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EFFECT OF TRACE ELEMENTS (Co, Cr) ON THE MICROSTRUCTURE AND PHYSICAL PROPERTIES OF Al-Si-Cu-Mg-Fe EXTRUDED ALLOY

Trace elements Co, Cr were added to investigate their influence on the microstructure and physical properties of Al-Si extruded alloy. The Co, Cr elements were randomly distributed in the matrix, forms intermetallic phase and their existence were confirmed by XRD, EDS and SEM analysis. With addition of trace elements, the microstructure was modified, Si particle size was reduced and the growth rate of β -(Al₅FeSi) phase limited. Compared to parent alloy, hardness and tensile strength were enhanced while the linear coefficient of thermal expansion (CTE) was significantly reduced by 42.4% and 16.05% with Co and Cr addition respectively. It is considered that the low CTE occurs with addition of Co was due to the formation of intermetallic compound having low coefficient of thermal expansion. The results suggested that Co acts as an effective element in improving the mechanical properties of Al-Si alloy.

Keywords: Al-Si alloy, Microstructure, Extrusion, Coefficient of thermal expansion, Trace elements

1. Introduction

In recent years, industries had shown considerable interest to mitigate environmental pollution, such as reducing carbon dioxide releasing rate in automobiles and eco-friendly energy. In automotive industries, the main cause of the emission of carbon dioxide into the atmosphere was the use of fossil fuels. Therefore, to reduce the carbon dioxide emissions, the weight of the internal combustion engine and the external body had to minimize for improving the fuel efficiency of transportation vehicles such as an automobile, a train, and an aircraft is actively interested. To achieve industries ambitions, Aluminum was an effective material to replace the existing alloys having distinct properties like low-weight, high specific strength, good corrosion resistance, and low coefficient of thermal expansion [1-5].

The Al-Si based alloy was the most important commercial alloy due to their superior casting characteristics, low thermal expansion, high strength to low weight ratio and high wear resistance. With these exceptional qualities, the Al-Si alloy utilized in large number of applications in automobile industries [6,7]. The reported results of Si content on Al-Si alloys show that as the amount of Si increases, the mechanical properties, wear resistance, and simultaneously casting were enhanced. However, it leads to impairment of mechanical, poor machinability and other properties which results in high cost and time-consuming process for application [8-10]. Therefore, to overcome the disadvantages in Al-Si alloy and to enhance their properties to implement in industrial sectors, different chemical elemental doping, and fabrication methods had implemented and succeeded.

The addition of various transition metals to the Al-Si alloy forms an intermetallic compound in the matrix, which affects the mechanical strength as well as the coefficient of thermal expansion. Kaya et al. [11] reported that elemental doping of Cu, Co, Ni, Sb and Bi in eutectic Al-Si alloy changes the microstructure with intermetallic compounds and consequently mechanical properties were enhanced. Li et al. [12] reported that adding of Sr, Fe and P to Al-Si-Cu modifies the dissolution of copper phases in solution heat treatment. According to the results of previous studies, the addition of Co and Cr have a special role in increasing the high temperature strength and stability of the alloy in common. Co has been reported to neutralize the influence of Fe in the Al-Si-Fe-X (X = Cu, Ni, Mg) alloy and Cr acts to inhibit grain growth by forming an intermetallic compound with Al, thereby increasing the mechanical strength [13,14].

Hot extrusion, which is one of the plastic working methods, is already widely used in the Al alloy industry due to its high plastic deformation and productivity, capable of modifying the microstructure by adjusting the temperature of the extruder container and the extrusion ratio of the mold. Application of hot extrusion in Al-Si alloys is an effective plastic deformation technique which can reduce the size of Si, intermetallic

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compounds and reduce pores to improve mechanical strength [15,16].

In this paper, we studied the influence of trace elements (Co, Cr) on the microstructure, mechanical and physical properties of Al-12.6Si-3Cu-0.6Mg-0.5Fe extruded alloy. We interested on the effect of trace elements upon extruded alloys due to most of the literature was focused on casted alloys. In this work, the effect of Co, Cr elements to Al-Si matrix was successfully interpreted by implementing proper experimental analysis.

2. Experimental procedure

In this study, trace elements (Co, Cr) were separately added based to Al-12.6Si-3Cu-0.6Mg-0.5Fe (Bare sample). The chemical composition of the alloys was shown in Table 1. Parent alloys (Al-Si, Al-Cu, Al-Mg, Al-Fe), elemental Co, Cr were weighted to 2 kg and melted in a high frequency induction furnace at 750°C, then charged into a stainless-steel mold to make gravity casting. The produced gravity casted alloys had a cylindrical shape with a diameter of 74 mm and a height of 150 mm in which 50 mm shrinkage hole was removed. The resultant casted alloys were hot extruded (500-ton extruder) at 400°C using 10:1 extrusion ratio, and the RAM speed was maintained at 4.5 mm/s. Preceding hot extrusion, the casted materials was pre-heated at 400°C for 1 hour.

Comparison of chemical composition in between target alloys and the extruded alloys [SEM-EDS results]

Alloy	Chemical Composition (wt.%)						
	Si	Cu	Mg	Fe	Co	Cr	Al
Alloy Design	12.6	3.0	0.6	0.5	0.5	0.5	Bal.
Alloy A	12.55	3.11	0.63	0.48		—	Bal.
Alloy B	12.63	3.16	0.65	0.51	0.48	—	Bal.
Alloy C	12.68	3.14	0.61	0.49		0.49	Bal.

The produced extruded bar had a diameter of 22 mm and a length of about 750 mm. The microstructure and mechanical properties of extruded bar were analyzed along parallel to the extrusion direction. Average silicon particle size was calculated using optical microscopy (GX41, Olympus) combined with image analyzer software (isolution DT) using auto threshold option and hardness measured by Vickers hardness tester respectively. X-ray diffraction (X-ray diffraction, miniflex 600, Rigaku) was performed for the phase analysis generated in the extruded material using 40 kV and speed of 2° /min.

The linear coefficient of thermal expansion for the extruded material was measured using a thermo mechanical analyzer (Q-400). The square (5 mm) shaped CTE specimens were processed at a test temperature from 20°C to 400°C at a rate of 10°C/min and subjected to a load of 0.5 N. The tensile strength was carried out at room temperature using tensile testing machine (UTM-T, R & B) with load cell of 7.5 KN and crosshead speed of 2.0 mm/min. The tensile specimen (ASTM A370 small size) has a diameter of 4 mm and gage length of 20 mm. The tensile test was carried out twice for reliability.

To identify the trace elements and the existence of intermetallic compounds in the bulk samples were revealed using a high-resolution scanning electron microscope (SEM-MIRA-LMH II, TESKAN) embedded with energy dispersive X-ray spectroscopy (EDS) analysis (X-flash 4010).

3. Results and discussion

Fig. 1 shows the optical microscope image of the Al-Si casted material with and without trace element. All casted materials had acicular shaped β-(Al₅FeSi) intermetallic compound formed by the addition of Fe, but the size of β -(Al₅FeSi) phase was different among those casted alloys. The size of acicular β -(Al₅FeSi) intermetallic phase was about 50 μ m (Fig. 1(a)) with absence of trace elements in Al-Si alloys, while the addition of Co, Cr elements in Al-Si matrix evidently refined the β -(Al₅FeSi) phase and reduces its size about 20 µm (Fig. 1(b, c)). The growth of β-(Al₅FeSi) intermetallic compound was not inhibited with addition of Co, Cr but uniformly distributed without being segregated in the matrix. By reducing the size of β -(Al₅FeSi), it is possible to cutoff the nucleation of pores which forms actively along the long sides of β -(Al₅FeSi) phase [17] which results in decreasing shrinkage cavity in Al-Si alloys. Table 1 shows the chemical composition of the extruded alloys observed through SEM-EDS analysis. The quantity percentage of different elements in the extruded alloys was mostly matched with targeted alloy.



Fig. 1. Optical microscope images of as-cast Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X [X = (a) : None, (b) : Co, (c) : Cr] alloys

TABLE 1



Fig. 2. Particle size analysis of Si in extruded Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X [X = (a) : None, (b) : Co, (c) : Cr] alloys and (d) Si Particle size distribution of extruded Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X alloys. [X = None, Co, Cr] alloys

Fig. 2 shows the analysis of Si particle size along parallel direction to extrusion in all three extruded samples. The quantitative analysis of Si particle size of the extruded material was measured using an image analyzer. The heavy deformation during hot extrusion, the Si particles were evenly distributed in the Al-matrix. The average Si particle size of the extruded material without trace elements (Fig. 2(a)) was 4.68 µm, while that of Co and Cr added extruded materials (Fig. 2(b) and (c)) was 4.15 and 4.17 μ m respectively. Fig. 2(d) shows the size distribution of Si in the extruded Al-Si matrix. The number of small Si particles (~ 0.1 -1 μ m) were mostly observed with Co, Cr doped alloys, and the number of large Si-size was primarily displayed by bare sample. Hence, it was concluded that addition of trace elements simultaneously decreases the size of intermetallic compound and primary Si particle which was beneficial for improving the mechanical properties. Reducing Si particle has influence on mechanical properties, Dighe et al. [18] reported that the crack propagation occurs primarily in extremum Si particles which deteriorate the mechanical properties in Al-Si alloys.

Fig. 3 shows the X-ray diffraction patterns of the extruded materials. All the diffraction peaks were matches with standard diffraction peaks of Al, Si, Q-(Al₅Cu₂Mg₈Si₆), and Al₅FeSi phases. Additionally, we identified XRD peaks regarding Al-

 $CrFe_2$ and $AlFeCo_2$ phases that were formed due to the trace elements. This kind of trend and the effect of Co, Cr on Al-alloys was identified that these elements can effectively convert the β -(Al₅FeS) phase into α -Al₁₅(Fe, Co, Ni)₃Si₂ and α -Al(Fe, Cr)



Fig. 3. XRD patterns of extruded Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X [X = (a) : None, (b) : Co, (c) : Cr] bars

Si phases respectively [13,14]. The XRD peaks belonging to Cr, Co added alloys slightly shifts towards lower angles and suggests that the lattice parameter was increased with addition of Co, Cr in eutectic Al-Si alloy.

Fig. 4 shows the Rockwell hardness values for the extruded alloys. The Rockwell hardness of Co, Cr added extruded alloys was significantly improved by 20% compared to the bare sample. The improvement of hardness values was attributed to effect of Co, Cr addition on the microstructure of extruded alloys. Based on the results of the above analysis (Fig. (1, 2)), the size of Si and the volume fraction of β -phase was decreases which was helpful in enhancing the hardness value.



Fig. 4. Rockwell hardness values of extruded Al-12.6Si-3Cu-0.6 Mg-0.5Fe-0.5X [X = None, Co, and Cr] alloys

Fig. 5 represents Young's modulus and the tensile strength values for the whole Al-Si extruded alloys. Engineering stress was analyzed to identify the influence of Co, Cr on mechanical property of extruded alloy. The Co and Cr containing extruded alloys shows high Young's modulus and tensile strength values about 5-10% compared to the bare sample. Among all extruded



Fig. 5. Engineering stress-strain curve of Al-12.6Si-3Cu-0.6Mg-0.5 Fe-0.5X (X = None, Co, Cr) extruded alloys

alloys, Co doped alloy exhibits higher Young's modulus and tensile strength of about 170 MPa and 230 MPa respectively. Kaya et al. [11] also observed high tensile value in Co doped Al-Si alloy while compared to Sb, Bi and Ni doped alloy. It was shown that some composites like potassium titanate can degrade tensile properties [20]. But, in deed, the Co, Cr doping moderately improved the tensile strength values and the results suggests that small amount of trace elements capable of enhancing the tensile strength of Al-Si alloy.

Fig. 6 shows the scanning electron microscope (SEM) images and EDS analysis of fracture surface of Co, Cr added tensile strength specimens. In both microstructure samples, dimples and ridges were observed and the dimples formation was an indication of ductility fracture which was observed through hot extrusion process. To interpret the effect of trace element on the microstructure and their distribution in Al-Si matrix, we performed EDS analysis on Co, Cr containing extruded tensile fracture specimens. From Fig. 6(a, b), it was clear that all the elements which were included in the alloy were present in the microstructure and most of the ridges were Al-phase, primary-Si was observed as granular shape having micrometers in range. The Co, Cr elements were randomly distributed in the matrix and forms intermetallic phases having granular (small size) and rod like structure. The existence of Co, Cr phases was also identified through XRD peaks. The enhancement of mechanical properties through trace element substitution was prescribed to the existence of Co, Cr intermetallic phases in the extruded alloys.

Fig. 7 shows the coefficient of thermal expansion (CTE) of the Al-Si extruded material with and without trace elements. The impact of trace elements was predominately shown on CTE property of extruded alloys. The coefficient of thermal expansion decreases by 42.4% and 16.05% for Co and Cr doped Al-Si alloys compared with bare sample. The small dimensional change of Cr containing alloy was also observed by Wu et al [20] by dispersing 30 Vol.% potassium titanate whiskers in Al-12Si alloy. The obtained results were improved than Ni and Mn containing Al-Si alloys [16] and the vast data produced by Hidnert et al. [21] respectively. Experimentally, it was proved that CTE for Al-Si alloy can be reduced by doping element having lower CTE than parent alloy and it also depends upon the formation of different kinds of phases in the matrix [19]. In general, the coefficient of thermal expansion of the trace additive elements Co (13.0 μ m \cdot m⁻¹ \cdot K⁻¹) and Cr (4.9 $\mu m \cdot m^{-1} \cdot K^{-1}$) was lower than aluminum (23.1 $\mu m \cdot m^{-1} \cdot K^{-1}$). Taking elemental CTE values into consideration, Cr doped alloy had to exhibit lower CTE than Co doped sample, indeed Co shows considerably lower value than Cr doped alloy. Chen et al [22] had extensively studied the CTE of intermetallic phases in Al-Si matrix and confirms that various intermetallic phases possess different CTE values. Considering this, the significant effect of Co than Cr on CTE was presumed to the formation of Co containing intermetallic phases having low CTE than other phases that results in exhibiting lower CTE value compared to other extruded alloys.



Fig. 6. Scanning electron micrograph and EDS-mapping was observed on fracture surface of extruded Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X [X = (a) : Co, (b) : Cr] alloys



Fig. 7. The coefficient of thermal expansions of the extruded Al-12.6Si-3Cu-0.6Mg-0.5Fe-0.5X [X = (a) : None, (b) : Co, (c) : Cr] alloys

4. Conclusion

In this study, eutectic Al-Si casted alloy containing trace elements were hot extruded to examine the changes occurs in microstructure and physical properties. The extrusion materials were prepared based on Al-12.6Si-3Cu-0.6Mg-0.5Fe composition and additionally 0.5 wt.% of different trace elements (Co, Cr) were added. Microstructure observation on the alloys showed that β -(Al₅FeSi) intermetallic compound and Si particle were modified and provided better properties to the Co, Cr added alloys. The coefficient of linear thermal expansion was intensively decreased with addition of Co (0.5 wt.%) to Al-Si alloy. Co and Cr-doped Al-Si extruded alloys have increased hardness and tensile strength compared to bare samples. Based on the SEM-EDS results, we confirmed that the trace elements form new intermetallic compounds appeared as small granules. From XRD analysis, AlCrFe₂ and AlFeCo₂ phases were also analyzed for Co and Cr added extruded alloys. As a result, the improvement of the β -(Al₅FeSi) phase and the formation of the intermetallic compound were contributed to the improvement of the properties in the extruded alloy.

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