

# Sintering Behaviour of Aluminium in Different Atmospheres

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## Abstract

The sinterability of pure aluminium powder was investigated in different sintering atmospheres, i.e.: nitrogen, hydrogen, argon, nitrogen/hydrogen and nitrogen/argon gas mixtures, and also in vacuum. Dimensional changes occurring during sintering were monitored by dilatometry. TG thermal analyze technique was used to recognize possible interactions between aluminium and nitrogen. It was shown, that only pure nitrogen is an active sintering atmosphere for aluminium, because it promotes shrinkage and sintered mechanical properties, as proved by bend test. Hydrogen very strongly lowers the sinterability of aluminium, even when present in small concentrations in a nitrogen atmosphere. Sintering experiments carried out in nitrogen on the loose aluminium powder clearly indicated, that the earlier suggestions known from the literature about the role of compaction step, in terms of cracking the aluminium oxide layers, are questionably. Auger electron spectroscopy was used to characterize the surface layers on aluminium powder particles, green compacts, and sintered samples. For green compacts and sintered samples surfaces obtained by fracture under ultra high vacuum conditions in the Auger microprobe were investigated. Distributions of aluminium, nitrogen, oxygen and other elements, present as impurities, were obtained by depth profiling measurements on this surfaces. The results pointed 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 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 the pure aluminium powders were used.

## 2. Experimental procedure

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  $\mu m$ , 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  $\mu m$ , delivered by ECKA GmbH.

Sintering processes were studied using a horizontal NETZSCH 402E dilatometer. For dilatometry investigations the rectangular (14x4x4 mm<sup>3</sup>) green compacts were produced by uniaxial cold pressing at 200 MPa. Die lubrication by glycerol was used. This resulted in about 83% green density. 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). The exact compositions of sintering atmospheres in vol.-% is given in Figs. 1-6. Nitrogen, hydrogen and argon used in current investigations were high purity gases with a dew point below  $-70^{\circ}\text{C}$  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  $600^{\circ}\text{C}$ , 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  $\Delta E/E = 0.6\%$ . 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  $\text{SiO}_2$  of about 3 nm/min.

Rectangular 3-point bend test samples ( $60 \times 5 \times 5 \text{ mm}^3$ ) were prepared by double action pressing at 200 MPa and die lubrication. These green specimens with 89% th.D. were sintered in a laboratory tube furnace accordingly to the same temperature-time program.

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  $50 \times 50 \times 50 \text{ mm}^3$  in size) formed in an alumina crucible was sintered in nitrogen. The temperature-time profile was the same as specified above.

### 3. Results and discussion

Figures 1-6 show dilatometric curves for aluminium sintering in different atmospheres. It is evident that nitrogen is the only atmosphere producing shrinkage (Fig. 1). The addition of hydrogen, even in small amounts, to nitrogen is detrimentally, because it strongly lowers sintering shrinkage. The higher purity ECKA powder seems to be more sensitive for hydrogen (Fig. 2 vs. Fig.3). The addition of argon to nitrogen also reduces shrinkage, but only at much higher contents than hydrogen (Fig. 4). Shrinkage may be quickly interrupted by the atmosphere change during sintering (Figs. 5 and 6).

The disturbance of the sintering process by 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) [10]. Volume diffusion involves the motion of vacancies and the

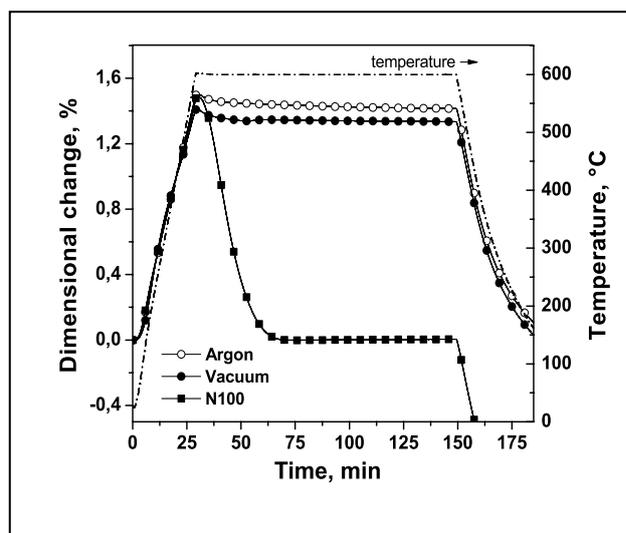


Fig. 1. Dilatometry curves for sintering Fluka Al compacts in different atmospheres and vacuum.

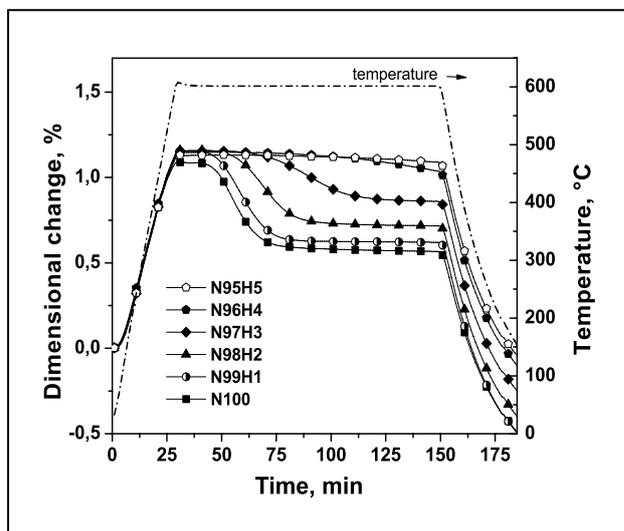


Fig. 2. Dilatometry traces for compacts made of Fluka Al powder sintered in nitrogen/hydrogen atmospheres.

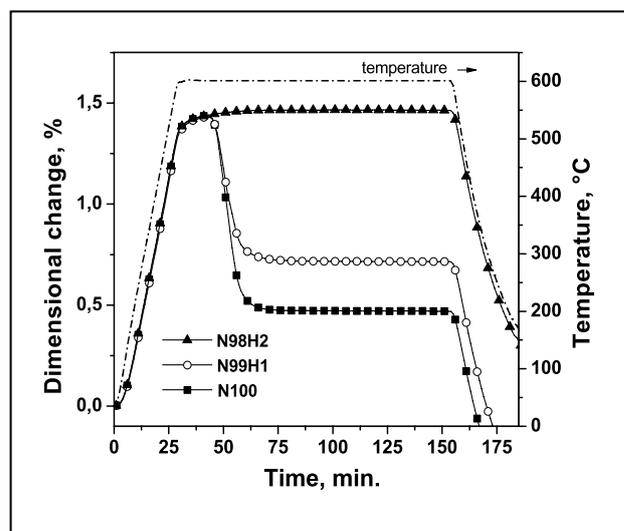


Fig. 3. Dilatometry traces for compacts made of ECKA Al powder sintered in nitrogen/hydrogen atmospheres.

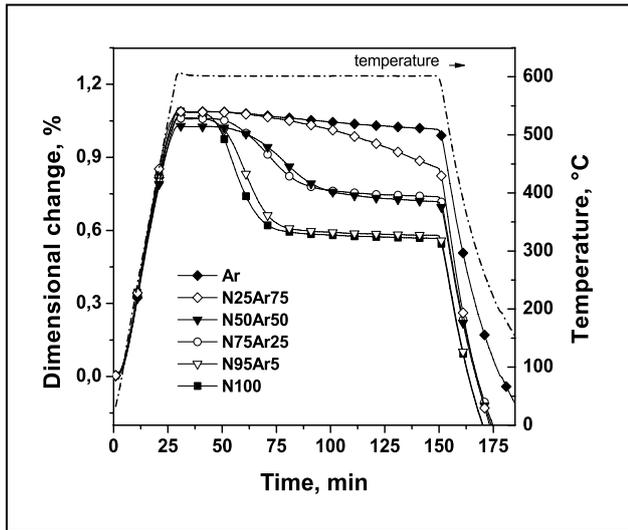


Fig. 4. Dilatometry traces for compacts made of Fluka Al powder sintered in nitrogen/argon atmospheres.

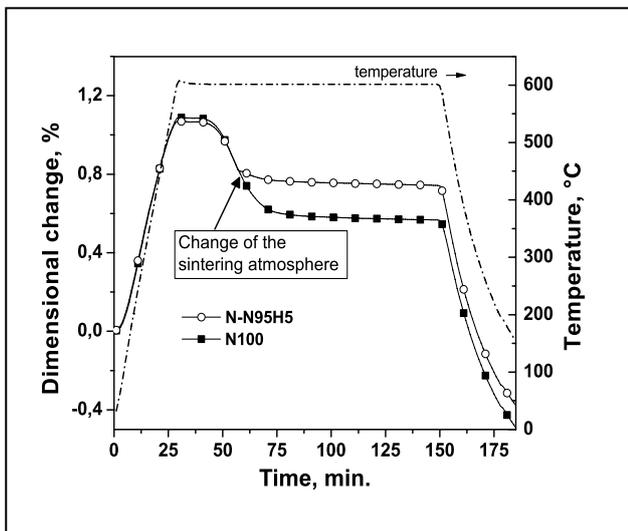


Fig. 5. Terminated shrinkage for Fluka Al compacts by atmosphere change: nitrogen → nitrogen/hydrogen.

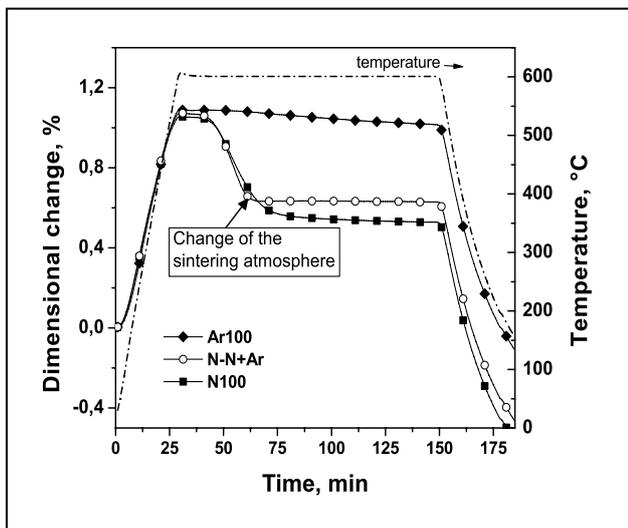


Fig. 6. Terminated shrinkage for Fluka Al compacts by atmosphere change: nitrogen → argon.

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 neighboring Al atoms into a vacancy and so the diffusion is hindered by hydrogen trapped in it.

Data collected in Table 1 and TG curve in Figure 7 clearly show, that the sintering shrinkage is associated with the nitrogen binding. Simultaneously, the increase in oxygen content is observed. 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 sufficient to diminish 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 questionable.

The enormous high shrinkage of loose packed Fluka Al powder particles (estimated to be about 30%) is accompanied by a very strong aluminium nitriding.

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 Al	N <sub>2</sub>	0.94	0.59
	N <sub>2</sub> /5%H <sub>2</sub>	0	0.80
	Ar	0	0.71
	Ar /5%H <sub>2</sub>	0	0.60
	Vacuum	0	0.50
Sintered compact of Fluka Al, surface layer	N <sub>2</sub>	0.44	0.70
		1.10	0.62
		0.83	0.53
Sintered specimen of loose Fluka Al powder, surface layer	N <sub>2</sub>	3.59	1.35
		5.45	0.33

Table 1. Nitrogen and oxygen content in investigated materials.

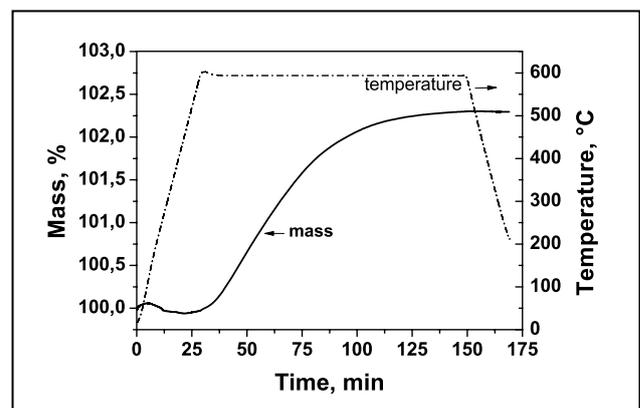


Fig. 7. TG curve of Fluka Al compact heated in nitrogen.

The X-Ray phase analyse performed on this material showed AlN as a product of Al powder – nitrogen atmosphere interactions. Additionally, this experiment proved, that the mechanical breaking of oxide layer due to particles deformation doesn't play a crucial role during sintering of aluminium.

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 <sub>2</sub>	243.1
2	N <sub>2</sub> /5%H <sub>2</sub>	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.

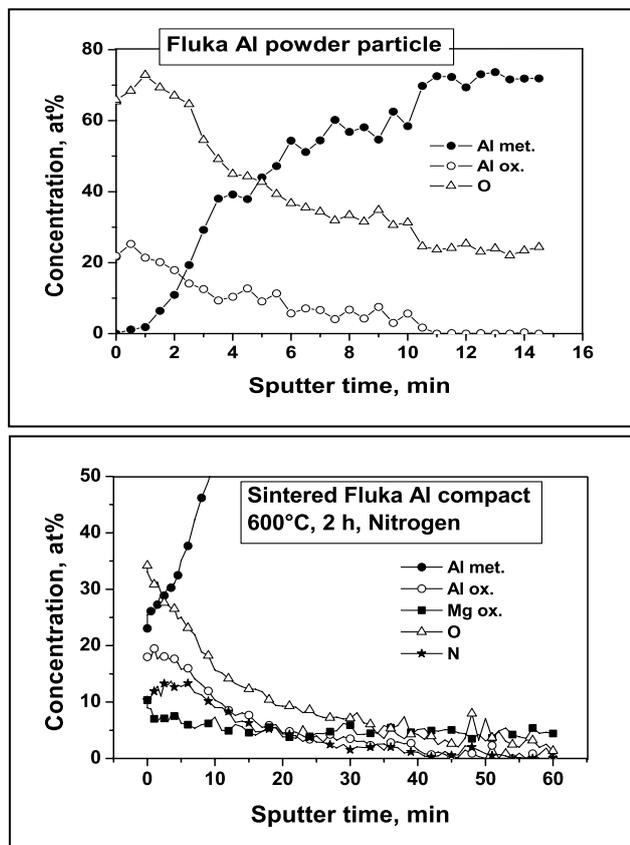


Fig. 8. AES concentration depth profiles for Fluka Al powder particle and fracture of sintered compact.

The Auger electron spectroscopy made on Fluka powder particles proved, that only Al oxide is present on a surface. Magnesium was not detected (Fig. 8 upper part). Kimura et al. [7] 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<sub>2</sub>O<sub>3</sub> 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. 8 lower part). Mg is 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<sub>2</sub>O<sub>3</sub> [8,9] and to degrade the oxide layer locally. Additionally, the revealed incorporation of nitrogen atoms enhances the destruction of Al<sub>2</sub>O<sub>3</sub> by potential formation of intermediate oxynitrides and subsequent AlN. Obviously, all of these reactions cause diffusion processes which could be responsible for the shrinkage observed when pure nitrogen atmosphere was used.

#### 4. Conclusions

Magnesium present in Al powder even in small amounts, concentrates on the surface of powder particles and supports sintering by local reduction of Al<sub>2</sub>O<sub>3</sub>. Pure nitrogen is the only active sintering atmosphere for aluminium producing shrinkage. The formation of aluminium nitride is thereby a key effect. In contrary, hydrogen strongly counteracts sintering shrinkage, probably due to the trapping hydrogen by lattice defects.

#### Acknowledgements

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