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Synthesis of bulk FeAl nanostructured materials by HVOF 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) to obtain bulk nanostructured materials from an Y_2O_3 reinforced Fe–40Al (at.%) milled powder. The microstructures of the sintered end-products were characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) in order to gain new insights in their microstructure formation mechanisms. HVOF spray forming is more effective to retain fine nanograins, in particular within retained unmelted powder particles. The drawbacks of this technique are that it inevitably leads to a high fraction of porosity and, because of lack of wetting, large areas (the melted zones) without any Y_2O_3 oxide. Comparatively, SPS has a much higher potential to create sub-micrometer microstructures within which the oxides are more homogeneously distributed.

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1. Introduction

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 [1–3]. 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 [4–6]. Taking all these factors into account, a Y_2O_3 strengthened Fe–40Al (at.%)–Zr–B powder was designed by CEA (Commissariat à l'Energie Atomique) for consolidation via extrusion or forging [7,8]. This powder is prepared by gas atomization and subsequent ball milling during which the Y_2O_3 phase is introduced [4,7]. The standard consolidation techniques usually result in materials having a grain size of the order of micrometers or slightly above [7–9]. The oxide particles are generally several tens of nanometers and fairly well distributed throughout the material. Using this milled powder as a precursor, two other consolidation processing techniques are being tested to synthesize bulk components with the goal of reaching even

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finer grain sizes: the High Velocity Oxy-Fuel (HVOF) thermal spray technique and Spark Plasma Sintering (SPS).

Thermal spraying is a process in which a fine powder is carried in a gas stream and passed through an intense combustion flame, where it becomes molten. The gas stream, expanding rapidly because of the heating, then sprays the molten powder onto the substrate where it solidifies. A deposit therefore builds up by the successive impact of individual powder particles. The resulting microstructure depends on the nature of the starting feedstock of powder particles, on their interaction with the flame in transit and, finally, on the interaction of each particle with the substrate to form the individual splats that are the “building blocks” of the deposit. HVOF thermal spraying of milled powder has already been successfully used for producing metallic nanostructured coatings, for example Ni-based alloys [10], Inconel 718 [11] or FeAl [12]. In addition, due to its high deposition rate, the technique has also been used to fabricate near net-shaped bulk nanostructured materials [13].

Spark Plasma Sintering has received increasing attention [14]. SPS shows similarities with conventional hot pressing in that the precursor is loaded in a die (typically made of graphite) and a uniaxial pressure is applied during synthesis. However, instead of using an external heating source, a pulsed direct current (DC) is allowed to pass through the sample and also through the electrically conducting pressure die. Consequently, SPS is claimed to use microscopic electric discharges between the particles under pressure [15] and to reduce significantly the synthesis and densification temperatures, limiting thereby the grain growth. The combination of mechanical activation of the powder with the SPS technique, often referred to as the MASPS process, has also been shown to be suitable for the production of materials having nanostructure and a controlled consolidation level [16]. It was proved to produce, from milled powders, bulk nanostructured $\text{Fe}_3\text{Al}-\text{C}$ [17] and $(\text{Al} + 12.5 \text{ at.}\% \text{ Cu})_3\text{Zr}$ [18] intermetallics that showed superior mechanical properties.

The aim of this paper is to give our first results concerning the comparison of the microstructure of bulk nanostructured materials obtained from milled oxide dispersion strengthened (ODS) $\text{Fe}-40\text{Al}$ (at.%) powder using the HVOF and SPS techniques.

2. Experimental

The feedstock milled powder was produced by CEA-DTEN (Département de Technologie pour l’Energie et les Nanomatériaux). Its nominal composition was $\text{Fe}-39.78\text{Al}-0.054\text{Zr}-0.01\text{B}-0.2\text{Y}_2\text{O}_3$ (mol%). Small amounts of Zr and B were added for fixing carbon impurities and improving grain boundary strength [5]. In addition, Y_2O_3 was introduced at the milling stage to create a fine yttria dispersion in the consolidated products [4,19,20]. This milled powder, which has a crystallite size of about 20 nm [12,21], was then used for the synthesis of bulk materials using the two different techniques.

Fig. 1(a,b) shows the sketches of the HVOF spray forming and SPS experimental set-ups, respectively. A Plasma-Technik CDS HVOF console and a CDS 100 torch were used to spray

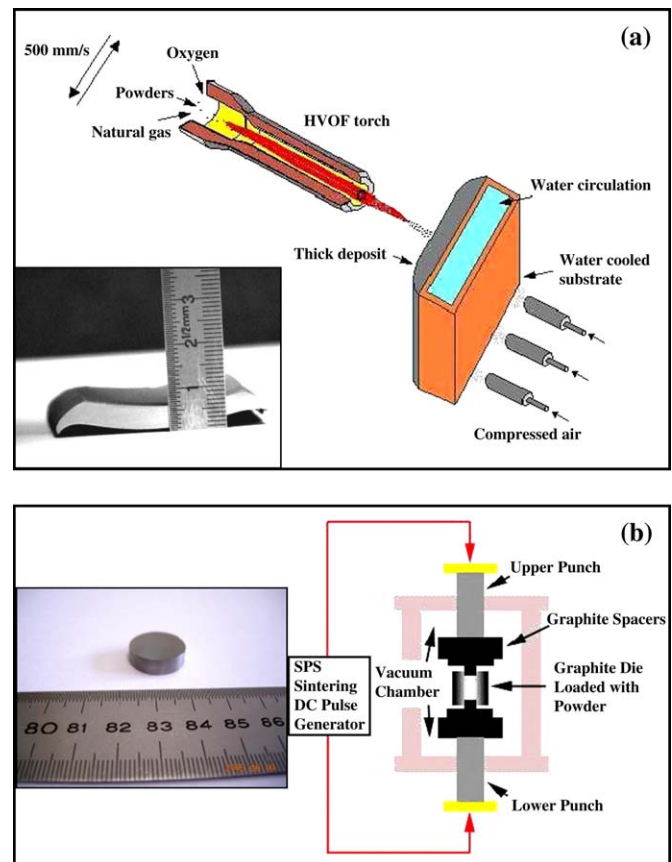


Fig. 1. Sketches of (a) the HVOF spray forming and (b) the SPS sintering experimental set-ups; insets are photos corresponding to the processed samples.

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. 1(a)). The HVOF flame was selected to guarantee a relatively low temperature and high velocity in order to retain unmelted nanostructured powder particles. The exact experimental conditions were detailed elsewhere [13]. A 1050 SPS apparatus, manufactured by the Sumitomo Coal and Mining Company [14], was used for the SPS sintering at the University of California-Davis. This machine consists of a uniaxial 100 kN press combined with a 15 V, 5000 A pulsed DC power supply. The pulse cycle used in this work consisted of 12 pulses on and 2 off. This means that there were 12 pulses of 3.2 ms each followed by a 6.4 ms (2 times 3.2 ms) off. An uniaxial load of 70 MPa was applied during the whole heating and cooling stages. The examples of microstructures shown here were prepared either (i) within a “low temperature” regime range where significant porosity was still present in the consolidated product or (ii) at, comparatively, higher temperatures for which the consolidation regime provided fully dense products. An example of end-product is shown in the inset of Fig. 1(b). It has dimensions 18.8 mm in diameter and 5 mm in height.

The samples were investigated by Scanning Electron Microscopy (SEM) as well as by Transmission Electron Microscopy (TEM) at the University of Metz with the goals of (i) asserting the presence of nanograins in the end-products

and (ii) depicting interesting fine scale features in the consolidated structures. SEM was done using a Jeol 6500F field emission gun microscope. TEM examinations were carried out using a Philips CM200 microscope operating at 200 kV. The chemical compositions were determined in the TEM using a PGT Spirit energy dispersive X-ray (EDX) spectrometry system. The analyses were carried out without the use of standards for neither the determination of the Cliff–Lorimer factors nor the measurements of local thin foil thicknesses. The results are therefore considered semi-quantitatively. All EDX spectra were displayed by plotting the intensity square root as a function of the energy in order to reveal low intensity peaks. This representation mode allows a better visibility of small peaks. However, it has the drawback of enhancing the artifact peaks such as Cr-K α from the microscope pole piece, Fe-escape and sum peaks related to high intensity peaks, Mo-K α and Mo-L peaks stemming from ion-milling induced contamination and mineral contaminants (S, Cl,...). In addition, the presence of the C and Cu peaks in the spectra is associated with contaminations from the electron beam and the copper sample holder, respectively. All these artifact peaks are indicated by stars in the EDX spectra given in this paper.

3. Results

Fig. 2 gives typical examples of the main characteristics of the deposits obtained by the HVOF technique. The HVOF spray formed material displayed typical microstructural features that were very similar to those observed in the HVOF nanostructured thin coatings [21]. They consisted of unmelted powder particles, melted and flattened particles (i.e. splats) and porosity [12,13,21]. Fig. 2(a) is an SEM image of such a structure. Contamination oxides, due to oxidation of the powder particles during their transit in the flame as well as after a subsequent passage of the spraying torch, are present at intersplat boundaries. A significant amount of porosity (about 10%) is also retained in the deposit because of poor flattening at the employed spraying conditions of the droplets under impact condition on the chilled surface [12,13]. TEM investigation showed that a nanograin zone was retained in the core of the unmelted powder particles [13]. The grain size was in the range from 30 to 90 nm. The grains, embedded in a still deformed matrix, resulted from a partial recrystallization of the original deformed structure from the milled powder [13,21]. The structure in the fully melted splats mainly consisted of

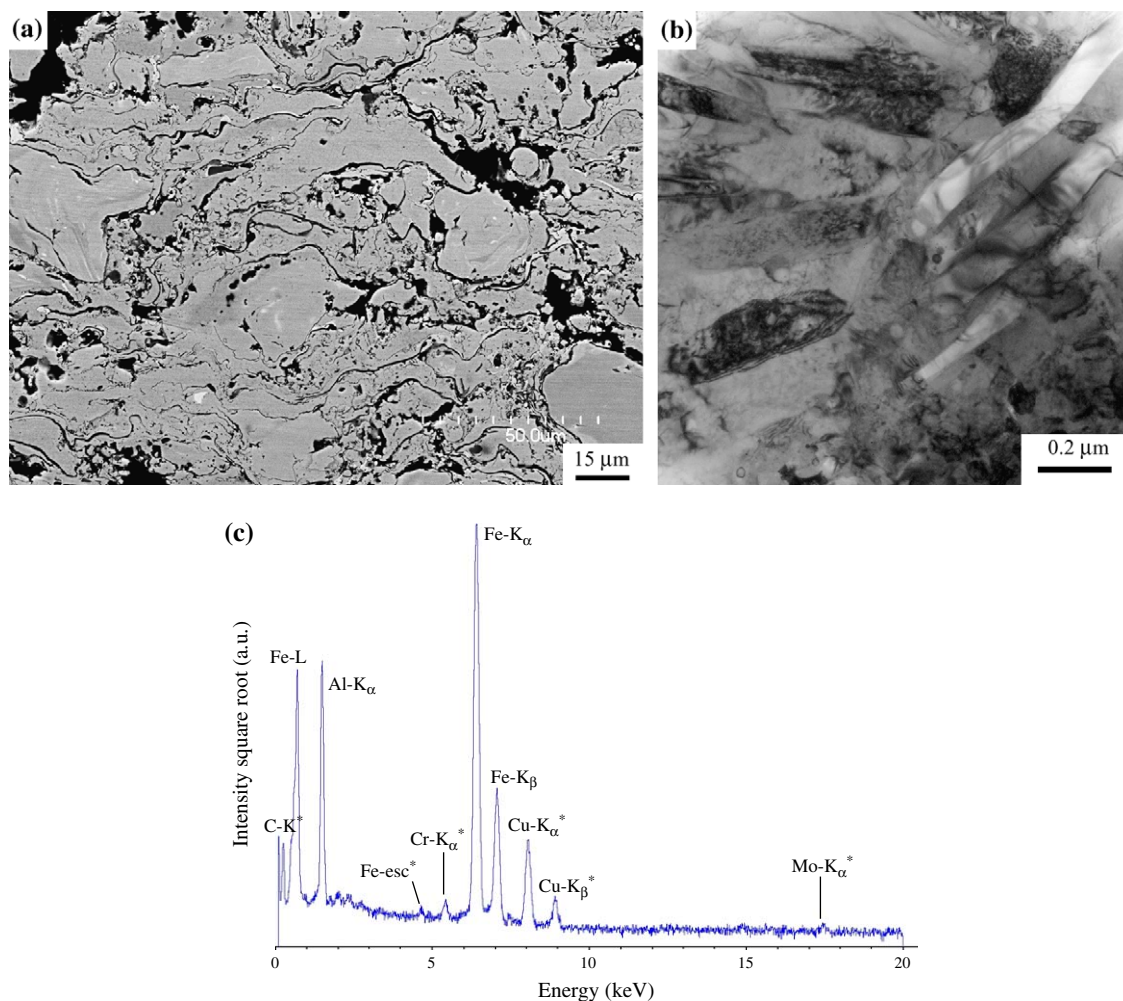


Fig. 2. (a) Backscattered electron SEM micrograph showing the details of the HVOF spray formed deposit, (b) TEM bright-field micrograph showing a columnar grain zone in the fully melted splats and (c) EDX spectrum recorded in one of the columnar grains.

sub-micrometer columnar grains [13]. They resulted from a rapid directional growth due to the intense heat extraction by heat conduction between the splats and the substrate (or the already deposited coating). An example of this type of columnar structure is shown in the TEM bright-field micrograph of Fig. 2(b). An interesting point revealed by the EDX analysis in the TEM was the fact that there was no yttrium left in the melted zones of the coatings. This is illustrated by the EDX spectra given in Fig. 2(c). Due to a lack of miscibility, yttrium was washed away from the melt and became trapped in the amorphous Al_2O_3 -based oxide present at intersplat boundaries where it substituted Al [22].

Fig. 3 shows two examples of SEM micrographs of the products consolidated using the SPS technique. The first SEM micrograph (Fig. 3(a)) was taken from a sample consolidated in the low temperature regime and a significant amount of porosity is clearly visible. Interestingly, the initial powder particles are clearly depicted in this image as they are all surrounded by a thin oxide layer that shows up with a very bright contrast. This oxide film must have been formed during the consolidation process by reacting with trapped gas under heating by the action of the applied current. Comparatively, when the processing is done in the high temperature regime that does not lead to

remnant porosity, the oxide layer is broken up into small pieces. This is clearly visible in the high magnification SEM image in Fig. 3(b) where small pieces of oxide, often of rectangular or squared shapes, are visible along former boundaries between adjacent powder particles. This break up of the external oxide layer is probably due to the effect of local pressure and plastic flow. In addition, electrical breakdown and arcing may be necessary to accommodate the current transfer through the non-conducting thin oxide layer. This mechanism can be accompanied by local melting and evaporation [23]. It is also clear from Fig. 3(b) that, in this high temperature consolidation range, some variability in grain size was visible. This was confirmed by an elaborate TEM analysis, as illustrated in Fig. 4(a,b). The small grains are of the order of 100–400 nm in size (Fig. 4(a)) while some larger grains would reach micrometer sizes (Fig. 4(b)). 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 which leads to fast sintering although the temperature inside the powder particles still remains fairly low. Thus, these local differences result in some heterogeneity in the microstructure of the end-products. TEM imaging revealed that some large grains in the consolidated products did not contain any Y_2O_3 oxide. As shown in Fig. 4(c), the EDX analysis of such grains did not reveal the presence of yttrium in these large grains. This means that this area of the microstructure underwent a solid–liquid phase transformation and that, as for the case of the HVOF sample depicted in Fig. 2, yttrium was washed away from the melt. This confirms that the high temperature consolidation regime combines the actions of plastic flow and liquid sintering mechanisms.

4. Discussion

The key to preparing bulk nanostructured materials with improved mechanical properties is to retain nanostructure while getting a high density of the end-products. The TEM results of these two consolidated types of products 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 [21]. In order to do that, special spray conditions such as low flame temperature, high particle velocity as well as rapid heating/cooling cycles must be selected. However, the drawback of these spraying conditions is that the quality of the particle flattening behaviour is not very effective. The consequence is to introduce porosity. Under the present conditions, the amount of porosity was about 9% while about 13% of unmelted powder particles were retained in the bulk material [13]. This porosity is difficult to avoid or reduce while keeping the ultra fine grain size present in the as-consolidated product. In addition, more than 85% of the consolidated product underwent a solid–liquid

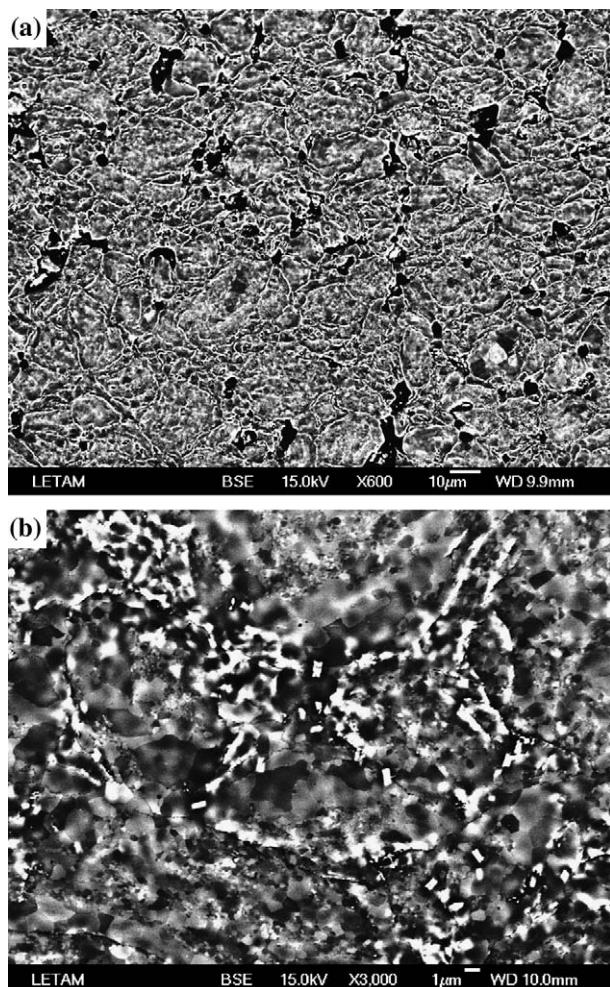


Fig. 3. Backscattered electron SEM micrographs of SPS samples consolidated (a) in the low temperature and (b) high temperature regimes.

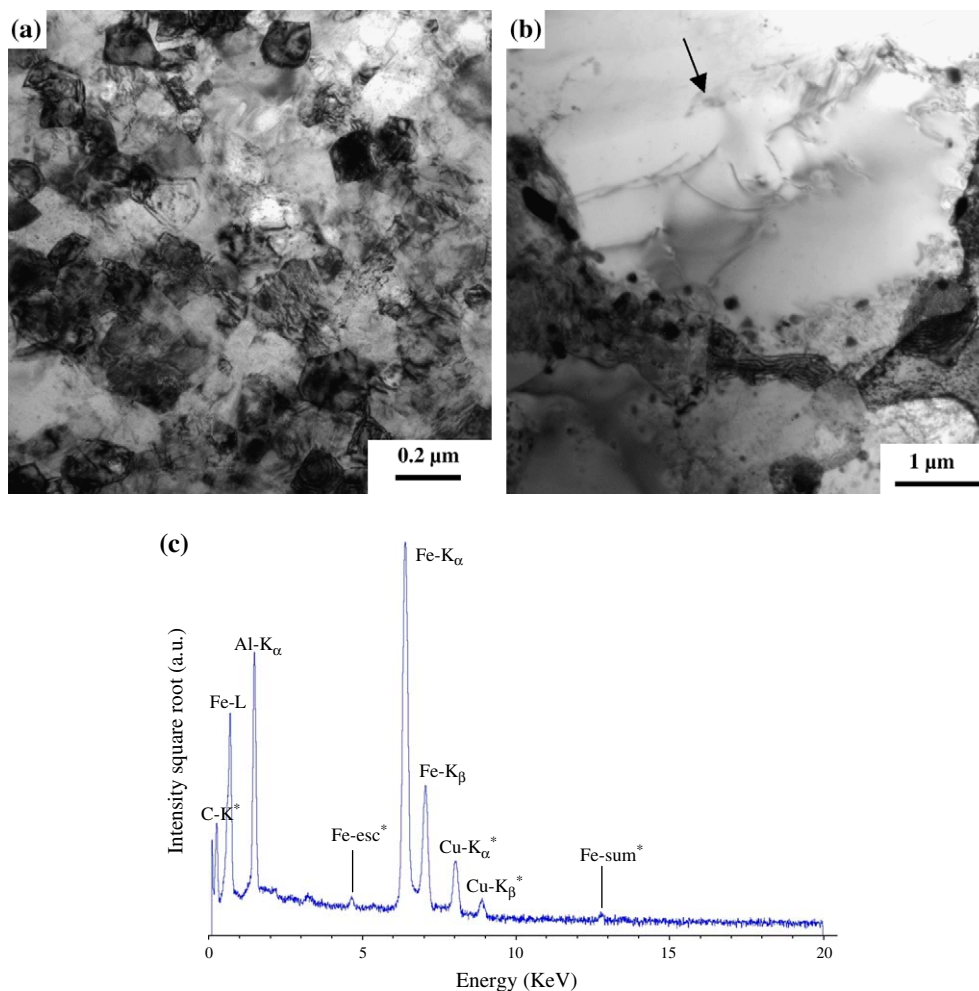


Fig. 4. TEM analysis showing (a) a bright-field micrograph of a nanograin zone and (b) a large grain (arrowed), (c) the EDX spectrum of the yttrium-free large grain.

state transformation. In other words, this also means that about 85% of the consolidated product does not contain any yttrium oxide in dispersion. This is a significant drawback for the development of these materials where Y_2O_3 is introduced to restrain grain growth during subsequent temperature exposure of the end-product. In the case of the SPS processing, the grain size is not as fine but the overall microstructure is more homogeneous. Furthermore, only a small part of the material underwent a passage through the liquid state. Therefore, the intentionally added Y_2O_3 oxides are better distributed in the SPS samples. In addition, the oxides that formed at the particle surfaces during the SPS processing itself have been shown to be broken up by plastic flow and arcing. Following this consolidation route, reduction in grain size to an even lower nanoscale size should be possible via optimization of the sintering procedure. Further work is now underway to optimize the processing conditions and to fully characterize the SPS samples to improve our understanding of the complex mechanisms taking place during the SPS processing. It is, however, clear that the high temperature consolidation regime provides good densification by the combined actions of plastic flow and liquid sintering mechanisms.

5. Summary and conclusions

The aim of this work was to examine the efficiency of two consolidation processing techniques: High Velocity Oxy-Fuel (HVOF) spray forming and Spark Plasma Sintering (SPS) to obtain bulk nanostructured materials from an Y_2O_3 reinforced Fe–40Al (at.%) milled powder. The main results are as follows:

- (1) The HVOF spray forming method is a very effective way to retain nanograins: columnar nanograins in the fully melted zones and, in particular, 30–90 nm sized equiaxed grains retained within the unmelted powder particles.
- (2) The HVOF processing has two major drawbacks. The required condition to bring or retain nanostructures in the HVOF deposits generates a high amount of porosity. In addition, due to their lack of miscibility with the liquid FeAl, the yttrium-based oxides are not present in the major part of the consolidated products. These two points should be harmful to the in-use properties of the HVOF sintered material.
- (3) Processing by SPS at low temperature creates a thin oxide layer at the powder particle surface. High temperature

processing causes a break up of this thin oxide layer by plastic deformation and arcing.

- (4) A good densification can be obtained by SPS through the combined mechanisms of plastic flow and local liquid sintering.
- (5) Because a major part of the material remains in the solid state, SPS has a much higher potential to create sub-micrometer microstructures within which the oxides are more homogeneously distributed.

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