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## Severe plastic deformation on powder metallurgy Cu–Al–Ni shape memory alloys

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### Abstract

High-pressure torsion has been successfully applied to polycrystalline Cu–Al–Ni shape memory alloys that had been prepared by a powder metallurgy methodology. The samples before and after high-pressure torsion were characterized by optical and electron microscopy and differential scanning calorimetry. After high-pressure torsion the alloys became ultra-fine grained and the present phases were identified.

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**Keywords:** Cu–Al–Ni; shape memory alloys; Severe plastic deformation; High pressure torsion; martensitic transformations; nano grains

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### 1. Introduction

Cu-based shape memory alloys (SMAs) have attracted much attention in the last years as an alternative to the conventional Ti–Ni binary alloys because they can exhibit higher transformation temperatures, a large superelastic window, small thermal hysteresis as well as high damping coefficient [1]. Furthermore, recent investigations on Cu–

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Al–Ni SMAs have confirmed a completely recoverable superelastic behavior even at nano-scale (less than 50 nm), what is not the case for Ti–Ni alloys [2,3]. However, Cu–Al–Ni SMAs are brittle in conventional polycrystalline state due to their high anisotropy and their large grain size. This problem can be overcome either using single crystals growth or reducing the grain size. Powder metallurgy of Cu–Al–Ni alloys has been particularly successful in the reduction of grain size and in the improvement of both ductility and shape memory behavior [4–8].

High-pressure torsion (HPT) is a well-established severe plastic deformation procedure for obtaining nanometer and submicrometer grains and microstructures or even an amorphous phase in bulk materials [9–11]. Both diffusive [12,13] and displacive phase transformations [14,15] promoted by HPT have been reported for different materials. In particular, this technique has already been used for NiTi SMAs quite extensively [11,15], however, this is not the case for Cu-based SMAs. The present work has been performed with the aim of analyzing the feasibility of applying HPT to Cu–Al–Ni SMAs in order to obtain nano-grained materials with improved thermo-mechanical and functional properties.

## 2. Materials and experimental procedure

Two Cu–Al–Ni SMAs (Alloy C: Cu–13.2 wt.% Al–3.3 wt.% Ni; Alloy B: Cu–14.4 wt.% Al–4.2 wt.% Ni) with slightly different concentration and, consequently, different transformation temperatures were selected according to [4,5,16]. The starting pure elements (99.99 % Cu, 99.99 % Al and 99.97 % Ni) were pre-alloyed in an Ar atmosphere and then atomized by Ar at 2.3 MPa using a Leybold Viga 2S vertical atomizer to obtain the Cu–Al–Ni SMA powders. The particle size fraction used was 25–50  $\mu\text{m}$ . Hot isostatic pressing (HIP) at 850°C, 140 GPa for 2 h in an ABB Autoclave Systems Inc. QIH-3 device was applied to compact the SMAs powders. Afterwards, the alloys were hot-rolled at 850 °C with a thickness reduction of 2% per step down to a thickness of about 0.8 mm. In the last step before HPT, the hot-rolled alloys were annealed at 900 °C, 0.5 h in Ar and quenched in cold water (0°C). As a result, one of the samples, B, is in austenite state at room temperature (Fig. 1a), whereas the second one, C, is in martensite state (Fig. 1b). For more details on the alloy production see Refs. [4,5].

For HPT processing the 0.6 mm thick discs (10 mm in diameter) were cut by spark erosion. HPT was performed at room temperature under a pressure of 5 GPa in a Bridgman anvil-type unit (5 rotations with a rate of 1 rpm) using a custom built computer controlled HPT device (W. Klement GmbH, Austria). The measured torsion torque increased during 1–2 anvil rotations and then remained unchanged (i.e. reached the steady-state as in Refs. [17,18]). The anvils/sample slippage is negligible. The sample thickness after HPT was slightly smaller than 0.6 mm.

Samples for microstructural and calorimetric investigations were cut from the HPT-processed discs at a distance of 3 mm from the sample center. Standard metallographic methods were applied to obtain polished specimens. The initial inspection was carried out using polarized light on an optical Leica DMRXA microscope. Scanning electron microscopy studies were also performed using Jeol JSM 6400/7000 F microscopes. Details about the fine microstructure and phase structure were investigated using a Philips CM200 super TWIN (200 kV) transmission electron microscope (TEM) equipped with an EDAX EDX system. Electron transparent lamellae were prepared by focused ion beam (FIB) standard methods using a FEI Helios NanoLab Dual Beam 650 equipment. Differential scanning calorimetry (DSC) measurements were performed in a TA DSC Q2000 equipment (heating rate 10 K/min).

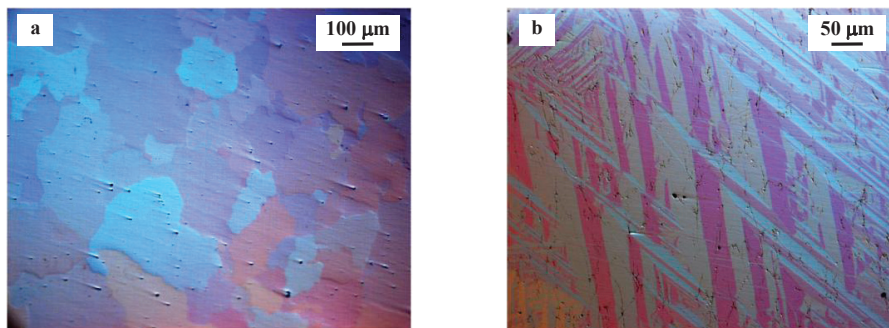


Fig. 1. Optical micrographs showing the overall microstructure of the Cu–Al–Ni SMA B (a) and C (b) after ice-quenching from 900 °C.

### 3. Results and discussion

Figure 2 shows the ultra-fine microstructure obtained in both Cu–Al–Ni polycrystalline SMAs upon HPT. A strong grain size reduction is evident with respect to the starting alloys. The particle diameter and/or the width of martensite self-accommodating groups are clearly smaller than 200 nm. It is important to emphasize that, to the best of our knowledge, severe plastic deformation, in particular HPT, was successfully applied for the first time on this type of SMAs at room temperature. Previous attempts of deformation at low temperatures lead directly to the falling apart of the material, due to its extreme brittleness, and, for this reason, hot-rolling at high temperatures was necessary to obtain polycrystalline Cu–Al–Ni bulk SMAs [4,5]. In the literature, only one work dealing with the microstructural evolution during mechanical alloying of an 82Cu–14Al–4Ni powder mixture mentioned severe plastic deformation in Cu–Al–Ni SMAs, but no results on bulk consolidated samples are reported [19].

Going to the details of the ultra-fine microstructure, TEM investigations of sample B indicated that the alloy consists mainly of martensite; no austenite was detected (Fig. 2a). According to the electron diffraction patterns (EDP) acquired, this martensite is a mixture of a very faulty orthorhombic  $\beta'$  martensite (see streaks along the basal plane in the upper EDP) and monoclinic  $\gamma'$  martensite (lower EDP). In the case of sample C, a duplex microstructure consisting of precipitates of the stable  $\gamma$  phase homogeneously distributed in a matrix was observed (Fig. 2b). The matrix is mainly a very faulty orthorhombic  $\beta'$  martensite (upper EDP), but regions in austenite state were also observed. According to the starting composition of alloy C, the material should be in austenite state [5]. A plausible explanation for that is that, as a consequence of the mass transport promoted by HPT, i.e. stable  $\gamma$  phase precipitation, an Al depletion in the matrix has taken place. According to EDS analyses the precipitates have an Al content higher than the matrix. This reduction in the Al content of the matrix leads to an increase of the martensitic transformation temperatures and this would be the reason for the martensite occurrence at room temperature in this alloy.

With the aim of analyzing the martensitic transformation behavior preliminary DSC measurements were performed. Figure 3 shows the DSC curves corresponding to Cu–Al–Ni SMA C before and after HPT. As expected from the presence of the stable  $\gamma$  phase, the amount of transforming material (enthalpy) is smaller for the sample after HPT than that for the sample before the severe plastic deformation. In addition, a clear shift of the martensitic transformation temperatures towards higher values together with a strong broadening is observed. This result indicates that even by applying an extremely heavy deformation the alloy functionality can be, at least, partly maintained. In other words, it is expected that ultra-fine grained Cu–Al–Ni SMAs with improve mechanical and functional properties can be produced by HPT. The reported results will open new opportunities to investigate the superelastic and shape memory effects in nanostructured Cu–Al–Ni alloys, which could be different from those reported for single crystal samples.

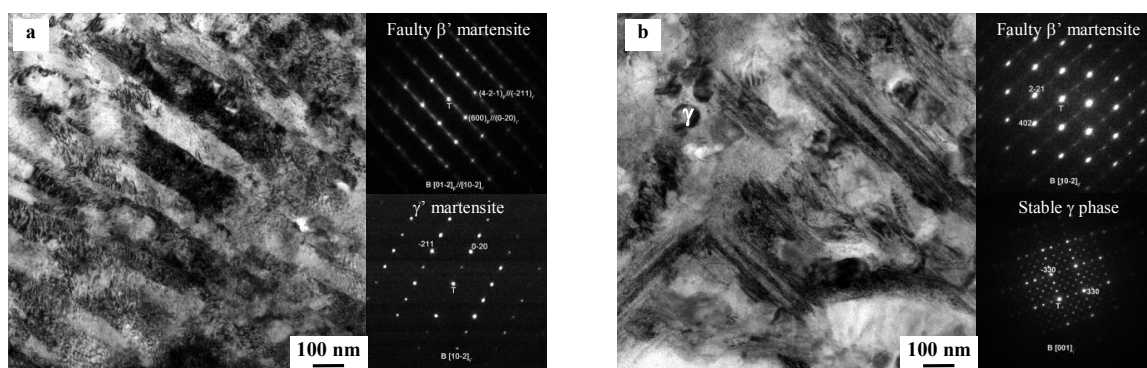


Fig. 2. Bright field TEM images acquired from Cu–Al–Ni SMA B (a) and C (b) after HPT.

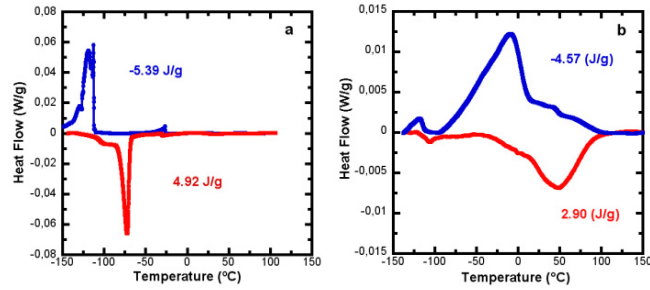


Fig. 3. DSC measurements performed on Cu–Al–Ni SMA C before (a) and after (b) HPT.

#### 4. Conclusions

- High-pressure torsion was successfully applied for the first time in polycrystalline Cu–Al–Ni SMAs.
- The phases present in severely deformed Cu–Al–Ni shape memory alloys were characterized.
- At least to a significant extent, the martensitic transformation has been observed via DSC in one of the severely deformed sample (alloy C).
- The reported results open new opportunities to investigate the superelastic and shape memory effects in nanostructured Cu–Al–Ni alloys, which could be different from those reported for single crystal samples.

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#### References

- [1] K. Otsuka, C.M. Wayman, *Shape Memory Materials*, Cambridge University Press, Cambridge, 1999.
- [2] J. San Juan, M.L. Nó, C.A. Schuh, *Adv. Materials* 20 (2008) 272–278.
- [3] J. San Juan, M.L. Nó, C.A. Schuh, *J. Mater. Res.* 26 (2011) 2461–2469.
- [4] J. San Juan, R.B. Pérez-Sáez, V. Recarte, M.L. Nó, G. Caruana, M. Lieblich, O. Ruano, *J. Phys. IV* 5 (1995) C8-919–924.
- [5] R.B. Pérez-Sáez, V. Recarte, M.L. Nó, O.A. Ruano, *J. San Juan, Adv. Eng. Mater.* 2 (2000) 49–53.
- [6] V. Recarte, I. Pérez-Landazabal, J. Campo, R.B. Pérez-Sáez, M.L. Nó, *J. San Juan, J. Phys. IV* 112 (2003) 605–609.
- [7] P.P. Rodríguez, A. Ibarra, A. Iza-Mendia, V. Recarte, J.I. Pérez-Landazabal, *J. San Juan, M.L. Nó, Mater. Sci. Eng. A* 378 (2004) 263–268.
- [8] A. Ibarra, J. San Juan, E.H. Bocanegra, M.L. Nó, *Mater. Sci. Eng. A* 438–440 (2006) 782–786.
- [9] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M.J. Zehetbauer, Y.T. Zhu, *JOM* 58 (2006) 33–39.
- [10] A.P. Zhilyaev, T.G. Langdon, *Prog. Mater. Sci.* 53 (2008) 893–979.
- [11] Y. Estrin, A. Vinogradov, *Acta Mater.* 61 (2013) 782–817.
- [12] X. Sauvage, A. Chbihi, X. Queleñec, *J. Phys.: Conf. Ser.* 240 (2010) 012003.
- [13] B. B. Straumal, A.R. Kilmametov, Yu.O. Kucheev, K.I. Kolesnikova, A. Korneva, P. Zieba, B. Baretzky, *JETP Letters* 100 (2014) 376–379.
- [14] Yu Ivanisenko, A.R. Kilmametov, H. Roesner, R.Z. Valiev, *Int. J. Mater. Res.* 99 (2008) 36–41.
- [15] S.D. Prokoshkin, I.Yu Khmelevskaya, S.V. Dobatkin, I.B. Trubitsyna, E.V. Tatyani, et al., *Acta Mater.* 53 (2005) 2703–2714.
- [16] V. Recarte, R.B. Pérez-Sáez, E.H. Bocanegra, M.L. Nó, *J. San Juan, Metall. Mater. Trans. A* 33 (2002) 2581–2591.
- [17] B.B. Straumal, S.G. Protasova, A.A. Mazilkin, E. Rabkin, D. Goll, G. Schütz, B. Baretzky, R.Z. Valiev, *J. Mater. Sci.* 47 (2012) 360–367.
- [18] B.B. Straumal, A.R. Kilmametov, Y. Ivanisenko, L. Kurmanaeva, B. Baretzky, Y.O. Kucheev, et al., *Mater. Lett.* 118 (2014) 111–114.
- [19] S.K. Vajpai, R.K. Dube, M. Sharma, *J. Mater. Sci.* 44 (2009) 4334–4341.