Journal of Alloys and Compounds 504S (2010) S456–S459

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

On the processing of hetero-nanostructured metals for improved strength/ductility balance by ECAE and SPS techniques

T. Grosdidier[a,*], D. Goran[a], G. Ji[a,1], N. Llorca[b]

[a] Laboratoire d'Etude des Textures et Application aux Matériaux (LETAM), CNRS 3143, Université Paul Verlaine – Metz, Ile du Saulcy, 57045 Metz Cedex 01, France
[b] Department of Materails Science and Metallurgical Engineering, Facultat de Química, University of Barcelona, C/Martí Franqués 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 5 July 2009
Received in revised form 16 February 2010
Accepted 2 March 2010
Available online 9 March 2010

Keywords:
Electric current assisted sintering (ECAS)
Spark plasma sintering (SPS)
Mechanical milling (MA)
Equal channel angular extrusion/pressing (ECAE/ECAP)
Nanostructured metals (hetero-nanostructure)

ABSTRACT

This paper has examined some recent findings concerning the processing of fully dense hetero-nanostructured materials (i.e. consisting of nano, ultrafine and micrometric grains) which can be produced by using the interplay between heavy deformation and recrystallization. By plastic deformation of bulk materials, an improved strength/ductility balance can be obtained directly by imparting high strain deformation (by equal channel angular extrusion) until the occurrence of recrystallization. Using a powder metallurgy route, the strong potential of electric field assisted sintering (ECAS) techniques for producing multi-scale microstructures when a conducting milled powder is used is demonstrated. In this case, in addition to modify the classic processing parameters (time/temperature of spark plasma sintering), altering the nature of the milled powder – by Y_2O_3 addition during the milling stage – is also a good way to delay the onset of recrystallization and, thereby, increase the fraction of ultrafine grains.

1. Introduction and background to present research

Nanostructured bulk materials can be produced by a number of processing methods, which essentially fall into two categories: (i) severe plastic deformation of bulk microstructured materials and (ii) consolidation of nanoparticles or ultrafine-grained powders. In addition to these two broad categories, pulsed electro-deposition is also a well established technique to reduce grain size – down to about a few nanometer – that is however restricted to thick (20 μm or so) deposits. The drawback of nanostructured bulk materials is their limited ductility of only a few percent of uniform elongation. For practical applications of nanostructured metals, it is therefore required to optimize the balance between strength and ductility. In a recent paper [1], Wang and Ma have explored – for intrinsically ductile metals – different ideas to remove or delay the plastic instabilities that hamper the useful ductility due to the presence of the nanostructure. One of the method was tailoring the grain size structure in order to get bimodal or multi-modal grain size distributions [1]. Even if the number fraction of larger grains in the nanostructure is low, their volume fraction can be sufficiently high to contribute to dislocation-based plasticity in the material [1]. Therefore, both thermo-mechanical and powder metallurgy approaches have been tested over the last years to produce this type of hybrid microstructures [2–5]. In many of the tested processes, the intrinsic heterogeneity of the recrystallization process was used to introduce some large recrystallized grains within a heavily deformed structure. The difficulty however lies in the exact control of the thermo-mechanical sequence to generate the suitable mixture in a fairly reproducible manner. Thus, alternative methods for processing materials with bimodal or broad grain size distributions such as electric current assisted sintering (ECAS) of milled powders [6] or direct current electro-deposition [7] have also been recently proposed. The aim of the present contribution is to illustrate some alternative ways of producing multi-modal sub-micrometer grain sized materials using techniques involving either (i) severe plastic deformation of bulk microstructured materials and (ii) consolidation of ultrafine-grained powders.

2. High strain deformation to induce recrystallization

Among the most advanced high strain deformation techniques are the high pressure torsion (HPT) [8,9], equal channel angular extrusion/pressing (ECAE/ECAP) [10,11], and accumulative roll-bonding (ARB) [12,13]. Due to structural and textural heterogeneities developed with these processes as well as a high content of stored energy, annealing of nanostructured metals is difficult to

* Corresponding author. Tel.: +33 3 87 31 71 30; fax: +33 3 87 31 53 77.
E-mail address: Thierry.grosdidier@univ-metz.fr (T. Grosdidier).
[1] Now with: Unité Matériaux et Transformations, CNRS UMR 8207 - Université 1, 59655 Villeneuve d'Aseq, France.

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.03.035

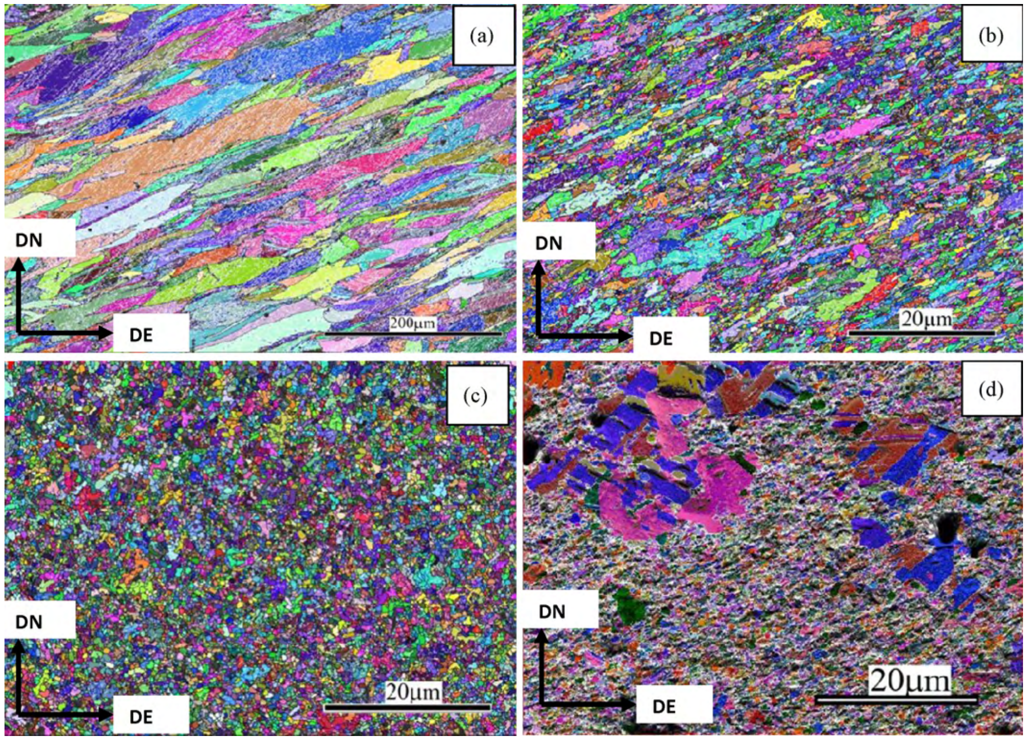

Fig. 1. Evolution of the microstructure with increasing number of passes (route Bc) of ECAE-Cu: (a) 1 pass, (b) 2 passes, (c) 8 passes and (d) 12 passes.

control because of the occurrence of non-uniform coarsening and recrystallization. These deformation heterogeneities are for example particularly present at the scale of the billet of ECAE processed materials [14–16]. Therefore, as also exemplified recently by the sub-surface heterogeneous recrystallized structures observed after one-step annealing of ARD deformed samples, a two-step annealing procedure is often required to avoid discontinuous recrystallization [17]. Another effective route to create grain size heterogeneities, as illustrated in Fig. 1, is to use recrystallization induced during the high straining process. Fig. 1 shows the microstructure evolution of a commercial purity Cu alloy processed by ECAE using the so-called route Bc, as detailed in [18], but for number of passes as high as 16. The development of texture and microstructure in ECAE Cu has been the subject of several publications [19,20]. The grain size reduction can be roughly described by the "fragmentation" of the initial grains and the creation of sub-grains having an increased amount of misorientation with increasing strain; thus leading to ultrafine grains separated by high misorientation boundaries. This is illustrated here by Fig. 1a–c. However, in the case of this Cu, the samples processed for 12 passes and more retained a very heterogeneous structure consisting of a mixture of patches having different microstructures. They were broadly made of 3 types of grains: ultrafine equiaxed (similar to those in Fig. 1c), coarse and fairly equiaxe (some are visible in Fig. 1d) and medium elongated (similar to those in Fig. 1b). A detailed characterization of this microstructure and its formation mechanisms will be published elsewhere [21]. In short, it is formed as a result of a complex combination of dynamic and fairly static recrystallization occurring at different stages of the ECAE process. Interestingly however, the microstructure was fairly similar after 12 or 16 passes. This indicates that pressing rods for many passes – at a controlled temperature depending on the deformed metal – can induce a balance between recovery/recrystallization and deformation processes to produce a multi-modal grain size distribution including a significant fraction of ultrafine grains.

Fig. 2 shows some tensile engineering stress–strain curves recorded on the ECAE-Cu samples deformed at different number of passes. It is clear from Fig. 2a that the strength of the material increases gradually with the number of passes from 1 to 8. These curves peak soon after yielding, in sharp contrast to the behavior of the initial coarse grain material. Such very limited strain hardening is common to severely plastically deformed Cu due to the low capacity of dislocation storage [1,22]. Comparatively, as more clearly visible in the enlarged image of Fig. 2b, the strain hardening capability could be improved for the case of the heterogeneous microstructure obtained for the higher number of passes (12 and 16 passes); leading to an improved strength/ductility balance. It is also interesting to notice in Fig. 2a that, despite different number of passes, the highly strained samples (12 and 16 passes) presented very similar mechanical responses.

3. Electric current assisted sintering (ECAS) of mechanically milled powders

A number of consolidation processes have been applied to fabricate nanostructured materials from milled powders such as cold pressing and hot extrusion [23–25], hot isostatic pressing and forging [25,26], thermal/plasma spraying of thick deposits [27–31], and, more recently, techniques for which an electric current was used to aid the pressure assisted sintering [32–37]. A very complete and extended review has recently been published on these electric current activated/assisted sintering (ECAS) techniques for which different names and acronyms have been used: spark plasma sintering (SPS), pulsed electric current sintering (PECS), pulsed discharge sintering (PDS), etc [38]. TEM analysis has recently established that SPS samples processed from conducting milled powders always contained a broad range of grain sizes varying from 10s of nanometer towards the micrometer range [35,39,40]. The large grain size distribution was in fact controlled by combination of (i) locally large temperature difference generated during the SPS process of conducting samples and (ii) the use of milled powder. Indeed, while fine grains are retained in the area where local temperature is relatively low, the Joule effect concentrates at the neck

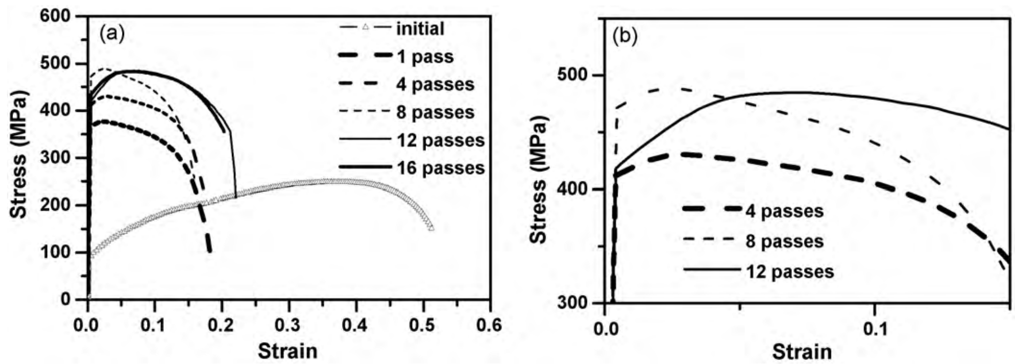

Fig. 2. Tensile engineering stress/strain curves of the Cu samples processed for different passes of ECAE (route Bc).

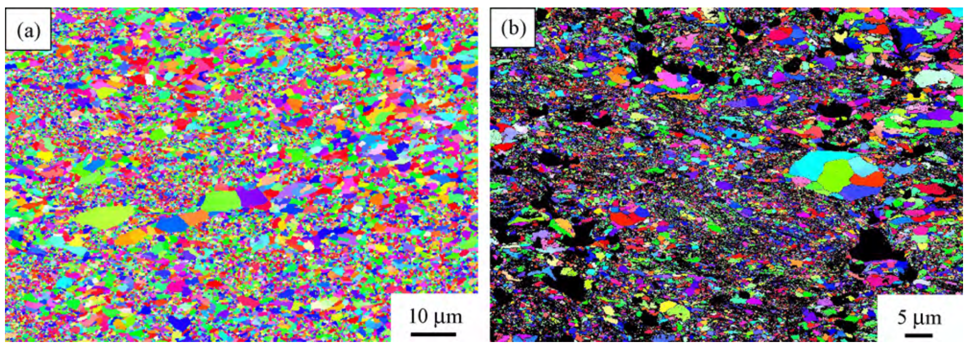

Fig. 3. Typical EBSD maps of samples processed by electric current assisted sintering from milled FeAl powder at (a) 900 °C (medium temperature range) and (b) 800 °C (low temperature range).

joining conducting powder particles so that recrystallization/grain growth occurred more rapidly in these overheated areas where larger grains could form. A detailed analysis of the microstructure of Y_2O_3 reinforced FeAl sintered samples indicated that local thermal gradient as high as 600 °C could be created during the ECAS sintering process [6,40]. These gradients, revealed at the scale of the powder, were witnessed by a detailed EDX and imaging analysis in the TEM [40] and the redistribution of Yttrium [40,41]. The EBSD maps in Fig. 3 show two examples of typical microstructures obtained by SPS of milled powder at, comparatively, low and high sintering temperatures [35,40]. As seen by the black patches visible in Fig. 3b, some porosity was still present for the low temperature regime. Comparatively, a good densification was obtained when the processing temperature reached 900 °C (Fig. 3a). The image in Fig. 3b also clearly reveals the presence of a badly milled powder particle for which 5 or 6 adjacent large grains are visible. In both cases however, the EBSD maps confirm that the variation in grain size of the materials obtained from the milled powder is quite considerable. The recent analysis of pure aluminium sintered by SPS from mechanically milled powders, performed by Kubota and Wynne [42], has also revealed a multi-modal grain size distribution. As could be expected from a powder metallurgy route, Kubota and Wynne have also shown that the sintered material was fairly isotropic (i.e. presenting no preferential texture component). Quantitative analysis of EBSD maps has been used to analyze quantitatively the effect of the nature of the initial powders – atomized (microcrystalline), milled (nanostructured) with or without Y_2O_3 reinforcement – on the grain size distribution [6]. All grains were above 1 μm with an average size close to 5 μm for the sample processed from atomised powder [6]. In contrast, the samples obtained from milled powders contained a multi-modal grain size distribution. The effect of the Y_2O_3 introduction during the milling procedure was essentially to delay the recrystallization process leading to more than 80% of the grains in the range +100/−500 nm that coexisted with about 10% of the grains in the size range +500/−1000 nm and <5% of micrometric grains. The tensile properties of SPS steels processed from milled powder were recently tested and improved strength/ductility balanced were obtained [43].

4. Conclusion

Hybrid microstructures (i.e. consisting of nano, ultrafine and micrometric grains) can be produced efficiently by using the interplay between heavy deformation and recrystallization processes. This can be done for example by imparting high strain deformation using ECAE/ECAP until the occurrence of recrystallization. The strong potential of ECAS/SPS technique when consolidating conducting milled powders is demonstrated. The two necessary conditions for the formation of such a multi-modal nano-grain structure are (i) the large temperature differences that are spontaneously generated during the ECAS/SPS process of conducting materials and (ii) the use of the milled powders within which the heavily deformed nanostructure is present.

Acknowledgment

The authors would like to thank Mr. N. Lugo (Barcelona) for his help with some of the ECAE experiments.

References

[1] Y.M. Wang, E. Ma, Acta Mater. 52 (2004) 1699.
[2] Y.M. Wang, M.W. Chen, F.H. Zhou, E. Ma, Nature 419 (2002) 912.
[3] X. Zhang, H. Wang, R.O. Scattergood, J. Narayan, C.C. Koch, A.V. Sergueeva, A.K. Mukherjee, Acta Mater. 50 (2002) 4823.
[4] T. Shanmugasundaram, V.S. Sarma, B.S. Murty, M. Heilmaeir, Mat. Sci. Forum 97 (2008) 584–586.
[5] B.Q. Han, E.J. Lavernia, Adv. Eng. Mater. 7 (2005) 457.
[6] T. Grosdidier, G. Ji, S. Launois, Scr. Mater. 57 (2007) 525.

[7] X. Shen, J. Lian, Z. Jiang, Q. Jiang, Mater. Sci. Eng. A 487 (2008) 410.
[8] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Prog. Mater. Sci. 45 (2000) 103.
[9] G. Sakai, Z. Horita, T.G. Langdon, Mater. Sci. Eng. A 393 (2005) 344.
[10] V.M. Segal, Mater. Sci. Eng. A 197 (1995) 157.
[11] R.Z. Valiev, T.G. Langdon, Prog. Mater. Sci. 51 (2006) 881.
[12] Y. Saito, H. Utsunomiya, N. Tsuji, T. Sakai, Acta Mater. 47 (1999) 579.
[13] N. Tsuji, Y. Ito, Y. Saito, Y. Minamino, Scr. Mater. 47 (2002) 893.
[14] A. Tidu, F. Wagner, W.H. Huang, P.W. Kao, C.P. Chang, T. Grosdidier, J. Phys. IV 10 (2000) 211.
[15] S. Li, I.J. Beyerlein, C.T. Necker, D.J. Alexander, M. Bourke, Acta Mater. 52 (2004) 4859.
[16] T. Grosdidier, J.-J. Fundenberger, D. Goran, E. Bouzy, S. Suwas, W. Skrotzki, L.S. Toth, Scr. Mater. 59 (2008) 1087.
[17] N. Kamikawa, X. Huang, N. Hansen, J. Mater. Sci. 43 (2008) 7313.
[18] N. Lugo, N. Llorca, J.M. Cabrera, Z. Horita, Mater. Sci. Eng. A 477 (2008) 366.
[19] H.W. Huang, L. Chang, P. Kao, C.P. Chang, Mater. Sci. Eng. A 307 (2001) 113.
[20] F. Dalla Torre, R. Lapovok, J. Sandlin, P.F. Thomson, Acta Mater. 52 (2004) 4819.
[21] T. Grosdidier, D. Goran, N. Ludo, N. Llorca, in preparation.
[22] Y.S. Li, Y. Zhang, N.R. Tao, K. Lu, Scr. Mater. 59 (2008) 475.
[23] D.G. Morris, M.A. Morris, Acta Metall. Mater. 39 (1991) (1763).
[24] K.I. Moon, K.S. Lee, J. Alloys Compd. 291 (1999) 312.
[25] A.P. Newbery, B. Ahn, T.D. Topping, P.S. Pao, S.R. Nutt, E.J. Lavernia, J. Mater. Proc. Technol. 203 (2008) 37.
[26] S. Revol, S. Launois, R. Baccino, B. Rigal, Fusion Eng. Des. 58 (2001) 751.
[27] T. Grosdidier, A. Tidu, H.L. Liao, Scr. Mater. 44 (2001) 387.
[28] J. He, J.M. Schoenung, Mater. Sci. Eng. A 336 (2002) 274.
[29] J. Gang, J.P. Morniroli, T. Grosdidier, Scr. Mater. 48 (2003) 1599.
[30] S.C. Tjong, H. Chen, Mater. Sci. Eng. Rep. 45 (2004) 1.
[31] G. Ji, T. Grosdidier, H. Liao, J. Morniroli, C. Codet, Intermetallics 13 (2005) 596.
[32] M. Omori, Mater. Sci. Eng. A 287 (2000) 183.
[33] S.H. Lee, K.I. Moon, H.S. Hong, K.S. Lee, Intermetallics 11 (2003) 1039.
[34] Y. Minamino, Y. Koizumi, N. Tsuji, N. Hirohata, K. Mizuuchi, Y. Ohkanda, Sci. Technol. Adv. Mater. 5 (2004) 133.
[35] T. Grosdidier, G. Ji, F. Bernard, E. Gaffet, Z.A. Munir, S. Launois, Intermetallics 14 (2006) 1208.
[36] G. Ji, D. Goran, F. Bernard, T. Grosdidier, E. Gaffet, Z.A. Munir, J. Alloys Compd. 420 (2006) 158.
[37] A. Zuniga, L. Ajdelsztajn, E.J. Lavernia, Metall. Mater. Trans. A 37 (2006) 1343.
[38] R. Orrù, R. Licheri, A. Locci, A. Cinti, G. Cao, Mater. Sci. Eng. Rep. 63 (2009) 127.
[39] G. Ji, T. Grosdidier, F. Bernard, S. Paris, E. Gaffet, S. Launois, J. Alloys Compd. 434–435 (2007) 358.
[40] G. Ji, T. Grosdidier, N. Bozzolo, S. Launois, Intermetallics 15 (2007) 108.
[41] T. Grosdidier, G. Ji, N. Bozzolo, Intermetallics 14 (2006) 715.
[42] M. Kubota, B.P. Wynne, Scr. Mater. 57 (2007) 719.
[43] B. Srinivasarao, K. Oh-ishi, T. Ohkubo, K. Hono, Acta Mater. 57 (2009) 3277.