

# Improvement of the Corrosion and Oxidation Resistance of Ni-based Alloys by Optimizing the Chromium Content

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## 論 文 内 容 要 旨

### 1. General context

Nuclear power plants (NPPs) are the main source of energy in France and considered as the principal source of electricity in Japan as well until march, 11<sup>th</sup> 2011. Thus, the majority of NPPs in Japan are suspended to improve their risk management. Nowadays, numerous thermal power plants are operating as substitutes for NPPs in Japan. Fossil fuel electric production contributes in many environmental concerns such as gas emissions. Moreover, fossil fuel such as oil, natural gas and coal are finites and their exploitation has considerable negative impact on the environment. Recently, in United Nations climate change summit September 2014 hold in New-York, It was strongly recommended that actions should be forthwith undertaken to reduce gas emission and to prevent the increase of global temperature. However, renewable sources of energy such as cellulosic biofuels, geothermal energy and solar still do not meet the present demand in respect of economic issues, hence those energy sources should be investigated and developed in the future. The world's growing demand for energy and the international commitments over its production and its use in environmentally safe manner make NPPs the favorite, in terms of efficiency and economic issues, alternative source of energy. Therefore, it is necessary to improve the degradation resistance of their structural materials.

Ni-based alloys are widely used in the structural compounds for both NPPs and thermal plants, operating in severe conditions. These materials are candidates also to use in future generation of power plants and to satisfy next challenges. Improving the degradation resistance of these materials is also required to extend the lifespan of structures. This fundamental study is focused on the influence of the chemical composition of Ni-based alloys on their corrosion behavior in simulated primary water of pressurized water reactors (PWRs) and in superheated steam for advanced ultra-supercritical power plant [1-3]. However, this work is not dedicated to a particular application. To design new structural material further investigations, taking into account the

synergetic degradation for instance, must be considered as well. To design new material, the metallurgical aspect must be considered also. Moreover, analytical approach, based on electrochemical measurements, is suggested to describe at the physical properties of protective oxides.

## **2. Objectives of the study**

Ni-based alloys are currently used in high temperature applications due to their good corrosion resistance [4,5]. This results from the ability of these materials to form a protective oxide layer which consists mainly of chromium oxide. In fact, the flux of species through the protective layer, such as inward and outward movement of oxygen anions and cation vacancies in sequence, is depressed as the amount of chromium in the alloys is increased to a critical threshold [15]. This is attributed to chromium enrichment in the Cr-oxide and the decrease of nickel-hydroxide or/and oxide portion. Indeed, Cr-oxides, called passive films, are assumed to act as barriers preventing the anodic dissolution, oxidation and thus protecting the structure. This may limit for instance the Ni release from Ni-based alloys in the primary circuit and consequently reduce its activity. However, in spite of the presence of those protective films, some detrimental corrosion degradations like Stress Corrosion Cracking (SCC) may occur in Ni-based alloys used in Light Water Reactors (LWRs) [6,7]. Some of the usually proposed mechanisms of SCC initiation rely on localized breakdown of the film: localized anodic dissolution and/or slip-dissolution model for instance [8,9,10]. Hence, it is necessary to understand and optimize the properties of the rate-limiting layer to prevent the degradations. To reach this purpose, the optimization of chromium content in the base metal is suggested. In this work attention was given to surface preparation to uncouple the possible contribution of surface cold-work. Then, exposition tests of Ni-xCr ( $14 \leq x \leq 30$ ) and Ni-xCr-8Fe ( $x= 14, 22$  and  $30$ ) model alloys were carried out in aqueous environments and superheated steam.

## **3. Results and discussions**

### *3.1. Aqueous corrosion*

The relationship between corrosion behavior of Ni-based alloys in simulated pressurized water reactor (PWR) environment (320°C, 14 MPa) and their chromium content is emphasized. H. Abe *et al.* [5] showed that increasing chromium content reduced the corrosion rate and SCC susceptibility of Ni-based alloys in primary water. For this reason, alloy 600 (16 wt.% Cr) has been replaced by alloy 690 (30 wt.% Cr) for vapor generator tubing in PWR system. Surface and cross-sectional observations using Scanning Electron Microscope (SEM) are performed to determine the morphology of resulting oxide scales. Further cross sectional characterization of the resulting oxides using Transmission Electron Microscope (TEM) are carried out as well. It is suggested that 20 % Cr is the critical amount of chromium required to form and maintain protective scale on cold-work free surface of Ni-Cr systems. Hence, it is assumed that oxide films formed on Ni-xCr alloys ( $x > 20$  wt.%) being unchanged in physico-chemical properties. Secondly, an analytical approach, based on electrochemical analysis, is suggested to investigate the passive film properties

at room temperature. The passive film acts as diffusion-migration barrier, controlling the flux of species such as Ni cations and oxygen anions. Thus, the corrosion resistance depends on the nature and the structure of the film. These film characteristics change with modifying the chemical composition of the substrate. Hence, understanding the effect of alloying elements on the passivation of Ni-based alloys is necessary. From the electrochemical behavior of Ni-Cr model alloys, the relationship between the Cr content and the properties of the passive films grown on these materials is clearly emphasized. Thus, an optimum threshold of chromium content (26 wt.%) in terms of aqueous corrosion resistance is determined. Increasing Cr content more than 26 wt.% has a detrimental effect on the properties of the passive film. This is due to the fact that the surface reactivity is increased. Iron is added to Ni-based alloys in order to reduce manufacturing costs and to improve their mechanical properties through solid-solution strengthening. P. Marcus *et al.* [11] considered iron as a passivity promoter. However, the selective dissolution of iron in Ni-Cr-Fe specimens led to the degradation of corrosion resistance. In fact, alloying Ni-Cr alloys with Fe may change the nature, the structure and the semiconductor features of the passive films. Thus, it is important to investigate the contribution of iron to the physical properties of the passive film.

### 3.2. Steam oxidation

Ni-based alloys are candidates for use in superheated steam generators in future generations of power plants, i.e., advanced ultra-supercritical power plants [1-3]. However, metal loss, internal oxidation, decarburization, and the decrease of heat transfer due to oxidation contribute to the degradation of the mechanical properties and performance of Ni-based alloys in water vapour [12]. Improvement of oxidation resistance of these materials is mandatory to satisfy future challenges. Although numerous investigations have been conducted to determine the oxidation behaviour of Ni-based alloys in dry atmospheres, relatively few oxidation studies of these materials in steam environments have been conducted to date. Steam can affect the solubility and/or diffusivity of oxygen in the alloy and thus its oxidation rate [12,13,14]; therefore, detailed knowledge regarding the oxidation behaviour of Ni-based alloys in steam environments is required for accurate prediction of their oxidation rates. This second part of the thesis focused on the effect of increasing the Cr content on the oxidation behaviour of model Ni-based alloys in superheated steam (700°C, atmospheric pressure). Attention was given to surface preparation to uncouple the effect of the alloying element and surface cold-work. Hence, reducing the hardened layer by mirror polishing is an accurate method to emphasize the influence of alloying elements on the oxidation rate. Electro-polishing results probably in prior establishment of Cr-oxide layer. This affects significantly the oxidation rate in the early stage of oxidation. However, SEM cross section views show similar oxide morphology, indicating that the hardened layer is efficiently reduced by mirror polishing, e.g. alumina powder down to 0.3  $\mu\text{m}$ . In agreement with the literature, oxidation rate of model alloys studied in the present investigation indicated that increasing the Cr content enhanced the oxidation resistance. This is attributed to the increase of volume fraction of nodular oxide and its coalescence into continuous barrier layer. The critical Cr content required to form a protective scale, consisting

mainly of chromia, in water vapour was reported by many authors [15]. However, the improvement of oxidation resistance by the optimization of Cr content has not been considered in previous studies. Optimal chromium content is investigated also in terms of oxidation resistance in superheated steam. Weight gain measurements and a meticulous characterisation of oxide scales elucidated the presence of an optimal Cr content (24 wt.%). Increasing Cr content to the optimal value allowed the growth and the maintenance of continuous Cr-enriched oxide. When the Cr content is larger than the optimal value a transition from internal to external diffusion and the appearance of Cr depleted zone beneath the rate limiting layer occurred simultaneously. Therefore, it is assumed that the Cr-content beneath this layer is not enough for its maintenance and consequently the growth of defective oxide takes place. Oxygen penetrates to the substrate through metallic nickel zone and the formation of Cr-oxide precipitates ensues. Oxidation rate in grain boundaries zone is depressed and thus it is suggested that grain fining can be an effective measure to improve the oxidation resistance in steam environment. In fact, the grain size becomes finer with increasing Cr content, synergetic effect between grain size and Cr content takes place in the oxidation process. This is linked to the fact that grain boundary provide fast diffusion path for chromium. Fe addition (8 wt.%) degrades Ni-base alloys properties in term of oxidation resistance. However, the presence of Fe does not alter the oxidation behavior of Ni-30Cr due to the establishment of Cr-oxide layer in the early stage which acts as barrier against the outward diffusion of Fe cation. Secondly, Fe diffuses to oxide/environment interface, tends to form Fe-oxide, the generation of cation vacancies occurred subsequently and thus condensation of these vacancies into pores is observed for ternary Ni-Cr-Fe materials. The comparison between the oxidation behavior of Ni-14Cr-8Fe and Alloy600-SA demonstrates that this fundamental study conducted on model alloys can be projected on some industrial materials. Hence, small deviation in the oxidation behavior between those tested materials is deduced.

#### **4. Conclusion**

This work contributes in the understanding of the effect of alloying elements on the high-temperature oxidation of Ni-based alloys by avoiding the synergetic effect with surface cold-work. This pioneer study emphasizes that the optimization of Cr content is more appropriate method for improving the corrosion resistance of nickel base-alloys and thus increasing the lifetime of structural compounds and enhance their integrity in high temperature environments. Hence, this study revealed the existence of optimal Cr content for better corrosion resistance. Increasing Cr content more than the optimal amount led to the degradation of the protective scale properties.

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# 論文審査結果の要旨

発電プラントの一層の高効率化と長期安定稼働を両立するためには、高温の水環境における合金の耐久性を一層向上させることが肝要である。本論文は、Ni 基合金の湿食ならびに水蒸気酸化に対する耐久性向上を図るための学術基盤確立に寄与するものであり、Ni-Cr 二元系および Ni-Cr-Fe 三元系合金の耐食性と耐酸化性に及ぼす Cr 含有量の影響を系統的な実験と分析により明らかにした基礎的研究である。

第1章は序論であり、エネルギー産業における Ni 基合金の現在ならびに将来の適用先ならびに耐食性、耐酸化性の重要性について論じ、本研究の背景と目的を述べている。

第2章では、加圧水型軽水炉の1次系環境ならびに過熱水蒸気環境に重点を置いて、高温の水環境での Ni 基合金の腐食ならびに酸化の機構と皮膜特性に関する従来の知見をレビューしている。両環境に共通して、Cr が高度に濃縮した酸化物による連続皮膜の形成が耐食性の要点であることを述べ、そのための Cr 含有量最適化の重要性を指摘している。

第3章では、本研究で用いた材料、試験・測定機器、試験・分析方法について詳しく述べている。本研究は、Ni 基合金の耐食性に及ぼす Cr 含有量の影響を系統的かつ詳細に明らかにすることを目的としているため、Cr 含有量を 14wt%~30wt%の範囲で 2%刻みに変えた実験合金を溶製して試験に供している。水溶液環境での耐食性評価に用いた種々の電気化学的測定・分析手法、すなわち、分極法、クロノアンペロメトリー、電極インピーダンス法、Mott-Schottky プロット法について、それらの原理から試験手順まで述べている。

第4章では、加圧水型軽水炉1次系模擬環境において Ni-Cr 二元系合金に形成される皮膜について Cr 含有量を変数とした高温高圧水中腐食試験により詳しく調べ、高い保護性が発揮されるためには 20wt%以上の Cr 含有量が必要であることを述べている。また、室温の硫酸中での各合金のアノード特性を電気化学的手法により調査した結果、Cr 含有量 26wt%付近に最適値が存在し、Cr 含有量をさらに高めると物質移動および反応の障壁としての皮膜の性能がむしろ低下する場合があることを明らかにした。これは、本研究により初めて明らかにされた重要な知見である。

第5章では、Ni 基合金の水蒸気酸化特性を明らかにしている。まず、細粒(2400番)エメリー紙を用いた湿式研磨によって合金のごく表層に導入される冷間加工が材料の水蒸気酸化特性に重大な影響を及ぼすことを見いだすとともに、材料本来の酸化速度を評価するためには電解研磨あるいはアルミナ懸濁液を用いた研磨によって仕上げた試料を酸化試験に用いるべきであることを指摘し、正確な酸化速度を得るための試験方法を確立している。次に、過熱水蒸気中での Ni 基合金の酸化速度は Cr 含有量 24wt%で最小となることを見いだしている。耐水蒸気酸化性の観点から Ni 基合金の Cr 含有量に最適値が存在することを初めて指摘したものであり、重要な成果である。また、8wt%の Fe 添加は耐酸化性を低下させることを指摘している。さらに、透過型電子顕微鏡を活用して各合金の酸化皮膜の構造および成分分布を詳細に調査して酸化律速過程をモデル化し、最適な Cr 含有量についての機構的解釈を与えている。

第6章は結論であり、本論文の成果を総括するとともに、今後取り組むべき研究の方向を整理して述べている。

以上、本論文は、発電プラント高温部材の長期信頼性確保の枢要である Ni 基合金の耐食性および耐酸化性の向上を目的として Cr 含有量の影響を詳細に調べ、最適値を明らかにしたものである。効率と安全性の向上が今後より高度に求められる発電設備において、最も過酷な部位に用いられる Ni 基合金に対して、その耐食性の一層の向上に寄与する極めて重要な知見を多数与えており、量子エネルギー工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。