Effect of fly ash addition on the magnesium content of casting aluminum alloy A535

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In the past few decades development efforts in the area of particle-reinforced metal matrix composites (MMCs) have focused mainly on age-hardenable aluminum alloy MMCs [1–14]. Particle-reinforced aluminum matrix MMCs are attractive for automobile, electronic packaging, and aerospace applications due to their low density, high specific strength and modulus, superior wear resistance and low coefficient of thermal expansion (CTE) [15, 16]. Most conventional particulate aluminum matrix MMCs are expensive and, as such, efforts are being made to produce aluminum alloy MMCs at lower costs and with similar, or possibly better, engineering application bases. Recent research into developing inexpensive aluminum alloy MMCs shows that fly ash can be used in forming inexpensive aluminum MMCs with improved mechanical properties that can compete favorably with other available particulate MMCs [16–28]. Fly ash is a lightweight coal combustion by-product (CCB) produced in upwards of 5 million tonnes annually in Canada by thermal generating utilities. It is separated from the exhaust gases of power plants with a suspension-fired furnace in which pulverized coal is used as fuel. It is generally finer than Portland cement and consists of small glassy spheres with varying sizes (ranging from less than 1 μm to more than 100 μm). Two major classes of fly ash are recognized, Classes C and F, which are related to the type of coal burnt [29, 30]. Class F fly ash, which is more suitable for the synthesis of MMCs because of its low CaO content, is generally obtained by burning anthracite or bituminous coal. The physical and chemical properties of fly ash make it useful for construction and industrial materials, especially in cement manufacturing, concrete, liquid waste stabilization, and hydraulic mine backfill. Using fly ash to reinforce aluminum alloy MMCs offers advantages of reducing disposal volumes for coal-powered utilities plants, providing a high value-added use of fly ash and producing composites with improved material properties (e.g., wear resistance and low density) at a reduced cost [16]. These composites can find useful applications in automotive and aerospace components, machine parts, sporting goods, and electronic packaging.

Aluminum casting alloy 535 (A535), (its chemical composition is given in Table I) is a non-heat treatable Al-Mg alloy with the highest combination of strength, shock resistance, ductility, and corrosion resistance of any as casting (non-heat treated) aluminum alloy. It develops its strength through solid solution strengthening. The fairly high Mg content gives it protection from mild alkalis, salt spray, seawater and mild acids such as fruit juices. The purpose of the present article is to document the effect of fly ash addition on the microstructure and mechanical properties of A535 reinforced with various weight fractions of fly ash and SiC. The matrix was reinforced with 5 wt% SiC + 5 wt% fly ash (A535 hybrid), 10 wt% fly ash (A535 + 10), and 15 wt% fly ash (A535 + 15) using a proprietary stir casting technique developed by CANMET, Ottawa, Canada. The chemical composition of the raw fly ash used in fabricating the composites (see Table II) was determined using a Bruker S4 Explorer X-ray Fluorescence Spectrometer (XFS). The samples were palletized with cellulose and analyzed with a 4-μm polypropylene film support under helium. As can be seen from Table II, the main constituents of this fly ash are oxides of silicon, aluminum, iron, calcium, and potassium, while the minor constituents include oxides of magnesium, sulphur, titanium, and sodium. According to ASTM C-618 requirements [29, 30], this fly ash is a Class-F fly ash since the sum of oxides of silicon, iron, and aluminum is greater than 70% of the total fly ash content. Specimens of the matrix alloy and the three MMCs were tested in the as-received and heat treated conditions in order to understand their properties and microstructure. Solution heat treatment was carried out at 450 ± 5 °C for 5 hrs, followed by water quenching. All the specimens were metallurgically polished using 1

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TABLE I Chemical composition of A535

Element	Mg	Cu	Mn	Si	Fe	Ti	Others	Al
Weight percent	6.5–7.5	0.10	0.25	0.20	0.20	0.25	0.15	Bal.

μm diamond paste. Hardness measurements were carried out in a Buehler Micromet II Vickers Microhardness Tester using a load of 100 g (resident time = 15 s). The hardness values reported here are the averages of at least seven readings. Microstructural analysis was carried out in a Jeol Model 5600 scanning electron microscope (SEM) equipped with an EDAX Genesis 7000 energy dispersive X-ray spectrometer (EDS). EDS elemental analysis was carried out at numerous locations on several specimens of the same material. The results presented here are therefore the average values of these readings.

Fig. 1a–c respectively show the microstructure of A535 hybrid, A535+10 and A535+15 fly ash composites produced by stir casting. It can be seen from these figures that the reinforcement particles are not uniformly distributed in the A535 matrix. In Fig. 1b and c, the fly ash particles appear to segregate along the aluminum dendrite boundary. Rohatgi and co-workers [19, 24] have attributed this segregation to lack of nucleation of α-aluminum dendrites on fly ash surfaces and the pushing of these particles by the growing α-aluminum dendrites during solidification. Also, extensive porosity occurred due to fly ash addition and this increases with increasing fly ash content. Fig. 2 shows the microhardness of the as-received (as-cast) and solution heat treated specimens of unreinforced A535 and its composites. It can be seen that the hardness of A535 decreased with increasing fly ash content. This is contrary to the results published by Rohatgi *et al.* [16, 24] for A356.2 aluminum alloy reinforced with precipitator fly ash in which a slight increase in hardness was observed with increasing fly ash content. Although A535 hybrid and A535+10 composites have the same total amount of reinforcement particles, the hardness of the former is substantially greater than that of the latter. This is an indication that fly ash is more effective in retarding the solid solution strengthening process in A535 alloy than SiC. It may also be noted from Fig. 2 that the hardness of the as-cast materials is lower than that of solution heat treated samples, thus showing the effectiveness of heat treatment in improving the mechanical properties of A535 alloy and its composites. From this result it is possible to conclude that the addition of fly ash is detrimental to the hardness and, by extension, the strength of A535 alloy.

The decrease in hardness was further investigated by elemental analysis using EDS. Since the main solid solution strengthening element in A535 alloy is magnesium, EDS was used to quantitatively determine its variation in the free matrix of the MMCs. Fig. 3 shows the variation of Mg content (wt%) with increasing weight fraction of reinforcements. It is evident that Mg content of A535 alloy decreases with increasing fly ash weight fraction. The implication is that there is substantial depletion of Mg from the matrix with the addition of fly ash. The chemical composition of fly ash is a fundamental parameter in determining its suitability for various industrial applications. In the case of MMC fabrication, it will determine the thermodynamics and kinetics of possible chemical reactions between molten alloys and the fly ash. Al and Mg are known to reduce SiO_2 [31–34] and Fe_2O_3 [20, 23, 27, 31] in molten aluminum alloys producing free Si and Fe, respectively.

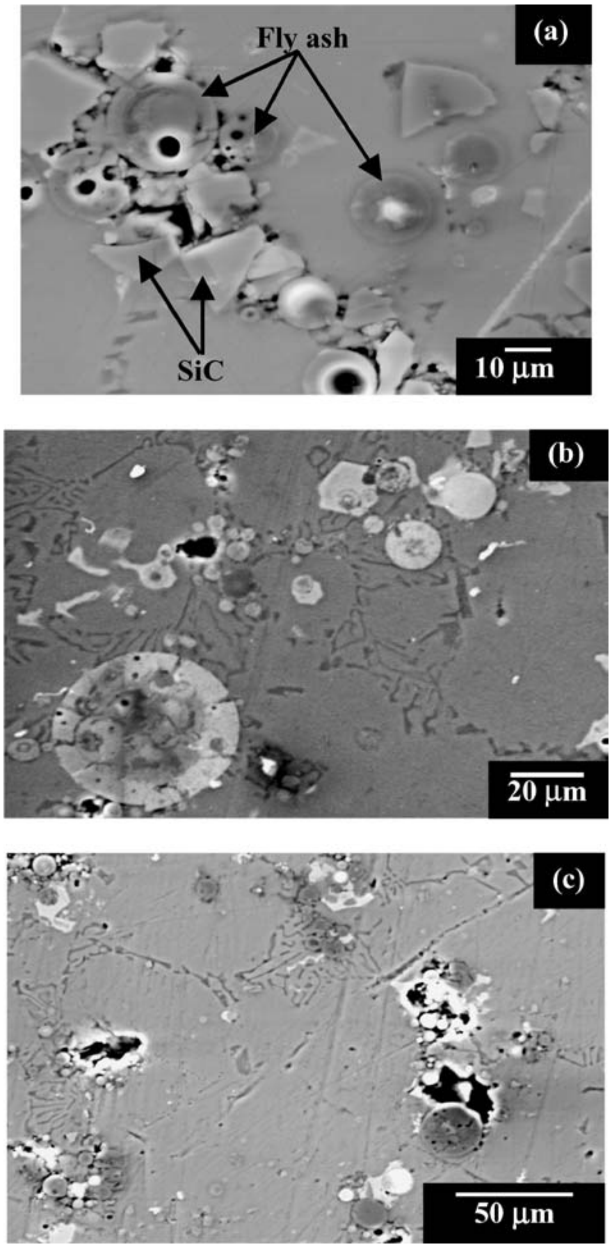

Figure 1 SEM micrographs showing the distribution of fly ash particles in A535 aluminum alloy: (a) A535 hybrid, (b) A535+10, and (c) A535+15.

TABLE II Chemical composition of raw fly ash

Compound	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO	K_2O	Na_2O	SO_3	Others
Weight percent	44.8	22.2	24.0	0.9	1.8	0.8	2.4	0.9	1.4	0.8

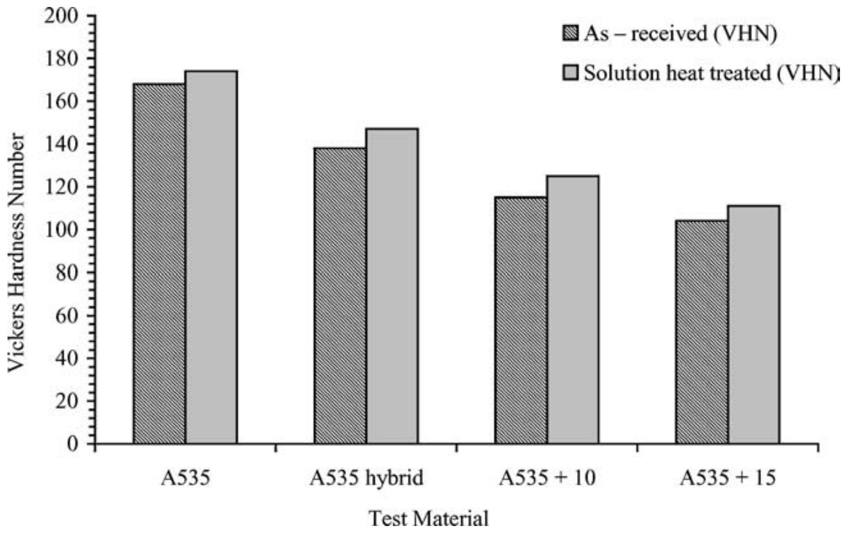

Figure 2 Hardness of as-received and solution heat treated samples.

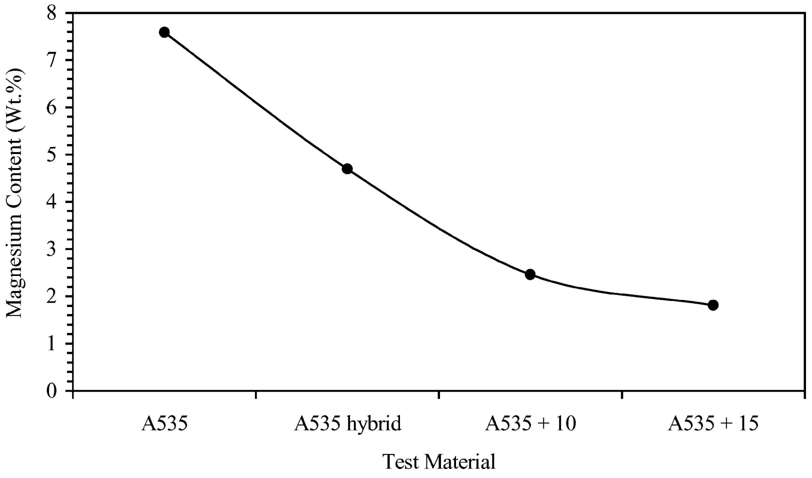

Figure 3 Effect of fly ash addition on the magnesium content of A535 alloy.

Also, Mg reduces Al_2O_3 [31–34]. At 1000 K, using the thermodynamic data in references [35, 36], the Gibbs free energy changes associated with the possible reduction reactions taking place between molten A535 and fly ash are:

$$SiO_2 + 2Mg \rightarrow 2MgO + Si \quad \Delta G^o = -255.6\ \text{kJ} \tag{1}$$

$$3SiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Si \quad \Delta G^o = -532.2\ \text{kJ} \tag{2}$$

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \quad \Delta G^o = -799.6\ \text{kJ} \tag{3}$$

$$Fe_2O_3 + 3Mg \rightarrow 3MgO + 2Fe \quad \Delta G^o = -917.0\ \text{kJ} \tag{4}$$

As can be seen, reactions (1) and (2) release Si while reactions (3) and (4) release Fe in the matrix. These metallic elements can migrate diffusively or convectively from the fly ash-A535 interface and alter the matrix chemistry. Depending on the prevailing processing conditions, the excess Si, for example, may combine with Mg to form Mg_2Si and other Si-rich compounds. The amount of the compounds formed will increase with increasing fly ash content. Experimental confirmation of this was obtained using SEM. Fig. 4a–c show the distribution of the Mg_2Si in fly ash reinforced A535 composites. It can be seen that as fly ash content increases, the complexity of Mg_2Si network decorating the matrix increases. The Mg_2Si phase is known to enhance precipitation hardening in age-hardenable A356 aluminum alloy [37] where it precipitates as fine particles. In the present case, it is too large to retard dislocation motion. As such, the Mg atoms which will usually participate in solid solution strengthening are tied up in a complex network of Mg_2Si that offers no appreciable strengthening to the material. Further, Mg has a greater affinity for oxygen than Al. In aluminum alloys, the reaction product Al_2O_3 (see reactions (2) and (3) might gradually change to either $MgAl_2O_4$ spinel or MgO. This will depend on the process temperature and the Mg content of the alloy. The possible reactions at 1000 K are [31, 32, 34]:

$$4Al_2O_3 + 3Mg \rightarrow 3MgAl_2O_4 + 2Al \quad \Delta G^o = -215.0\ \text{kJ} \tag{5}$$

$$MgAl_2O_4 + 3Mg \rightarrow 4MgO + 2Al \quad \Delta G^o = -84.9\ \text{kJ.} \tag{6}$$

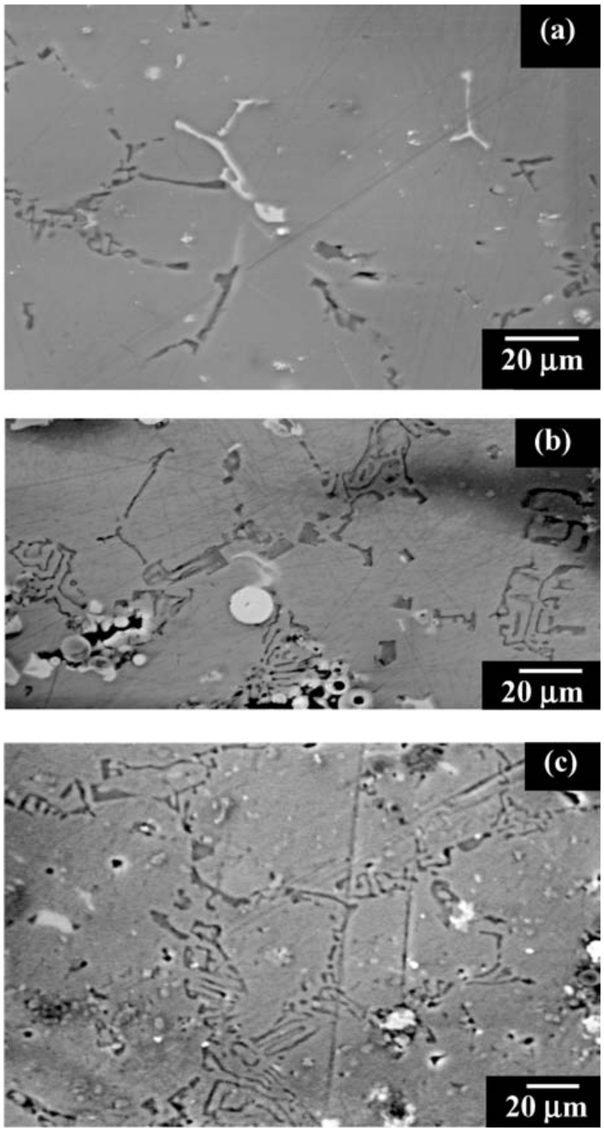

Figure 4 SEM micrographs showing the morphology and distribution of Mg_2Si phase in: (a) A535 hybrid, (b) A535+10, and (c) A535+15.

Since reactions (5) and (6) are thermodynamically possible, whichever of them runs concurrently with Mg_2Si formation in Equations 1 and 2 will exacerbate the unavailability of Mg for solid solution strengthening in the composites. In conclusion, the addition of fly ash to A535 aluminum alloy leads to Mg depletion in the matrix and subsequently to smaller solid solution strengthening.

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References

1. J. M. PAPAZIAN, *Metall. Trans.* A **13A** (1982) 761.
2. C. M. FRIEND and S. D. LUXTON, *J. Mater. Sci.* **23** (1988) 3173.
3. H. J. RACK, in "Dispersion Strengthened Aluminum Alloys", edited by Y.-W. Kim and W. M. Griffith (TMS, Warrendale, PA, 1988) p. 649.
4. S. SURESH, T. CHRISTMAN and Y. SUGIMURA, *Scripta Metall.* **23** (1989) 1599.
5. J. L. PETTY-GALIS and R. D. GOOLSBY, *J. Mater. Sci.* **24** (1989) 1439.
6. K. K. CHAWLA, A. H. ESMAEILI, A. K. DATYE and A. K. VASADEVAN, *Scripta Metall.* **25** (1991) 1315.
7. M. P. THOMAS and J. E. KING, *J. Mater. Sci.* **29** (1994) 5272.
8. I. DUTTA, F. N. QUILES, T. R. MCNELLEY and R. NAGARAJAN, *Metall. Mater. Trans.* A **29A** (1998) 2433.
9. I. N. A. OGUOCHA and S. YANNACOPOULOS, *Sci. Engrg. Comp. Mater.* **7** (1998) 299.
10. L. F. LIU, L. H. DAI and G. W. YANG, *J. Mater. Sci. Lett.* **20** (2001) 2097.
11. K. B. LEE and H. KWON, *Metall. Mater. Trans.* A **33A** (2002) 455.
12. C. H. CACERES and W. J. POOLE, *Mater. Sci. Engrg.* A **332** (2002) 311.
13. B. G. PARK, A. G. CROSKY and A. K. HELLIER, *J. Mater. Sci.* **36** (2001) 2417.
14. M. TAN, Q. XIN, Z. LI and B. Y. ZONG, *ibid.* **36** (2001) 2045.
15. D. J. LLOYD, *Int. Mater. Rev.* **39** (1994) 1.
16. P. K. ROHATGI, *JOM* **46** (1994) 55.
17. D. M. GOLDEN, *EPRI J.* Jan/Feb (1994) 46.
18. P. K. ROHATGI, J. K. KIM, R. Q. GUO, D. P. ROBERSTON and M. GAJDARDZISKA-JOSIFOVSKA, *Metall. Mater. Trans.* A **33A** (2002) 1541.
19. P. K. ROHATGI, R. Q. GUO, P. HUANG and S. RAY, *ibid.* A **28A** (1997) 245.
20. R. Q. GUO and P. K. ROHATGI, *ibid.* B **29B** (1998) 519.
21. P. K. ROHATGI, R. Q. GUO, B. N. KESHAVARAM and D. M. GOLDEN, *Trans. Amer. Found. Soc.* **103** (1995) 575.
22. P. K. ROHATGI, R. Q. GUO and B. N. KESHAVARAM, *Key Eng. Mater.* **104–107** (1995) 283.
23. R. Q. GUO, D. VENUGOPALAN and P. K. ROHATGI, *Mater. Sci. Engrg.* A **A241** (1998) 184.
24. P. K. ROHATGI and R. Q. GUO, *Proc. Amer. Power Conf.* **58** (1996) 657.
25. R. Q. GUO, P. K. ROHATGI and D. NATH, *J. Mater. Sci.* **31** (1996) 5513.
26. *Idem.*, *ibid.* **32** (1997) 3971.
27. P. K. ROHATGI, R. Q. GUO, H. IKSAN, E. J. BORCHELT and R. ASTHANA, *Mater. Sci. Engrg.* A **A244** (1998) 22.
28. T. MATSUNAGA, J. K. KIM, S. HARDCASTLE and P. K. ROHATGI, *ibid.* **A325** (2002) 333.
29. J. K. TISHMACK, in Proc. Coal Combustion By-Products Associated with Coal Mining: Interactive Forum, Oct. 29–31, 1996 (Southern Illinois University, Carbondale, USA, 1996) p. 13.
30. Y. P. CHUGH, D. DEB and C. B. RAJU, in Proc. The Use and Disposal of Coal Combustion By-Products at Coal Mines: A Technical Interactive Forum, April 10–13, 2000 (Morgantown, West Virginia, USA, 2000) p. 26.
31. R. ASTHANA, *J. Mater. Sci.* **33** (1998) 1959.
32. J.-C. LEE, J.-P. AHN, Z. SHI, J.-H. SHIM and H.-I. LEE, *Metall. Mater. Trans.* A **32A** (2001) 1541.
33. P. K. ROHATGI, B. C. PAI and S. C. PANDA, *J. Mater. Sci.* **14** (1979) 2277.
34. D. J. LLOYD, H. P. LAGACE and A. D. MCLEOD, "Controlled Interphases in Composite Materials", edited by H. Ishida (Elsevier Sci. Pub. Co., Inc., 1990), p. 359.
35. R. C. WEAST, in "CRC Handbook of Chemistry and Physics," 70th ed. (CRC Press, Boca Raton, Florida, USA, 1990) p. D-33.
36. M. W. CHASE, C. A. DAVIES, J. R. DOWNEY, JR., D. J. FRURIP, R. A. MCDONALD and A. N. SYVERUD (eds.), "JANAF Thermochemical Tables," 3rd ed. (J. Phys. Chem. Ref. Data, 1985) Vol. 14, Suppl 1.
37. K. Y. WEN, W. HU and G. GOTTSTEIN, *Mater. Sci. Technol.* **19** (2003) 762.

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