Spark plasma sintering of gas atomized Al$_{87}$Ni$_8$La$_5$ amorphous powder

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Abstract: Bulk samples were prepared by in-situ devitrification and consolidation of gas atomized Al$_{87}$Ni$_8$La$_5$ amorphous powder. Consolidation was carried out at different temperatures by spark plasma sintering, which leads to highly dense bulk specimens with a microstructure consisting of fcc aluminum together with Al$_{11}$La$_3$ and Al$_3$Ni intermetallic compounds. The consolidated powder displays a remarkably high compression stress, which depends on the sintering temperature and ranges between 900 and 1000 MPa, combined with plastic strain varying between 10 and 20 %. These results indicate that the mechanical properties of the samples can be tuned within a wide range of strength and ductility as a function of the sintering temperature used.

1. Introduction

In the last few years, considerable efforts have been devoted to the production of high-strength amorphous, partially amorphous and nanocrystalline or ultra-fine grained (UFG) Al-based alloys [1-5]. Such high-strength materials are particularly attractive for automobile and aerospace industries due to their low density, high specific strength and good wear resistance [1,2]. Among the different amorphous materials, Al-based alloys with more than 85 at.% Al have shown very high strength levels on the order of 2-3 times higher than for conventional Al-based alloys [5,6]. The mechanical properties can be further improved by the partial crystallization of Al-based amorphous precursors to create a homogeneous distribution of nanoscale fcc Al or nanosized intermetallic compounds within a residual amorphous matrix [7-11]. Due to their limited glass-forming ability, Al-based amorphous alloys are generally produced in form of ribbons, flakes or powder [2]. Such a small size limits their engineering applications. To overcome this limitation, powder metallurgical methods, such as gas atomization followed by powder consolidation, have been employed to create bulk Al-based samples with the desired microstructure [4].

Among the different consolidation techniques, spark plasma sintering (SPS) has been recognized as a suitable consolidation technique to obtain highly dense samples with desired microstructure and properties [12,13]. SPS is a relatively new technique which combines conventional hot pressing with sintering through a low voltage pulsed DC current which flows through the punch-die-sample-assembly resulting in an optimum thermal and electrolytic diffusion between the powder particles.
The SPS process does not require long sintering time and high sintering temperatures to obtain fully dense compacts, as needed for conventional sintering [13-17]. In the present work SPS was used to produce bulk nanocrystalline/UFG samples from gas atomized amorphous powder with composition Al$_{87}$Ni$_{8}$La$_{5}$. The simultaneous consolidation and devitrification of the amorphous precursor leads to highly dense specimens with promising mechanical properties that strongly depend on the sintering temperature.

2. Experimental
Gas atomized powder (GAP) with nominal composition Al$_{87}$Ni$_{8}$La$_{5}$ (purity > 99.9 wt. %) was used as starting material. The microstructure of the samples was studied by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (Co-K$_{\alpha}$ radiation), by scanning electron microscopy (SEM) using a JEOL JSM 6400 microscope, by optical microscopy (OM) with a Zeiss Axioskop 40 and by transmission electron microscopy (TEM) using a FEI Tecnai F30 microscope operated in scanning TEM mode at 300kV. The thermal stability of the powder was investigated by differential scanning calorimetry (DSC) with a Perkin-Elmer Diamond calorimeter at 40 K/min heating rate under a continuous flow of purified argon. Cylindrical specimens with 10 mm diameter and 8 – 10 mm length were produced by consolidation of the gas atomized powder under high vacuum by spark plasma sintering at different temperatures (573, 643 and 713 K) with a heating rate of 10 K/min and an applied pressure of 500 MPa for 3 minutes. The density of the consolidated samples was measured using the Archimedes principle and was found to be about 98 % of the theoretical density. The microhardness was measured by using a HMV Shimadzu Vickers hardness testing machine with a load of 15 g with 10 s dwell time. Parallelepiped specimens with 3.5 mm x 3.5 mm area and 7 mm height were carefully prepared from the SPS samples. Room temperature compression tests were carried out using an INSTRON 8562 under quasistatic loading with a strain rate of 8x10$^{-4}$ s$^{-1}$.

3. Results and discussion
The X-ray diffraction pattern of the as-atomized Al$_{87}$Ni$_{8}$La$_{5}$ powder is shown in figure 1. The pattern displays the broad maxima typical of an amorphous phase together with few broad diffraction peaks from crystalline fcc Al and Al$_{11}$La$_3$ phases. The isochronal DSC scan of the as-atomized powder (figure 2), reveals two exothermic peaks at 457 and 620 K, respectively, corresponding to the precipitation of fcc Al from the amorphous matrix followed by the transformation of the residual glassy phase into Al$_3$Ni and Al$_{11}$La$_3$ intermetallic compounds.

The XRD patterns of the samples consolidated by SPS at different temperatures (figure 1) reveal the formation of fcc Al, Al$_3$Ni and Al$_{11}$La$_3$ phases. No traces of the amorphous phase are visible at this stage, which indicates that complete crystallization of the powder took place during consolidation. In addition, the diffraction peaks of fcc Al become sharper with increasing sintering temperature, suggesting that the grain size of the phases increases when increasing the sintering temperature during consolidation.
SPS. Indeed, the grain size of fcc Al, evaluated by the Scherrer equation \[18\], increases from about 50 nm for the sample consolidated at 573 K to about 100 nm for the powder sintered at 713 K.

As a typical example, figures 3 and 4 show the microstructure of a sample sintered at 643 K studied by OM and SEM. The OM image shows a uniform particle distribution and reveals the formation of a bright interface layer between the particles, which indicates that good densification and efficient bonding between the powder particles has taken place during consolidation. Only few pores are visible (black points), corroborating the high density of the sintered samples evaluated by density measurements. The SEM micrograph in figure 4 shows that the particles mostly retain their original spherical shape. The black interface between the particles visible in figure 4 (corresponding to the bright areas in figure 3) is not due to porosity. Detailed TEM and EDX investigations (figure 5) reveal that the particle interface mostly consists of an fcc Al matrix along with some nanometer-scale particles, most likely corresponding to Al\(_{11}\)La\(_3\) and/or Al\(_3\)Ni intermetallics.

Figure 6 shows the room temperature compressive true stress-true strain curves of the SPS samples sintered at 573, 643 and 713 K. The sintered samples exhibit a very high yield stress in the range of 750 to 900 MPa, an ultimate compressive stress (UCS) ranging between 900 and 1000 MPa together with a large plastic strain of about 10 - 20 %. After reaching a maximum, the stress gradually decreases with increasing strain for all the tested specimens, giving rise to a work softening-like behavior, an aspect frequently observed in nanocrystalline as well as in ultrafine-grained materials [19-23].

Figure 7 shows the influence of the sintering temperature on hardness and ultimate compressive stress. The hardness of the different SPS samples shows a continuous decrease with increasing sintering temperature. For example, the hardness of the specimen consolidated at 573 K is 345 HV and it decreases to 240 HV for the sample sintered at 713 K. A similar trend can be observed for the ultimate compressive stress, which decreases from 1030 MPa for the sample consolidated at 573 K to 930 MPa for the sample sintered at 713 K. The decrease of both hardness and UCS is most likely due to the
increase of the grain size with increasing sintering temperature, as observed in figure 1. The grain size strongly influences the mechanical properties of a material [24]. For example, a remarkable increase of hardness has been observed by decreasing the grain size up to 25 nm for different Fe-based nanocrystalline materials [25], which suggests that the decrease of hardness and UTS observed in the present work is due to the grain size effect.

Figure 6. Room temperature true stress-true strain curves of the samples consolidated by SPS at 573, 643 and 713 K.

Figure 7. Hardness and ultimate compressive stress of the consolidated samples as a function of the sintering temperature.

As a typical example, figures 8(a)-(c) show the fracture surface after compression of a sintered sample consolidated at 573 K. The specimen breaks along the compression direction and the fracture surface displays a decohesive-like rupture [26] and inter-granular crack propagation. Decohesive-like rupture, in contrast to what is observed in Fig. 8(a), would imply little or no plastic deformation [26]. However, small dimples are visible on the surface of the particles [see arrows in figure 8(c)], suggesting that some local plastic deformation has occurred at the particle interface before rupture. In order to get a better understanding of the fracture mechanism, the fracture surface of the SPS sample shown in figures 8(a)-(c) was polished and then observed by SEM [figure 8(d)]. This allows to study the microstructure of the deformed sample and to compare it to the original as-consolidated sample in figure 8(b). The SEM investigation reveals that after deformation the particles are elongated perpendicularly to the compression direction, explaining the macroscopic plastic deformation. The brittle-like fracture observed in figure 8 is most likely linked to the behavior of the particle interface, as suggested by the inter-granular crack propagation characterizing the SPS samples. Locally, at the particle interfaces, microcracks can be found [see arrows in figure 8(d)]. Initially, for small
deformations, microcracks are isolated and non-interacting. For large deformations, the microcracks join together to form a macrocrack that rapidly propagates through the sample, leading to the decohesive-like rupture shown in figure 8 and explaining the large macroscopic plastic deformation and the brittle-type fracture surface.

4. Summary
Nanocrystalline bulk samples were produced by SPS of gas-atomized Al$_{87}$Ni$_{8}$La$_{5}$ amorphous powder. The microstructure of the consolidated samples comprises fcc Al and nanosized intermetallic phases. Thus, the SPS process leads to simultaneous consolidation and devitrification of the amorphous precursor powder. Room temperature compression tests of the sintered samples reveal very high yield stress as well as ultimate compression stress, along with a large amount of plastic strain. The ultimate compressive stress, yield stress and hardness values decrease as the sintering temperature increases, most likely as a consequence of grain growth.

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6. References
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