}Fe_{2} | 40 (FeAl)          | 945                    | 4.465          |
| Al_{60}Fe_{18}Ti_{13}Ni_{5} | Al_{3}Fe+ τ2     | 930                  | 4.283                  |                |
| Al_{50}Fe_{25}    | Al_{3}Fe_{2}      | 32                   | 862                    | 3.988          |
| Al_{80}Fe_{20}Ge_{6} | bcc              | 742                  | 3.817                  |                |
| Al_{80}Fe_{14}B_{6} | bcc              | 38                   | 737                    | 3.578          |
| Al_{80}Fe_{17}    | bcc              | 36                   | 630                    | 3.604          |
| Al_{80}Fe_{15}    | bcc + ?          | 34                   | 613                    | 3.416          |

4. Conclusions
In this study, several ways of bulk nanocrystalline Al-based alloys production by high-pressure compaction were explored. The effect of chemical composition and different compaction parameters...
on the characterisation and properties of the final bulk samples were studied. Several conclusions can be established:

(i) in the case of bulk Al-Mm-Ni-(Fe,Co) alloys obtained starting from ribbons:
- the best compacted samples are those compacted at high temperature,
- pressure affects the quality of compaction and the microhardness of samples pressed at room temperature,
- crystallisation temperature increases with the increase of compacting pressure,
- microhardness increases as the crystalline volume fraction of $\alpha$-Al phase increases,
- maximum microhardness was achieved in the sample compacted at 275 °C and 7.7 GPa (which results in an bulk amorphous material) and subsequently annealed for 20 min at 235 °C (540HV);

(ii) in the case of bulk Al-Si-(Ni,Fe)-Mm alloys obtained starting from ribbons:
- the hardness of bulk nanocrystalline samples achieved values five times higher than that of commercial 4xxx series Al alloy,
- fracture surface of bulk nanocrystalline alloys is similar to that of brittle alloys,
- it is possible to recycle commercial 4xxx series Al alloys into high-strength nanocrystalline materials;

(iii) in the case of bulk Al-Fe Al-Fe-(Ti, Si, Ni, Mg, B) alloys obtained starting from mechanically alloyed powders:
- consolidation of nanocrystalline powders under the pressure of 7.7 GPa at 1000 °C causes limited growth of grains in the material,
- consolidation of amorphous powders under the pressure of 7.7 GPa at 1000 °C causes crystallisation into nanocrystalline phases,
- the quality of compaction preserving nanocrystalline structure as well as of the compaction yielding nanocrystalline structure from the amorphous one is satisfactory and the products’ microhardness is relatively high.

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