

Sintering Atmosphere Effects on the Densification of Al-SiC Compacts

Tadeusz Pieczonka, Jan Kazior

Abstract—The influence of SiC powder addition on densification of Al-SiC compacts during sintering in different atmospheres was investigated. It was performed in a dilatometer in flowing nitrogen, nitrogen/hydrogen (95/5 by volume) and argon. Fine, F500 grade of SiC powder was used. Mixtures containing 10 and 30 vol.% of SiC reinforcement were prepared in a Turbula mixer. Green compacts of about 82% of theoretical density were made of each mixture. For comparison, compacts made of pure aluminum powder were also investigated. It was shown that nitrogen is the best sintering atmosphere because only in this atmosphere did shrinkage take place. Its amount is lowered by ceramic powder addition, i.e. the more SiC the less densification occurs. Additionally, the formation of clusters, enhanced in compacts containing 30 vol.% SiC, is also responsible for limiting the shrinkage. Microstructural examinations of sintered composites revealed that sintering of compacts occurs in the presence of the liquid phase exclusively in nitrogen.

Keywords—Al-SiC composites, densification, sintering atmosphere.

I. INTRODUCTION

ECOLOGICAL requirements of the automotive industry include future components with lower densities than iron-based parts, including those manufactured by Powder Metallurgy, PM. Thus aluminum-based PM materials have recently gained considerable attention [1]-[10]. The replacement of the sintered steel parts by the aluminum-based ones has additional economic benefits, because of the relatively low temperature of sintering in cheap and safe nitrogen. Already there are several aluminum based PM materials in use [4], [5], including aluminum metal matrix composites (MMCs), of which those reinforced with SiC particles are the most significant [11]-[14]. Developed for aerospace and defense applications, they have found, up to now, limited use in the automobile industry.

The main goal of our previous investigations on sintered Al-SiC MMCs [15]-[17] was microstructural examination, especially the arrangement of SiC particles in the aluminum matrix. Compacts used in those experiments were sintered conventionally in a nitrogen atmosphere, since it has been demonstrated unambiguously that nitrogen is the most suitable sintering atmosphere for aluminum [18]-[20]. We have also already observed [15], [21] that, when compared to other sintering atmospheres, processing of Al-SiC MMCs in pure nitrogen produces the highest shrinkage.

T. Pieczonka is with the AGH University of Science and Technology, Al. Mickiewicza 30, PL- 30-059 Krakow, Poland, (phone: +48-12-6173027; fax: +48-12-6173190; e-mail: pieczonk@agh.edu.pl).

J. Kazior is with Cracow University of Technology, Ul. Warszawska 24, PL- 31-155 Krakow, Poland (e-mail: kazior@mech.pk.edu.pl).

It should be recalled that, due to the extremely high affinity of aluminum for oxygen, a thin (few nm) and transparent aluminum oxide layer is always present on an aluminum surface. Since Al_2O_3 oxide is thermodynamically very stable, it cannot be reduced by any practical gaseous reductants. As the surfaces of aluminum powder particles are covered by this oxide layer, it influences the sintering process; it being expected that the skin will impede the process. Pure aluminum oxide powder requires significantly higher sintering temperatures than aluminum based powders (about 1600 vs. below 600°C, respectively). Thus successful processing of aluminum powder at low temperatures must involve destroying the continuous Al_2O_3 oxide layer - to make a direct metallic contact between the neighboring powder particles. As loosely packed aluminum powder particles were successful sintered in nitrogen [22], it is clear that the rupture of the brittle oxide layer during compaction is not a processing requisite. The difference in thermal expansion coefficients between alumina and aluminum may result in an oxide rupture during heating, but then the oxide skin can immediately be rebuilt by binding with oxygen, necessarily present, even in a trace amounts, in the surrounding atmosphere. The disruption of the stable oxide skins can also result from the formation of a liquid phase [19], [23].

Considering all of the above mentioned possible mechanisms of destroying Al_2O_3 , it is concluded that the only explanation for the effective solid state sintering of an aluminum powder are reactions between Al_2O_3 , impurities (or alloying elements) present in the powder and the sintering atmosphere, though the influence of the atmosphere on the dimensional changes occurring during sintering is still not completely clear. In an attempt to elucidate this, the current paper presents and considers new results on Al-SiC powder mixtures sintered in different atmospheres.

II. EXPERIMENTAL PROCEDURE

A. Materials

The starting materials were:

- air atomized, 99.5% purity AGC100 grade aluminum powder of $\sim 100\mu m$ average particle size, delivered by Alpoco, and
- ball milled fine SiC F500 grade powder characterised by particle sizes $d_3 \text{ max.} - 38.2\mu m$, $d_{50} - 15.2-17.8\mu m$ and $d_{94} \text{ min.} - 4.6\mu m$. Before mixtures were prepared, the SiC powder was cleaned in acetone, then washed in cold water and dried.

Mixtures containing 10 and 30vol.-% of SiC were prepared

in a turbula mixer with a mixing time of 30 minutes. Additionally, for comparison, as-delivered aluminum powder was the next investigated composition.

B. Green Compacts

Rectangular ($15 \times 4 \times 4 \text{ mm}^3$) green compacts of ~82% of theoretical density were produced by uniaxial cold pressing with glycerol die wall lubrication.

C. Sintering

Sintering was performed in a horizontal NETZSCH 402E dilatometer in different protective gas atmospheres, flowing through the furnace tube of 35mm inner diameter at 100ml/min. The sintering atmospheres used were:

- pure nitrogen (52),
- 5 vol.-% hydrogen and 95 vol.-% nitrogen, and
- pure argon.

All gases used were high purity with a dew point below -70°C (which was the lowest point on a dew-point-meter's scale), and oxygen content below 5ppm.

Dimensional changes were monitored during the whole temperature-time program: heating at $20^\circ\text{C}/\text{min.}$ to the isothermal sintering temperature of 620°C , at which the samples were held for 2 hours, and cooling at $20^\circ\text{C}/\text{min.}$ to room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 clearly demonstrates that sintering atmosphere (N_2 , Ar or $\text{N}_2+5\%\text{H}_2$) exerts a strong influence on the sintering densification of Al-30vol.% SiC compacts. Two completely different types of dilatometric curves can be distinguished: for sintering in pure nitrogen and in other atmospheres. This observation is valid for all compositions investigated, i.e. the amount of SiC, in contrast to the atmosphere type, does not change the type of dimensional behavior during sintering (Fig. 2). Additionally, the results show that the sintering atmosphere is a dominant factor, determining not only the sintering mechanisms, but also generating the sintering shrinkage.

While both heating and cooling segments are similar for all mixtures investigated, the essential dimensional changes are observed during isothermal sintering. Independently of the sintering atmosphere, the heating period is characterized by continuous thermal expansion up to the isothermal step at 620°C . However, the expansion rate becomes lower as the amount of ceramic powder added is increased (Fig. 2). It is well known that the main function of SiC constituent in the Al-SiC composites is limiting the thermal expansion of the matrix.

It has already been shown [18], [23] that densification occurring during sintering of aluminum is connected with its nitriding and even a small amount of hydrogen in a mixture with nitrogen will strongly impede the sintering shrinkage. The current results clearly document that only pure nitrogen is an active sintering atmosphere also for Al-SiC compacts producing their shrinkage. Similarly to the sintering behavior of unalloyed aluminum, the isothermal shrinkage developed in Al-SiC compacts in nitrogen at high shrinkage rate may

suggest that a liquid phase contributes to the shrinkage. The appearance of the liquid phase in the system at 620°C is possible due to the highly exothermal aluminium nitriding reaction, which may result in a local increase of the temperature above the aluminium melting point.

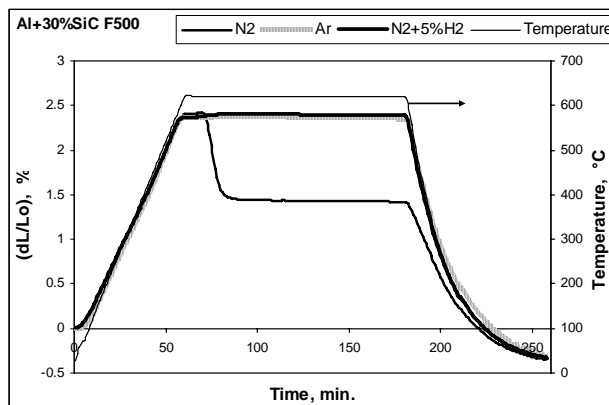


Fig. 1 Dilatometry trials showing the sintering atmosphere effect on densification of Al-30vol.% SiC compacts. Green density ~82% of theoretical, isothermal sintering temperature 620°C and time – 2h

Microstructure investigations carried out on sintered compacts confirm the presence of the liquid phase during sintering of Al-SiC compacts in nitrogen (Fig. 3). As can be seen, the liquid phase partly wets the ceramic surface, which supports densification.

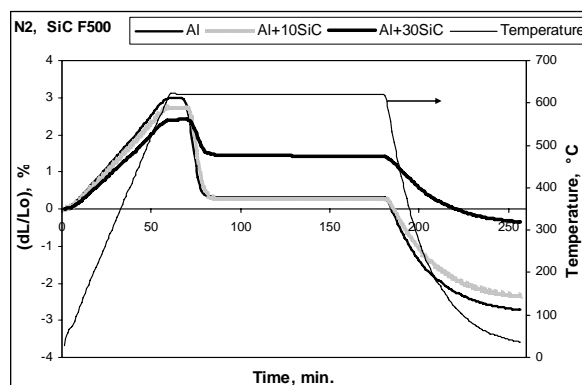
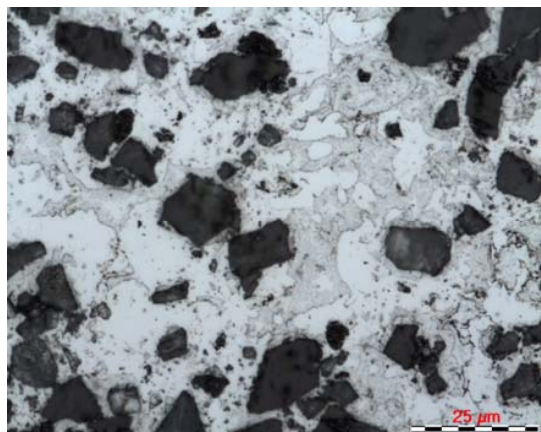
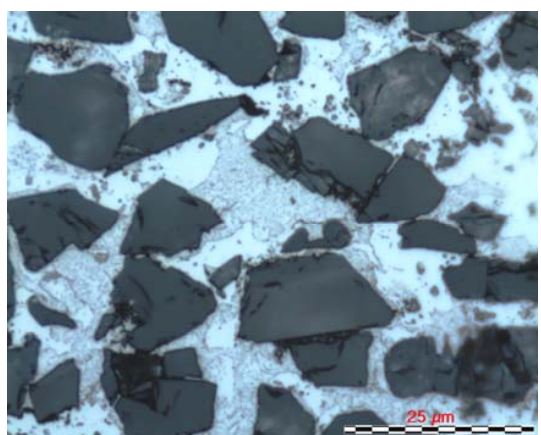


Fig. 2 Dilatometry trials showing the effect of reinforcement amount on densification of Al-30vol.% SiC compacts. Green density ~82% of theoretical, isothermal sintering temperature 620°C and time – 2h



(a)



(b)

Fig. 3 Microstructure of Al-SiC compacts sintered in nitrogen: (a) – 10vol. % SiC, (b) – 30vol. % SiC. Structural components of the matrix document the presence of the liquid phase during sintering

It seems, however, that some unresolved questions remain, e.g. whether nitrogen completely impedes the reaction between Al and SiC and whether the Al-Si liquid phase is formed, at all, in nitrogen.

IV. CONCLUSIONS

Densification during sintering of Al-SiC powder mixtures depends strongly on the composition of gaseous atmosphere used; only pure nitrogen produces shrinkage.

Nitriding of aluminum matrix, evolved only in pure nitrogen atmosphere, is responsible for the liquid phase formation during isothermal sintering carried out at temperatures even lower than the melting point of aluminum. Since the melt partly wets the solid phases, the densification of compacts proceeds.

It seems that nitriding of the aluminum matrix dominates over the reaction between aluminum and silicon carbide producing Al_4C_3 and thus the latter can be avoided in the sintered structure, which is highly desired.

ACKNOWLEDGMENT

This work was supported at the Krakow University of Technology by a Polish grant POIG No. 01.01.02-00-015/09-00, which is gratefully acknowledged. Special thanks are due to The Aluminium Powder Company Limited (ALPOCO) from Skawina in Poland for donating the high purity aluminum powder.

REFERENCES

- [1] G.B. Schaffer, S.H. Huo "On Development of Sintered 7xxx Series Aluminium Alloys", Powder Metallurgy, vol. 42, 1999, 3, 219-225.
- [2] F.V. Beaumont "Aluminium P/M: Past, Present and Future", Int. J. Powder Metallurgy, vol. 36, 2000, 6, 41-43.
- [3] Ch. Lall, W. Heath "P/M Aluminium Structural Parts – Manufacturing and Metallurgical Fundamentals", Int. J. Powder Metallurgy, vol. 36, 2000, 6, 45-50.
- [4] W.H., Jr. Hunt "New Directions in Aluminium – Based P/M Materials for Automotive Applications", Int. J. Powder Metallurgy, vol. 36, 2000, 6, 51-60.
- [5] G.B. Schaffer, D. Apelian "Aluminum Powder Metallurgy: Process, Properties and Design Solutions", Booklet published by The Aluminum Association, 2000.
- [6] H. Weber "Sintering of New PM Aluminium Alloys: New Sintering Furnaces Concept for Stringent Sintering Process Conditions", Proc. of EURO PM'2001, European Congress and Exhibition on Powder Metallurgy, vol. 2, pp. 171-176.
- [7] W.A.G. McPhee, J. Drennan, G.B. Schaffer "Iron and Microstructural Development During Sintering of Al-Cu-Mg Alloys", PM²TEC 2001, Advances in Powder Metallurgy & Particulate Materials - 2001, Proc. of the 2001 Int. Conf. on Powder Metallurgy & Particulate Materials, New Orleans 2001, pp. 9-139 – 9-147.
- [8] N. Myers, R.M. German "Sintering of Aluminium Flakes for Lightweight Applications", PM²TEC 2001, Advances in Powder Metallurgy & Particulate Materials - 2001, Proc. of the 2001 Int. Conf. on Powder Metallurgy & Particulate Materials, New Orleans 2001, pp. 9-192 – 9-198.
- [9] H.C. Neubing, J. Gradl, H. Danninger "Sintering and Microstructure of Al-Si P/M Components", PM²TEC 2002, Advances in Powder Metallurgy & Particulate Materials - 2002, Proc. of the 2002 Int. Conf. on Powder Metallurgy & Particulate Materials, Orlando 2002, pp. 13-128 – 13-138.
- [10] H. Weber, P. Delarbre, M. Krehl, K. Link "Sintering of High Performance PM Aluminium Alloys", PM²TEC 2002, Advances in Powder Metallurgy & Particulate Materials - 2002, Proc. of the 2002 Int. Conf. on Powder Metallurgy & Particulate Materials, Orlando 2002, pp. 13-150 – 13-156.
- [11] K.C. Ramesh, R. Sagar "Fabrication of Metal – Matrix Composite Automotive Parts", Int. J. Adv. Manuf. Technol., vol. 15, 1999, pp. 114-118.
- [12] R.R. Phillips "High Strength Aluminum Metal Matrix Composites", PM²TEC 2000, Advances in Powder Metallurgy & Particulate Materials - 2000, Proc. of the 2000 Int. Conf. on Powder Metallurgy & Particulate Materials, New York 2000, pp. 12-63 – 12-69.
- [13] S. Yamagata, M. Imamura, Y. Hirose, T. Sugiyama, O. Suwata, K. Kamitake, M. Omachi, Y. Abe, A. Fukui "P/M Al-SiC Composite Through Sintering Process for Heat Spreader in Semiconductor Devices", "Proc. Powder Metallurgy World Congress and Exhibition PM'2000, Kyoto, Eds. K. Kosuge, H. Nagai, vol. 2, 1174-1177.
- [14] K. Tomolya "Production and Investigation of Aluminum-base and SiC Particles Reinforced Composites", Thesis, University of Miskolc, 2001.
- [15] Z. Gácsi, T. Pieczonka, J. Kovács, Á. Kovács, M. Szigethy, G. Buza "Characterization of Microstructure of Sintered and Laser Remelted Composites", in "Materials Development and Processing, -Bulk Amorphous Materials, Undercooling and Powder Metallurgy", Ed. L. Schultz, D. M. Herlach, J. V. Wood, Vol. 8. (2000) p. 375.
- [16] Z. Gácsi, J. Kovács, T. Pieczonka "Investigation of Sintered and Laser Surface Remelted Al-SiC Composites", Surface & Coatings Technology. Vol. 151-152 (2002) p. 320.
- [17] Z. Gácsi, J. Kovács, T. Pieczonka "Particle Arrangement Characterization by the Pair Correlation Function", Powder Metallurgy Progress. Journal of Science and Technology of Particle Materials, vol.

- 3, 2003, 30-38.
- [18] T. Pieczonka, Th. Schubert, S. Baunack, B. Kieback "Dimensional behaviour of aluminium sintered in different atmospheres", *Materials Science and Engineering A*, vol. 478, 2008, 251-256.
- [19] T. Pieczonka, S.C. Mitchell, A.S. Wronski, J. Kazior, M. Hebda „Postulation of a mechanism of nitrogen sintering of aluminium“, *PM²TEC 2008, Advances in Powder Metallurgy & Particulate Materials - 2008, Proc. of the 2008 World Congress and Exhibition on Powder Metallurgy & Particulate Materials*, vol. 5, 25-40.
- [20] G.B. Schaffer, B.J. Hall "The Influence of the Atmosphere on the Sintering of Aluminum", *Metallurgical and Materials Transactions A*, vol. 33A, 2002, 3279-3284.
- [21] T. Pieczonka, Z. Gácsi, F. Kretz, J. Kovács "Sintering Behavior of Al-SiC Powder Mixtures Controlled by Dilatometry", *Proc. PM2004 World Congress & Exhibition, Vienna, 2004, Vol. 2*, 95-100.
- [22] Th. Schubert, T. Pieczonka, S. Baunack, B. Kieback "The Influence of the Atmosphere and Impurities on the Sintering Behaviour of Aluminum", *Proc. EURO PM2005 Congress & Exhibition, Prague 2005, vol. 1*, 3-8.
- [23] T. Pieczonka „Powder Metallurgy Processing of Aluminium ”, in „*Polish Metallurgy 2006-2010 in Time of the Worldwide Crisis*“, Committee of Metallurgy of the Polish Academy of Sciences, Ed. E. Swiątkowski, vol. 1, 37-57.