Influence of Aluminium on Dimensional Change of Sintered 430 Ferritic Stainless Steel

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ABSTRACT. Aluminium is added to decrease matrix chromium losses on 430 stainless steel sintered on nitrogen atmosphere. Three different ways were used to add a 3% (in weight) aluminium: as elemental powder, as prealloyed powder, and as intermetallic Fe-Al compound. After die pressing at densities between 6.1-6.5 g/cm^3, samples were sintered on vacuum and on N_2-5%H_2 atmosphere in a dilatometric furnace. Therefore, dimensional change was recorded during sintering. Weight gain was obtained after nitrogen sintering on all materials due to nitrides formation. Sample expansion was obtained on all nitrogen sintered steels with Al additions. Microstructure showed a dispersion of aluminium nitrides when pre-alloyed powders are used. On the contrary, aluminium nitride areas can be found when aluminium is added as elemental powders or as Fe-Al intermetallics. Also nitrogen atmosphere leads to austenite formation and hence, on cooling, dilatometric results showed a dimensional change at austenitic-ferritic phase transformation temperature.

Keywords: Dimensional change, ferritic stainless steels, aluminium additions

1 INTRODUCTION

Ferritic sintered stainless steels are widely used on applications with moderate corrosion resistance and ductility, low temperature or magnetic applications since they are relatively weak at high temperature. The addition of other alloying elements to the nominal composition looks for enhancing certain properties. Improved corrosion resistance by road salt with molybdenum, intergranular corrosion stabilization with niobium, better machinability with sulfur or manganese sulfur, are some examples. On the contrary, elements such us nitrogen, usually introduced during sintering on nitrogen base atmospheres, leads to the formation of chromium nitrides, which may adversely affect stainlesss steel corrosion resistance. Ceramic or metallic additions could be added to combine with nitrogen during sintering. Nitrides so formed allowed keeping the content of chromium on steel matrix.

On the other hand, aluminium addition is exceptionally effective in enhancing the oxidation resistance of Fe–Cr alloys by the formation of a stable layer of α-Al_2O_3, rather than of Cr_2O_3 [1]. This has been exploited commercially in a number of materials, such us Fe– 20Cr– 5Al as substrate materials for catalytic converters that can be used at temperatures of up to 1375°C in the preoxidized condition. An improvement in the oxidation resistance for 316L stainless steel powders is achieved when a combination of grain refinement and alloying with 6 wt.% Al is employed. Mechanical milling (cryomilling and using SPS) is the process of choice for the fabrication of alloyed powders [2].

On the present work, aluminium and intermetallics Al-Fe are added to 430L ferritic stainless steel. Iron aluminide intermetallics are among the promising engineering materials to substitute stainless steel or Ni-based superalloys in high-temperature applications due to their low cost, high specific strength, high melting points, excellent corrosion resistance under oxidizing, carburizing and sulfidizing atmospheres, relatively high electrical resistivity, and low thermal conductivity [3]. The absence of a persistent liquid phase on Fe-Al alloys is overcome when is used Fe-Al intermetallics, meanwhile with elemental powders, a permanent liquid phase is present up to intermetallics formation. This leads to important dimensional changes which would make pressed parts far from the near net shape after sintering. Dimensional changes will be analyzed through a dilatometric study, within a microstructural study of sintered materials.

Vacuum sintering allowed a lower sintering density on 430L stainless steel without additions than N_2/H_2 sintering atmosphere (Table 1) due to weight gain and a low dimensional change. Low melting point of Al and intermetalics $FeAl_2$ (1165ºC) and Fe_2Al_5 (1169ºC) leads to a liquid phase on 430L with additions and densification will be carried out on semi-solid state. On the contrary, formation of C_2N and AlN due to sintering nitriding leads to a differential densification rate [3]. Dimensional change depends on atmosphere since shrinkage is observed on vacuum meanwhile swelling is obtained on N_2-$5H_2$ (Table 1). Liquid phase content with Al and Al/Fe intermetallic addition justifies the different swelling on behaviour of intermetallics in vacuum or in N_2-$5H_2$. Liquid phase nitriding from aluminium or intermetallics melt could reduce the diffusion rate resulting in lower dimensional change. The presence of aluminium leads to highest weight gain, especially on prealloyed 16Cr-3Al powder (2.98%).

Table 1. Density and dimensional change of green and sintered materials on vacuum and N_2/H_2

Material	Green density g/cm^3	Vacuum Sintering		$N_2/5\%H_2$ Sintering		
		SD% theo.	Change in Length %	SD% theo.	Change in Length %	Weight gain, %
430L	6.46-6.50	83.4	-1.20	83.9	0.05	0.4
Fe-16Cr-3Al	6.27-6.30	82.7	-0.30	83.2	1.85	2.98
430L+3Al	6.33-6.40	78.0	0.95	83.4	0.9	1.25
430L+FeAl$_2$	6.26-6.30	80.7	0.85	84.5	0.28	1.10
430L+Fe$_2$Al$_5$	6.21-6.26	80.7	0.80	82.5	0.44	1.15

3.2 Dimensional change and microstructure of 430L and Fe-16Cr-3Al. Low shrinkage and high swelling are found on prealloyed stainless powders sintering on N_2/H_2 as a consequence of chromium and aluminum nitruration (point A on curve N_2-$5H_2$, figures 3 and 4). Also austenite formation is obtained since on cooling, a dimensional change is obtained on the interval of transformation gamma-alpha (Point B on N_2-H_2 curve, figures 3 and 4). 430L nitruration decreases diffusion mechanisms and leads to a lower shrinkage than on vacuum. Sintered density on vacuum is close to that obtained on N_2/H_2 due to the weight gain (Table 1).
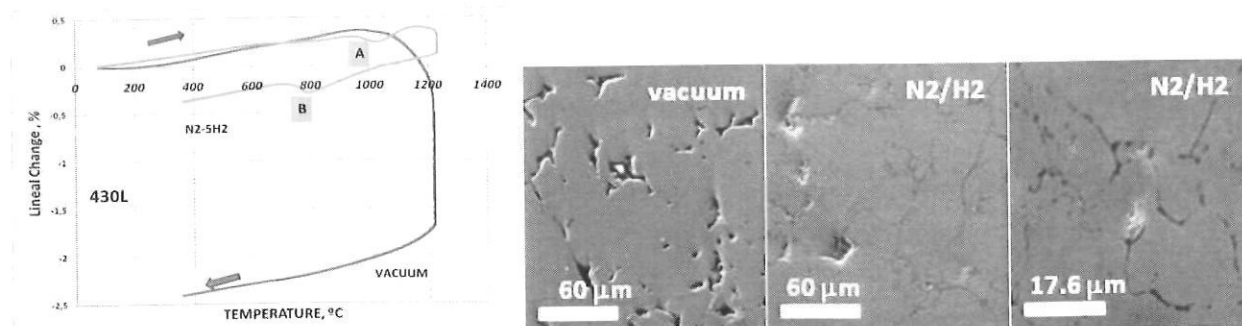

Figure 3. Dimensional change on dilatometric tests under vacuum and N2-5H2 atmosphere and microstructure of vacuum and N_2/H_2 (right) 430L sintered samples

At 1000ºC densification starts on 430L, but nitruration leads to a further swelling over 1050ºC (Point A, curve N2-5H2, figure 3). Fe-16Cr-3Al spherical particles retain their identity and internal porosity on sintered material and appear with internal porosity (Figure 4). From sintered steels microstructures, lamellar constituents of Cr_2N are not observed (Figures 3 and 4). The grain boundary nitrides and the mixture of Cr_2N with ferrite are clearly observed (Figure 3) on 430L sintered on N_2/H_2.

Solid state sintering on N_2/H_2 of Fe-16Cr-3Al steel is carried out without dimensional change (Figure 4) over 1150ºC on heating up to 1050ºC on cooling. Densification due to diffusion mechanism and steel nitruration could justify this dimensional behaviour at high temperature. Nitruration starts at temperatures slightly higher than aluminium melting point (Figure 4, Point A), leading to a high swelling. A complete

2. EXPERIMENTAL PROCEDURE

2.1 Raw materials. As base material, a water atomized stainless steel 430L powders (16.19%Cr; 0.1Ni; 0.14Mn; 1.11%Si , 0.007%C, 45-125 µm, 7.75g/cm^3, using inverse rule of mixture) were used. They have irregular particle morphology (Figure 1). As a reference material, Fe-Cr-Al powder (Fe-16Cr-3Al, 40-100 µm, 7.43 g/cm^3, using inverse rule of mixture) was used. This powder was gas atomized to avoid Al oxidation [4] and thus, its particle shape is spherical. Since reference prealloyed powder has 3%Al; elemental Al powder (99.5% Al, 0.07Fe, 0.04Si, particle size < 150 µm) and intermetallic $FeAl_2$ (49.1%Al, < 100µm) and Fe_2Al_5 (54.70%Al,< 100µm) powders were added to 430L base powder in order to get a final composition close to Fe-16Cr-3Al. Intermetallic powders show a brittle morphology particle [5] as it can be seen on Figure 1. X-ray diffraction verified the presence of the crystal structures Fe_2Al_5, $FeAl_2$ (Figure 1). After mixing, powders were die lubricated and pressed close to 700MPa into dilatometric samples. Dilatometric green compact sample was 20mm in length with rounded ends and a surface of 0.75 cm^2.
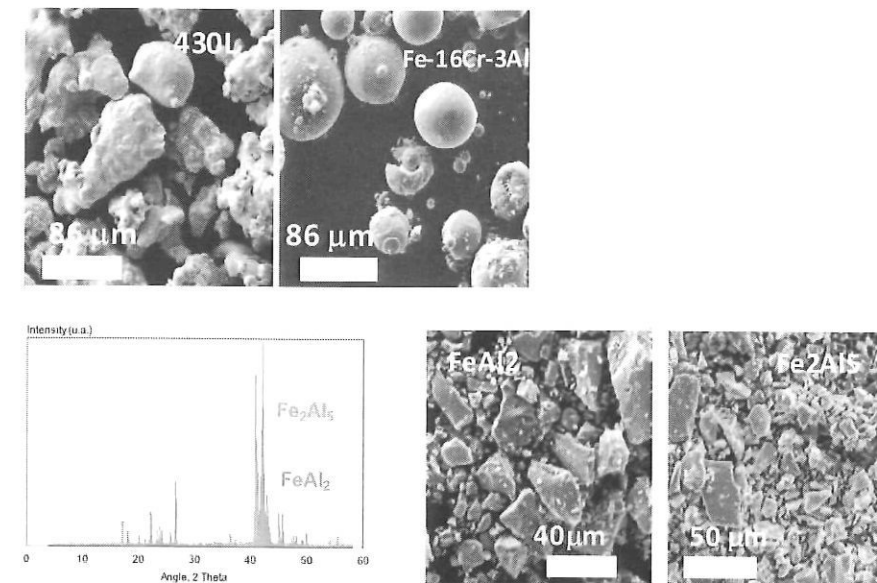

Figure 1. Morphology of powders: 430L and Fe-16Cr-3Al, Xray diffraction of intermetalics $FeAl_2$, Fe_2Al_5 .

2.2 Dilatometric tests. DIL805 Bahr equipment was used to perform the dilatometric analysis. A heating rate of 10K/min up to 1220ºC was applied. Holding time at this temperature was 30 min and cooling rate was 15K/min. Two dilatometric tests were carried out for each material. Two sintering atmospheres were used: vacuum and N_2-$5\%H_2$. Lineal change (%) was recorded as a function of sintering time and temperature.

2.3 Sintered samples characterization. Sintered densities of the samples were determined by dimensional measurements as well as theoretical sintered density (SD%). Also, dimensional change and weigh gain on nitrogen sintered samples was measured. Microstructure was determined on each material using scanning electron microscopy, as well as a micro-hardness study was carried out.

3 RESULTS AND DISCUSSION

3.1 Influence of sintering atmospheres on physical properties. Ferritic stainless steels green density was on the range: 6.21-6.50g/cm^3. Aluminum density and hardness of intermetallics leads to lower green density on 430L with Al or Al-Fe powders addition than 430L powders (Table 1). Also Al diffusión into prealloyed Fe-16Cr-3Al powders decreases their green density [4].

3.4 _Dimensional change and microstructure of 430L with intermetallics._ As it can be seen on figures 6 and 7, from 900°C-1000°C on N_2/H_2 atmosphere, lineal change is kept constant. Once intermetallic melting point is achieved, lineal change did not increase and it slowed down. On the contrary, vacuum atmospheres showed a change on lineal change from 1000°C up to sintering temperature. Lower diffusion of Al into Fe leads to a transient liquid with a lower Al content and at higher temperatures than with Al additions.
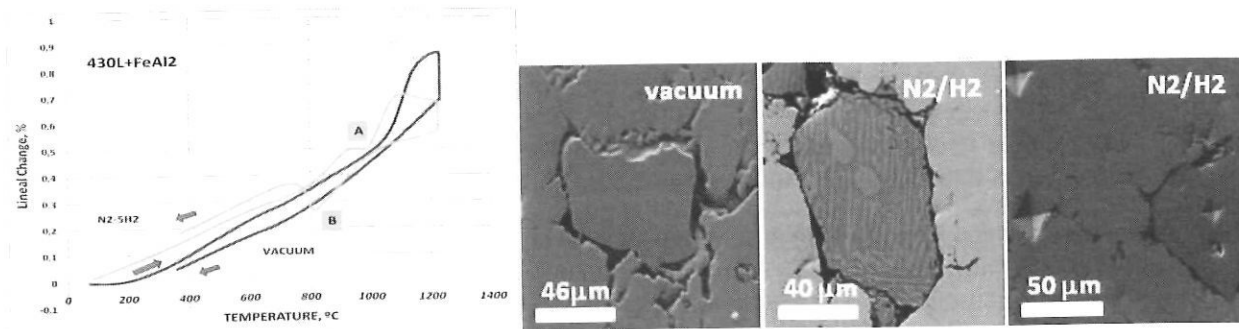

Figure 6. Dimensional change on dilatometric tests and microstructure of vacuum and N_2/H_2 (right) 430L+FeAl$_2$ sintered samples. Microhardness: 220MHV0.1 (matrix), 778MHV (Intermetallic)[5]

Once the additive melts, rapid rearrangement of the solid particles occurs during liquid phase sintering when liquid volume is enough. This stage is followed by a rapid densification and chemical potential gradient across the solid and liquid interface. On Fe-Al and Fe-Intermetallic Al/Fe, once aluminium has diffused across the liquid/solid (430L) interface, liquid transient phase disappears and solid state sintering mechanisms govern sintering densification of a clearly inhomogeneous material. When transient liquid solidifies, it is expected a lower Kinkerdall porosity at additive particle sites than during liquid phase sintering.

The lower diffusion rate of aluminium from intermetallic powder into the iron compared with elemental Al powder in Fe, coupled with a fast heating rate (150K/min), leads to allow minimal Fe-Al inter diffusion during heating [6].
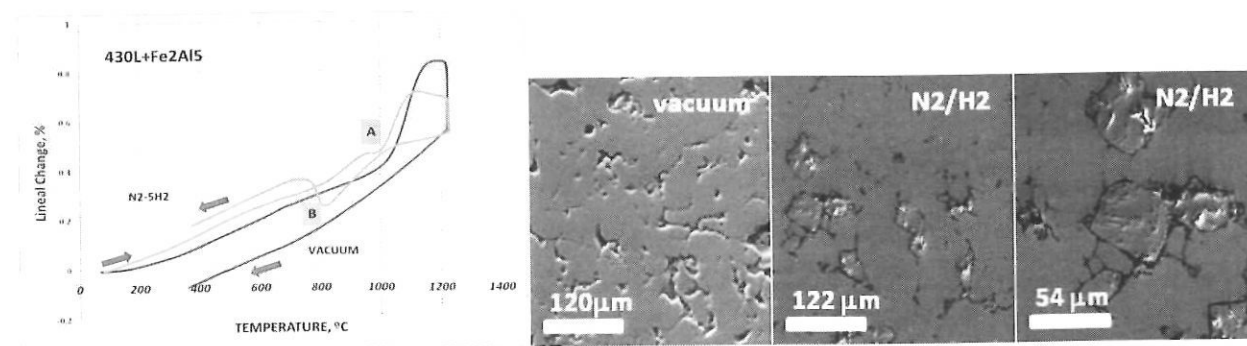

Figure 7. Dimensional change average on dilatometric tests and microstructure of vacuum and N_2/H_2 (right) 430L+Fe$_2$Al$_5$ sintered samples

SEM microscopy suggests [6] that agglomerated intermetallic Fe/Al particles are responsible for a significant portion of the remaining porosity in high sintered density compacts. Intermetallic particles form a liquid during sintering and creating stable pores after melting (Figure 7). FeAl$_2$ particles retain their identity and they appear as a mixture of FeAl and Fe$_2$Al$_5$ phases. At 1000°C reaction Fe+Fe$_2$Al$_5$ would lead to complete FeAl formation [7]. On vacuum a high intermetallic particle size allows to find intermetallic phases that should not be present over 1162°C [6]. The formation of intermetallic or

aluminium nitruration as well as low diffusion mechanisms justifies steel dimensional behaviour on heating over 1150°C up to the end of sintering holding time.
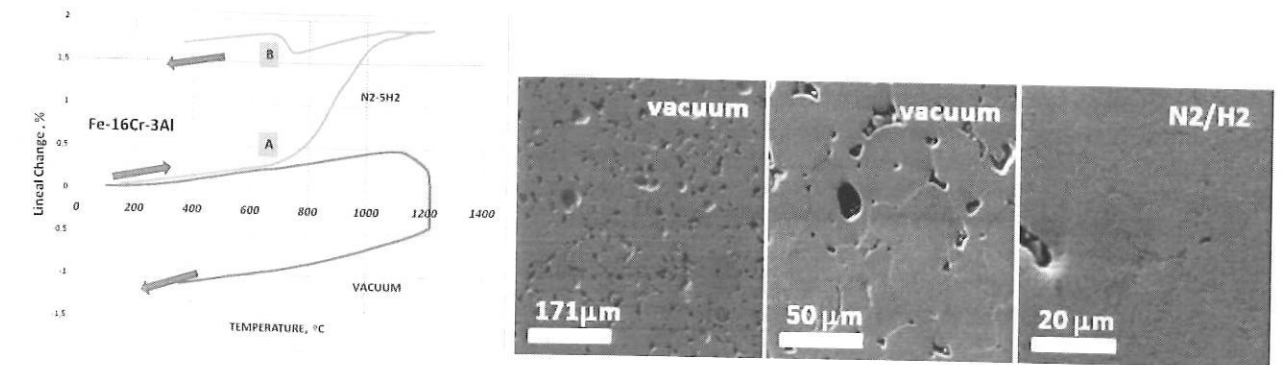

Figure 4. Dimensional change on dilatometric tests and microstructure of vacuum and N_2/H_2 (right) Fe-16Cr-3Al sintered samples

3.3 _Dimensional change and microstructure of 430L+Al._ In the Fe-Al system, Kirkendall porosity forms at aluminium particle sites after diffusion of aluminium into iron, resulting in swelling, lowering of the average density and the formation of various stable iron–aluminium compounds around pores, which prevent any further densification [6]. Thus swelling is achieved on vacuum and N_2/H_2 atmospheres with 430L+Al. The most promising route to a high sintered density when a free nitrogen sintering atmosphere is used, is through the use of suitable prealloyed powders, such as prealloyed powder Fe/Al, as a transient liquid forming constituent [6].

Over 900°C on vacuum, and 1000°C on N_2/H_2 atmosphere, a rapid volume expansion during the formation of the intermediate phase (such as Fe$_2$Al$_5$) and finally FeAl intermetallic can be seen on Figure 5. This allows obtaining porous Fe-Al [2] by reactive synthesis (around 950-1050°C) with Fe and Al powders.
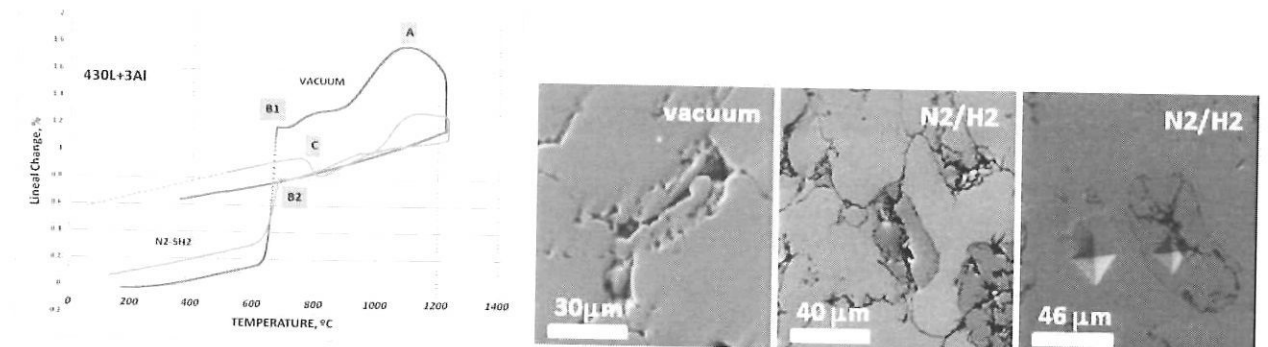

Figure 5. Dimensional change (average) on dilatometric tests and microstructure of vacuum and N_2/H_2 (right) 430L+3Al sintered samples. Microhardness: 194HV0.1 (Matrix), 363HV0.1 (Al diffusion area)

Influence of sintering atmosphere can be seen on 430L+Al over 850°C (Figure 5).Thus, aluminium melting point leads to a high swelling (Point B1 figure 5) following by Al diffusion into iron. Intermetallics Fe/Al leads to further swelling up to intermetallics melting (Point A, Figure 5).On N_2/H_2, nitruration of aluminium diffused areas (dark grey, Figure 5) decreases densification and increases microhardness. A network of chromium nitrides surrounding aluminium diffusion areas can be seen on microstructure.
On both sintering atmospheres, linear change is similar, but nitruration leads to higher density on ferritic stainless steel as well as a phase transformation gamma-alpha during cooling (Point C, figure 5).
The presence of large pores shortly after liquid formation suggests that remaining porosity is largely due to powder agglomeration during mixing.

intermediate phases (aluminides of Fe and Cr) at 800°C–1100°C can be expected on the basis of binary and ternary phase diagrams, but they have not been found clearly on studied microstructures.

4. CONCLUSIONS

Nitruration of ferritic stainless steels leads to austenite stabilization and its transformation to ferrite during cooling. Nitrides are present as fine particles uniformly distributed on prealloyed Fe-16Cr-3Al stainless steel meanwhile a nitrides network can be seen on 430L stainless steel without additions as well as on 430L stainless steel with Al and Al/Fe intermetallics additions. Dimensional change behaviour of prealloyed powders was shrinkage when sintering is carried out under vacuum and swelling when N_2/H_2 sintering atmosphere is used.

Although N_2/H_2 atmosphere leads to higher density, densification is lower due to nitruration. Several transient liquid phases appear during sintering, due to Al or intermetallics melting. Diffusion of liquid into solid and liquid nitruration changes the dimensional behavior during sintering of 430L ferritic stainless steel.

REFERENCES

[1] Wolff I.M.; Iorio L.E.; Rumpf T.; Scheers P.V.T.; Potgieter J.H. Materials. Oxidation and corrosion behaviour of Fe-Cr and Fe-Cr-Al alloys with minor alloying additions. Science and Engineering: A, 241, 1, January 1998 , 264-276

[2] Almathami, A., Brochu, M. Microstructure and transformation of Al-containing nanostructured 316L stainless steel coatings processed using spark plasma sintering. Journal of Materials Processing Technology 210, 2010, 2119–2124.

[3] Shen, P.Z.; Song, M.; He, Y.; Gao, H.; Zou, J.; Xu, N.; Huang, B.; Liu, C. Synthesis and characterization of porous Fe-25 wt.% Al alloy with controllable pore structure Powder Metallurgy and Metal Ceramics, 49, 3-4, July 2010, 183-192.

[4] Ruiz Iglesias, J.; Cambronero, L.E.G.; Ruiz Román, J.M.; Ruiz Prieto ,J.M.; Suarez,J.C.; Influencia del aluminio en la microestructura y propiedades de los aceros inoxidables ferriticos sinterizados. III Congreso Nacional de Pulvimetalurgia, Valencia, 13 y 14 June 2010, 415-421.

[5] Cambronero, L.E.G.; Herranz, J.D.; Ruiz-Roman J.M.; Ruiz-Prieto J.M.; Properties and microstructure of aluminum reinforced with Fe-Al intermetallics. AMPT01 Leganes, Spain, 2001, 1521-1526

[6] Xydas, N.K.; Gabbitas, B.L.; Xu, X.X.; Salam, L. A.; Transient liquid phase sintering of high density Fe3Al using Fe and Fe2Al5/FeAl2 powders Part 1: Experimentation and results. Powder Metallurgy 46, 1, April 2003, 68-72.

[7] Gao, H.Y.; He, Y.H.; Shen, P.Z.; Xu, N.P.; Zou, J.; Jiang, Y.; Huang, B. Y.; Liu, C.T. .Effect of heating rate on pore structure of porous FeAl material. Powder Metallurgy, 51, 2, June 2008 ,171-175.