Chemical Modification of Iron – Rich Beta Intermetallic Phase in Aluminium-Silicon Alloys: A Short Review

Deni Ferdian[1,*], *Nida* Fauziah[1], *and Jacques* Lacaze[2]

[1]Dept.of Metallurgy and Materials Engineering, Universitas Indonesia, Indonesia
[2]CIRIMAT, Université de Toulouse, ENSIACET, BP 44362, 31030 Toulouse, Cedex 4, France

Abstract. Iron-rich intermetallic phases normally form during solidification of aluminium – silicon alloys with low level of iron. This type of phases is known for creating a mechanical properties degradation, especially the beta intermetallic phase (β-$Al_9Fe_2Si_2$). Various studies and researches have led to mitigate the harmful effect of these phases through physical separation, thermal treatment or microstructure alteration by chemical neutralization such as with Mn addition which changes their structure into cubic alpha phase (α-$Al_{15}(Fe,Mn)_3Si_2$). In this paper, the effect of chemical addition was reviewed and discussed in terms of effectiveness of modifying the crystal structure or morphology of beta intermetallic phase

1 Introduction

Iron is a common element in industrial Al-Si alloys and usually forms iron-rich intermetallic phases such as alpha, beta or delta phase. The study of aluminium - iron - silicon (Al-Fe-Si) ternary phase diagram can be traced back to the work by Gwyer and Phillips [1], with further details by Mondolfo [2] and more recent work by Belov et al. [3] in relation to commercial alloys. The liquidus projection of this ternary phase shows 11 stable ternary compounds which are labelled as τ_1 to τ_{11}, see Fig. 1. Furthermore, other metastable phases have also been reported in the system [4,5].

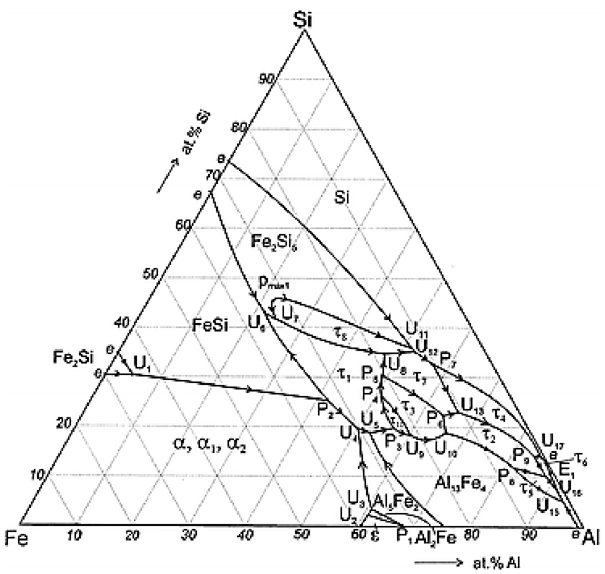

Fig 1. Liquidus projection of Al-Fe-Si ternary phase system [4].

In equilibrium condition, the Al corner of the liquidus projection shows that the intermetallic phase that must be present at the end of solidification is the τ_2-$Al_9Fe_2Si_2$ (beta phase) along with (Al)-Si eutectic as three phase solidification. Nevertheless, precipitation of other iron rich intermetallic phase such as delta phase might occur as well due to non-equilibrium conditions caused by finite cooling rate or due to chemical additions.

1.1 Beta Intermetallic Phase

Rosenhein et al. [6] reported beta phase has a monoclinic structure, and this has been confirmed by others [7-9]. Compared with other iron-rich intermetallic phase, beta phase is known to have a negative effect to the material mechanical properties. The beta phase provides a path for crack propagation due to its brittle properties [10]. Other researchers suggested that this damaging effect might be related to the beta phase morphology [11,12]. Minimazing the size of the phase below 50 microns showed improving the mechnanical properties [13]. 2D micrograph characterisation of the phase showed beta phase has a needle like appearance, but more recent 3D image analysis using serial sectioning or X-ray tomography indicated a plate like structure with interconnection among the precipitates [14,15].

1.2 Beta Phase - Chemical Modification

Efforts to minimize the harmful effect of beta phase have been carried out using several methods such as physical removal or chemical modification by the addition of minor elements that alter the growth of the

* Corresponding author : deni.ferdian@ui.ac.id

beta phase or transform it into a different phase during solidification. Manganese addition is known to neutralize the beta phase into cubic alpha phase $Al_{15}(Mn,Fe)_3Si_2$ that has a Chinese script appearance. This transformation has been investigated by Phillips and Varley in relation with establishing the effect of the manganese content in quaternary Al-Fe-Mn-Si alloys [16]. Munson [17] also showed the transformation into $Al_{15}(Mn,Fe)_3Si_2$ cubic structure which is isomorph with the structure of the Al_8Mn_2Si phase in the Al-Mn-Si system. Consequently, the addition of manganese causes the precipitation of the cubic alpha phase instead of the monoclinic beta phase.

Fig 2. 3D image of beta phase by serial sectioning [13].

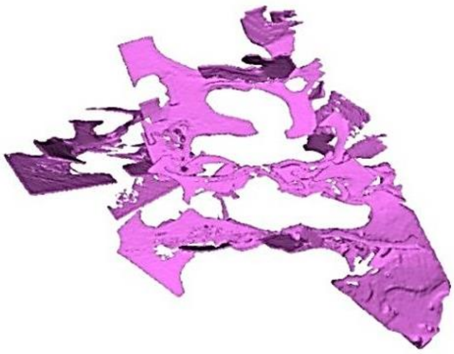

Fig 3. 3D image of beta phase by X-ray tomography [14].

Further efforts to chemically modify the beta phase were carried out with the addition of strontium. In low-Si Al-Si alloys, observations by Samuel et al. [18] indicated that strontium adsorption prevents silicon diffusion towards the hexagonal alpha phase which reduces the peritectic transformation of this hexagonal phase into the beta phase, and thus decreases the quantity of the latter. Other work by Liu et al. [19] showed fragmentation of beta phase due to strontium addition, though the effect was diminished with higher iron level. Work by Santos et al. [20] revealed that strontium addition increases the size of the beta precipitates during solidification at low cooling rate, but showed also that increasing the cooling rate reduced the amount of beta phase in comparison with un-modified strontium alloys.

Calcium also has been studied in relation to the beta phase modification. Calcium additions modify the silicon precipitates in the Al-Si eutectic and reduce the size of the beta phase [21,22]. However, the results of Cadena and Valdes [23] contradict the latter conclusion: in their work, the addition of calcium increased the beta phase, although the refinement of eutectic silicon took place.

Addition of transition element, such as vanadium or molybdenum, also showed modification of the beta phase although not much documentation could be retrieved. Work by Dichtl [24] demonstrated that molybdenum is altering platelet intermetallic into compact star shape appearance. Moreover, work by Skinner et al. [25] and Rao [26] showed some effect of vanadium on the modification of beta intermetallic phase.

2 The Effect of Rare Earth Elements

Early work of the effect of rare earth elements on the microstructure and properties of aluminium alloys can be found in the work by Podergin [27] who studied the effect of rare earths on the hardness of aluminium matrix. Work by Grebenkin and Dyzkovich [28] showed that cerium can neutralize the harmful effect of tin and lead in aluminium alloys. Addition of rare earth elements also refines the eutectic silicon as seen in the work by Shi et al. [29,30], Pandee et al. [31] and Yu et al.[32].

In 1xxx series of commercial alloys, Fu et al. [33] reported that rare earth elements can modify the needle like beta phase into a sphere or stick-shape precipitate of the complex AlFe(Ce,Nd,La) phase. Other studies on the effect of lanthanum and cerium in 6xxx series showed that lanthanum addition refined the eutectic silicon and stimulates the formation of Chinese script α-AlFeSi [34]. Unfortunately, this effect was not shown with cerium addition. The effect of lanthanum and ytterbium was studied by Li and Yan [35] who showed the reduction of the amount of beta phase although no morphology changes occurred to the intermetallic.

In most studies, rare earth elements were added to commercial alloy so that the effect on the beta phase precipitation and growth might be influenced by other element in the system. Study of the rare earth element effect was performed by Ferdian et al. [36] upon controlled system by using a synthetic alloy of Al-7Si-1Fe added with neodymium. The result showed the beta phase size reduced as the neodymium addition increases, though no alteration occurred to the beta phase morphology. Micro-chemical analysis also indicated the precipitation of a neodymium-rich intermetallic phase. Moreover, the addition of samarium also showed the same result as neodymium. EDS analysis showed precipitates of samarium-rich intermetallic phase which corresponds to Al_2Si_2Sm, as seen in Figure 4. EDS mapping in Figure 5 showed the distribution of the phases and of samarium-rich intermetallic phase within the aluminium matrix. It is worth noting that no quaternary phase was formed with rare earth element addition

Measurement of the beta phase length distribution showed the shifting of beta phase length to a lower size with increase in samarium addition, as seen in Figure 6. Without the addition of samarium, observation showed that no beta phase size smaller than 150 µm was observed even at cooling rate of 30 oC min-1. However, when samarium was added, a shift to a lower beta phase length occurred.

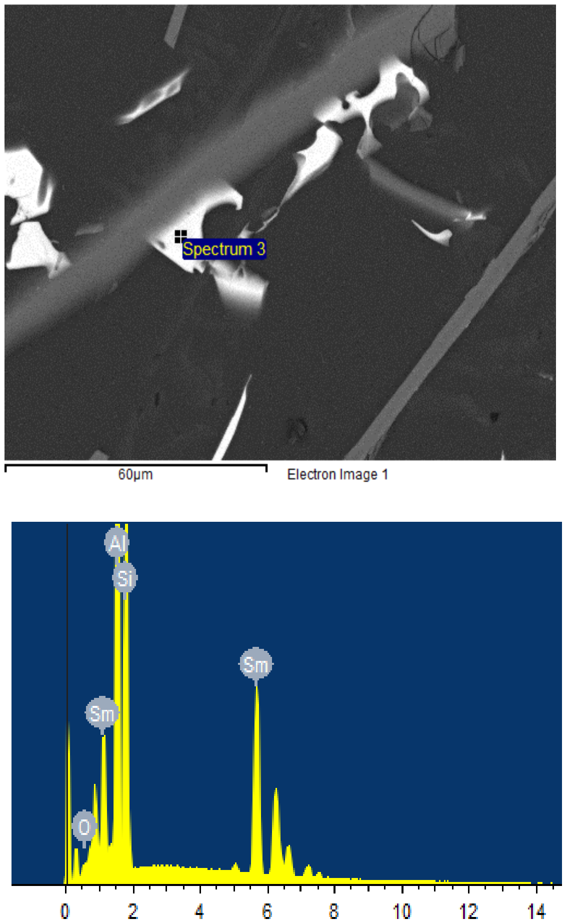

Fig 4. EDS spectrum analysis corresponds to the samarium rich intermetallic phase.

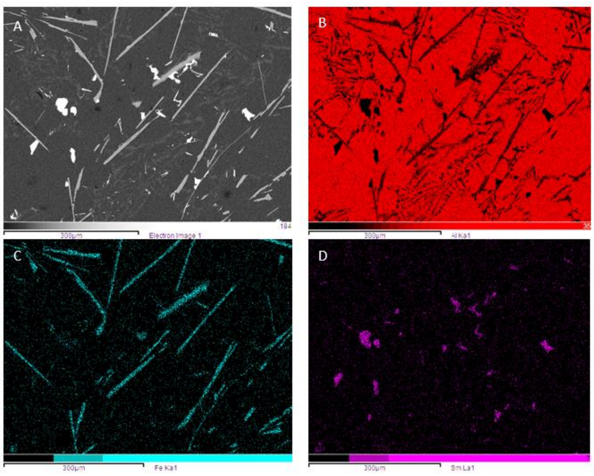

Fig 5. Backscattered electrons SEM micrograph from Al–7Si–1Fe–1Sm alloy (a) and associated EDS mappings of aluminium (b), iron (c) and samarium (d).

From the analysis, rare earth addition appeared to promote the beta phase size reduction probably by blocking of the transfer of silicon and iron atoms during the precipitation and growth of beta phase. Addition of rare earth element also changes the precipitation within the matrix where rare earth rich intermetallic phase alters the liquid composition and liquid fraction during solidification, although no formation of quaternary phases due to the addition of rare earth element was observed. In addition, no change in morphology was observed apart from the reduction in the size of the intermetallic phase.

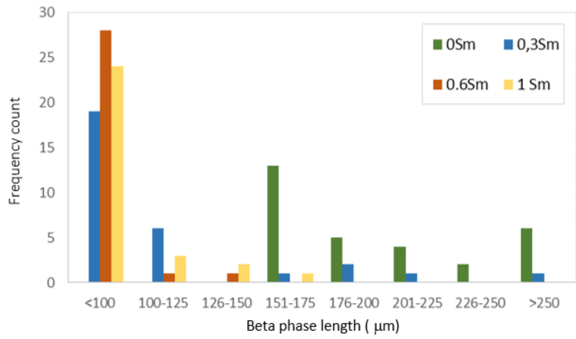

Fig 6. Distribution of beta phase length with different samarium additions (wt.%).

3 . Conclusion

The chemical modification by manganese addition alters the crystal structure of beta phase into cubic structure. Addition of rare earth elements did not change the crystal structure and the platelike morphology of the beta phase. However rare earth addition changed the beta phase size and reduced its length dimension. One of the proposed mechanisms related to this refinement is through adsorption blocking of Fe or Si during beta phase growth.

References

1. A.G.C. Gwyer and H.W.L. Phillips, J. Inst. Metals. 38 (1927) 35-44.
2. L.F. Mondolfo, Aluminium alloys, structure and properties, Butterworths, London ,1976.
3. N.A. Belov, A.A. Aksenov, and D.G. Eskin. Iron in aluminium alloys: impurity and alloying element, Taylor and Francis Inc., London and New York, 2002.
4. G. Ghosh, Aluminium-iron-silicon, in: Light metal systems: Phase diagrams, crystallographic and thermodynamic data, vol. IV of Landolt-Börnstein (New Series), Springer-Verlag, Berlin, 2008.
5. N. Krendelsberger, F. Weitzer and J.C. Schuster, Metall Mater Trans A. 38A (2007) 1681-1691.
6. W. Rosenhain, S.L. Archbutt, D. Hanson, Some Alloys of Aluminium-Light Alloys, London, 1921
7. V. Hansen, B. Hauback, M. Sundberg, C. Romming, J. Gjonnes, Acta Crystallogr. 54B (1998) 351–357.
8. G. Phragmen, J. Inst. Met. 77 (1950) 489–552.
9. C. Romming, V. Hansen, J. Gjonnes, Acta Crystallogr. B50B (1994) 307–312.

10. O. Elsebaie, A. M. Samuel and F. H. Samuel, J. Mat Sci. 46 (2011) 3027-3045.
11. S. Murali, K. S. Raman and K. S. S. Murthy, Mater. Sci. Eng. A. 151 (1992) 1–10.
12. M.A. Moustafa, J. Mater. Process. Technol. 209 (2009) 605–610.
13. L.Kuchariková, D. Medvecká, E. Tillová, J Belan, M. Kritikos, M. Chalupová, and M. Uhríčik, Materials, 14(8), (2021), 1943
14. C.M. Dinnis, J.A. Taylor, Scr. Mater. 53 (2005) 955–958.
15. D Ferdian, L Salvo, J Lacaze, C Tenailleau, B Duployer and B Malard, IOP Conf. Ser.: Mater. Sci. Eng. 117 (2016) 012018
16. H.W.L. Phillips, P.C. Varley. JIM 69 (1943) 317.
17. D. Munson, J. Inst. Met. 95 (1967) 217–219.
18. A.M. Samuel, F.H. Samuel, H.W. Doty, J. Mat Sci. 31 (1996) 5529-5539.
19. L. Liu, A.M.A. Mohamed, A.M. Samuel, F.H. Samuel, H.W. Doty, And S. Valtierra, Metall. Mater. Trans. A. 40A (2009) 2457-2469.
20. J. Santos, A.E.W. Jarfors, A.K. Dahle, Metall. Mater. Trans. A. 50A (2019) 4148–4165.
21. S.S. Sreeja Kumari, R.M. Pillai, B.C. Pai, K. Nogita and A.K. Dahle, Metall. Mater. Trans. A. 37A, (2006) 2581-2587.
22. T. Kobayashi, H.J. Kim, M. Niinomi, Mater. Sci. Technol. 13 (1997) 497-502.
23. A.A Zaldivas Cadena, A. Flores Valdes, Mater. Charact. 58 (2007) 834-841.
24. H.J. Dichtl, Aluminum. 46 (1970) 362–364.
25. D.J. Skinner, R.L. Bye, D. Raybould, A.M. Brown, Scr. Metall. 20 (1986) 867–872.
26. A.K. Prasada Rao, Trans Indian Ins. Met. 64 (2011) 447-451.
27. V.A. Podergin, Soviet Powder Metallurgy and Metal Ceramics. 5 (1966) 656–664.
28. V. S. Grebenkin, I. Ya. Dzykovich, Met. Sci. Heat Treat. 10 (1968) 786–788.
29. Z.M Shi, Q. Wang, G.Zhao, R.Y.Zhang, Mater. Sci. Eng. A. 626 (21050 102–107.
30. Z. Shi, Q. Wang, Y. Shi, G. Zhao, and R. Zhang, J. Rare Earths. 33 (2015) 1004–1009.
31. P.Pandee, C.M. Gourlay, S.A. Belyakov, R. Ozaki, H. Yasuda, C. Limmaneevichitr, Metall. Mater. Trans. A. 45A (2014) 4549-4560.
32. Yu-Chou Tsai, Cheng-Yu Chou, Sheng-Long Lee, Chih-Kuang Lin, Jing-Chie Lin, S.W. Lim, J. Alloys Compd. 487 (2009) 157–162.
33. G. Fu , F. Su, L. Ren, W. Chen, K. Qian, J. Rare Earth. 20 (2002) 61-66.
34. M. Hosseinifar and D.V. Malakhov, J. Mat Sci. 43 (2008) 7157-7164.
35. Z. Li and H. Yan, J. Rare Earths. 33 (2015) 995-1003.
36. D Ferdian, K.S Irawan, J Lacaze, Trans. Indian Inst. Met. 71 (2018) 2671–2676.