Tuning the microstructure and mechanical properties of Al-based amorphous/crystalline composites by addition of Pd

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The microstructure and mechanical properties of Al86Ni6Y6Co2Pd x (x = 0, 0.5 and 1) rods, with a 1 mm diameter, have been investigated. The Al86Ni6Y6Co2 alloy consists of ductile fcc-Al and hard Al3Ni intermetallic phases embedded in the matrix. Replacing Y by Pd in the Al86Ni6Y6Co2 alloy promotes precipitation of additional crystalline phases, producing composite materials with tuneable mechanical behaviour. Compared to conventional Al-based crystalline alloys, the Al86Ni6Y6Co2 rod is relatively hard (395 HV) but exhibits a brittle behaviour when compressed at room temperature. The compressive plasticity increases to 1.5% in the Al86Ni6Y6Co2Pd0.5 alloy but the hardness decreases in this case. The plasticity, hardness and elastic properties of these alloys depend on the amount and intrinsic properties of the different constituent phases, as well as on the resulting microstructure obtained after the casting process (i.e., the size and shape of the precipitates).

1. Introduction

Al-based metallic glasses represent an important family of amorphous metals since they combine unique mechanical properties, such as high specific strength, with good corrosion resistance and rather low density, thus making them suitable candidates for lightweight applications (e.g., automotive or aerospace industries). Fully amorphous (Al–Fe, Co–B) ribbons exhibiting a brittle behaviour were first successfully fabricated in 1981 by melt-spinning [1]. Alloys of the Al–Ni–Y system showing not only good ductility (180° in bending) but also reasonable strength were obtained several years later [2,3]. However, the use of Al-based alloys to fabricate bulk metallic glasses (BMGs) (>1 mm diameter) is so far rather scarce due to their low glass-forming ability (GFA). The addition of proper concentration of Co to the Al–Ni–Y system was found to improve the glass-forming ability and further increase the mechanical strength with no detriment of the bend ductility [4]. A maximum critical glass-forming thickness of 850 μm was attained with the Al86Ni6Y6Co2 alloy by wedge casting [5]. In Al86Y2Ni10–xMx (M = Mn, Fe or Co) ribbons with certain concentrations of Mn, Fe or Co [6], precipitation of α-Al particles was detected. These particles increase the tensile strength and hardness of the alloys, as compared to the monolithic amorphous specimens. The addition of Pd to Al–Ni–Y–Co alloys further promotes the formation of highly dispersed primary α-Al nanoparticles (of about 5 nm) in the glassy matrix of the as-spun ribbons [7,8].

In this article, the influence of Pd addition on the microstructure and mechanical behaviour of bulk Al86Ni6Y6Co2 samples is studied. By adjusting the Pd content the volume fraction of crystalline phases can be tuned to optimize the compressive plasticity and strength of the investigated alloys.

2. Experimental

Ingots were prepared by arc-melting mixtures of the high-purity elements (>99.9 at.%) in an argon atmosphere purified by Ti-gettering. Each alloy was re-melted at least three times to attain good chemical homogeneity. Rod samples with a diameter of 1 mm were obtained by remelting the master alloy in a quartz tube and subsequent injection into a copper mold in an inert gas atmosphere. The cross-sections of the as-cast rods were structurally characterized by X-ray diffraction (XRD) in a Rigaku D/max 2400 diffractometer with monochromated Cu Kα radiation. The microstructure of the three specimens and the morphology of the indents were observed using an optical microscope (OM) and...
a scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analysis.

The elastic properties were evaluated by means of ultrasonic measurements (pulse-echo overlap technique), using ultrasonic pulser-receiver model 5072PR and oscilloscope model TDS 2022B Textronix, along with density assessment (Archimedes’ method). The standard formalism for isotropic solids, based on Aleksandrov’s method, was employed [9]. The total error in the measurement of the elastic constants is about 5% which include the error of the acoustic measurements (error of the oscilloscope delay time), the error of the sample thickness measurements (normally ± 1 or 2 microns) and the error in density measurements (±0.02 g/cc). To evaluate the mechanical properties, cylindrical specimens were cut with an aspect ratio of 2:1 and uniaxially compressed at room temperature until fracture (using an Shimadzu testing machine with 50 kN maximum load), according to the American Society for Testing and Materials (ASTM) standards (E9-09), at an initial loading rate of 5 × 10⁻⁴ s⁻¹. To shed light on the deformation mechanisms, in-situ tensile tests on a ribbon with composition Al₈₆Ni₆Y₅.₅Co₂Pd₀.₅ and Al₈₆Ni₆Y₅Co₂Pd₁ rods. The microstructure of the surroundings on the EDX signal. This result is consistent with previous observations. Fig. 2 reveals that the XRD technique has a quantification limit and that the composition of the alloys containing Pd is close to that of Al₈₆Ni₆Y₅Co₂ a small volume fraction of amorphous phase, especially close to the outer surface, could be expected. However, as these alloys have a gradient microstructure it is difficult to get this information of the samples from TEM observations.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD patterns of the 1 mm diameter Al₈₆Ni₆Y₆Co₂Pdₓ (x = 0, 0.5 and 1) rods. For the alloy without Pd high intensity XRD peaks associated to the face-centered cubic (fcc) Al₁₃Ni (a = 0.409496 nm) phase along with small peaks of primitive orthorhombic Al₃Y (a = 0.6622 nm, b = 0.5473 nm, c = 0.4682 nm) phase are detected. These peaks are superimposed on a broad halo suggesting the presence of an amorphous or nanocrystalline matrix. For the Al₈₆Ni₆Y₅.₅Co₂Pd₀.₅ and Al₈₆Ni₆Y₅Co₂Pd₁ alloys additional peaks of primitive monoclinic mP22 Al₈₆Co₂ (a = 0.62163 nm, b = 0.62883 nm, c = 0.85587 nm), primitive rhombohedral hR₃₆ Al₈₆Y (a = b = 0.6221 nm, c = 2.1160 nm) phases are detected. The relative intensity of the XRD peaks associated to fcc-Al solid solution (α-Al) has been calculated comparing the peaks of maximum intensity of the different phases. For the alloy containing 0.5% Pd the intensity of the Al₃Ni (111) reflection relative to the intensity of the Al₃Ni (211) reflection (at 35.55°) and to the intensity of the Al₃Y (024) reflection (at 37.45°) is about 4.6 and 3.3, respectively. These values are higher than those of the alloy containing 1% Pd as the intensity of α-Al (111) reflection relative to the intensity of the Al₃Ni (211) reflection (at 35.55°) is 2.5 and to the intensity of the Al₈₆Co₂ (310) reflection (at 46.24°) is 2.3. These results indicate that the volume fraction of the α-Al phase compared with that of the intermetallic phases is the largest for the alloy containing 0.5% Pd. The addition of Pd decreases the glass-forming ability (GFA) of the alloys as can be deduced from the lack of broad halo in the XRD scan, which is consistent with previous observations [8]. Considering that the XRD technique has a quantification limit and that the composition of the alloys containing Pd is close to that of Al₈₆Ni₆Y₅Co₂ a small volume fraction of amorphous phase, especially close to the outer surface, could be expected. However, as these alloys have a gradient microstructure it is difficult to get this information of the samples from TEM observations.

Fig. 2 shows the optical images corresponding to the cross-section of the 1 mm diameter as-cast Al₈₆Ni₆Y₆Co₂, Al₈₆Ni₆Y₅.₅Co₂Pd₀.₅ and Al₈₆Ni₆Y₅Co₂Pd₁ rods. The microstructure of the Al₈₆Ni₆Y₅Co₂ rod (Fig. 2a) consists of two crystalline phases with dendritic shape dispersed heterogeneously in the matrix. The magnified image of the region marked with a red rectangle in Fig. 2a is shown in Fig. 2b. Two different phases can be identified from their different tonality. According to the EDX measurements the composition of the brighter phase is Al₅₅Ni₇Y₅Co₀.₅ which is richer in Al than the nominal composition of the alloy so it might be associated to α-Al phase. Despite it is also detected small amounts of other elements (e.g. Ni, Y, Co) it may be due to the influence of the surroundings on the EDX signal. This result is consistent with a previous report where almost pure α-Al phase was detected in the Al–Ni–Y–Co system [7,12]. In fact, the angular positions of the peaks in the XRD scans match very well with those tabulated for the α-Al phase. Additionally, a dark phase with dendritic shape was observed which, according to the EDX analysis, shows the composition Al₃Ni₃Y₇Y₁Co₂. This phase can thus be associated to the intermetallic Al₃Ni with Y and Co in solid solution. Fig. 2b reveals that most of the dendrites whose size is smaller than about 7 μm (indicated by small white arrows) are constituted by a brighter phase in their core suggesting that the Al₃Ni phase grows from the α-Al phase. It appears that when the Al₃Ni dendrites achieve a critical size from 7 to 13 μm (large white arrow of Fig. 2b)
the \( \alpha \)-Al phase grows enough to reach the Al\(_3\)Ni/matrix interphase. Moreover, once the Al\(_3\)Ni phase attains a spanning length of 55 \( \mu \)m the growth of the \( \alpha \)-Al phase is so large that it can encapsulate the Al\(_3\)Ni dendrite (large black arrow). This observation suggests that after the Al\(_3\)Ni phase nucleates from the primary \( \alpha \)-Al phase, both phases grow simultaneously (Fig. 2b) so it appears that it corresponds to a eutectic-like reaction [13] which is consistent with the eutectic microstructure of \( \alpha \)-Al and Al\(_3\)Ni reported by Watkins et al. [14]. For the Al\(_{86}\)Ni\(_6\)Y\(_{5.5}\)Co\(_2\)Pd\(_{0.5}\) (Fig. 2c) and Al\(_{86}\)Ni\(_6\)Y\(_5\)Co\(_2\)Pd\(_1\) (Fig. 2d) rods two different regions with different microstructures can be distinguished depending on the distance from the outer surface. The difference is particularly remarkable for the alloy containing 0.5\% Pd (Fig. 2c) for which a well defined bright outer region with a thickness of about 47 \( \mu \)m is observed. Region 1 is rather featureless and probably corresponds to an amorphous or a nanocrystalline phase. Conversely, region 2 (in which the cooling rate was slower) is constituted by several crystalline phases. These results indicate that the addition of Pd decreases the GFA of the Al–Ni–Y–Co system, as was previously reported [7,8]. The microstructure of the inner part (region 2) of the Al\(_{86}\)Ni\(_6\)Y\(_5\)Co\(_2\)Pd\(_{0.5}\) rod is shown in more detail in the SEM image of Fig. 3. According to the EDX analysis the brighter and elongated phase corresponds to Al\(_3\)Ni with small contents of Y and Co in solid solution, similar to those
detected in the same phase of the alloy without Pd. This phase is embedded in a matrix mainly constituted by α-Al phase as well as by other scarce phases whose composition could not be accurately assessed by EDX owing to their small size. Analogous microstructure was observed in the inner part of the Al$_{86}$Ni$_6$Y$_5$Co$_2$Pd$_1$ rods.

3.2. Mechanical behaviour

3.2.1. Macroscopic compression tests

Fig. 4 shows the uniaxial compressive stress—plastic strain curves for the Al$_{86}$Ni$_6$Y$_{x}$Co$_2$Pd$_1$$_x$ (x = 0, 0.5 and 1) rods. Due to the small dimensions of the samples no strain gage could be used to measure the Young’s modulus quantitatively, therefore the results shown in Fig. 4 are affected by the compliance of the testing machine [15]. However, it is clear that the Young’s modulus and yield stress decrease when 0.5 at.% Pd is added to the Al–Ni–Y–Co system and increase with further addition of Pd (e.g., 1 at.%). The evolution of the compressive plasticity with the Pd content is the opposite: it increases to a maximum of 1.5% for the alloy containing 0.5 at. % Pd and then decreases to 0.8% when 1 at.% Pd is added. The difference in mechanical behaviour of the three alloys, despite their similar composition, can be attributed to the microstructure which changes dramatically with small Pd additions.

The mechanical properties of a composite can be roughly described by the rule of mixtures. In isostrain conditions $P_{c, p} = \sum(V_i P_i)$ [16] where $P_i$ is the property of the phase $i$ while $V_i$ is its volume phase percentage. Hence, the larger the volume fraction of the softer phase with respect to the brittle phase, the closer will be the mechanical properties of the composite to that of the soft phase. α-Al phase is very soft (17 HV) [17] while the intermetallic phases are widely known to be hard and brittle [18]. For example, the hardness of Al$_3$Ni is about 714–786 HV [19] and for Pd$_x$Al$_{1-x}$ it is about 670 HV [20]. The Young’s modulus of α-Al phase is 70 GPa [17] which is also lower than that of intermetallic compounds (e.g. 140 GPa for Al$_3$Ni [21]). Thus, the volume fraction of ductile α-Al phase, as compared to the volume fraction of the brittle intermetallic phases, is likely to be crucial in the compressive plasticity behaviour. Indeed, this may explain why among the two crystalline samples, the one with $x = 1$ (containing larger percentages of intermetallic phases) exhibits larger Young’s modulus and higher yield stress than the sample with $x = 0.5$. It is also noteworthy that the compressive fracture of the Al$_{86}$Ni$_6$Y$_{0.5}$Co$_2$Pd$_{0.5}$ rod occurs at an angle of around 40° with respect to the loading axis instead of at 45° (as it would occur for polycrystalline metals following the Von Mises or Tresca yield criteria). This indicates that the alloy is governed by a pressure-dependent yield behaviour. This result is consistent with previous works which showed that the flow stress in aluminum alloys is pressure-sensitive [22] and was associated to the effect of pressure on the motion of dislocations.

To gain further understanding on the influence of the α-Al phase on the mechanical behaviour of the Al–Ni–Y–Co–Pd system, a ribbon with the composition Al$_{86}$Ni$_6$Y$_4$Co$_2$Pd$_2$ was investigated by in-situ tensile tests performed inside a TEM. To promote the formation of the α-Al phase, the ribbon was previously annealed at 553 K. Note that this specific composition was selected because the temperature of the first transformation (associated with the formation and/or growth of the α-Al phase) decreases with the increase in Pd content; moreover, this annealing treatment results in the formation of large amounts of α-Al nanocrystallites embedded in the amorphous matrix (see Fig. 5). A hole was made at the center of the ribbon and the specimen was then tensile tested in-situ in the TEM (Fig. 5) to generate a stress concentration that could favour the formation of cracks which would eventually interact with the α-Al phase. The SAED pattern of the upper inset shows a diffuse ring and small spots, confirming the annealing-induced formation of small α-Al nanocrystals embedded in an amorphous matrix. According to the XRD patterns shown in the lower inset, all the nanocrystals correspond only to α-Al. It should be noted that the processing conditions to obtain the α-Al phase are

![Fig. 4. Engineering stress—plastic strain curves for 1 mm diameter Al$_{86}$Ni$_6$Y$_{x}$Co$_2$Pd$_1$$_x$ (x = 0, 0.5 and 1) rods. Note that, for the sake of clarity, the stress—strain curves were shifted along the strain axis.](image)

![Fig. 5. TEM bright-field image of the Al$_{86}$Ni$_6$Y$_4$Co$_2$Pd$_2$ ribbon annealed (553 K) and then tensile tested in-situ showing the propagation of a crack. Upper inset: SAED pattern. Lower inset: XRD patterns in the as-spun and annealed (553 K) condition.](image)
different in the bulk sample (quenching) and the ribbon (quenching and annealing). Remarkably, the crack tip follows a rather straight path with only a small deviation which suggests that the interaction of the crack with the nanocrystals is small probably due to the small size of the α-Al nanoparticles. This is consistent with the observation of Lund et al. [23] who suggested that to achieve a strong interaction between shear bands and the crystalline phase, the crystals should be larger than the shear band width, which is typically about 10–15 nm [24].

The lack of interactions between the shear bands and the amorphous/nanocrystalline matrix of the Al86Ni6Y6Co2 alloy can be inferred from the rather semi-circular shape of the bands (Fig. 6a), which are very similar to those observed in monolithic metallic glasses [25]. As the size of the Al phase increases, a dendritic shape develops (samples Al86Ni6Y5.5Co2Pd0.5 and Al86Ni6Y5Co2Pd1), then the length of the interfaces increases favouring the interaction with the bands. These results evidence that the deformation behaviour of the dual nanocrystal-amorphous phase alloy not only depends on the intrinsic properties of the constituent phases but also on morphological and microstructural features, such as the size and shape of the grains composing the alloy.

3.2.2. Vickers microhardness

Table 1 shows the results of the Vickers microhardness measured in the three alloys, Al86Ni6Y6Co2, Al86Ni6Y5.5Co2Pd0.5 and Al86Ni6Y5Co2Pd1. A maximum hardness of 395 ± 21 HV is measured in the matrix of the Al86Ni6Y6Co2 alloy which is higher than the hardness of the outer regions of the Al86Ni6Y5.5Co2Pd0.5 (285 ± 5 HV) and Al86Ni6Y5Co2Pd1 (281 ± 4 HV) rods. It is known that, due to the lack of dislocations and grain boundaries, metallic glasses are typically harder than the corresponding crystalline alloys with analogous compositions. Hence, these trends in HV values can be attributed to the microstructure which tends to get closer to the fully crystalline state with the increase in Pd content. However, comparing the hardness values of the inner parts of the rods it is observed that the Al86Ni6Y5.5Co2Pd0.5 rod is softer (166 ± 5 HV) than the Al86Ni6Y5Co2Pd1 rod (180 ± 7 HV), probably because the relative volume fraction of soft α-Al phase (17 HV) is larger in the alloy containing 0.5% Pd.

To better understand how different bands interact with the crystalline phases, the band structure activity around the indents has been investigated. This study was performed on the Al86Ni6Y6Co2 alloy, since the alloy microstructure is simpler in this case. Fig. 6a shows an optical image of an indent performed on the amorphous/nanocrystalline matrix of the aforementioned alloy.

<table>
<thead>
<tr>
<th>Al86Ni6Y6Co2</th>
<th>Al86Ni6Y5.5Co2Pd0.5</th>
<th>Al86Ni6Y5Co2Pd1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Inner region</td>
<td>Outer region</td>
</tr>
<tr>
<td>H (HV)</td>
<td>395 ± 21</td>
<td>166 ± 5</td>
</tr>
<tr>
<td></td>
<td>285 ± 5</td>
<td>180 ± 7</td>
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<tr>
<td></td>
<td>281 ± 4</td>
<td>281 ± 4</td>
</tr>
</tbody>
</table>

Table 1: Vickers microhardness (HV) for the three alloy compositions.

![Fig. 6](https://example.com/fig6.png)

**Fig. 6.** Optical images of the indentation in the Al86Ni6Y6Co2 alloy. (a) Formation of shear bands in the amorphous/nanocrystalline matrix with a slip-step distance \(d = 1.7 \mu m\) (100 g). Propagation of slip bands (b) parallel and (c) perpendicular to the crystalline Al3Ni fingers (300 g), (d) SEM image corresponding to a more general view of Fig. 6b. The continuous arrows indicate the direction of propagation of slip bands. The dashed arrows indicate the direction of propagation of the Al3Ni fingers.
with a load of 100 g. A few shear bands are found to emanate from the edge of the indent at an angle a bit lower than 45° (angle between the shear band tangent and the normal to the edge of the indent) suggesting that the material obeys the Mohr-Coulomb yield criterion, which implies that plastic yielding is sensitive to pressure [26]. This is, to a certain extent, expected because many metallic glasses and composite materials are known to follow a pressure-dependent yielding criterion [27,28]. Fig. 6a also shows that the density of shear bands generated by the indent is very small and the distance between slip-steps is large (d = 1.7 μm) which is consistent with the brittleness of the Al89Ni5Y5Co1 alloy. This result confirms that the lack of plasticity from the compression test does not stem from the presence of flaws but it is an intrinsic property of the alloy. Fig. 6b–d show the interaction between slip bands and the crystalline phases of the Al89Ni5Y5Co1 alloy. One should note that the darkest phase in the optical image (Al3Ni) is seen as the lightest one in the SEM image and vice-versa for the α-Al phase. The observations reveal that when slip bands collide with the crystalline phases (α-Al and Al3Ni phases) they stop mainly at the α-Al/Al3Ni interfaces. Despite cracks and bands tend to be attracted towards regions that are in tension [29], this is not expected to be the case for the α-Al/Al3Ni interfaces as the thermal expansion coefficient of aluminum (23.1 × 10⁻⁶ K⁻¹) is only about 1.4 times larger than that of Al3Ni [30]. For this reason, the detection of slip bands at the α-Al/Al3Ni interfaces could be attributed to the large difference in mechanical behaviour between the two phases. Indeed, the difference in hardness between the intermetallic Al3Ni (714–786 HV) [21] and the α-Al (17 HV) phase is larger than between the matrix of the Al89Ni5Y5Co1 alloy (395 ± 21 HV) and any of both phases. For this reason during compression there is maximum strain mismatch at the α-Al/Al3Ni interfaces which accounts for the detection of many slip bands in this region. Their propagation is strongly affected by the crystalline phase. Indeed, they sometimes spread parallel to the crystalline interfaces instead of simply emanating from the corner of the indent (Fig. 6c). For this reason most bands do not exhibit the typical semi-circular morphology [26] but they have irregular shapes. Fig. 6b and c show that the angle at which the bands emanate from the edge of the indent is variable but in all cases very far from 45° (contrary to what occurs in the matrix), which further confirms the strong interaction between slip bands and the α-Al/Al3Ni interface. Note for example that while from the edge of the indent in Fig. 6c that is in contact with the crystalline phases the bands emanate at about 22°, the angle tends to approach 45° on the other edge of the indent and the bands appear to vanish as they approach the corner of the Vickers indent where the microstructure is amorphous or nanocrystalline (i.e., the dendrite in this case seems to promote slip band activity). These results clearly reveal the strong influence that the crystalline phases have on the propagation of slip bands. It is also interesting that despite the presence of the brittle Al3Ni phase no cracks at the corner of the indent are formed. The SEM image shown in Fig. 6d corresponds to the same indentation as that in Fig. 6b; however, in this more general view additional details can be detected. Note for example that there are some areas close to the dendrites constituted by dark and bright spots arranged alternatively forming a microstructure that appears to be eutectic (indicated by white arrows). According to the EDX analysis the composition of the dark spots is Al89Ni5Y5Co5, hence slightly richer in Al than the nominal composition of the alloy, thus probably corresponding to α-Al phase. The microstructure of these regions is slightly elongated in the radial direction towards the center of the Al3Ni dendrite suggesting the existence of directional solidification. A similar pattern but constituted by spots that are even more elongated is marked by black arrows in Fig. 6d suggesting that the solidification in that part of the rod is more directional.

The extent of the plastic zone size of the indent of Fig. 6a can be predicted from the expanding spherical cavity model [31] using the following equation [32]:

$$\delta = \frac{3P}{2\pi\sigma_y}$$

(1)

where δ is the plastic zone size (distance between the center of the indent and the last band), P is the applied load and σ_y the yield stress. This expression was experimentally validated for polycrystalline aluminum [32].

The hardness H and yield stress σ_y of metals can be related through the following relationship [33]:

$$\sigma_y = \frac{H}{C}$$

(2)

where C is the constant factor that depends on the type of specimen and indenter and on other experimental parameters and is usually around 3 for metallic alloys. Eqs. (1) and (2) allow estimating the plastic zone size from hardness measurements. For a Vickers hardness of 395 HV (Table 1) and C = 3 then σ_y is 1.296 GPa, which is close to the fracture strength obtained from compression tests (Fig. 4). For a load P of 100 g, Eq. (2) yields a value of δ around 19 μm, which is about 40% larger than the experimental value (13 μm) (Fig. 6a). Similar differences between the experimental and theoretical value were previously reported for a Pd-based BMG by Ramamurty et al. [26]. However, the size of the plastic zone can vary widely when the band structure interact with the crystalline phases. When slip bands propagate parallel to the direction of the finger of the α-Al/Al3Ni dendrite (see discontinuous and continuous black arrows in Fig. 6b and d) the interaction between the slip bands and the crystalline phase is small. Conversely, when slip bands propagate perpendicular to the finger of the α-Al/Al3Ni dendrite (see arrows of Fig. 6c), the interaction is larger so the distance the slip bands can travel is shorter. In both cases the load is the same (300 g), resulting in a theoretical plastic zone size of δ = 28 μm, which is smaller than 36.10 ± 0.78 μm estimated from Fig. 6b. These observations confirm that the strain misfit of the α-Al/Al3Ni fingers favours the propagation of the slip bands along the interfaces.

### 3.2.3. Acoustic and nanoindentation investigation

To better characterize the mechanical behaviour of the samples, acoustic and nanoindentation measurements were performed. The former are known to provide more accurate values of the Young’s modulus than macroscopic compression tests. Listed in Table 2 are the density (ρ), shear modulus (G) and bulk modulus (B) values of the three alloys evaluated by acoustic measurements. From the density it has been calculated that the specific strength ranges from 3.69 × 10³ Nm Kg⁻¹ to 2.74 × 10³ Nm Kg⁻¹ for the alloy without Pd and with 0.5 at.% Pd, respectively. These values are very high considering that for a fully amorphous Al-based BMG the specific strength reported is 3.34 × 10³ Nm Kg⁻¹ [5]. The values of Young’s modulus (E) and Poisson’s ratio (ν), estimated from B and G using the relationships $B = E/(3(1-2\nu))$ and $G = E/(2(1+\nu))$, are also shown in Table 2. The minimum values of the elastic constants (G, B, E, ν).

### Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Al86Ni6Y6Co2</th>
<th>Al86Ni6Y5.5Co2Pd0.5</th>
<th>Al86Ni6Y5Co2Pd1</th>
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<td>ρ (g/cm³)</td>
<td>3.362</td>
<td>3.401</td>
<td>3.395</td>
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<tr>
<td>G (GPa)</td>
<td>36.1</td>
<td>32.0</td>
<td>32.2</td>
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<tr>
<td>B (GPa)</td>
<td>100</td>
<td>90.4</td>
<td>96.7</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>96</td>
<td>86</td>
<td>87</td>
</tr>
<tr>
<td>ν</td>
<td>0.34</td>
<td>0.35</td>
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and $E$) are obtained by the alloy containing 0.5% Pd and increase slightly for the alloy containing 1% Pd. It is noteworthy that this behaviour can be deduced intuitively from the rule of mixtures [16] because the relative volume fraction of the soft $\alpha$-Al phase (with $G = 26$ GPa and $B = 76$ GPa [17]) is maximum for the alloy containing 0.5 at.% Pd.

To better compare the plastic flow of the different alloys the nanoindentation technique was employed. This technique is useful because only small sample volumes are involved thus minimizing the influence of flaws or other instabilities. Fig. 7 shows the load–displacement ($P–h$) nanoindentation curves for the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{6}\text{Co}_{2}, \text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$ and $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5}\text{Co}_{2}\text{Pd}_{1}$ alloys with a large applied load of 300 mN. This load is high enough to get information from all the phases composing the alloy microstructure and hence it provides a representative average value. The three curves are very smooth and no pop-ins are detected despite the formation of band structure in the vicinity of the indents could be detected by SEM. This is mainly due to the lack of resolution of the nanoindenter for this large value of applied load. The mechanical properties that were evaluated from nanoindentation are the following: hardness ($H$), reduced elastic modulus ($E_r$), ratio of plastic energy vs total energy ($U_{\text{plastic}}/U_{\text{total}}$) and maximum indentation displacement ($h_{\text{max}}$). The values of these mechanical properties for the three compositions are shown in Table 3. The hardness $H$ is calculated from the following expression:

$$H = \frac{P_{\text{max}}}{A}$$

where $P_{\text{max}}$ is the maximum load and $A$ is the projected area of the indent. The reduced Young’s modulus is related to the specimen’s Young’s modulus and Poisson’s ratio as follows:

$$1 \frac{E}{E_r} = 1 - \frac{\nu^2}{E} + 1 - \frac{\nu^2}{E_i}$$

where $E$ and $\nu$ are the Young’s modulus and Poisson’s ratio of the specimen, respectively, and $E_i$ and $\nu_i$ are the Young’s modulus (1140 GPa) and Poisson’s ratio (0.07) of the diamond tip. The nanoindentation results reveal that the ratio $U_{\text{plastic}}/U_{\text{total}}$ and the displacement into the sample $h_{\text{max}}$ are maximum for the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$ alloy whereas the reduced elastic modulus $E_r$ is minimum for this alloy (in agreement with the results from compression tests and acoustic measurements). Table 3 also shows that the softest alloy is the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$. Indeed, a maximum hardness of 5.5 GPa is attained in the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{2}\text{Co}_{2}$ alloy (probably because of its mainly amorphous character) and the hardness value decreases sharply to 2.5 GPa with the addition of 0.5 at.% Pd. Further increase of Pd (up to 1 at.%) increases the hardness to 3 GPa. Note that the hardness obtained with the nanoindenter (Berkovich tip) is slightly larger than that obtained with the microindenter. This can be attributed to the so-called indentation size effect (ISE), i.e., a decrease of $H$ with $h_{\text{max}}$ since the load (and thus the indentation depth) is larger for the Vickers measurements. According to Nix and Gao [34] the ISE originates from strain gradient effects related to the need to create geometrically necessary dislocations in order to accommodate the indentation plastic strains in exceedingly small indentations and the density of these dislocations is proportional to the inverse indentation depth. The three techniques employed in this work (compression tests, acoustic measurements and nanoindentation) agree that the lowest elastic moduli and maximum plasticity are attained in the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$ alloy. Indeed, the $U_{\text{plastic}}/U_{\text{total}}$ ratio is larger for this alloy, corroborating its larger ability to store plastic energy (and show plasticity) during deformation. Furthermore, the mechanical properties of the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{2}\text{Co}_{2}$ alloy are distinctly different than those measured in samples containing Pd mainly due to its very different microstructure, particularly because of the existence of the amorphous matrix. The fact that Vickers indentations performed on the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{2}\text{Co}_{2}$ alloy (Fig. 6) create a band structure only visible on the side of the indent where the crystalline phases are situated suggests that the fully plastic regime has not been reached in the matrix but only on the Al–Al3Ni crystalline phases. This observation is consistent with the lower $E/\sigma_y$ value [35] of the amorphous regions compared to the crystalline counterparts. Assuming that the $E$ and $\sigma_y$ of the matrix roughly correspond to those of the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{2}\text{Co}_{2}$ alloy (96 and 1.836 GPa respectively — see Table 2 and Fig. 4) and those of the Al–Al3Ni crystalline phases correspond to those of the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$ alloy (86 and 0.83 GPa respectively) then $E/\sigma_y$ would be 52 for the matrix and 104 for the Al–Al3Ni crystalline phases. These values are close to the $E/\sigma_y$ values reported for bulk metallic glasses (about 50) and for crystalline metals (about 120) [36]. A large contribution to the low $E/\sigma_y$ ratio of the crystalline phases is the large volume fraction of almost pure $\alpha$-Al phase which has a yield stress of only around 0.11 GPa. The constraint factor has been calculated for the three alloys also considering the values of $H$ obtained by nanoindentation. From the $H$ and $\sigma_y$ values obtained from compression tests (700 MPa and 800 MPa for the alloys containing 0.5 at.% and 1 at.% Pd) a C value slightly higher than 3 is obtained. This result also suggests that the alloys are pressure-sensitive, which is consistent with the fracture angle of 40° (Fig. 4) of the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{5.5}\text{Co}_{2}\text{Pd}_{0.5}$ alloy. Note that for the $\text{Al}_{86}\text{Ni}_{6}\text{Y}_{2}\text{Co}_{2}$ alloy, using $C = 3$ and the hardness obtained by nanoindentation ($H = 5500$ MPa), the calculated $C$ would be about 1800 MPa (Eq. (2)). From Eq. (1), a load of 100 g and $\sigma_y = 1800$ MPa leads to a plastic zone size $\delta$ of 16 $\mu$m, thus rather close to the 13 $\mu$m obtained experimentally.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$H$ (GPa)</th>
<th>$E_r$ (GPa)</th>
<th>$U_{\text{plastic}}/U_{\text{total}}$</th>
<th>$h_{\text{max}}$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al86Ni6Y6Co2</td>
<td>5.5</td>
<td>98</td>
<td>0.66</td>
<td>1.7</td>
</tr>
<tr>
<td>Al86Ni6Y5.5Co2Pd0.5</td>
<td>2.5</td>
<td>88</td>
<td>0.78</td>
<td>2.3</td>
</tr>
<tr>
<td>Al86Ni6Y5Co2Pd1</td>
<td>3</td>
<td>91</td>
<td>0.76</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3: Hardness ($H$), reduced elastic modulus ($E_r$), ratio $U_{\text{plastic}}/U_{\text{total}}$ and maximum indentation depth ($h_{\text{max}}$) obtained from nanoindentations for the three alloy compositions.
4. Conclusions

In conclusion, the influence of Pd addition on the microstructure and concomitant mechanical properties of bulk Al-based samples has been investigated by X-ray diffraction, optical and electron microscopies, compression tests, acoustic measurements and nanoindentation. The dramatic microstructural changes that occur with small Pd additions is responsible for the large difference in mechanical behaviour. By carefully controlling the concentration of Pd, the compressive plasticity can be enhanced by favouring the formation of ductile α-Al phase against the growth of brittle intermetallic particles. Moreover, the dendritic shape of the crystalline regions favours the initiation, arrest and multiplication of slip bands, which introduces moderate plasticity in the alloy. The obtained results indicate that yielding in these composite materials is influenced by pressure. Moreover, these alloys exhibit relatively large Young’s modulus combined with a high specific strength and are thus suitable materials for certain light-weight engineering applications.

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References