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Bulk FeAl nanostructured materials obtained by spray forming and spark plasma sintering

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Abstract

This paper examines the efficiency of two consolidation processing techniques high velocity oxy-fuel (HVOF) spray forming and spark plasma sintering (SPS) which allow to obtain bulk dense nanostructured materials. An oxide dispersion strengthened (ODS) Fe–40Al (at.%) based milled powder (with a nanostructure < 30 nm in size) was used as a precursor. The microstructures of the sintered end-products were characterized by transmission electron microscopy (TEM). The results indicated that, under the present processing conditions, the HVOF spray forming is more effective to retain nanograins (30–90 nm in size) within unmelted powder particles. However, the SPS processing shows its potential to fully densify the material while retaining ultrafine grains having sizes in the range 100–400 nm together with larger micrometer grains.

Keywords: Iron aluminides (based on FeAl); High velocity oxy-fuel spray forming; Spark plasma sintering; Nanostructures; Transmission electron microscopy (TEM)

1. Introduction

Although considerable progress in basic understanding of nanostructured material has been made, the shift from basic science to technological applications of bulk nanostructured parts is being slow. One main reason for this is that it is relatively easy to create powders and thin films with nanoscaled structures; while it is much more difficult to obtain the same materials in the bulk forms generally needed for structural applications [1].

It has already been reported that nanocrystalline bulk materials can be produced by several approaches such as powder synthesizing and consolidation [2–4], structural refinement involving severe plastic deformation [3–6] and annealing of bulk amorphous materials [7]. Various thermal spray techniques have also been considered as efficient processes to produce nanostructured coatings (up to several hundreds of micrometers in thickness). For example, the high velocity oxy-fuel (HVOF) technique has already succeeded in producing metallic nanostructured coatings of Ni based alloys [8], Inconel 718 [9], Cr_3C_2–NiCr [10], WC/Co [11] and FeAl [12]. Due to their high deposition rates, they have also been used to produce near net-shaped parts (several mm in thickness) by spraying nanostructured powders [13,14]. In addition, flash techniques such as spark plasma sintering (SPS) have also being tested to produce bulk materials having ultra fine grain size. The SPS process uses a pulsed direct current, which was claimed to create weak plasma, discharge impact and electric field, to sinter (or simultaneously synthesize and consolidate) materials within a die [15]. It was

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proved to be very potent to retain the ultrafine microstructure from the original milled powder to produce bulk nanostructured materials (NMs). For example, it has been reported that dense nanostructured Fe_3Al–C [16] and (Al + 12.5 at.% Cu)$_3$Zr [17] intermetallics sintered by the SPS processing of milled powder showed superior mechanical properties.

FeAl intermetallic alloys are attractive materials for industrial applications at medium to high temperatures because they combine good mechanical properties, low density, low cost and availability of raw materials and excellent corrosion and oxidation resistances [18–20]. However, their use has been limited by their brittleness at room temperature and poor creep resistance. These drawbacks can be improved by grain boundary and oxide dispersion strengthenings as well as grain size reduction [21–23]. Taking all these factors into account, an Y_2O_3 strengthened Fe–40Al (at.%)-Zr–B powder was designed and prepared by gas atomization and subsequent ball milling in a semi-industrial mill [22,24]. Using this milled powder as precursor, this paper gives our first results concerning the comparison of the microstructure of bulk NMs obtained from milled ODS Fe–40Al (at.%) powder using the HVOF and SPS techniques. Transmission electron microscopy (TEM) was employed to exactly assert the presence of the nanograins in the end-products.

2. Experimental

The feedstock milled powder was produced by CEA-DTEN. Its nominal composition was Fe–39.78Al–0.054Zr–0.01B–0.2Y_2O_3 (at.%). Small amounts of Zr and B were added for removing carbon impurities and improving grain boundary strength [22]. In addition, Y_2O_3 was added during the milling stage to introduce a fine yttria dispersion [21,25,26]. This milled powder was then used for the synthesis of bulk NMs using the two different techniques.

Figs. 1a and 1b show the sketches of the HVOF spray forming and SPS experiment set-ups, respectively. A Plasma-Technik CDS HVOF console and a CDS 100 torch were used to spray form the sieved milled powder. A copper tube, cooled by internal water circulation, was used as a substrate to deposit a 5 mm thick deposit (see inset photo in Fig. 1a). The HVOF flame was selected to establish relatively low temperature and high velocity to retain unmelted nanostructured powder particles. The exact experimental conditions were detailed elsewhere [14]. A 515S SPS apparatus (Sumitomo Coal and Mining Co., Ltd.) was used for the SPS sintering. A uniaxial load of 70 MPa was applied during the whole heating and cooling stages. Temperatures were measured on the external surface of graphite die by a k-type thermocouple. The selected sintering temperature was 1050 °C. The heating rate was about 250 °C/min. The end-product is shown in the inset of Fig. 1b. It has a dimension of 18.8 mm in diameter and

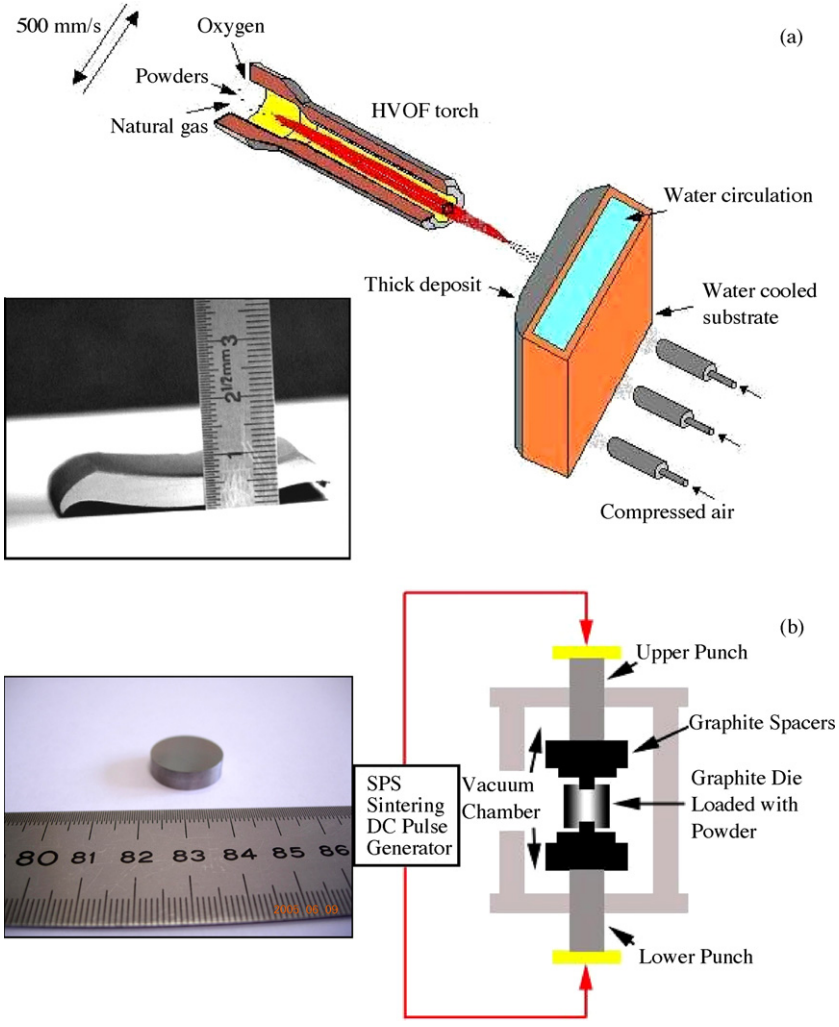

Fig. 1. Sketches of (a) the HVOF spray forming and (b) the SPS sintering experiment set-ups, insets are photos corresponding to the processed samples.

5 mm in height. Microstructure characterizations were carried out by TEM using a Philips CM200 microscope, operating at 200 kV.

3. Results and discussion

The HVOF spray formed material displayed typical microstructural features that were very similar to those observed in the HVOF nanostructured thin coatings [27]. They consisted of unmelted powder particles, melted and flattened particles (e.g. splats) and porosity [12,14,27]. Fig. 2a is a TEM bright-field micrograph showing a nanograin zone retained in the unmelted powder particle. The grain size was in the range from 30 to 90 nm. The grains are embedded in the deformed matrix. It has been established that they resulted from a partial recrystallization of the original deformed nanostructure (nanosized domain below 30 nm [27]) from the milled powder [14,27]. The structure in the fully melted splats mainly consisted of sub-micrometer columnar grains. They resulted from a rapid directional growth due to the intense heat extraction by heat conduction between the splat and the substrate (or already deposited coating). An example of this type of columnar structure is shown in the TEM bright-field micrograph of Fig. 2b.

The SPS material was characterized by a heterogeneous grain size. This is illustrated in Figs. 3a and 3b. The small grains are of the order of 100–400 nm in size (Fig. 3a) while the larger grains can reach a size of about several micrometers (Fig. 3b). At the beginning of the SPS processing, necks connecting powder particles can be quickly formed with the aid of a pulsed direct current running through the sample. The temperature at the neck must be much higher than that in the rest of the powder particles, due to the higher current density. Such effect associated with the applied uniaxial pressure allows the growth and softening of the neck to a fast sintering although the temperature inside the powder particles still remains fairly low. Thus, these local differences result in heterogeneity of the microstructure in the end-products.

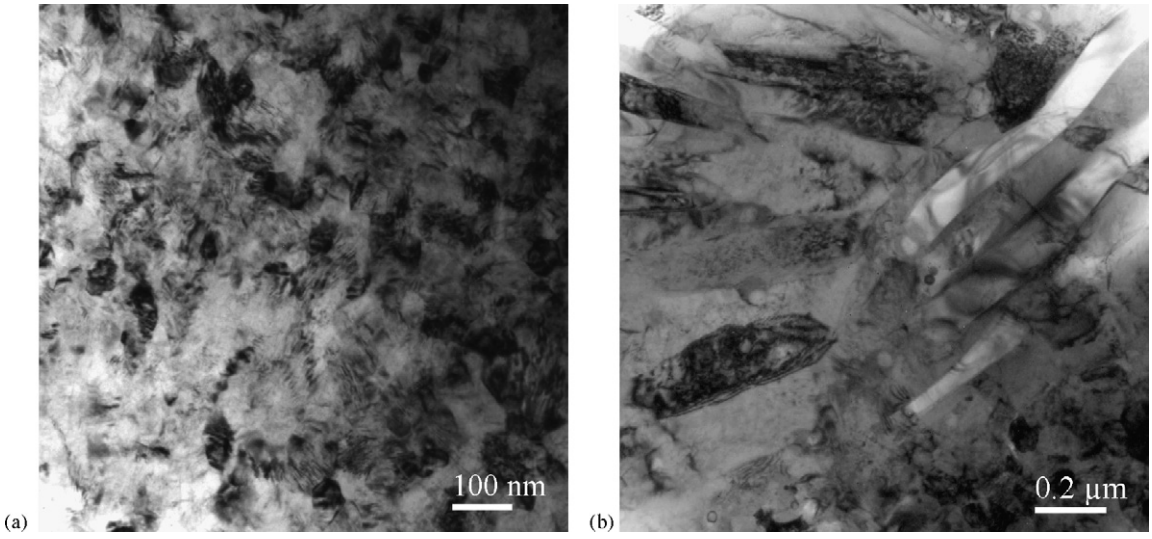

Fig. 2. TEM bright-field micrographs showing: (a) an equiaxed nanograin zone and (b) a columnar grain zone present in the HVOF spray formed deposit.

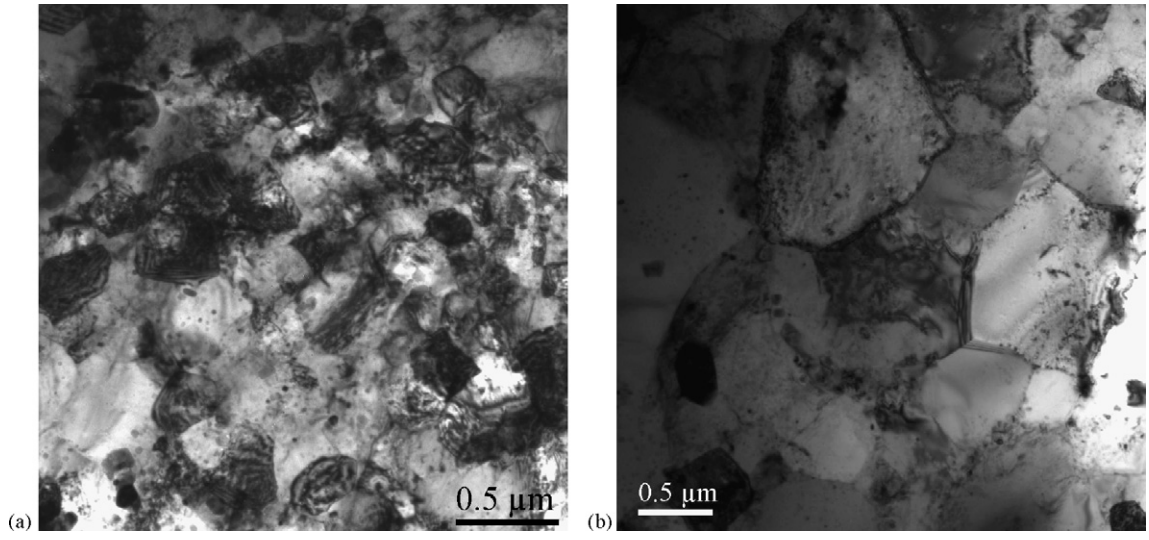

Fig. 3. TEM bright-field micrographs showing: (a) a fine-grained zone and (b) a coarse-grained zone present in the SPS sintered sample.

The key to prepare bulk NMs with improved mechanical properties is to retain nanostructure while getting a high density of the end-products. The TEM results of these two consolidated materials clearly indicate that the HVOF spray forming is more efficient to retain a nanostructure, in particular within the unmelted powder particles where the structure is very similar to the original nanostructure of the milled powder. In order to do that, special spray conditions such as low flame temperature, high particle velocity as well as rapid heat cycles must be selected. However, the drawback of these spraying conditions is that the quality of the particle flattening behaviour is less effective. The consequence is to introduce porosities. In the present spraying case, the amount of porosity was about 9% while 12% of unmelted powder particles were retained in the bulk material [14].

Previous studies on the as-extruded ODS FeAl material obtained by hot extrusion showed that this fully dense material owns a yield strength above 1000 MPa combined with reasonable ductility [28]. In addition, after having examined different factors that can modify the ductility of FeAl, Morris and Muñoz-Morris [29] pointed out that further refinement in grain size is the most attractive way to improve ductility. The hot extrusion is generally carried out at 1100 °C, which inevitably results in grain growth to reach an average grain size of about 1.1 μm in the final product [21,26]. A SPS run at the high temperature of 1050 °C has already shown its potential to obtain the fully dense sample containing very fine sub-micrometer grains (Fig. 3a). Following this consolidation route, reduction in grain size to a nanoscale should be possible by using lower sintering temperatures and improved experimental processing conditions. At this level, a proper increase of the applied load and holding time will be needed to ensure a high consolidation density.

4. Summary and conclusions

(1) The HVOF spray forming of nanostructured milled powder (nanosized domain < 30 nm) is a very effective way to retain nanograins (30–90 nm in size) within the unmelted powder particles. However, this technique introduced a high amount of porosity which may be harmful to properties of the as-sintered material.
(2) For the SPS processing of the same type of the milled powder, the microstructure of the SPS sample is fairly heterogeneous. It presents a bimodal size distribution consisting of (i) ultrafine grains in the range of 100–400 nm and (ii) larger micrometer grains.
(3) The SPS processing performed at 1050 °C has already shown its potential to obtain a fully dense material within which ultrafine grains were retained. Optimization of the SPS conditions is likely to further reduce the grain size to the nanoscale while keeping a high density.

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