Fast synthesis and consolidation of porous FeAl by pressureless Spark Plasma Sintering

D V Dudina\textsuperscript{1,2,3}, A E Brester\textsuperscript{2,3}, A G Anisimov\textsuperscript{1}, B B Bokhonov\textsuperscript{2,4}, M A Legan\textsuperscript{1,3}, A N Novoselov\textsuperscript{1}, I N Skovorodin\textsuperscript{5} and N F Uvarov\textsuperscript{2,3}

\textsuperscript{1}Lavrentyev Institute of Hydrodynamics SB RAS, Lavrentyev Ave. 15, Novosibirsk, 630090, Russia
\textsuperscript{2}Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze str. 18, Novosibirsk, 630128, Russia
\textsuperscript{3}Novosibirsk State Technical University, K. Marx Ave, 20, Novosibirsk, 630073, Russia
\textsuperscript{4}Novosibirsk State University, Pirogova str. 2, Novosibirsk, 630090, Russia
\textsuperscript{5}Institute of Automation and Electrometry SB RAS, Koptyug Ave. 1, Novosibirsk, 630090, Russia

E-mail: dina1807@gmail.com

\textbf{Abstract.} We report one-step fast synthesis and consolidation of iron aluminide FeAl of high open porosity by pressureless reactive Spark Plasma Sintering (SPS). The starting material of the Fe-40at.%Al composition was a mixture of an iron powder with an average particle diameter of 4 µm and an aluminum powder with an average particle diameter of 6 µm. The rationale behind the choice of the SPS as a processing technique and fine and comparable sizes of the two reactants for the synthesis of high-open porosity FeAl was realization of fast full chemical conversion of Fe and Al into single-phase FeAl reducing the time available for the compact shrinkage. According to the XRD phase analysis, single-phase FeAl compacts formed after SPS at 800 and 900°C. These compacts had open porosities of 41 and 46%, respectively. The transverse rupture strength of the compacts sintered at 700-900°C was found to change little with the sintering temperature in the selected range.

1. Introduction

Porous iron aluminides FeAl and Fe\textsubscript{3}Al are promising materials for making high-temperature gas filters due to their high corrosion resistance in sulfur-containing atmospheres [1]. Reactive sintering presents an efficient fabrication method of porous iron aluminides. Gao \textit{et al} [2-3] used this approach and obtained porous FeAl by cold pressing and sintering of Fe+Al mixtures in a vacuum furnace. Relatively coarse powders were used and sintering was conducted at 1200°C for 1 h. The formation mechanism of porous structures during the reaction between iron and aluminum powders remains a matter of active discussion [2-5]. A successful processing method of porous FeAl would be the one that allows achieving fast chemical transformation of the reaction mixture into a single-phase product while maintaining high porosity (limiting shrinkage of the compact).

The advantages of using electric current as a means of heating of the reaction mixture is fast heating and reactivity enhancement relative to conventional processes of heating in a furnace. As was reviewed by Orru \textit{et al} [6], Spark Plasma Sintering (SPS), a sintering technique that uses DC
pulses, can be used for the production of both dense and porous materials. In recent years, there has been a growing interest to the possibilities that SPS can offer in the area of porous materials [7-10]. Two main approaches can be used for the synthesis of porous materials by SPS: sintering using space holders [7-9], which are removed from the compact after consolidation, and sintering without the application of pressure [5, 10].

In this work, we report, for the first time, one-step fast synthesis and consolidation of single-phase high-open porosity iron aluminide FeAl by reactive pressureless SPS.

2. Materials and Methods

Carbonyl iron (99%, average size 4 µm, “Syntez-PKZh”, Dzerzhinsk, Russia) and gas-atomized aluminum (99.9%, PAD-6, average size 6 µm, “VALKOM-PM”, Volgograd, Russia) were used as the reactants. The mixture of the Fe-40at.%Al composition was prepared. The powders were dry-mixed in a horizontal low-energy mixer for 3 h. Spark Plasma Sintering was carried out using a SPS Labox 1575 apparatus (SINTER LAND, Inc., Japan). The temperature during the SPS was controlled by a pyrometer focused on a near-through hole in the die wall. The powder mixtures were sintered into 3-mm thick compacts of 20 mm diameter at 700, 800 and 900°C. The heating rate was 70°C min⁻¹ and the holding time at the maximum temperature was 3 min. Very fast synthesis was also attempted using a heating rate of 100 °C min⁻¹ and no holding at the maximum temperature. The as-mixed Fe-40at.%Al powders were not pressed before the SPS. The powders were poured into the die and the upper surface of the loosely packed powder sample was rendered flat by a long punch with a diameter equal to that of the punch inserted in the die cavity during the SPS. Then the long punch was extracted from the die and a short punch was inserted. The density of the powder mixture before sintering was 38% (calculated using the theoretical density of the Fe-40at.%Al composition). A schematic of the set-up used for the pressureless SPS experiments is shown in Figure 1. The pressureless SPS experiments had good reproducibility in terms of the resultant sample thickness, porosity and phase composition. Comparative experiments were conducted using a hot press at a heating rate of 50°C min⁻¹.

The X-ray diffraction (XRD) patterns were recorded using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu K alpha radiation. The microstructure of the compacts was studied by Scanning Electron Microscopy using a Hitachi-Tabletop TM-1000 microscope (Japan).

The open porosity of the sintered compacts was determined by measuring the weight and calculating the volume of ethanol absorbed by the porous compacts, as described in ref. [11].

The transverse rupture strength (TRS) of the compacts was measured using a method described in refs. [12-13]. A steel ball of 6 mm diameter was used as an indentor to fracture the samples of 20 mm diameter. A universal testing machine Zwick/Roell Z100 (Germany) was used. Three tests were
conducted for each sintering temperature. The Poisson’s ratio of the porous material was calculated using the value of the Poisson’s ratio of the fully dense FeAl and the values of the total porosity of the compacts, as described in ref. [13].

3. Results and Discussion
In our previous investigation [5], it was found that during SPS and hot pressing, the same sequence of reactions takes place in the Fe-40at.%Al mixtures of the micrometer-sized powders:

\[ \text{Fe} + \text{Al} \rightarrow \text{Fe} + \text{Fe}_2\text{Al}_3 \rightarrow \text{Fe} + \text{FeAl} \rightarrow \text{FeAl}. \]

The range of the SPS temperatures used in that work was 500-650°C. Compacts of 10-mm diameter sintered at 650°C were composed of FeAl as a major phase and Fe (residual) as a minor phase. In the present study, the choice of the SPS as a processing technique, sintering temperatures and fine and comparable sizes of the two reactants was dictated by the goal of conducting fast full chemical conversion of Fe and Al into single-phase FeAl reducing the time available for the compact shrinkage.

Figure 2 and Figure 3 show the XRD patterns and fracture surfaces of the 20-mm Fe-40at.%Al compacts sintered 700 and 900°C, respectively. The phase composition of the 20-mm diameter compact sintered at 700°C was similar to that of the 10-mm compact sintered at 650°C [5]. The single-phase FeAl, according to the XRD analysis, formed after the SPS at 800°C. It was also shown that even faster heating (100°C min⁻¹) of the reaction mixture in the SPS up to 900°C without holding at the maximum temperature allows synthesizing single-phase FeAl from the selected reaction mixture. The presence of the AlFe₃C phase in the compacts was due to the presence of carbon in the initial iron powder [5].

![Figure 2](image1.png)

**Figure 2.** XRD patterns of the Fe-40at.%Al compacts obtained by pressureless SPS at 700°C (a) and 900°C (b).

The porous compacts had a uniform structure and did not contain any macrodefects on the sample size scale. Structural differences between the porous materials obtained at 700 and 900°C can be observed. In the former, particles with smooth surfaces - those of the residual iron - can still be distinguished (Fig.3 (a)). The characteristic feature of the latter is the presence of ligaments with a string-like morphology (Fig.3 (b)) indicating a higher degree of chemical transformation of the mixture into the reaction product.

Table 1 summarizes the phase composition, total and open porosity and transverse rupture strength of the FeAl compacts. The content of iron in the compact sintered at 700°C was estimated from the XRD data. The total porosities were calculated based on the precise measurements of the samples’ dimensions and using the theoretical density of FeAl (5.67 g cm⁻³). Karczewski et al [14-15] produced FeAl with an open porosity of more than 45-49% using pore forming agents.
decomposing during sintering and releasing gaseous products. In the present work, high open porosities - 41-46% - were achieved without the use of pore forming agents; therefore, any possible contamination (for example, by carbon) of the porous material caused by decomposition of the pore formers is avoided. A comparative sintering experiment in the hot press at 800°C produced single-phase FeAl with an open porosity of 33%. A lower open porosity can be related to lower heating and cooling rates in this experiment.

The TRS of the compacts sintered at 700-900°C was in the 53-67 MPa range: it did not change significantly with the sintering temperature. Based on these data, a temperature of 800°C can be selected as the processing temperature of porous FeAl by reactive SPS from the selected reactants. At the same time, to reach a slightly higher open porosity and ensure the reaction completeness (some residual iron may still be present in the material sintered at 800 °C in concentrations below the detection limit of the XRD), the synthesis should be conducted at 900°C. The values of TRS of the porous Fe-40at.%Al materials obtained at temperatures below 650°C and still containing the Fe$_2$Al$_5$ phase were very low (less than 50% of the TRS of the porous single-phase FeAl).

![Figure 3](image-url) Fracture surfaces of the Fe-40at.%Al compacts obtained by pressureless SPS at 700°C (a) and 900°C (b).

| SPS temperature (°C) | Phase composition | Total porosity (%) | Open porosity (%) | TRS (MPa) | Standard deviation of TRS (MPa) |
|----------------------|-------------------|--------------------|-------------------|-----------|-------------------------------|
| 700                  | FeAl+5 vol.%Fe    | 47                 | 41                | 53.4      | 5.5                           |
| 800                  | FeAl              | 47                 | 41                | 67.3      | 15.9                          |
| 900                  | FeAl              | 53                 | 46                | 63.0      | 5.9                           |

4. Conclusions
In this work, we presented the results of the structural characterization and mechanical testing of porous FeAl synthesized and consolidated using reactive pressureless SPS of the Fe-40at.%Al loosely packed powder mixtures. High open porosities of 41-46% are achieved without the addition of pore forming agents using a heating rate of 70°C min$^{-1}$ in the SPS and a holding time at the maximum temperature of 3 min. According to the XRD analysis, single-phase FeAl could be obtained by SPS of the mixtures at 800°C. The porous compacts had a uniform structure and were
free from macrodefects. The TRS of the compacts sintered at 700-900°C did not change significantly with the sintering temperature.

The main advantages that are offered by the SPS technique for the synthesis of porous FeAl are the possibilities of high heating rates and relatively high cooling rates of the samples. A limited time of exposure of the reaction mixture to high temperatures allows conducting the synthesis while limiting the shrinkage of the porous material.

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