	パチャラポン　タンタウィルーン
氏　　　　名	Phacharaphon Tunthawiroon
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）材料システム工学専攻
学位論文題目	Effect of Si Addition on Properties of Co–Cr–Mo Alloys Used as Aluminum Die-casting Dies
論文審査委員	主査　東北大学教授　千葉　晶彦　東北大学教授　加藤　秀実 東北大学教授　成島　尚之

論文内容要約

Die casting is a cost effective conventional techniques for producing Al part with high dimension accuracy, good surface finish and also available for complex near net shape. The die performance and service life are usually constrained by several parameters, such as erosion, corrosion and thermal fatigue. For Al die casting, the conventional hot work tool steels, AISI grade steel H11 and H13, have been commonly used. Although, they are high Cr contents, low corrosion resistance to molten Al, low fatigue resistance and high oxidation rate were reported. Recently, Co-based alloys become the alternative materials for replacing current hot work tool steels. This is attributed to the high corrosion and fatigue cracking resistant properties. In addition, oxidation treatment had been suggested to be an effective way to improve the corrosion resistance of Co-based alloys to molten Al. However, the formation of nonhomogeneous oxide was considered to induce the local corrosion of alloy. Therefore, this research intend to develop properties of Co–Cr–Mo alloys for using as an Al die casting die by optimizing the alloying Si. To investigate the effects of Si in Co–Cr–Mo alloys, the materials used for the present research are composed of 28-29 wt% Cr, 6wt% Mo and Si of 0.1, 0.5 and 1.0 wt% with the rest of the alloys dominantly containing Co. The corresponding alloys are named as Co–Cr–Mo–0.1Si, Co–Cr–Mo–0.5Si and Co–Cr–Mo–1.0Si, respectively.

Chapter 2. Effects of Si addition on microstructures and mechanical properties of Co–Cr–Mo alloys

Prior to oxidation and corrosion test, three alloys were heat treatment at 800 °C for various durations and investigated microstructures and mechanical properties. Fortunately, microstructure of cast and hot-deformed alloys with different Si contents displayed the similar structure, mainly consisting of γ fcc structure and no precipitation phase. During the aging treatment at 800 °C, phase transformation (from γ fcc structure to ε hcp structure) also exhibited the same nature. Strength of all alloys at room temperature was strongly influenced by an increase in the ε hcp fraction. However, the presence of precipitates, σ and μ phase, was found to degrade the ductility of alloys. Following this observation, it can be indicated that the addition of Si up to 1.0 wt% does not have any harmful effects on the microstructures and mechanical properties of the Co–Cr–Mo alloys.

Chapter 3. Oxidation behaviour of Co–Cr–Mo alloys with different amounts of Si contents

To characterize the effects of Si addition on oxidation and corrosion properties, iso-thermal oxidation for various temperature (700–1000 °C) and static immersion test at 700 °C were performed. In an investigation of oxidation behaviour of Co–Cr–Mo–(0.1, 0.5 and 1.0)Si alloys, it was found that Si promoted the selective oxidation of Cr_2O_3. The beneficial effects of selective oxidation yielded the formation of a single, homogeneous, smooth and compact of external Cr_2O_3 films with low defects. In addition, formation of SiO_2 distinctly observed at the outmost oxide-matrix interface reduced the inward and outward diffusion of O and Cr, resulting in the slower oxidation rates compared with the lower Si containing alloys. Furthermore, the presence of SiO_2 improved the oxide scale adhesion to Co–Cr–Mo alloy matrix by suppressing and eliminating voids and cavities. In the sample with a low Si contents, oxidation proceeded much faster coexisting with duplex oxides of CoO and Cr_2O_3, and the oxide layer gradually lost contact with the alloy matrix because of the inadequate amount of SiO_2 barrier which could inhibit the diffusion of both Cr and O, leading to failure of the oxide layer through spalling. The relationship between oxide thickness and oxidation time followed the parabolic rate law. The increase in Si could reduce the parabolic rate constant, especially at high temperature greater than 700 °C (Fig. 1a). The calculated activation energies for oxidation of Co–Cr–Mo–0.1Si, Co–Cr–Mo–0.5Si and Co–Cr–Mo–1.0Si indicated the different oxidation kinetic rates in low and high temperature (Fig. 1b). It is because of the role of Si that obviously appears at the high temperature oxidation. At low temperature (700 °C), activation energies were almost the same in all alloys (245-250 kJ/mol). However, at high temperature, activation energies increased with increasing of Si contents and the values for alloys with 0.1, 0.5 and 1.0Si were 56.5, 84.1 and 99.6 kJ/mol, respectively. The activation energies at low temperature obtained in three alloys are similar to those of self-diffusion of Cr in Cr_2O_3 and Co matrix. Therefore, the growth of oxide is controlled by the diffusion of Cr. In contrast, oxide film becomes thicker and forms rapidly at high temperature, activation energies are low and similar to those of diffusion of O in oxide film indicating that oxidation rate is limited by the absorption rate of oxygen not by the diffusion of Cr ion though the oxide film. In this case, the rate-limiting control is dominant the oxidation process.

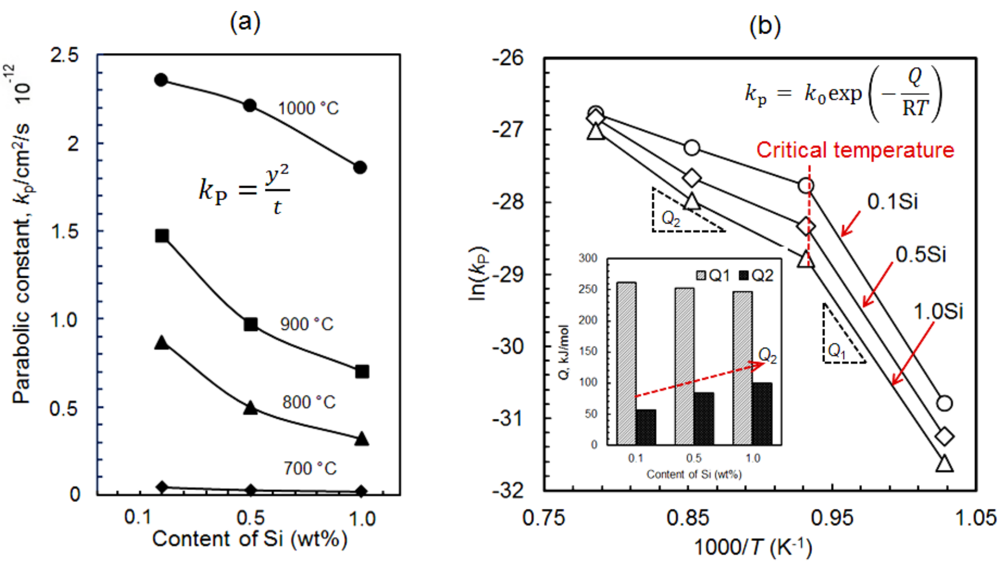

Fig. 1. (a) Parabolic rate constant (k_p) of Co–Cr–Mo alloys at 700 – 1000 °C with various Si contents and (b) activation energies for oxidation of Co–Cr–Mo–0.1Si, Co–Cr–Mo–0.5Si and Co–Cr–Mo–1.0Si.

Chapter 4. Effects of Si addition and oxidation treatment on corrosion resistance to molten Al

In the static immersion test of the oxidised Co–Cr–Mo–0.1Si, Co–Cr–Mo–0.5Si and Co–Cr–Mo–1.0Si alloys at 700 °C for 24 h, the corrosion resistance properties were in accordance with the oxide film morphologies. The Cr_2O_3-dominant film was more effective in enhancing the corrosion resistance than the duplex film of CoO and Cr_2O_3 films. In addition, local defects such as the cracks acted as initiation sites of failure in oxide film were reduced by the presence of Si. The influences of Si added in Co–Cr–Mo alloys are also considered to be a potentially second barrier to prohibit the growth of corrosion by molten Al by the formation of the internal oxidation of SiO_2. Ascribed to its higher stability, SiO_2 particles beneath the oxide film retarded the reaction between Al and matrix even after the failure of oxide film. According to the thermodynamic parameters of molten Al and oxide compounds at 700 °C, the Gibbs free energies for reaction between molten Al and three oxide compounds, CoO, Cr_2O_3 and SiO_2 were calculated to be −1094.33, −510.019 and −341.184 kJ/mol. Reaction between molten Al and CoO was found to have the lowest free energy among all oxide implying that CoO would be destroyed by molten Al prior to Cr_2O_3 and SiO_2. In other words, the driving force of the reaction between molten Al and CoO was higher than that of reaction between molten Al and Cr_2O_3 or SiO_2. Therefore, the formation of Cr_2O_3 protective film promoted by the Si addition could effectively inhibit the corrosion from molten Al resulting in low thickness loos comparing to the untreated samples (Fig. 2).

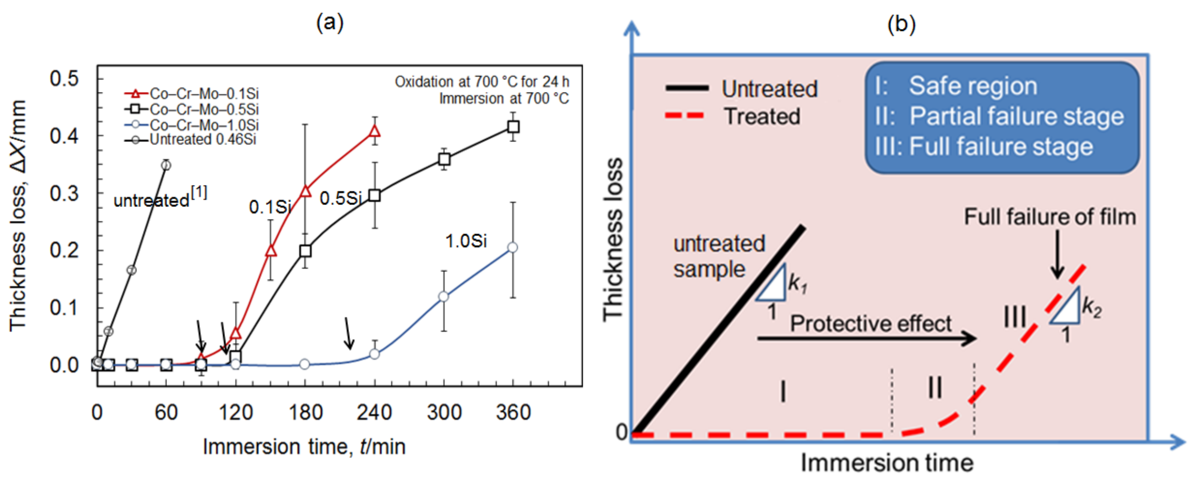

Fig. 2. (a) Reduction in thickness of oxidised Co–Cr–Mo–0.1Si, Co–Cr–Mo–0.5Si and Co–Cr–Mo–1.0Si alloys at 700 C for 24 h; for comparison, the thickness loss of untreated samples (Tang et al., Corros. Sci. 53, 2011, 2324–2326) was plotted together, and (b) thickness loss-immersion time curve of oxidised samples schematically divided into 3 stages following the thickness loss behaviour in Fig. 3a; stage I, effective protection of film; stage II, partial failure in film and stage III, full failure of film.

Chapter 5. High temperature fatigue test of Co–Cr–Mo alloys and effects of Si addition

Finally, in order to characterize the cyclic temperature and loading on die casting die, the high temperature fatigue tests (out of phase thermo-mechanical (OP-TMF) fatigue and iso-thermal fatigue (IF) techniques) were performed to simulate the fatigue behaviour. The out of phase thermo-mechanical (OP-TMF) fatigue technique in which the opposite phase-shift between mechanical and temperature cycles were closed to the realistic loading of die casting, was performed at the maximum and minimum temperature at 700 and 400 °C for a Co–Cr–Mo–0.5Si alloy. Under the OP-TMF cyclic loading, the cause of fatigue failure was involved the oxidation damage mode. Oxide easily formed and covered the fatigue specimen at high temperature. Subsequently, Brittle cracking of oxide occurred due to the decrease in temperature and the reversed loading from compression to tension. Some of oxide films spalled off from the specimen surface due to the mismatch in elastic properties and thermal expansion properties. Exposes of the fresh surface was attributed to the re-oxidation which results in the loss of thickness or mass. As a result, cracks were preferentially begun within these areas. However, IF tests were used to characterize the effects of Si additions on the high temperature fatigue behaviour. Fatigue life of alloys increased with increasing Si content, in spite of insignificantly different cyclic stress and plastic strain responses. Si is responsible for improving the oxidation resistance of the alloys and SiO_2 is probably the barrier for the further oxidation, especially, along the grain boundaries of the alloys, leading to the long fatigue life. Comparison of hysteresis loops (stress versus mechanical strain) of IF and OP-TMF tests obtained at the same applied mechanical strain revealed the significant different in maximum tensile stress portions. For IF tests, the tensile peak stress occurred at the temperature of 700 °C whereas the highest tensile stress of OP-TMF tests existed at the lower temperature at 400 °C. However, the compressive stress almost occurred same magnitude due to the same environmental temperature. For this reason, mean stress of OP-TMF tests was higher than that of IF conditions. In addition, it was found that mean stress of the IF test was located in the compressive region whereas the tensile mean stress was observed in OP-TMF test. The higher magnitude of tensile stress was a great influence on oxide film cracking and fatigue life. However, fatigue life can be improved by the addition of Si as investigated under the IF test.

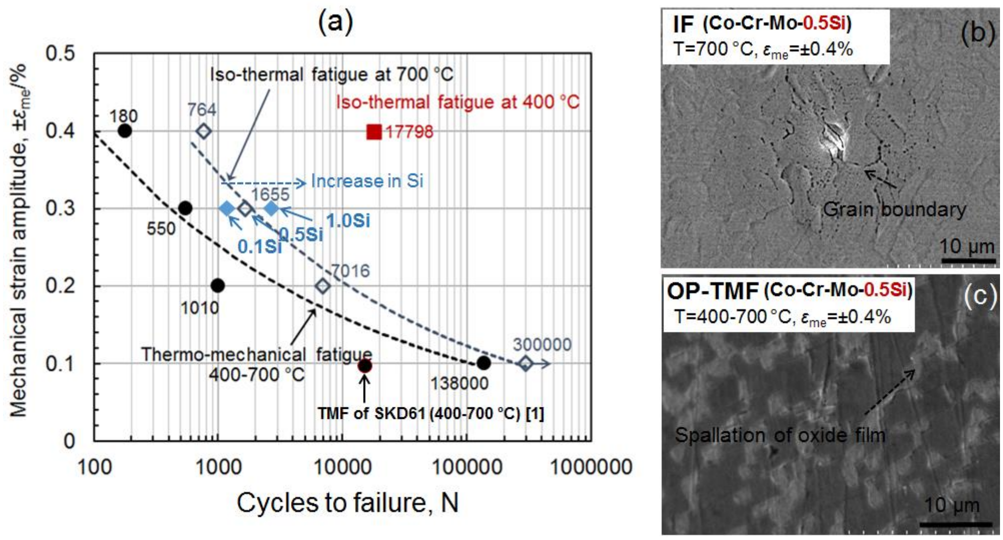

Fig. 3. (a) Strain amplitude–fatigue life curve of IF and OP-TMF test for various mechanical strain amplitudes, (b) grain boundaries oxidation observed on the surface of IF samples, and (c) breaking or spallation of oxide film morphologies on the surface of OP-TMF samples.

Prospects

Form effects of Si addition on the properties of Co–Cr–Mo alloys for using in Al die casting die, the obtained data indicates that the oxidation and corrosion properties were improved as well as high temperature fatigue resistance. Therefore, it is expected that these carried out results may be helpful for industry to design die materials. However, in actual die casting, occurrences of damage are much complex due to several simultaneous operating parameters, oxidation, corrosion and fatigue. For the laboratory test, those complex conditions were limited and testing results are still insufficient. To elucidate each damage mode individually and keep closing actual die-casting conditions, series of experiment are needed. Cyclic oxidation and immersion test should be considered. In addition, holding time effects on high temperature fatigue test should be carried to examine the high-temperature fatigue and creep–fatigue interactions.