The Influence of the Atmosphere and Impurities on the Sintering Behaviour of Aluminium

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Abstract

Green samples of aluminium pressed using air atomised powders of different purity were sintered under vacuum, argon, nitrogen, nitrogen/hydrogen gas mixtures. Only pure nitrogen is an active sintering atmosphere for aluminium, because it promotes shrinkage and sintered mechanical properties, as proved by bend test. A key feature in the use of nitrogen is the formation of aluminium (oxy)-nitrides. Hydrogen very strongly lowers the sinterability of aluminium, even when present in small concentrations in a nitrogen atmosphere. Auger electron spectroscopy was used to characterize the surface layers on aluminium powder particles and sintered samples. Distributions of aluminium, nitrogen, oxygen and magnesium, present as impurities, were obtained by Auger depth profiling measurements on these surfaces. These investigations revealed a strong surface segregation of Mg in the early stage of the sintering process. In addition, the sintering response of aluminium was influenced by the content of the Mg impurity; higher concentrations of Mg accelerated the sintering process. The results point, that enhanced concentration of magnesium within the surface film on powder particles may support sintering of aluminium.

1 Introduction

The advantages of the production and application of aluminium based sintered materials are well known starting since 1960-ties. Despite this the usage of PM parts made of aluminium is still waiting for the substantial growth. During the last decade, however, the interest to involve more sintered aluminium based structural parts to the automobile industry has dramatically increased, which strongly supports the investigations on sintered aluminium [1]. In fact, the number of papers on this topic is currently quickly growing.

The role of the sintering atmosphere on sintering behaviour and sintered properties belongs still to the unsolved fundamental problems in powder metallurgy of aluminium. The presence of a very stable Al_2O_3 layer on the aluminium powder particles is a specific feature affecting the aluminium powder technology, particularly the sintering process, because the oxide cannot be reduced during sintering. It is obvious, that the oxide layer has to impede the sintering process. However, aluminium powder can successfully be sintered even at very low temperature despite the high temperature resistant aluminium oxide. Therefore, the sintering atmosphere acts in more complex way as compared with its common functions against e.g. iron. It is a well known fact in powder metallurgy, that dry nitrogen is the most suitable sintering atmosphere for aluminium based compacts, because it simply produces the best sintered properties. To the best knowledge of the authors of the current paper there is no up to now unambiguous explanation of this behaviour. It should also be noted, that there are only very few publications showing the results of interactions occurring between aluminium based compacts and the sintering atmosphere [2-6]. In consequence, there are some questions

remaining. One of them is the role of hydrogen in aluminium sintering. Contrary to the most sintered systems, hydrogen seems to be a highly detrimental component of the sintering atmospheres used both for aluminium [4] and for aluminium alloys [2,5,6], because it strongly reduces the shrinkage. The main purpose of this paper is to show the influence of the sintering atmosphere on the dimensional changes of aluminium compacts during solid state sintering. To eliminate the effect of alloying additions and of a liquid phase on the sintering behaviour high purity aluminium powders were used.

2 Experiments

As starting materials were used:
− air atomized, 99.5% purity aluminium powder (impurities specified by supplier: Si - 0.15, Fe - 0.15, Mg - 0.02 and Cu - 0.03 wt.-%), particle size: 28% <20 / 23% 20-40 / 49% >40 µm, delivered by Fluka,
− air atomized, 99.94% purity aluminium powder, (Mg content − 2.3 ppm) particle size: 48,7% <20 / 42,9% 20-40 / 8,5% > 40 µm, delivered by ECKA Granulate GmbH.

For dilatometry investigations the rectangular (14x4x4 mm^3) green compacts were produced by uniaxial cold pressing at 200 MPa. Die lubrication by glycerol was used. This resulted in about 83% green density. Rectangular bend test samples (60x5x5 mm^3) were prepared by double action pressing also at 200 MPa and die lubrication. The green density of these samples was about 89%. Sintering processes were studied using a horizontal NETZSCH 402E dilatometer. Different sintering atmospheres were used: nitrogen, nitrogen/hydrogen mixtures, argon, argon/hydrogen mixtures and vacuum (10^{-3} Pa). The gas flow rate was 100 ml/min through the dilatometer's furnace tube (the inner diameter 35 mm). Nitrogen, hydrogen and argon used in current investigations were high purity gases with a dew point below −70°C and oxygen content below 5 ppm. Dimensional changes were monitored during the whole realized temperature-time program: heating at 20 K/min to the isothermal sintering temperature of 600°C, at which the samples were held for 2 hours, and cooling at 20 K/min to RT.

Nitrogen and oxygen content in sintered specimens was measured by LECO analyzer. Surface analysis on "fresh" fracture surfaces of sintered compacts was made by Auger electron spectroscopy. These measurements were performed in a Scanning Auger Microprobe PHI660 (Physical Electronics, USA) with primary electrons of 10 keV, 40 nA and an energy resolution of ΔE/E = 0.6 %. Under the given conditions the beam diameter was about 400 nm. Fracture was carried out under ultra high vacuum conditions by the impact fracture stage of the PHI660. For depth profiling the samples were sputtered by 1.5 keV argon ions with an equivalent sputtering rate in SiO_2 of about 3 nm/min. Bend test specimens were sintered in a laboratory tube furnace accordingly to the same temperature-time program. 3-point bend test for green and sintered compacts were performed.

To revise a well known hypothesis that the rupture of the brittle oxide layer occurring during compaction supports sintering of aluminium, a loose Fluka Al powder layer (about 50x50x50 mm^3 in size) formed in a steel crucible was sintered in nitrogen. The temperature-time profile was the same as specified above.

3 Results and Discussion

Figures 1-2 show dilatometric curves for aluminium sintering in different atmospheres. It is evident, that nitrogen is the only atmosphere producing extensive shrinkage compared to argon or vacuum. The addition of hydrogen, even in small amounts, to nitrogen is detrimental because it strongly lowers sintering shrinkage (Fig. 2). In addition, the shrinkage may be quickly interrupted by the atmosphere change from pure N_2 to N_2/H_2 mixtures during sintering.
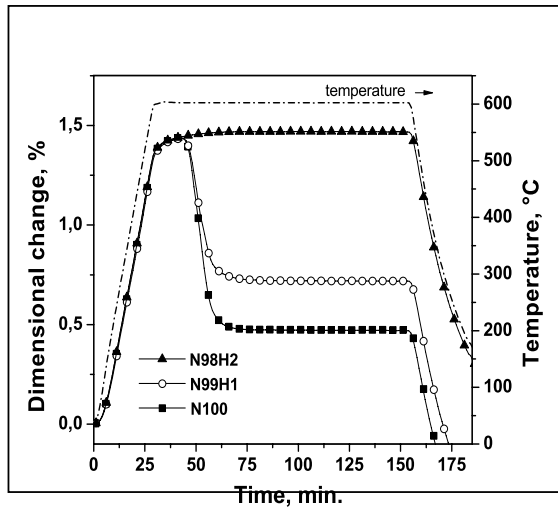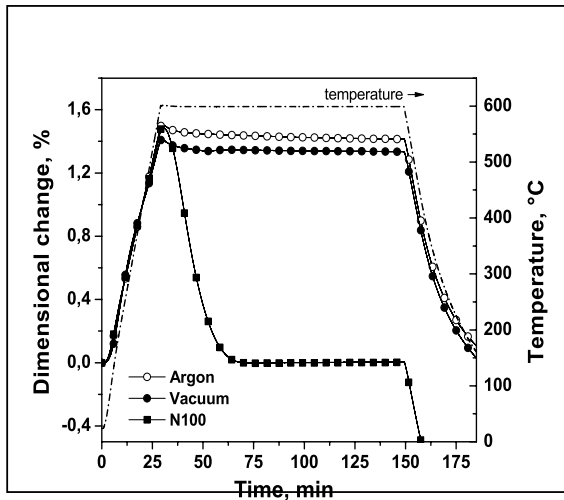
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Fig. 1. Dilatometry curves for sintering Fluka Al99,5 compacts in different atmospheres and vacuum.

Fig. 2. Dilatometry traces for compacts made of ECKA Al99,94 powder sintered in nitrogen/ hydrogen atmospheres.

The disturbance of the sintering process by hydrogen due to the formation of gaseous Al hydrides was suggested in [6]. But, no liquid phase is available during the sintering of pure aluminium, and therefore no effect on pore filling can be discussed. Even though the solubility and diffusion of hydrogen is small in aluminium and its alloys, it can be enhanced by trapping hydrogen by lattice defects, e.g. lattice vacancies, dislocations, grain boundaries. The binding energy between vacancies and hydrogen has been reported to be around 0,5 eV, the binding enthalpy to grain boundaries is lower (about 0,15 eV) [7]. Volume diffusion involves the motion of vacancies and the equilibrium vacancy concentration, which increases with temperature, dictates the volume diffusion contribution to sintering. Although volume diffusion is not the dominant mass transport process, it is active in most materials. It is supposed, that the jump of neighbouring Al atoms into a vacancy and so the diffusion is hindered by hydrogen trapped in it.

Data collected in Table 1 clearly show, that the sintering shrinkage is associated with the nitrogen binding. Simultaneously, the increase in oxygen content is observed.

Material	Sintering atmosphere	Nitrogen, wt.-%	Oxygen, wt.-%
Fluka Al99,5 powder, as delivered	-	0	0,36
ECKA Al99,94 powder, as delivered	-	0	0,22
Sintered compact of Fluka Al99,5	N_2	0,94	0,59
	$N_2 + 5\%H_2$	0	0,80
	Ar	0	0,71
	Vacuum	0	0,50
Sintered compact of ECKA Al99,94	N_2	0,66	0,42
Sintered compact of Fluka Al, surface layer inter layer interior part	N_2	0,44 1,10 0,83	0,74 0,62 0,53
Sintered specimen of loose Fluka Al powder, surface layer internal region	N_2	3,59 5,45	1,35 0,33

Table 1. Nitrogen and oxygen content in investigated materials.

The nitrogen distribution on the sintered cross sections, shown also in Table 1, suggests, that the self-gettering mechanism [3] can take place during sintering of Al. But, this gettering effect appears not to dimish the oxygen partial pressure within the pore network to an adequate level. Thus, the proposed direct reduction of Al_2O_3 oxide by gaseous nitrogen [3] seems to be questionably.

The favourable influence of nitrogen on primary Al particles bonding, formed during sintering, is shown in Table 2:

No.	Sintering atmosphere	Bending strength, MPa
1	N_2	243.1
2	$N_2/5\%H_2$	123.2
3	Ar	164.7
4	Green compacts	21.5

Table 2. 3-point bend test results for specimens made of Fluka Al99,5 powder.

The Auger electron spectroscopy made on loose Fluka powder particles proved, that only Al oxide is present on a surface and magnesium was not detected (Fig. 3). Kimura et al. [8] showed a tendency of magnesium atoms to migrate from the inner region to the surface of Al particles at temperatures above 500°C. Using X-ray photoelectron spectroscopy they observed Al on the particles surface in the metallic state, which was attributed to the reduction of Al_2O_3 by Mg. Thus, Al can directly react with gaseous nitrogen and aluminium nitride is formed in situ. The AES results presented here confirm the enrichment of Mg on the surface of the aluminium particles (Fig. 3).
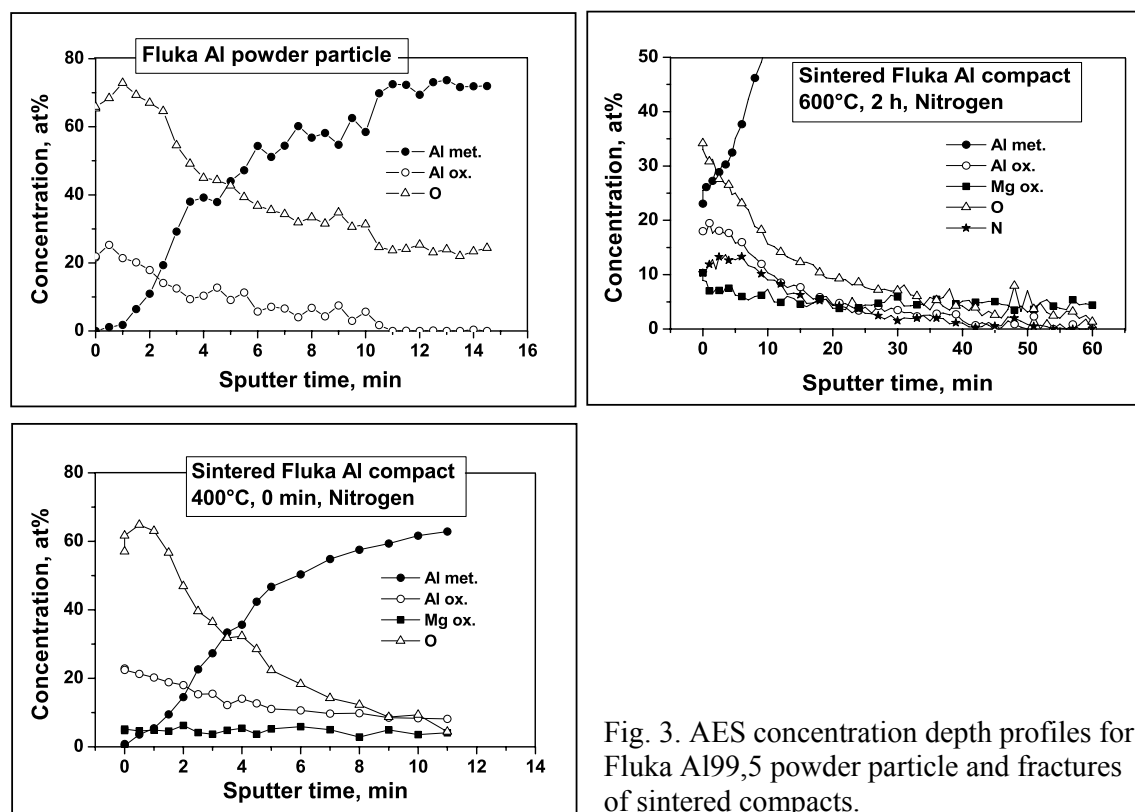

Fig. 3. AES concentration depth profiles for Fluka Al99,5 powder particle and fractures of sintered compacts.

This segregation process of Mg was already revealed at 400°C, and therefore it occurs prior to the pickup of nitrogen by aluminium starting at about 520°C. Mg is always present in the

oxidic state, as concluded from the position of the Mg(KLL) peak. Whereas the impurity level for Fluka Al is about 200 ppm, up to 10 at.% Mg are found at the surface. This level is sufficiently to reduce Al_2O_3 [9,10] and to degrade the oxide layer locally.

In case of sintered samples of the purer ECKA Al99,94 these highly enriched Mg levels at the particle surfaces were not detected by AES. But, provided that the same enrichment of the impurity level of 2,5 ppm Mg would occur, the segregation only results in 0,1 at.% Mg at the surfaces, which is clearly beyond the detection limit of AES. Apparently, these lower Mg levels can already attack the oxide layers and support the sintering, but this process seems to be retarded (Fig. 4). A incubation time of some minutes is necessary to start the shrinkage during sintering of the ECKA Al99,94 compacts compared to Fluka Al99,5.
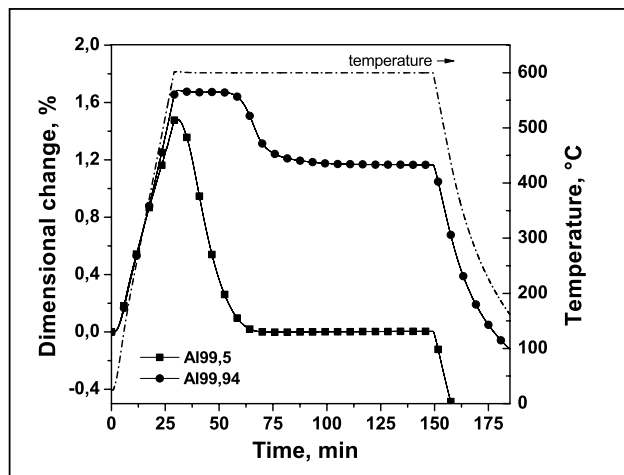

Fig. 4. Dilatometry curves for sintering Fluka Al99,5 and ECKA Al99,94 compacts in pure nitrogen.

It is obvious, that the revealed incorporation of nitrogen atoms enhances the destruction of Al_2O_3 by potential formation of intermediate oxynitrides (Fig. 5) and subsequent AlN. After a short-time sintering of the aluminium compacts some rosette-like precipitations as the first reaction products corresponding to about $Al_2MgO_{3,5}N_{0,5}$ decorate the powder particle surfaces Obviously, all of these reactions

$$3\,Mg + 4\,Al_2O_3 \rightarrow 3\,Al_2MgO_4 + 2\,Al$$

$$2\,Al + N_2 \rightarrow 2\,AlN$$
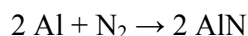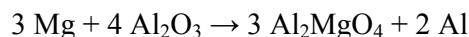
cause diffusion processes which could be responsible for the following shrinkage observed, when pure nitrogen atmosphere was used.
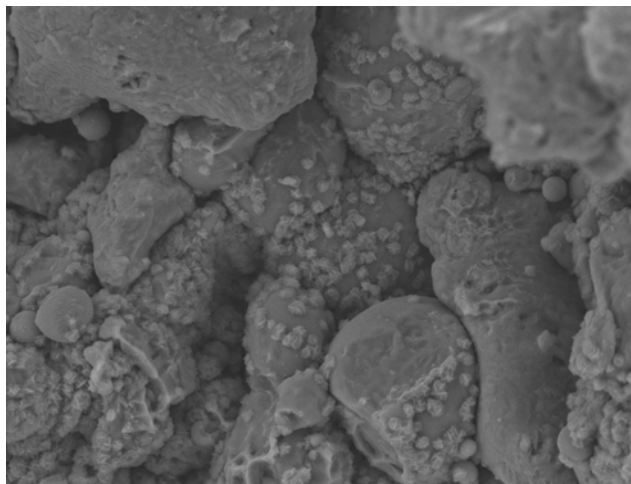
Fig. 5. SEM picture of fractured Fluka Al99,5 compact sintered at 600°C for 10 min.

4 Conclusions

Pure and sufficiently dry nitrogen is the only active sintering atmosphere for pure aluminium producing shrinkage. The formation of aluminium oxynitride and nitride is thereby a key effect. A direct reduction of Al_2O_3 by gaseous nitrogen seems unlikely, because magnesium, even in small amount present in Al powder, concentrates on the surface of powder particles and supports sintering by local reduction of Al_2O_3 prior to the incorporation of nitrogen.

In contrary, hydrogen strongly counteracts sintering shrinkage, probably due to the trapping hydrogen by lattice defects, and thus the reduction of their mobility and so their contribution to the sintering process.

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