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MECHANICAL MILLING AND FIELD ASSISTED SINTERING CONSOLIDATION OF NANOCRYSTALLINE Al-Si-Fe-X ALLOY POWDER

机械研磨的方法合成纳米晶体Al-Si-Fe-X合金粉末

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Abstract. Rapidly solidified pre-alloyed Al-17Si-5Fe-3.5Cu-1.1Mg-0.6Zr (wt.%) powder was mechanically milled using stearic acid and ethyl acetate as process control agents. The resulting nanocrystalline powder was degassed in a furnace at 350 °C for 5 hrs in vacuum. Both as-milled and degassed powders were consolidated using field-assisted sintering (FAST) in steel dies in vacuum at 375 to 500 °C. Some experiments were also carried out with an additional in-situ degassing step at 470-500 °C for 1 to 5 minutes. Shrinkage along the pressure axis, temperature and applied pressure were automatically stored through a data acquisition system.
As-milled powder and sintered compacts were characterized using optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and microhardness measurements. The crystal size, calculated from the line broadening of the X-ray diffraction peaks using Williamson-hall plots, of the mechanically alloyed powders and FAST sintered mechanically alloyed materials was in the range of 23-70 nm, depending on the type and amount of process control agent used during milling and the FAST parameters. As-milled powders with furnace degassing (350 °C/5h) could not be fully densified due to remaining entrapped gasses. An in-situ degassing (500 °C/5min) step included during FAST sintering however resulted in the consolidation of fully densified bulk nanostructured compacts. Microstructure and hardness showed strong dependency on the type of process control agent used during milling.

使用机械合金的方法将Al-17Si-5Fe-3.5Cu-1.1Mg-0.6Zr粉末快速合金化。在研磨的过程中加入不同的添加剂对样品的微结构和硬度都有很大影响。

1. INTRODUCTION

PM processed Al-Si-Fe-X alloys are of significant interest in automotive and aerospace applications due to improved properties and high thermal stability resulting from extended solid solubility and refined microstructures [1-3]. To further explore the potential of these alloys preparation of nanostructured powders and consolidation into bulk material can be very challenging. Although there are numerous techniques to produce nanostructured materials, mechanical milling is relatively cheaper to produce large quantities of nanostructured powders. Since Shingu *et al.* [4] produced nanocrystalline Al-Fe alloy through mechanical alloying, much attention was given to high-energy mechanical milling and it is now established as a major potential process for producing nanostructured powders. However, consolidation of mechanically milled aluminium based powders to full density can be extremely difficult due to the inherent oxide layer present on aluminium powder [5,6] as well as the high surface area due to reduced particle size and entrapped gases.

Additionally ball-milled powders may cause serious grain growth during high temperature consolidation because of high interfacial energies. In general, ball milled powders can be consolidated to full density though conventional powder metallurgy tech-

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niques such as hot pressing, but retaining the nanostructure is not possible due to long term exposure to high temperatures. Recently, success in forming dense bulk nanostructured systems was looked by using of two forms of activation i.e., mechanical activation by high-energy ball milling and field activation by the use of high-density currents [7,8].

In this work, nanostructured Al-Si-Fe-X alloy powders were fabricated by mechanical milling using two varieties of process control agents and the bulk nanostructured alloy was consolidated by means of Field Assisted Sintering Technology (FAST), which is comparable to Spark Plasma Sintering (SPS). Fully densified compacts were characterized using XRD, scanning electron microscopy and hardness.

2. EXPERIMENTAL PROCEDURE

Rapidly solidified air atomised powder with an Al-17Si-5Fe-3.5Cu-1.1Mg-0.6Zr (wt.%) composition and in the size range from 45 μm to 250 μm was ball milled using *Retsch PM4* planetary ball mill. The container (500 ml) and balls (∅ 6 mm) are made of hardened chromium steel. During milling, the rotation direction of the supporting disc and the bowl are opposite. The centrifugal forces alternately are synchronized and opposite. The grinding balls and the charge alternatively roll on the inner wall of the mill and are lifted and thrown off across the bowl at high speed. To prevent excessive cold welding of Al-alloy, 1.5 wt.% of Stearic acid [$CH_3(CH_2)_{16}COOH$] or 5.5 wt.% Ethyl acetate [$CH_3COOC_2H_5$] was added to the pre-alloyed powder as process control agent (PCA). A ball-to-powder weight (BPR) ratio of 20:1, milling time of 6 h and a milling speed of 230 rpm were employed in all experiments. Milled powders were degassed in a furnace in vacuum at 350°C for 5 hrs.

Milled powders in both degassed and undegassed condition were analyzed using X-ray diffraction (*XRD- Seifert 3003 T/T*) with Cu$K\alpha$ radiation to measure the crystallite size of fcc-Al. The XRD peak broadening was attributed to the refinement of crystals, introduction of internal strains and instrumental effects.

The average grain size and the internal strain are calculated by the Hall–Williamson method [9,10]. The Hall–Williamson equation is expressed as:

$$\beta_{sample}\cos\theta = \frac{K\lambda}{d} + 2\varepsilon\sin\theta. \qquad (1)$$

where β_{sample} is the full width at half-maximum (FWHM) of the milled powders, K the Scherrer constant (assumption K = 1.0) , d the grain size, λ the wavelength (0.154186 nm) of the X-ray used, ε the internal strain introduced by milling, and θ the Bragg angle. FWHM was evaluated using a Pseudo Voigt fit with double $K(\alpha)$ peak separation. β_{sample} is given as:

$$\beta^2_{sample} = \beta^2_{exp} - \beta^2_{inst}. \qquad (2)$$

where β_{inst} is the FWHM of the standard reference material (LaB_6: *NIST SRM/RM660a*) used for calibration, and β_{exp} the FWHM evaluated.

Both degassed and undegassed powders milled using 1.5 wt.% SA and 5.5 wt.% EA were consolidated in vacuum in steel dies using Field Assisted Sintering Technology (FAST) *(model HP D 25/1, FCT Systeme GmbH, Rauenstein, Germany).* In the FAST technique, the powder is consolidated by simultaneous application of a mechanical load and a pulsed electric current. In the present experiments, applied mechanical load, maximum test temperature and holding time at maximum test temperature are key process variables to study the consolidation behaviour. All experiments were conducted with an on/off DC pulse rate, of 5/5. A *K*-type thermocouple was inserted into an inclined hole drilled in the upper punch, which is positioned at 2 mm from the top surface of the compact to measure and control the sintering cycle. Aiming to achieve 100% theoretical density, a variety of sintering schedules were planned. Fig. 1 shows a schematic diagram of two important sintering cycles.

The density was measured in water, according to the Archimedes method (*Sartorius AG, Germany*). The hardness was determined using a Zwick (*model 3202, Zwick, Ulm, Germany*) hardness tester with an indentation load of 0.25 kg. The reported values are the mean of at least 10 indentations. The microstructure of polished cross-sectioned powder and densified samples was studied by scanning electron microscopy (*SEM, XL-30FEG, FEI, The Netherlands*).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

XRD patterns of the milled powders with 1.5 wt.% SA, 5.5 wt.% EA as well as that of consolidated compacts using these powders are shown in Fig. 2(a). XRD patterns of milled powders showed relatively broad peaks due to the fine grain size and internal strain. Based on the broadening of the X-

使用德国莱驰PM400对样品进行研磨，500ml铬钢研磨罐，6mm铬钢研磨球。球料比为20：1
在230转/分钟的转速下研磨时间6小时。在研磨过程中使用正反转交替模式。为了避免在研磨
过程中产生过多的冷合金副产物，在研磨时加入硬脂酸和乙酸乙酯。

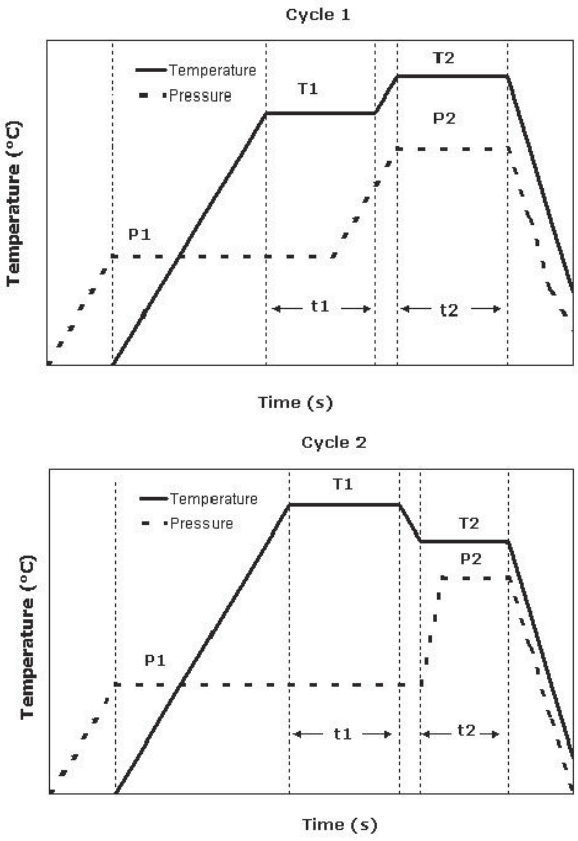

Fig. 1. Schematic diagram of the two of FAST sintering schedules followed to densify the milled powders.

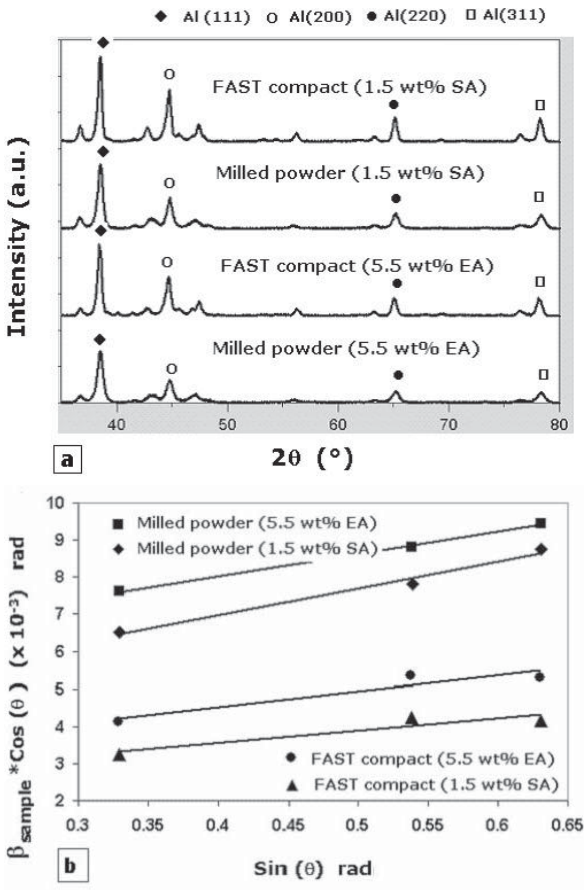

Fig 2. (a). X-ray diffraction patterns of the as milled powders and compacts after FAST. (b). Williamson-Hall plots of as milled powders and compacts after FAST plotted using Al(111), Al(220) and Al(331) reflections.

ray diffraction peaks shown in Fig. 2(a), the crystallite size of the fcc-Al was determined using Williamson-Hall plots as shown in Fig 2(b). The Al(200) peak reflection was not included in the Williamson-Hall plots due to an overlap with peaks from intermetallic phase. From the intercepts of the plotted straight lines, the crystallite size was determined. The crystallite sizes and micro strains determined using Williamson-Hall plots are given in Table 1.

3.2. Density

For the investigated Al-Si-Fe-X alloy, a density of 2.84 g/cm^3 can be considered as fully dense. Table 2 and Table 3 summarises the resulting densities from various FAST-sintering cycles for 1.5 wt.% SA and 5.5 wt.% EA milled powders respectively. From Table 2 and Table 3, it can be seen that sintering cycle 1 (see Fig. 1) is not effective to produce fully dense samples even with furnace degassed (350 °C/5 h) powders.

In cycle 1, powders were sintered at 450 °C / 500 °C for 5 minutes but gasses were unable to escape from the compact due to a large magnitude of preload. In view of that, cycle 1 was modified with a minimum preload of 15 MPa during the in-situ degassing stage to allow gasses to escape. This resulted in a marginal increase in density but 100 % theoretical density (%TD) was not obtained. Hence cycle 2 was designed to perform in-situ degassing at high temperatures and under minimum load in the first stage of the cycle, followed by a densification stage with relatively higher compaction pressures and lower temperatures in comparision to the first stage of the cycle. Cycle 2 (see Fig. 1) proved to be very effective in obtaining fully dense samples with both prior degassed and undegassed samples while preserving the nano-structure. One of the key achievements in the present work is the optimiza-

Table 1. Crystallite sizes and micro-strains obtained from XRD-profile analysis of milled powders and FAST sintered compacts.

Material condition	Intercept (10^{-3})	Crystallite size (nm)	Microstrain (10^{-3})
Milled powder (5.5 wt.% EA)	5.6192	27	6.02
Milled powder (1.5 wt.% SA)	4.0741	38	7.23
After FAST (5.5 wt.% EA)	2.8234	55	4.21
After FAST (1.5 wt.% SA)	2.2172	70	3.34

Table 2. Summary of FAST sintering parameters and the resulting densities for the powder milled with 1.5% SA.

T_1 (°C)	t_1 (s)	P_1 (MPa)	T_2 (°C)	t_2 (s)	P_2 (MPa)	Density (kg·m^{-3})	%TD (%)	Remarks
400	0	229	–	–	–	2740	96.5	♣, •
400	0	253	–	–	–	2750	96.8	♣, •
350	1	100	400	5	283	2770	97.5	♣, •
400	1	100	450	1	253	2780	97.9	♣, •
400	1	15	450	5	253	2790	98.2	♣, •
400	2	15	500	1	253	2800	98.6	♣, •
500	5	15	400	5	283	2840	100.0	♣, ♦, Θ
470	1	15	400	1	283	2840	100.0	♣, ♦, Θ

• cycle 1, Θ cycle 2, ♣ degassed powder, ♦ as milled powder

Table 3. Summary of FAST sintering parameters and the resulting densities for the powder milled with 5.5% EA.

T_1 (°C)	t_1 (s)	P_1 (MPa)	T_2 (°C)	t_2 (s)	P_2 (MPa)	Density (kg·m^{-3})	%TD (%)	Remarks
400	0	253	–	–	–	2740	96.5	♣, •
400	0	283	–	–	–	2750	96.8	♣, •
470	5	15	375	1	283	2750	96.8	♣, Θ
500	5	15	400	1	283	2810	98.9	♣, Θ
500	5	15	425	1	283	2840	100.0	♣, ♦, Θ

• cycle 1, Θ cycle 2, ♣ degassed powder, ♦ as milled powder

Table 4. Hardness of the fully dense compacts consolidated by FAST.

Max. T (°C)	Max. P (MPa)	Density (kg·m^{-3})	Hardness ($HV_{0.25}$) (GPa)	PCA used during milling
500	283	2840	2.67 ± 0.23	1.5 wt.% SA
500	283	2840	4.15 ± 0.14	5.5 wt.% EA

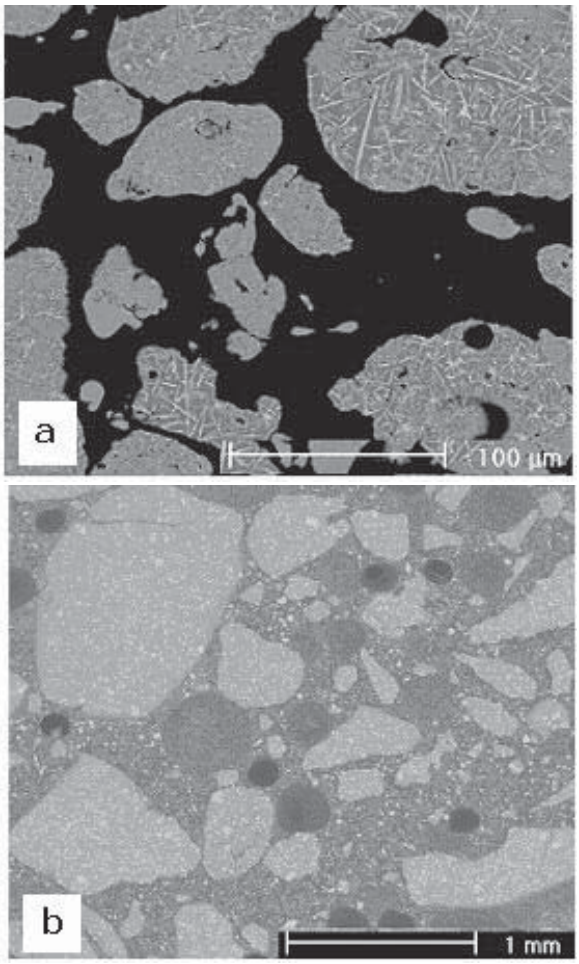

Fig. 3. Morphology of (a) air-atomised powder (b) powder milled with 5.5 wt.% EA.

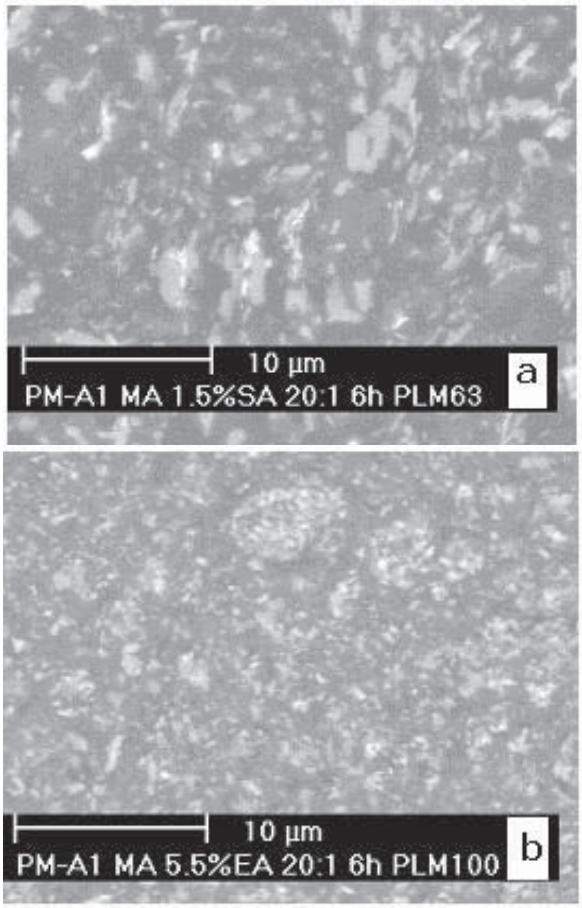

Fig. 4. Scanning electron micrographs of (a) compact consolidated at 500 °C by FAST technique using powder milled with 1.5 wt.% SA. (b) compact consolidated at 500 °C by FAST technique using powder milled with 5.5 wt.% EA.

tion of a process window to obtain fully dense solid nanostructured materials are clearly defined for each variety of powders investigated. Moreover, the FAST process s proved to be very effective in consolidating nano crystalline milled powders without a prior furnace degassing.

3.3. Microstructural characterization

The Morphology of the air-atomised and milled powder is shown in Fig. 3. In air-atomised powder, large particles that were subjected to relatively lower cooling rates during air atomisation show coarse needles of AlFeSi intermetallic phases. On the other hand, the smaller particles or the particles splashed on the larger particles contain finer needles due to a higher cooling rate [11]. Common for small and large particles is the absence of primary silicon particles that are typically observed in Al-Si alloys processed by conventional routes [12]. A close examination of the milled powders (see Fig. 3b) and fully densified samples consolidated using FAST (see Figs. 4a & 4b) indicates that the needle like features of the air-atomised powder is modified into a homogeneous distribution of fine dispersoids in an Al matrix during milling. No significant changes in microstructural features occurred during FAST at different temperature/load combinations and the microstructure of the milled powders is preserved during FAST.

3.4. Hardness

The Vickers hardness was measured on selected fully densified samples consolidated from different categories of milled powders. Milled powders are in different size ranges and are not suitable to establish a common hardness value; hence hardness of the milled powders is not reported here. The hard-

ness of the compacts produced using powders milled with 5.5 wt.% EA is 1.5 times higher than that of compacts produced using powder milled with 1.5 wt.% SA as shown in Table 4. This fact was also reflected in the microstructure as shown in Fig. 4, where the former grade has a finer distribution of intermetallic phase. The crystallite size and microhardness investigated in the present study are higher, but in agreement with the reported results on comparable alloy Al-Fe-Cr-Ti powders milled for 6 hrs [13].

4. CONCLUSIONS

Consolidation of mechanically milled nanostructured Al-17Si-5Fe-3.5Cu-1.1Mg-0.6Zr (wt.%) powder into fully dense compacts was possible by means of Field Assisted Sintering Technology (FAST). In-situ degassing can be incorporated during the FAST process hence prior degassing, typically required during other powder metallurgical consolidation routes is not needed. The XRD spectra of milled powders and fully dense compacts were analysed using the Williamson-Hall method revealing that powder milled with 1.5 wt.% of SA and 5.5 wt.% EA have crystal size, in the range of 27-38 nm. The fully dense compacts after FAST show minimal grain growth and the crystal size is the 55 & 70 nm range respectively. Experimental work revealed that a mechanical load of 283 MPa was needed at 400 °C to fully densify the powder with a prior in-situ degassing step at 470 °C to 500 °C for 1 to 5 minutes, depending upon the type of PCA used. Significant microstructural changes were observed after FAST, when compared to the pristine air-atomised powder. Mechanical milling resulted in a morphological change of the alloy microstructure by breaking down the long intermetallic needles into uniformly distributed finer dispersoids. The Vickers hardness of the dense compacts exhibited a strong dependency on the type of process control agent used during milling. The hardness of the compacts produced using powders milled with 5.5 wt.% EA is 1.5 times higher than that of compacts produced from powder milled with 1.5 wt.% SA.

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