Research Article

Control of FeAl Composition Produced by SPS Reactive Sintering from Mechanically Activated Powder Mixture

S. Paris,^{1,2} E. Gaffet,² and F. Bernard¹

¹ ICB UMR 6303 CNRS/Université de Bourgogne, 9. Avenue A. Savary, BP 47870, 21078 Dijon Cedex, France

² IJL UMR 7198 CNRS/Université de Lorraine, Parc de Saurupt, CS 50840, 54011 Nancy Cedex, France

Correspondence should be addressed to F. Bernard; fbernard@u-bourgogne.fr

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The effects of mechanically activated powder mixture (Fe + Al) on the microstructure and the chemical composition of FeAl compound produced by reactive sintering implying an exothermic reaction were studied. Firstly, the characteristics of Fe/Al mechanically activated powder mixtures were investigated in terms of their phase composition and microstructure. The high-energy milling allowed the formation of micrometric agglomerates composed of nanometric crystallites of iron and aluminum. Three aggregate sizes class A: $\phi < 125 \mu\text{m}$, class B: $125 \mu\text{m} \leq \phi < 250 \mu\text{m}$, and class C: $\phi \geq 250 \mu\text{m}$ were considered. The latter class enhanced the reactivity of powder mixtures due to an increase of interfaces in contact as an analogy to nanostructured multilayer systems. Interrupted SPS experiments were performed on these mixtures to understand the origin of chemical heterogeneities observed after the reactive sintering. Formation of the intermediate phase Fe_2Al_5 at $\sim 510^\circ\text{C}$ was accompanied by an exothermic reaction and a linear expansion and followed by the formation of small amount of FeAl. The conversion to FeAl was complete at temperatures higher than the melting point of Fe_2Al_5 (1170°C). Finally, a phase evolution between Fe and Al versus the temperature during the reactive sintering is suggested.

1. Introduction

Obtaining dense FeAl compounds with a perfectly controlled microstructure is of interest because of improved hardness and strength but also because of expectations of better ductility and toughness for these intrinsically brittle materials [1]. Techniques for producing ultrafine grained bulk materials have been extensively studied over the last decade [2–9]. They include consolidation from nanostructured milled powder by using conventional hot compaction [2, 3], thermal spraying by different processes such as high velocity oxy-fuel (HVOF) [4–6] as well as the spark plasma sintering (SPS) [7–9]. Prior works reported that SPS was an effective method for the synthesis of monolithic FeAl compounds using powders prepared via ball-milling [10–12]. Consequently, it is crucial to control the microstructure of mechanically activated powder mixtures (called hereafter MAP-mixture) which can be considered as agglomerates composed of nanoreactants. Such MAP-mixtures are reported to be combustion synthesis nanoreactors [13]. Indeed, the combustion front reaction

propagates in individual aggregate from the surface to the core. In addition, this fine multilayers system inside MA-agglomerates allows to improve the combustion synthesis parameters such as an increase of the combustion front velocity (by a factor 3 or 5 in the case of Mo/2Si [14] and of Fe/Al systems, resp. [15]) or decrease the ignition temperature of the exothermic reaction between Fe and Al by 100°C down to about 400°C [16]. However, the decrease of the grain size down to the nanometer scale is not the only pertinent parameter. Indeed, the quality and the size of the exchange surface between reactants are essential, especially when a mechanical pressure is applied during a liquid-solid reaction [17]. Such contacts between particles play a major role in the heat conduction and the kinetics of the reaction. For example, in contrast to combustion synthesis of MAP-mixtures, the reaction from Fe/Al nanostructured powders prepared by evaporation-condensation in cryogenic media [18] leads to the formation of alumina with some minor FeAl compounds [19]. The purpose of this work is to control the characteristics (morphology, structure, chemical

composition, analogy with fine multilayers systems without any mechanical alloyed phases) of mechanically activated powder mixtures. In addition, to understand the origin of the FeAl chemical heterogeneities, SPS-stop experiments (i.e., when the current is switched off) were performed at desired temperatures determined from the SPS shrinkage curve. Consequently, each stage of the synthesis and the consolidation of FeAl by SPS reactive sintering were investigated.

2. Experimental Procedure

The synthesis process to produce dense nanostructured FeAl from elemental powders (Fe + Al) is composed of two steps [20]: (i) mechanical activation of the elemental powder mixture by a short duration treatment in a high energy planetary ball-mill and, (ii) synthesis and densification of FeAl in one step by reactive sintering using SPS equipment.

The Al and Fe reactants are taken in the stoichiometric ratio 53 at.% Fe. 10 g mixture of elemental powders of Al (Cerac, 15–20 μm in particle size, and 99.5% purity) and Fe (Prolabo, 10–15 μm in particle size, and 99.5% purity) was co-milled in confined air via a planetary ball vario-mill Fritsch Pulverisette 4 [22, 23]. Based on previous works [10, 16], a specific ball-milling condition was established at 150 rpm (rotation per minute) for the disk rotation speed, –200 rpm for the absolute vial rotation speed, and 4 h uninterrupted milling duration. The charge ratio C_R (ball to powder mass ratio) was 7. The powders being constituted of quite abrasive materials, a short duration of milling has been selected to avoid any contamination of the product by the milling tools. In fact, in order to limit the powder contamination by the milling tools but also to increase simultaneously the yield of MAP-mixtures, three millings without cleaning milling tools have been carried out. Indeed, under these conditions, the ductile character of powders induced the formation of FeAl coating on the vial surface aging as a protective liner against the abrasion on the surface of tempered steel tools. In addition, the milling parameters were selected to be short to avoid the formation of mechanically induced phases but still sufficiently long for producing MA-agglomerates. In fact, fracture and welding are the two basic events which cause a permanent exchange of matter between particles and ensure a mixing of components at a nanometer scale level [10, 16]. To perform study of the aggregate size effect, two sieves of 125 and 250 μm mesh size were selected in order to prepare three granulometric classes.

Then, these MA-powders were introduced in the SPS apparatus [24] for performing reactive sintering implying an exothermic reaction. The mechanically activated powders were first cold compacted into green body in a cylindrical graphite die lined with graphite foil using a uniaxial pressure of 80 MPa during 2 min. The relative density of the green sample resulting from the cold compaction was about 70%, determined by geometrical measurements. The graphite die containing the cold-compacted sample was set inside the SPS chamber. SPS process is a pressure-assisted pulse-current sintering in which by repeated application of DC pulses, spark point discharges and Joule heating points result in efficient

sintering with low power consumption. The experimental procedure is well detailed elsewhere [11]. A uniaxial pressure of 14 kN (i.e., 70 MPa) was applied both during the reaction and during the cooling. A high DC current was generated, increasing from 0 to 1750 A in 20 s then held at the maximum value for 160 s. Thus, the total duration for applying DC pulse current from the beginning of the heating to the beginning of the cooling is equal to 4 minutes. Temperatures were measured by means of a K-type thermocouple inside a hole located at 3 mm of sample surface. The end-products were typically disks of 18.8 mm in diameter and from 2.2 up to 5.5 mm in height. Before characterization, samples were first polished with 180-grit silicon carbide and down to 1 μm with diamond paste and, finally cleaned in an ultrasonic ethanol bath in order to remove surface contamination from graphite foil. The density of sintered products was evaluated by Archimede's method.

For each “quenched” sample corresponding to SPS stop experiments, a phase and a chemical analysis were carried out, respectively, by X-ray diffraction (XRD) and by scanning electron microscopy (SEM). These quenching means freezing the different stages from shrinkage curve at desired temperatures of the SPS process by shutting off the electric current. X-ray powder diffraction (XRD) measurements were performed using a D5000 Siemens high-resolution diffractometer with a monochromatic Cu-K_β beam ($\lambda = 0.1392 \text{ nm}$) focused with a secondary curved graphite monochromator. Pattern decomposition was achieved by means of the profile-fitting. At the same time, a least-square refinement program was used to determine the cell parameter of reactants. A JEOL 6400F Scanning Electron Microscope (SEM) with a field emission gun (FEG) and coupled with a LINK OXFORD Energy Dispersive X-Ray Spectrometry (EDXS) was used to analyze, respectively, the grain morphology and the local chemical composition of materials. Consequently, MAP-mixtures were embedded and polished whereas dense materials were cut along the axial direction and were embedded in carbon charged resin (Konductomet). A back-scattered electron (BSE) technique was also used to determine the elemental chemical distribution. To estimate the global chemical composition, EDXS measurements were also performed on FeAl products annealed at 950°C in vacuum during 48 hours in order to get a reference material; these analyses were performed on square surfaces ($100 \times 100 \mu\text{m}^2$). The chemical composition was determined from 50 measurements. An ICP plasma torch (ICP OES Vista Pro commercialized by Varian) coupled with a Meinhardt nebulizer and cyclonic chambers (200 kPa, 1.3 kW) was also used to check the Fe and Al contents.

3. Results and Discussion

3.1. The MAP-Mixture. The microstructure analysis deduced from XRD, SEM, and ICP experiments of all MAP-mixtures including polydisperse mixture is reported in Table 1. In comparison with the classical mixture (Turbula) composed of micrometer sized grains (10–15 μm and 20 μm for Fe and Al, resp.) [15], the mechanical activation stage allows

TABLE 1: Average characteristics in terms of chemical composition and microstructure parameters (crystallite size, microdistortion level, and lattice parameter) for each class of MAP-mixtures (Fe + Al) in comparison with those obtained by a TURBULA classical mix. $a_{\text{JCPDS Al}} = 0.4049 \text{ nm}$, $a_{\text{JCPDS Fe}} = 0.2866 \text{ nm}$. * Average characteristics $i = \sum(\text{Characteristic } i \times \text{yield of each granulometric class})$. $\diamond$ Grain size given by suppliers.

Characteristics	TURBULA powders	MA powders resulting from the third ball-milling				
		Polydispersity	Seaved—grain-size ranges Φ (μm)			
		Average*	3rd milling	Class A < 125	Class B 125–250	Class C ≥ 250
Yield (%)	100%		96%	8 ± 4	17 ± 2	75 ± 03
Chemical composition						
Global—ICP (%at. Fe)	53 ± 1	53 ± 3	53 ± 3	45 ± 3	47 ± 4	55 ± 3
Global—EDXS (%at. Fe)	53 ± 1	53 ± 2	53 ± 2	46 ± 2	49 ± 2	54 ± 1
Microstructure						
Fe						
Crystallite size (nm)	$10\text{--}15 \mu\text{m}^\diamond$	53	50	90 ± 5	67 ± 4	45 ± 3
Microdistortion level (%)		0.13	0.13	0.10	0.12	0.14
Lattice parameter (nm)	0.2866 (3)	0.2867 (1)	0.2867 (2)	0.2866 (9)	0.2867 (4)	0.2868 (3)
Al						
Crystallite size (nm)	$20 \mu\text{m}^\diamond$	70	70	110 ± 7	87 ± 5	62 ± 3
Microdistortion level (%)		0.09	0.08	0.08	0.08	0.09
Lattice parameter (nm)	0.4049 (2)	0.4049 (9)	0.4050 (4)	0.4050 (2)	0.4050 (6)	0.4049 (7)

FIGURE 1: X-ray diffraction pattern of Fe/Al MAP-mixtures (theoretical XRD peak position of FeAl phase from ICDD n° 01-1257).

FIGURE 2: SEM (BSE mode) micrographs showing and comparing different morphologies of MAP-mixtures (53 at.% Fe/Al) in function of the granulometry class (P4 (150/–200/4h)). The bright layers and the dark ones are Fe and Al phase, respectively [21].

the formation of micrometer size MA-powders (ranging from $0.4 \mu\text{m}$ up to $800 \mu\text{m}$) constituted of Fe and Al with an average crystallite sizes of 50 nm and 70 nm, respectively.

The size distribution of MAP-mixtures is very wide and may be responsible for some heterogeneity after SPS reactive sintering. Taking into account the detection limit of the apparatus, XRD patterns which performed MAP-mixtures confirm that no mechanical alloyed phase is formed during the milling (Figure 1). In fact, only Fe and Al XRD peaks were observed and any modification of the lattice parameters of these phases was highlighted. The internal microstructure of the MA powders depended on the aggregate size (Figure 2). From chemical composition, microstructure, and structure, the yield of each aggregate size was calculated (Table 1). The yield was improved when the size of MA-powders increased; as an example 75% of MAP-mixtures had larger size than $250 \mu\text{m}$. The size difference can be explained by an activation degree of powder which increases with the agglomerate size. This operation allowed selecting three classes of MA-agglomerates, having different particle sizes: (i) class A: $\phi < 125 \mu\text{m}$, (ii) class B: $125 < \phi < 250 \mu\text{m}$, and (iii) class C: $\phi > 250 \mu\text{m}$. A fourth batch of powder labeled as “polydisperse” was also studied, that is, without any size separation.

From SEM observations of the MA-aggregate cross-sections (Figure 2), it is obvious that the morphology and the microstructure between each class are heterogeneous and may be responsible for the chemical contrast observed in sintered products [10, 12]. Indeed, SEM observations of MA-agglomerates (Figure 2) revealed that the chemical distribution between Fe (white color) and Al (dark color) is different from one type of aggregates to another one. Even after a mechanical activation step, the initial grain size of Fe ($10\text{--}15 \mu\text{m}$) and Al ($20 \mu\text{m}$) is still observed in smaller MA-aggregates (Class A, Figure 2(a)). In addition, concerning the medium MA-agglomerates (Class B, Figure 2(b)), some grains of Fe and Al are slightly elongated and had a thickness in the range of few micrometers. Finally, only large MA-aggregates (i.e., Class C, Figure 2(c)) may be considered

as Fe/Al multilayers. Indeed, this latter is comparable to the Fe/Al diffusion couples. Moreover, a variation of the aggregate morphology inside this lamellar structure can be observed on the larger agglomerate (Class C). The analogy with multilayers structure is improved from the surface to the center of the agglomerate. In comparison to the initial powders, the thickness reduction of Al elongated grains (i.e., layers) is greater than those of Fe especially at the center of aggregates (i.e., ranging from 100 nm to 500 nm). Similar behavior has been reported for other systems such as Al-Cr [25] and Al-Mo [26]. In the center of agglomerate, it can be assumed that the microstructure of the powder particles could not be solved using SEM, since the size of layers has been reduced below 0.2 micrometer. Between the finest multilayers, it is possible to distinguish the presence of a new intermediate color (gray) (Figure 3(a)) that consisted of 53 at.% Fe from chemical analyses (Figure 3(b)). These confirm the well-established Fe/Al diffusion couples, the improvement of powder reactivity, and, therefore, the conversion rate. In fact, according to Fe/Al binary phase diagram [27] and to the schematic diagram showing the possible hierarchy of phase formation in the case of a diffusion couple [28], this interfacial intermediate phase may correspond to an amorphous phase, a Fe or Al rich solid solution, and/or another intermetallic phase like Fe_2Al_5 formed at higher temperature [29]. This latter intermetallic is assumed to form after an annealing of Fe/Al multilayer thin films [30].

From Table 1, the crystallite sizes of reactants are in the nanometric range for both Al and Fe parts. In particular, the crystallite size of Fe (idem for Al) decreases when the size of MA-aggregates increases whereas the Fe microdistortion rate decreases (no evolution is observed for Al). In addition, whatever the granulometry, overestimated value of aluminum amount (70 at.%) was determined. Similar results were obtained for powders mixed during 4 h in Turbula. This difference can be explained by the higher analyzed XRD depth (~7 times) of Al (30 μm) in comparison with that of Fe (2.4 μm) for a similar fraction of irradiated area. Nevertheless, as the Fe particles seem to be embedded by an aluminum layer, a careful interpretation is needed. In addition, whatever the granulometry, no contamination (mainly by Cr) from milling tools has been observed (Figure 3(b)). Nevertheless, the global chemical analysis of aggregate shows a significant amount of oxygen (<10 at.%) which increases with the grain size, that is, 5, 7, and 9 at.% for the smallest (Class A), the medium (Class B), and the larger (Class C) agglomerates, respectively. Similar results were reported by Godlewska et al. [31]. However, the origin of the oxygen may be due to the milling atmosphere (confined air) containing oxygen. Nevertheless, these oxides are not detected by XRD (in the detection limit of the apparatus). This study confirms the interest to use high-energy ball-milling without cleaning vials in order to avoid any contamination. Moreover, the formation of passive layer around the micrometric aggregate surface will reduce considerably the reactivity towards ambient air of the isolated nanometric particles allowing storage, transport, and handling.

Although the ball-milling conditions are identical for each granulometric class (P4 (150/–200/4 h), noticeable heterogeneities have been found to appear whatever the scale observation (from macroscopic to microscopic levels) in micrometric Fe/Al MA-aggregates. Transverse observations have shown that aggregates are heterogeneous and that they are responsible for the chemical contrast present on reactive sintered compound. Similar behavior was observed in the case of the Mo/2Si agglomerates [32]. Heterogeneities of Fe/Al aggregates depend on their size. Consequently, the control of the MA-aggregates features (chemical composition, microstructure, intergranular porosity, etc.) is crucial in order to elaborate intermetallic compounds with expected properties. Such a result is emphasized because Fe/Al MA-aggregates can be considered as combustion synthesis nanoreactors [13]. To adjust the specific characteristics of MA-aggregates for expected foreseen applications, it is necessary to understand the origin of such heterogeneities. A similar behavior, that is, the observation of heterogeneous micrometric aggregates composed of nanostructured reactants was already reported in the case of the production of items from cold-rolling process [33]. A nanometer size multilayers system and the chemical homogeneity are obtained when the number of cycle is increased and when the mechanical pressure is higher. Consequently, it is possible to assume that the difference of MA-aggregate characteristics must be due to a modification of plastic deformation mechanism during the ball-milling process [34, 35]. In MA techniques, the repeated fracture-welding process results in an intimate mixture of the two constituents with a concomitant increase of the defect concentration and strain in the mixture. In the case of ductile-ductile powder mixture (such as Fe/Al system), milling refines the grain size further to a lamellar structure and even greater number of defects are introduced [36–38]. Ball-milling conditions have an influence on the nature and, also on the concentration of defects and, consequently on the chemical homogeneity. High energy planetary ball-mill (especially pulverisette P4), in which the rotation speeds of vials and the plate can be selected independently, allows extending the milling investigation for producing powders with the desired characteristics [39–44]. Oleszak and Shingu [34] reported that the shape of agglomerates with different chemical composition from 50 to 100 at.% Fe is more regular when the milling duration is prolonged. According to El-Eskandarany et al. [45], the large distribution of the MA-aggregates size indicates that the growth mechanism of aggregates to obtain powders with optimal characteristics is not complete. It can be stipulated that the heterogeneity can be due to a difference of co-milling effective duration. Milling injects an additional energy to the reactant system in the form of the interfacial and strain energies and effectively lowers the activation barriers. In fact, in a few minutes to one hour, the lamellar spacing (Figure 3(a)) usually becomes small (few micrometers) and the crystallite size is refined to nanometric dimensions. Moreover, the presence of structural defects (i.e., dislocations, vacancies, stacking faults, grain boundaries, etc.) enhances the diffusivity of dissolved elements into the matrix. Additionally, the slight temperature increase during milling

FIGURE 3: (a) BSE micrographs showing the transverse cut of coarser agglomerates (class C) to reveal the multilayer structure in each MAP-mixtures. The bright layers (A) are Fe phase, and the dark ones (B) are Al phase. Between the finest multilayers (A and B), a layer with a intermediate color (C) is observed and corresponds to a mix of Fe and Al. The EDX spectra of each contrasted layer (A, B, and C) are reported in (b).

	Class A- ϕ (μm) < 125	Class B- $125 \leq \phi$ (μm) < 250	Class C- ϕ (μm) ≥ 250
Corresponding SPS products

FIGURE 4: SEM (BSE mode) micrographs of products synthesized by SPS. These are performed on the transverse cut of each of them. The bright layers and the dark ones are Fe and Al phase in the agglomerates, respectively. Contrast of brightness is characteristic of the heterogeneity such as brighter area which can correspond to higher % at. Fe content.

supports the diffusion and, consequently, a true alloying takes place among the constituent elements.

3.2. SPS Reactive Sintering. These MAP-mixtures were introduced in the SPS apparatus for performing reactive sintering according to conditions previously described. The control of the SPS processing parameters has been found to allow

the formation of a dense FeAl compound (close to 99%) forming a microstructure with nanosized coherently diffracting domains [12]. TEM analyses have been found to reveal that the nanoorganization, especially the nanosize of the coherently diffracting domain size, was due to dislocation networks [12]. The beneficial effect of the SPS process on the densification was demonstrated elsewhere [11] showing

FIGURE 5: Evolutions of (a) the voltage (V), intensity (I/10) and pressure (kN $\times$ 10) and of (b) the temperature (T) and the displacement versus the time of a sample sintered at 1750 A and 70 MPa.

that the relative density increased with the heating rate, the applied pressure, and the holding time up to a critical value. SEM observations (Figure 4) of the sintered sample showed clearly the presence of heterogeneous chemical compositions which differ versus MA-agglomerate size. In order to explain the origin of these heterogeneities, SPS-stop experiments were carried out using only larger MA-agglomerates (Class C) in which the chemical contrast seems to be stronger and also closer to expected FeAl stoichiometry (53% at. Fe, Table 1). Figure 5(a) presents the evolution of SPS processing parameters versus the time during the reactive sintering from Fe + Al. In addition, as presented in Figure 5(b). From a fine analysis of such curves associated to reaction mechanisms, it is possible to describe the different sintering stages of the process leading to the formation of FeAl during a reactive sintering implying an exothermic reaction, that is, temperatures at which expansion and phase transformation take place. Such analysis allows selecting “interesting” temperatures that is performing SPS “stop.” From Figure 5, five distinct successive stages can be highlighted labeled as zones I to V. XRD patterns from the SPS end-products quenched

from different temperatures are presented in Figure 6. The corresponding microstructure contrast due to the difference in chemical composition is presented in Figure 7. The phase identification deduced from XRD characterization analysis and the chemical composition determined by EDX are also reported. It can be clearly stated that the nature of the phases determined by XRD (Figure 6) and microstructure observed by SEM (Figure 7) change versus the temperature. For describing all stages of the reactive sintering in the Fe/Al system, the linear expansion (deduced from Figure 5(b)) and the relative density evolutions were plotted versus the temperature (Figure 8).

In Zone I, as can be observed (Figure 8), the displacement increases slowly from the room temperature to 400°C. A SPS-stop experiment carried out at 350°C revealed the absence of chemical interaction. The sample contained only Fe (bright layers) and Al (dark layers) like the initial green sample which is validated by the XRD analysis (Figure 6(b)). This confirms that no significant reaction occurs from RT up to 400°C. Consequently, the slight expansion in Zone I was caused by the thermal expansion of particles, die, and gas.

FIGURE 6: X-ray diffraction patterns (from (b) to (f)) versus temperature for quenched specimens to room temperature.

FIGURE 7: SEM (BSE mode) micrographs showing and comparing microstructure of samples quenched from different temperatures. Temperatures are characteristics of each zone relative to the reaction sequence of FeAl formation determined from the evolutions of the XRD patterns curves (Figure 6).

In Zone II, from 400°C to 500°C, a slight shrinkage of the sample is observed (Figure 8(a)).

At 450°C, for the sample quenched from 450°C, an intermediate color can be observed at the Fe(s)/Al(s) interfaces (Figure 7(a)). Using energy dispersive spectroscopy (EDS), the dark gray phase surrounded by iron gets an atomic percent Fe equal to 30 ± 2 . This latter can be identified as an amorphous or crystallized intermetallic phase rich in Al (such as Fe_2Al_5 according to the Fe-Al phase diagram [27])

and/or as a solid solution of Fe(Al) or Al(Fe). In particular, Thompson [46] has pointed out that an interdiffusion is necessary between pure components at the interface before the nucleation of any intermetallic compound. In addition, it was reported [21] that at temperatures below 300°C, the interdiffusion of Fe in f.c.c Al is faster for Al-Fe diffusion couple. Above this temperature, the diffusion behavior is opposite; that is, interdiffusion of Al in b.c.c. Fe is faster. From calculated free energy at 450°C, intermetallic compound can

FIGURE 8: Evolution of (a) of the linear expansion during a SPS reactive sintering from Fe + Al mixture. Red points correspond to XRD phase analysis presented in Figure 6. A zoom of the temperature profile showing the fast increase of the temperature characteristic of the exothermic reaction is inset. (b) Dependence of relative density of interrupted sample, that is, of the different phases (detected by XRD from Figure 6), as a function of temperature. In addition, five zones in agreement with Figure 5 are presented.

nucleate within the aluminum solid solution [47]. However, the amount of solute content (Fe) in solid solution of Al is too small to be detected.

In Zone III, a sharp temperature elevation ($3780^{\circ}\text{C}\cdot\text{min}^{-1}$) from 500°C to 600°C is observed simultaneously as a significant shrinkage which is validated by the faster stage of densification (Figure 8). These evolutions are characteristics of the exothermic reaction occurring between Fe and Al powders. This latter is confirmed by X-ray analysis which shows the presence of an unreacted Fe and the formation of the aluminum rich Fe_2Al_5 (Figure 6(d)) and of a minor amount of FeAl. The formation of Fe_2Al_5 is detectable only from 600°C whereas it can exist at lower temperature. As previously observed, the dark gray phase is confirmed as Fe_2Al_5 ($\sim 30\%\text{at. Fe}$). The intermetallic compound is formed around the partially unreacted Fe particle (bright layer). The interface between the Fe_2Al_5 layer and Fe grain is irregular due to the tongue-like morphology of the Fe_2Al_5 layer. Similar morphology was observed during dipping solid Fe in liquid aluminum [48, 49]. It can be concluded that at this stage, despite the fact that melting point of Al was not reached (660°C), aluminum has totally reacted to form iron aluminide and left behind large pores (Figure 7(b)) certainly due to

FIGURE 9: SEM (BSE mode) micrographs of a homogeneous single phase FeAl after thermal treatment (1000°C , 30 min) on sample containing Fe + Fe_2Al_5 + FeAl phases presented in Figures 6(e) and 7(c).

a local temperature higher than measured temperature. As reported by different authors [29], the reaction demonstrated to be always accompanied by an expansion of the sample due to the solid state exothermic reaction $2\text{Fe(s)} + 5\text{Al} \Rightarrow \text{Fe}_2\text{Al}_5$ which occurred at $\sim 560\text{--}565^{\circ}\text{C}$.

Then, in Zone IV from 600°C to 1100°C , it can be seen that the amount of FeAl increases on the expense of Fe_2Al_5 and Fe (Figure 6(e)). These observations are confirmed by high resolution SEM images (Figure 7(c)). Three uniform well-distinguished phases which differ in contrast can be observed. However the amount of FeAl is very small even after the second reaction. The EDS analysis obtained from these regions indicate that between Fe (bright grain) and aluminum rich Fe_2Al_5 there is another layer (light grey layers) exhibiting narrow morphology rings with Fe concentration much higher (55% at.) than expected in Fe_2Al_5 (Figure 7). These may be the rings of the aggregates. These layers are believed to be consisting of FeAl or a mixture of FeAl with Fe or Fe_2Al_5 . At higher temperature (1100°C), according to SEM analysis (Figure 7(d)), the amounts of Fe_2Al_5 and Fe still decrease whereas the quantity of FeAl increases. Such observations can be explained from diffusion couple of species. As reported by Maitra and Gupta [30] during the formation of FeAl, the microstructure of the diffusion couple has revealed that exist two Kirkendall planes: one at the Fe/FeAl interface and, the other at the FeAl/ Fe_2Al_5 interface on the Fe_2Al_5 side. For the Kirkendall plane at Fe/FeAl interface, it can be inferred that Fe diffused faster ($\sim 10^4$) than Al in the Fe-rich part of FeAl. A similar conclusion can be drawn for the other Kirkendall plane in agreement with the diffusivity values [50]. These observations are confirmed from activation energy for the growth of the FeAl layer. The activation energy for the growth of the FeAl layer is larger ($180\text{ kJ}\cdot\text{mol}^{-1}$) than that for the diffusion of iron atoms into Fe_2Al_5 ($141\text{ kJ}\cdot\text{mol}^{-1}$) and is smaller than that for the diffusion of aluminum atoms into FeAl ($340\text{ kJ}\cdot\text{mol}^{-1}$) [51]. It was identified that the growth of all intermetallic layers was controlled by the diffusion of Fe atoms into the Al-richer intermetallic layers [52]. The growth of the FeAl layer was likely controlled by the diffusion of iron atoms into the Fe_2Al_5 layers.

FIGURE 10: Phase evolution from Fe/Al MAP-mixtures for producing pure FeAl compound by reactive sintering.

Finally, in Zone V from 1100°C to 1235°C , the evolution of the SPS curves corresponds to the formation of FeAl. At 1180°C , only XRD peaks of FeAl are observed (Figure 6(f)). FeAl compound was formed to exhibit a micrometric grain size ranging from 1 to $6\text{ }\mu\text{m}$ [12]. Nevertheless, from the observation of BSE micrograph, whereas the previous areas corresponding to Fe and Fe_2Al_5 disappear, a modulation of contrast can be clearly observed (Figure 7(e)). Such observations can be explained by the chemical contrast present at the submillimeter-scale (EDX) [10, 11] with a variability of Al content in the range of 36–47%. The specificities can be introduced by the melting of Fe_2Al_5 at 1171°C according to the Fe-Al phase diagram [27]. Hence, the melting of Fe_2Al_5 allows a faster shrinkage and leads to a fully dense compound; that is, the density of the compact reaches 99.5% TD. No macroporosity can be observed in SEM image (Figure 7(e)) which is confirmed from Hg porosimetry analysis, and no open porosity was detected. It is obvious that hot pressure applied during SHS allows full-densification of material.

To confirm the role of Fe_2Al_5 in the formation of FeAl, an additional experiment was performed on the sample quenched from 800°C in order to get FeAl from solid state reaction between $\text{Fe}_{(s)}/\text{Fe}_2\text{Al}_{5(s)}/\text{FeAl}_{(s)}$ phases. The sample was heated for 30 min at 1000°C , below the melting point of Fe_2Al_5 . Compared to previous FeAl compounds formed, a single phase material (with pores) was formed (Figure 9) with 94% relative density. After polishing of the sample to eliminate oxide layers, local phase analysis (EDS) on several zones showed that the sample composition is homogeneous and corresponds to the expected composition (53 at.% Fe, Figure 9). Characteristics are consistent with those obtained by Gedevisanishvili and Deevi [29] at 900°C . Homogeneous

FeAl compounds can be formed via a solid state reaction. Consequently, it is expected that the new FeAl phase formed during the melting of Fe_2Al_5 has a different formation mechanisms than the FeAl synthesized at lower temperature. This study confirms the necessity on the one hand, to follow the evolutions of the phase nature and of their respective domains of composition and, on the other hand, to understand the sequence of phase formation, the interface type, the morphology of interfaces, and the growth mechanism. Thus, it is possible to suggest a reaction mechanism for producing pure FeAl (Figure 10). Whatever the SPS conditions, the formation of FeAl occurred in three steps: the formation of a solid solution Fe (Al) followed by a solid state reaction of Fe_2Al_5 to the interfaces of $\text{Fe}(s)/\text{Al}(s)$ and, then FeAl. Nevertheless, it is not possible to conclude the fact that such reactions are competitive or successive. The formation of Fe_2Al_5 is prejudicial to elaborate dense FeAl in one step from Al liquid phase [15]. To limit the reaction duration, it is necessary to go through the melting of Fe_2Al_5 . This latter phase, combined to the presence of $\text{Fe}(s)$, is responsible for the original characteristics of the FeAl compounds. In agreement with others intermetallics, an increase of the heating rate will reduce the duration of precombustion reaction and, consequently the formation of Fe_2Al_5 . A higher heating rate will promote Fe-solid-Al-liquid reaction which results in the production of pure nanostructured FeAl compounds [53] whereas the presence of Fe_2Al_5 leads to a stoichiometry gap. Consequently, the heterogeneous characteristics of MA-agglomerates according to their size which are considered as SHS microreactors reinforce the obligation of their check. They are responsible for the FeAl chemical heterogeneities which depend on the reaction path.

4. Conclusion

This study gives a fine description of the formation of Fe/Al MA-agglomerates using a high energy planetary ball-mill. It has been demonstrated that mechanical activation resulted in the formation of micrometer size aggregates composed of nanostructured Fe/Al multilayers with heterogeneous characteristics themselves. These latter are responsible for the heterogeneous characteristics of the subsequent dense “nanostructured” FeAl compounds synthesized by SPS reactive sintering. A system presenting an “ideal” nanometer size multilayer system is obtained when the larger aggregates are formed. Consequently, for this ball-milling conditions, that is, P4 (150/–200/4 h), the optimal mixture resulted from the 3rd ball-milling without cleaning tools and had the coarsest studied granulometry ($\phi \geq 250 \mu\text{m}$, i.e., Class C). In addition, it is essential for each agglomerate size to adapt reactive sintering parameters for limiting FeAl chemical heterogeneities.

The dense FeAl intermetallics synthesized via a mechanically activated reactive sintering process have been shown to exhibit some chemical heterogeneity. To produce FeAl materials with perfectly controlled characteristics, the sequences of phases formed during the sintering of MAP-mixtures (Fe + Al) were identified by X-ray diffraction, scanning electron microscopy back scattered electrons coupled with energy dispersive X-ray spectrometry, and density measurements. The results were correlated to the temperature profile and the shrinkage curve occurring during flash sintering. It was found that the formation of the intermediate phase Fe_2Al_5 at $\sim 510^\circ\text{C}$ was associated with an exothermic reaction and a linear expansion and followed by the formation of small amount of FeAl. The conversion to nanoorganized FeAl is complete at higher temperatures than the melting point of Fe_2Al_5 (1170°C). The formation of two types of iron aluminide intermetallics. (i.e., with distinct reaction mechanisms) seems to be at origin of the FeAl specificities. Consequently, it is essential to limit the formation of Fe_2Al_5 by solid state reaction and to promote the direct reaction between Fe(s) and Al(l) by a control of the mechanical activation and reactive sintering conditions.

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