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学位論文題名

Development of Advanced High Temperature Corrosion Resistant Alloy for Coating Applications

（耐高温腐食性先進コーティング材料の開発）

学位論文内容の要旨

In the present study, a further understanding of the behavior of boiler material exposed to the high temperature and corrosive atmosphere containing aggressive coal contaminants has been performed. Based on the results obtained, the development of corrosion resistant coating has been then taken into consideration for the purpose of improving the corrosion resistance of boiler materials. In order to accomplish the aforementioned effort, therefore, a particular focus of study was subsequently placed on the development of high corrosion resistant alloy for coating applications. Three clusters of alloys as CoNiCrAlY – Si, $CrSi_2$ – Ni and $CrSi_2$ – CoNiCrAlY with different alloy composition were fabricated by a spark plasma sintering technique. The resistance of these alloys against aggressive elements of coal contaminants at high temperature was studied at the same atmospheric conditions as aformentioned. The addition of varying content of Si to CoNiCrAlY, Ni to $CrSi_2$ and CoNiCrAlY to $CrSi_2$ alloys was performed as means to promote the formation of a protective oxide layer on the alloy surface and to identify the materials that offer great promise as a candidate coating material for applications in coal-fired boiler atmospheres. Here is a summary of each chapter.

In chapter 1, a brief overview of this study, research objectives and outline of the thesis were presented.

In chapter 2, the high temperature corrosion behavior of boiler material, STBA21 steel, at 650°*C* in the simulated fireside corrosion atmospheres of coal - fired boiler conditions: gas phase and liquid phase of Na_2SO_4 and NaCl was investigated. The results demonstrated that the alloy steel has experienced a severe corrosion attacks in both corrosive environments.The sulfides formation can be observed frequently at the outer/inner scale interface and on the steel surface. In particular, however, the STBA21 steel was corroded more severely in the liquid phase than that in the gas phase. This is due to the fact that the constituents of the salts and oxygen can detach the steel grain boundaries easily, leading to the steel grain spallations. As exposure time increases, the detached grains then tend to become easily corroded and the salt constituents and oxygen continue to migrate inwardly, resulting in acceleration in the consumed thickness of alloy. These results strongly suggest that the development of a protective coating on the alloy surface has become an indispensable component for improving their high temperature corrosion resistance.

In chapter 3, the resistance of CoNiCrAlY – Si alloys to the high temperature corrosion was studied at 650°*C* in the gas phase and liquid phase of Na_2SO_4 -NaCl. It was apparent that the CoNiCrAlY alloy suffers from internal corrosion in both corrosive atmospheres. The beneficial effect of Si addition on the corrosion resistance of CoNiCrAlY alloy depends on the alloy composition and atmospheric condition. Metallographic observation suggests that CoNiCrAlY – Si alloys form mainly Al_2O_3 – spinel, Al_2O_3 or Al_2O_3 – SiO_2 scale. In the given atmospheres, the CoNiCrAlY alloy with 30 mass% Si content shows an excellent corrosion resistance due to the formation of oxide scale consisting mainly of Al_2O_3 and SiO_2. Moreover, the formation of SiO_2 has also an outstanding advantage for suppression of the growth of external scale and formation of internal corrosion products.

In chapter 4, the high temperature corrosion of $CrSi_2$ – Ni alloys in the atmosphere containing Na_2SO_4 -NaCl at 650°*C* was discussed. The results revealed that the $CrSi_2$ – Ni alloys form a SiO_2 scale in these atmospheres, independing on the alloy constituent and demonstrate an excellent corrosion resistance at this temperature. Nevertheless, in the gas phase corrosion, a continuous SiO_2 formation on the $CrSi_2$ alloy with 0 mass% Ni content leads to Si-depletion and Cr-enrichment in the

alloy surface. The addition of Ni to the $CrSi_2$ alloy provides benefit in promoting the formation of a denser and continuous SiO_2 scale on the alloy surface. However, the thickness of a SiO_2 scale is likely to increase with the addition of Ni. Accordingly, the $CrSi_2$ alloy with 10 mass% Ni content seems to be the most effective materials for application in the corrosive atmospheres containing Na_2SO_4 and NaCl.

In chapter 5, the corrosion resistance of $CrSi_2$ – CoNiCrAlY alloys against aggresive elements of coal contaminants at 650^oC was investigated. The obtained results indicated that the addition of CoNiCrAlY to the $CrSi_2$ alloy contributes in the formation of a continuous and dense oxide scale on the alloy surface. As the result, the attack of aggressive elements of the salts doesn' t occur the underneath alloy. The establishment of an Al_2O_3 scale at the SiO_2/alloy interface has beneficial effect in retarding inward diffusion of oxygen and other aggressive elements, leading to suppression of the consumed thickness of alloy in longer exposure time. Considering the alloy fabrication, microstructure and corrosion resistance, the $CrSi_2$ alloy with 20 mass% CoNiCrAlY content offers the highest performance for high temperature corrosion applications.

Additionally, in chapter 6, to overcome an increasing demand on material for applications at higher temperatures (> 650^oC), the high temperature corrosion resistance of CoNiCrAlY – Si, $CrSi_2$ – Ni and $CrSi_2$ – CoNiCrAlY alloys was investigated at elevated temperatures of 800 and 1000^oC. Similarly to at 650^oC, the results show that the main advantage of the addition of Si to CoNiCrAlY, Ni to $CrSi_2$ and CoNiCrAlY to $CrSi_2$ alloy is determined by the alloy constituent and atmospheric condition. The most striking results provide additional evidence that the formation of a continuous and dense SiO_2 scale and oxide scale consisting of SiO_2 and Al_2O_3 offer a protective barrier against internal corrosion in both corrosive atmospheres.

In chapter 7, turning now to the results, some important points were pointed out. In the case of pure alumina-former as CoNiCrAlY alloy, first, the formation of transient alumina phases in the initial stage of corrosion may not act as an effective barrier for the aggressive elements of the salts and oxygen. In addition, Al-depletion beneath the oxide layer seems to accelerate the degradation of an Al_2O_3 scale. Accordingly, the constituents of the salts and oxygen may be more likely to diffuse and/or penetrate inwardly to form the internal corrosion. Second, cracks in the oxide scale in the gas phase corrosion at 1000^oC that may be formed due to the volume shrinkage based on Al_2O_3 phase transformation: transient to a stable phase, quicken the formation of internal attacks. Meanwhile, the addition of Si seems to enhance the formation of a protective Al_2O_3 scale and an oxide scale consisting mainly of Al_2O_3 and SiO_2. On the other hand, for a SiO_2 - forming material, a smaller ion radius and interatomic spacing of oxygen compared with sulfur and chlorine appear to give a potential beneficial effect for the formation and growth of a SiO_2 scale (n - type semiconductor) in the complex atmospheres containing oxidant and aggressive coal contaminants because they allow oxygen to inwardly - diffuse more preferentially. Hence, at the scale/substrate interface, an increase in the activities of the salts constituents can be decelerated. However, there is a considerable problem that at 800^oC, $CrSi_2$ alloy doesn' t form a continuous SiO_2 layer on the alloy surface. Consequently, the constituents of salts are able to attack the underneath alloy. Meanwhile, the addition of Ni to $CrSi_2$ and CoNiCrAlY to $CrSi_2$ reinforce the formation of a protective SiO_2 scale and an oxide scale consisting of SiO_2 and Al_2O_3, respectively on the alloy surface. This results in providing a protective barrier against severe internal corrosion in both corrosive atmospheres. Further promising result in SiO_2-formers showed that the oxide scale has a strong adhesion to the underneath alloys. Accordingly, it becomes favorable for high temperature applications under cyclic conditions.

In chapter 8, the general conclusion and future direction of this study were presented. From the results, it has been recognized that CoNiCrAlY-30 mass% Si, $CrSi_2$ -10 mass% Ni and $CrSi_2$ -20 mass% CoNiCrAlY seem to hold great promise as candidate coating material for application in corrosive atmospheres of coal-fired boiler conditions. In order to provide the practical applications, further study is needed to explore which material that has a good compatibility with the boiler materials.

学位論文審査の要旨

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学位論文題名

Development of Advanced High Temperature Corrosion Resistant Alloy for Coating Applications

（耐高温腐食性先進コーティング材料の開発）

現在、石炭火力発電用ボイラ伝熱管には *STBA* 系などの鋼材が広く使用されている。しかし、将来の高効率化、CO_2 排出削減に対する要求を満たすため、さらなる高温・高圧環境での使用が求められている。このような過酷環境では、腐食性ガスや溶融塩による高温腐食、さらには燃焼灰の衝突によるエロージョンなどが原因で材料劣化が一層激しくなることが容易に予想される。このような状況から、今後耐高温腐食性および耐摩耗性に優れた基材あるいはコーティング材料の開発が求められている。

本論文は、現在および将来を想定した石炭燃焼発電用ボイラ伝熱管に対する新しいコーティング材料の開発に関する研究成果を纏めたものであり、特にシリサイドをベースとしたシリカ皮膜形成型材料が優れた耐高温腐食特性を有することを明らかにしている。

本論文は全 8 章から構成されており、各章の概要は以下の通りである。

第 1 章は緒論であり、現在石炭火力発電用ボイラ伝熱管に使用されている材料、将来の使用環境の動向など工学的背景について述べ、それに基づいて本研究の必要性について述べている。

第 2 章では、現在使用されている鋼材 (*STBA*21) の $NaSO_4$ と $NaCl$ を含む環境での高温腐食試験 (650 ℃での高温ガス腐食試験および溶融塩埋没試験) を行い、形成される腐食層の構造を明らかにするとともに、硫化物や塩化物の生成機構について考察している。

第 3 章では、コーティング材料として広く使用されている *CoNiCrAlY* 合金をベースに Si を添加した合金を開発し、その高温腐食特性 (腐食条件は第 2 章と同じ) について調べた結果について述べている。30% の Si を添加した合金は Al_2O_3/SiO_2 複層皮膜を形成し、硫化物および塩化物の生成を完全に抑制できることを明らかにしている。

第 4 章では、上述した試験条件のもとで $CrSi_2-Ni$ 系合金の高温腐食試験を行って得た結果について述べている。高温ガス腐食および溶融塩埋没ともに、10% 以上の Ni 添加合金で SiO_2 皮膜が形成され、極めて優れた耐高温腐食特性を示すことを明らかにしている。また、Ni の高濃度添加は SiO_2 皮膜の成長を促進するが、緻密な SiO_2 皮膜の形成に寄与することを見出している。この SiO_2 皮膜形成によって硫化物および塩化物の生成を完全に抑制できることを明らかにしている。

第 5 章では、上述した試験条件のもとで $CrSi_2-CoNiCrAlY$ 系合金の高温腐食特性について調べた結果について述べている。$CrSi_2$ への 20%*CoNiCrAlY* の添加は連続的で緻密な酸化皮膜 (SiO_2/Al_2O_3) の形成に寄与し、硫黄および塩素の内方拡散を顕著に抑制する効果が高いことを明

らかにしている。また、複層酸化皮膜の形成機構についても考察を行っている。

第6章では、将来的なボイラ伝熱管の使用環境の過酷化を想定し、さらに高い温度域(800 ℃および1000 ℃)での$CoNiCrAlY-Si$系、$CrSi_2-Ni$系、および$CrSi_2-CoNiCrAlY$系合金の高温腐食挙動について検討した結果について述べている。SiO_2皮膜およびSiO_2/Al_2O_3皮膜形成材料はいずれも高い温度域でも優れた耐高温腐食性を示すことを見出している。

第7章では、$CoNiCrAlY-Si$系、$CrSi_2-Ni$系、および$CrSi_2-CoNiCrAlY$系合金をAl_2O_3皮膜形成材料、SiO_2/Al_2O_3皮膜形成材料、SiO_2皮膜形成材料に分類し、その耐高温腐食性について比較検討している。Al_2O_3皮膜形成材料の場合、腐食初期での遷移Al_2O_3の形成とそれに起因したクラック発生による溶融塩成分の内方浸入、さらに長時間腐食での酸化皮膜直下でのAl濃度枯渇層の形成などを原因として、酸化皮膜/合金界面および合金内での硫化物や塩化物の生成が起こりやすいことを明らかにしている。一方、SiO_2皮膜形成材料では、硫黄および塩素よりも酸素の拡散係数が大きいSiO_2皮膜が形成されるため、酸化皮膜/合金界面での硫黄および塩素のポテンシャル上昇が起こり難く硫化物や塩化物の生成を抑制できること、さらにSiO_2皮膜と合金下地との密着性にも優れていることを明らかにしている。また、SiO_2/Al_2O_3皮膜形成材料は比較的短時間では優れた耐高温腐食性を示すが、長時間腐食に伴うAl_2O_3皮膜厚さの増加および熱サイクル条件では、Al_2O_3/合金界面で剥離しやすくなる欠点を持っていることを指摘している。

第8章は本論文の総括であり、高効率石炭火力発電ボイラ伝熱管用コーティング材料として最適な高温腐食特性を示す合金組成は、$CoNiCrAlY-30mass\%Si$、$CrSi_2-10mass\%Ni$、$CrSi_2-20mass\%CoNiCrAlY$合金であることを提案している。

これを要するに、著者は各種組成のコーティング材料の高温腐食特性について検討を行い、その結果に基づいて将来の高効率石炭火力発電ボイラ伝熱管用コーティング材料の開発にきわめて重要な指針を与えた。よって、著者は北海道大学博士(工学)の学位を授与される資格あるものと認める。