

Development of High-Strength Anti-Corrosive Ni-Co-Cr-Mo-Cu Alloys

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論文内容要旨

Chapter 1

Developing materials with both high strength and high resistance to hydrofluoric acid (HF) is of great importance for industrial applications such as the fabrication of chlorofluorocarbon compounds, components in injection molding of polyfluoroalkoxy resin (PFA), and high-pressure containers used in the chemical industry. The commercially used alloys that meet this condition include Ni-16Cr-15Mo-6Fe (Ni-Cr-Mo, wt.%) alloys, recognized for their high corrosion resistance to HF solution. Various studies have indicated that Ni-Cr-Mo alloys can offer excellent corrosion resistance to HF solutions because a Mo-oxide-dominant passive film can form on the sample surface; the passive film is both compact and inert to any further attack by hydrofluoric. Therefore, Ni-Cr-Mo alloy is widely used in HF conditions despite their lower strength compared to Co-Cr-Mo alloys. Previous research has indicated that substituting Co for Ni by up to 30 wt.% can greatly increase the strength and hardness of the alloy without sacrificing its corrosion resistance to HF solutions. This is made possible by greatly reducing the stacking fault energy (SFE) of the alloy by alternating its plastic deformation mechanism because the cross slip is significantly inhibited in low-SFE materials, leading to higher work hardening of materials and therefore higher hardness or strength. The strength of Ni-30Co-16Cr-15Mo-6Fe (Ni-Co-Cr-Mo, wt.%) alloys can be further enhanced by cold working, although the corrosion resistance of the deformed Ni-Co-Cr-Mo is greatly reduced in comparison to that of Ni-Cr-Mo.

Hot forging at high temperatures, which results in grain refinement via dynamic recrystallization is an effective method of increasing the hardness of metallic materials. However, when substituting approximately 30 wt.% Co for Ni in a Ni-16Cr-15Mo-6Fe alloy, below approximately 1070 °C, the second phase, a π phase with tetragonal crystalline structure in the Ni-16Cr-15Mo alloy, was replaced by a hexagonal crystal μ phase below approximately 1220 °C in an equilibrium state. This implies an enhanced formation trend of the μ phase after Co addition, where both precipitates contain extremely high quantities of Mo (about 40 wt%). Hot forging

Ni-30Co-16Cr-15Mo-6Fe alloys below the μ phase precipitation point was detrimental to its HF acid solution corrosion resistance because of the Mo-rich μ phase, which lowered the Mo concentration of the alloy matrix, especially in areas near the precipitates. Severely corrosion occurs as a result of the selective dissolution of the Mo-depleted region around the precipitated μ -phase. This prevented the formation of a homogenous, compact Mo-rich passive film across the entire sample surface. The formation of μ phase make it impossible to further enhance the hardness and strength of Ni-Co-Cr-Mo alloys by cold forging and subsequent aging treatment (strain-aging). It is necessary to clarify the influence of Mo concentration on the corrosion behaviour in HF acid solution and then find another way to further improve the corrosion resistance. As a relatively noble element under reducing conditions, Cu has been proved to exhibit a strong resistance to HF and other acids. Cu addition should be a choice to further improve the corrosion resistance of Ni-Co-Cr-Mo alloys. Both the effect of Mo and Cu will be discussion in detail. The final objective of this research is to develop a novel screw material with both excellent mechanical properties and excellent corrosion resistance.

Chapter 2

The effect of Mo concentration on the corrosion resistance of both Ni-30Co-16Cr-6Fe-xMo and Ni-30Co-16Cr-6Fe-2Cu-xMo ($x = 7, 9, 11, 13, 15$, wt.%) alloys was investigated by immersion testing in 5.0 M HF solution at 100 °C. The corrosion behaviour and sample surface microstructure before and after the immersion test were analysed in detail based on EBSD and LSM. The concentration of alloy elements in the solution after immersion test were analysed by using ICP-OES method. The alloys with and without Cu addition were analysed in detail on the basis of XPS analysis, STEM, and STEM-EDS elemental distribution. The main conclusions derived from this detailed analysis are summarized in the following paragraphs.

In the Ni-30Co-16Cr-6Fe-xMo ($x = 7, 9, 11, 13, 15$) alloys, the weight loss follows a Boltzmann equation relative to the Mo concentration, allowing a critical Mo concentration to be obtained. With decreasing Mo concentration, the Ni-30Co-16Cr-6Fe-xMo alloys first lost the Mo protection on the grain boundaries, followed by the annealing twin boundaries, and finally on the grain matrix, which then led to a homogenous corrosion across the sample surface.

In the Cu-containing alloys, decreasing the Mo content did not give rise to an increased sample weight loss, but led to a preferential dissolution in both grain and annealing twin boundaries. No significant change in the grain matrix was observed with decreasing Mo concentration.

Results of passive film analysis indicated that a small addition of Cu yielded a tremendous improvement in the corrosion resistance of Ni-30Co-16Cr-xMo-6Fe alloys. The passivation of Ni-30Co-16Cr-6Fe-xMo alloys by a Mo-oxide-dominated passive film completely changed to passivation by a Cu-dominated one in Ni-30Co-16Cr-6Fe-xMo-2Cu alloys during immersion in HF solution. It is considered to be due to the segregation behaviour of Cu was much stronger compared to that of Mo. Mo become less

important owing to the formation of Cu-dominant passive film during dealloying process in hydrofluoric acid solution. It is possible to perform hot deformation at lower temperature by decreasing the Mo concentration in the alloy with Cu addition.

Chapter 3

The electrochemical behavior of both Ni-Co-Cr-Mo and Ni-Co-Cr-Mo-Cu alloys with Mo concentration varying from 7 wt.% to 15 wt.% has been investigated by polarization test and electrochemical impedance spectroscopy (EIS) measurement using a typical three-electrode system. The disks of both Cu-free and Cu-containing alloys as working electrode (WE) was fixed in a Teflon electrode holder with an O-ring leaving the area for measurement. The diameter of the sample surface exposed for measurement is 10 mm. A Pt foil as counter electrode (CE) and saturated silver chloride electrode (Ag/AgCl) as reference electrode (RE) was fixed in the cell. The counter electrode was covered with Teflon film and the reference electrode was using with a Teflon salt bridge. In the present study, an aqueous hydrofluoric (HF) acid solution with a concentration by approximately 0.5 mol/L was used to evaluate the corrosion resistance of both Cu-free and Cu-containing alloys. All the potentials mentioned in this research are reported vs. Ag/AgCl reference electrode. All experiment has been carried out at room temperature (25 ± 1 °C) controlled by an electro-thermostatic water bath. The main important results of this experimental work can be summarized as follows:

For Ni-Co-Cr-Mo alloys in hydrofluoric acid solution, the alloys show significantly different polarization behaviors. Alloys with Mo concentration below 9 wt.% exhibits active-passive behavior and alloys with higher Mo concentration exhibits spontaneous passive behavior. Mo plays a significant role in the formation of the passive film for Ni-Co-Cr-Mo alloys, thus the improvement of corrosion resistance. However, for alloys with 2 wt.% Cu additions, Mo become less important owing to the formation of Cu-dominant passive film during dealloying process in hydrofluoric acid solution.

The existence of Cu-rich layer is considered have a corrosion inhibition effect on anodic reaction owing the positive shifted corrosion potential after Cu addition. Ni-30Co-16Cr-7Mo-6Fe alloy exhibits the greatest corrosion inhibition efficiency after Cu addition in the present condition.

Chapter 4

The influence of Cu concentration on mechanical properties and corrosion behavior during immersion in HF solution of Ni-30Co-16Cr-15Mo-6Fe-xCu ($x = 0.5, 1, 2, 4, 6$, wt.%) alloys have been investigated in detail and the following conclusions have been obtained:

For mechanical properties, Cu concentration is observed have no significantly influence on the hardness of Ni-Co-Cr-Mo-Cu alloys after homogeneous treatment. Alloys with low Cu concentration exhibits similar ultimate tensile strengths (700 – 800 MPa) and elongations around 90%. However, both the UTS and elongation sharply decrease to 355 MPa and 11.3%, respectively, as the Cu concentration in Ni-Co-Cr-Mo-Cu alloy increased to 6 wt.%. In addition, no significantly influence of Cu concentration in yield strengths is observed.

For corrosion resistance, even the addition of 0.5 wt.% Cu greatly enhanced the corrosion resistance of Ni-Co-Cr-Mo alloy to HF solution. Cu demonstrates a positive effect in terms of enhancing the corrosion resistance of the alloy, which is characterized by the extremely low mass loss during immersion testing and a Cu-rich passive film on the sample surface. Such a small addition of Cu completely changed the passivation mechanism of Ni-Co-Cr-Mo alloys from Mo-dominated passivation into Cu-dominated passivation in HF solution. In addition, even no obvious improvement of corrosion resistance is observed for alloys with Cu concentration higher than 0.5 wt.%, the thickness of the passive film increased greatly from approximately 7.5 nm to 60 nm as the Cu concentration increase from 0.5 wt.% to 6 wt.%.

Chapter 5

Finally, the effects of prior plastic deformations and subsequent aging treatment on mechanical properties and corrosion resistance of the investigated alloy when exposed to various temperatures have been investigated. Discs with a thickness of approximately 1 mm were cut perpendicular to longitudinal axis using an electron discharge machine. These discs were then exposed to temperatures of 600, 700 and 800 °C for 1 h and subsequently quenched in water. To investigate the microstructures, the quenched discs were ground using grinding paper and then polished using an automatic lapping machine. The discs were subsequently etched in a solution mixed with 45% sulfuric acid (H₂SO₄), 43% nitric acid (HNO₃) and 12% phosphoric acid (H₃PO₄) at room temperature at a voltage of 9 V for 15 s. Microstructure observation were taken using field-emission scanning electron microscope (FESEM) and transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM-EDS).

The results show that the hardness and strength has been significantly improved by cold rolling and subsequent aging treatment via the Suzuki segregation, for both Cu-free and alloys with Cu addition.

The Co- and Mo-rich μ -phase is the main precipitate in all alloys after aging at temperature higher than 700 °C. And the formation of μ -phase was observed greatly decreased the Mo concentration in the matrix. The prior plastic deformations promoted the precipitation of the μ -phase via the Suzuki segregation, which occurred during aging after the plastic deformations. The solutes Mo, Co, and Cr, which segregated at the stacking fault ribbons, acted as nucleation sites for the μ -phase.

The corrosion resistance of Cu-free alloys has been greatly influenced by the cold working and aging temperature. Nevertheless, the corrosion resistance became not influenced by the cold working and aging even with the existence of μ -phase. Alloys with higher Cu concentration results in a lowered hardness after immersion.

Conclusions

In summary, both the hardness and strength of Cu-modified Ni-Co-Cr-Mo alloys have been improved significantly by cold deformation and subsequent aging treatment even with as small as 0.5 wt.% Cu addition. At the same time, the weight loss remains low even after severe cold deformation and aging treatment. Finally, we successfully developed a novel Ni-Co-Cr-Mo-Cu alloy with both excellent mechanical properties and excellent corrosion resistance.

論文審査結果の要旨

フッ素樹脂射出成形機スクリー用金属材料としては一般にNi-Cr-Mo 基合金が使用されている。当該合金はフッ化水素に対する耐食性に優れるが、耐摩耗性に劣り、異種/同種金属との摺動時に焼き付きが生じ易く、摩耗により発生する摩耗粉が製品に混入し、製品品質の低下の原因となっている。このため、耐食性を確保しながら同時に耐摩耗特性にも優れた合金の開発が急務の課題となっている。本研究は優れた強度と耐摩耗性及びフッ酸水溶液中で高耐食性を発現する合金開発に関するものであり、全6章から構成されている。

第1章は序論であり、本研究の背景や目的について示している。

第2章では、合金のMo濃度の変化が、5mol/L フッ酸水溶液中において、Ni-Co-Cr-Mo系とNi-Co-Cr-Mo-Cu系合金の耐食性に与える影響について調査している。Cuの添加有り、無しのNi-Co-Cr-Mo合金にMo添加量を変化させた試料を作製した。結果として、Moの濃度が低下すると、Moの不働態被膜の形成が不十分となり、フッ酸に対する耐食性が著しく劣化することを明らかにしている。しかしながら、この問題は微量のCu添加により改善されることを見出した。この耐食性改善機構は、Moの不働態被膜にかわり、デアロイング機構により形成される数十nm厚さの金属Cu被膜が100℃のフッ酸水溶液中で電気化学的に安定に存在することに起因することを示した。

第3章では、電気化学的手法であるアノード分極曲線測定やターフェル外挿法を用いた腐食速度の測定、開放電位の経時変化測定を行い、0.5mol/L フッ酸水溶液中Ni-Co-Cr-MoとNi-Co-Cr-Mo-Cu合金の不働態化挙動へのMoの影響を調査している。その結果、Ni-Co-Cr-Mo合金の耐食性がMoの濃度に大きく影響されるが、Cu添加により、アノード反応が抑えられ、腐食電位と腐食電流密度が大きく改善することを明確化した。

第4章では、5mol/L フッ酸水溶液における開発合金の耐食性へのCu濃度の影響について調査している。その結果、微量のCu添加により、耐食性が著しく改善することを示した。Cuの濃度が増加すると、Cu原子が粒界や粒内に偏析し、ナノサイズの析出物を形成するが、その粒成長が極めて遅いことを見出した。これより、開発合金はハイエントロピアロイ合金に分類されるべきものであり、ナノサイズ析出物の粒成長抑制は、当該合金に認められる拡散遅延 (Sluggish diffusion) 効果の発現によって説明されることを示した。

第5章では、開発合金における高強度化と、それに伴って発現する耐食性劣化の問題について詳細に調査し、その解決策を提示している。開発合金は冷間加工とその後の時効熱処理により著しく強化され、2700 MPaを超える引張強さを示し、100℃フッ酸水溶液中においてもこれまで開発されただの合金よりも優れた耐食性を示すことを明らかにした。

第6章は本論文の結論であり、本研究で得られた成果について総括している。

以上、本研究は耐摩耗特性に優れかつフッ酸水溶液中で高い耐食性を示す合金開発に成功し、さらに耐食性改善機構について電気化学的理論に基づいて説明した。これまでにない、優れた力学特性と耐フッ酸腐食性を有する合金開発に成功しており、材料システム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。