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論文名	Corrosion Behavior and Environment Induced Cracking of Nickel- Base Intermetallic Compounds (ニッケル基金属間化合物の腐食挙動と環境誘起割れ)
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論文要旨

The nickel base intermetallic compounds such as $\text{Ni}_3(\text{Si},\text{Ti})$ with and without additions (Mo, Cr, and Al) and $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ with and without additions (Nb, Co, Cr, Ta and W), showing a high melting temperature, have advantages of lightweight and high temperature oxidation resistance compared with conventional materials such as steels and nickel based alloys. Therefore, the intermetallic compounds are considered to be one of the candidates as materials of high temperature oxidation resistance. However, up to the present, these intermetallic compounds have not systematically been investigated for general corrosion and pitting corrosion in aqueous solutions. Furthermore, although they are found to be susceptible to hydrogen embrittlement in moist environment at or near room temperature, there is little study on the environment induced cracking (EIC) of the intermetallic compounds in aqueous solutions.

The main objectives of this thesis are (1) to elucidate the general corrosion of these intermetallic compounds in acidic solutions by using weight loss and electrochemical methods, (2) to clarify the pitting corrosion of these intermetallic compounds as functions of test temperature and chloride concentration in chloride solutions, and (3) to obtain the basic information of their EIC in chloride solutions by using constant load method and to propose an EIC mechanism.

In chapter 1, the background of this work and, objectives and content of this thesis were described.

In chapter 2, the structure and mechanical properties of nickel-based intermetallic compounds were investigated by using XRD (X-ray diffraction), SEM (scanning electron microscope) and tensile test. All of the observed diffraction lines of $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo intermetallic compounds were indexed as the $L1_2$ structure. In particular, for $\text{Ni}_3(\text{Si,Ti})$ with 2Mo, it was known that in the two phase mixture of $L1_2$ and fcc nickel solid solution (Ni_{ss}) formed by the addition of a small amount of Mo to $\text{Ni}_3(\text{Si,Ti})$, the lattice spacings of the Ni_{ss} phase was almost identical with those of the $L1_2$ phase. The presence of the Ni_{ss} phase was not confirmed by XRD as well as $\text{Ni}_3(\text{Si,Ti})$ with 2Cr and 4Al. Therefore, $\text{Ni}_3(\text{Si,Ti})$ is composed of single phase with $L1_2$ structure, while $\text{Ni}_3(\text{Si,Ti})$ with 2Mo, 2Cr and 4Al consisted of $L1_2$ and ($L1_2 + \text{Ni}_{ss}$) mixture region. On the other hand, the addition of Mo enhanced the tensile and yield strengths of $\text{Ni}_3(\text{Si,Ti})$ compared to $\text{Ni}_3(\text{Si,Ti})$ without Mo, and reduced the elongation of $\text{Ni}_3(\text{Si,Ti})$ compared to $\text{Ni}_3(\text{Si,Ti})$ without Mo. Furthermore, the tensile and yield strengths for both as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ with or without Mo were higher than those for both as-annealed $\text{Ni}_3(\text{Si,Ti})$ with or without Mo but the elongation of both as-cold rolled compounds was smaller than that of both as annealed compounds.

All of the observed diffraction lines of $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ intermetallic compounds were indexed as the $L1_2$ structure (Ni_3Al) and D0_{22} (Ni_3V). In present results, all compounds exhibited the two-phases composed of the cuboidal $L1_2$ precipitate and ($L1_2 + \text{D0}_{22}$) channel region. The mechanical properties of homogenized $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ dual phase intermetallic compound without additions (Nb, Co, Cr, Ta and W) were investigated in air at room temperature. The ultimate tensile stress, and yield stress of homogenized $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ was lower than those of both as-annealed or as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ with or without addition of Mo. Furthermore, the elongation of homogenized $\text{Ni}_3\text{Al}/\text{Ni}_3\text{V}$ dual phase intermetallic compounds was lower than that of as-homogenized $\text{Ni}_3(\text{Si,Ti})$ and both as-annealed $\text{Ni}_3(\text{Si,Ti})$ with and without addition of Mo, but showed the reverse elongation compared to both as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ with or without addition of Mo.

In chapter 3, the general corrosion of homogenized $\text{Ni}_3(\text{Si,Ti})$ intermetallic compounds consisting of a $L1_2$ -single phase and the Al-,Cr,-and Mo-added $\text{Ni}_3(\text{Si,Ti})$ consisting of $L1_2$ -single phase and a two phase mixture of $L1_2$ and fcc Ni_{ss} was examined in 0.5 kmol/m³ HCl, H₂SO₄ and

HNO₃ solutions at 303K. The Ni₃(Si,Ti) with 4Al had the lowest corrosion resistance in all acidic solutions, while Ni₃(Si,Ti) with 2Cr had the highest corrosion resistance in H₂SO₄ and HNO₃ solutions, although Ni₃(Si,Ti) with 2Cr was less corrosion-resistant than Ni₃(Si,Ti) in HCl solution. Furthermore, the preferential dissolution of L1₂-single-phase region took place in all acidic solutions. In addition, Ni₃(Si,Ti) with 4Al and Ni₃(Si,Ti) with 2Cr showed intergranular corrosion in HNO₃ solution. The corrosion behavior of the Ni₃Al/Ni₃V two-phase intermetallic compounds with and without minor elements such as Nb, Co and Cr consisting of L1₂ phase (Ni₃Al) and a mixed phase of L1₂ (Ni₃Al) and D0₂₂ (Ni₃V) has been investigated in 0.5 kmol/m³ HCl, H₂SO₄, and HNO₃ solutions. Those compounds showed the higher corrosion resistance in HCl solution and the lower corrosion resistance in HNO₃ solution than homogenized Ni₃(Si,Ti) and type 304 austenitic stainless steel. In all acidic solutions, preferential dissolution of (L1₂ + D0₂₂) phase was found in Ni₃Al/Ni₃V but without intergranular attack, whereas the intergranular attack took place on Ni₃(Si,Ti).

In chapter 4, the pitting corrosion of homogenized Ni₃(Si,Ti) and Ni₃(Si,Ti) with 2Mo was investigated as functions of test temperature and chloride concentration in NaCl solutions. The pitting potential obtained for both compounds decreased with increasing chloride concentration and test temperature. Furthermore, the pitting potential of Ni₃(Si,Ti) with 2Mo was higher than pure nickel, but lower than that Ni₃(Si,Ti). A critical chloride concentration (Cl_{crit}) of Ni₃(Si,Ti) with 2Mo was found to be higher than that of Ni₃(Si,Ti), where the specific pitting potential (E_{pit^{specific}}) was found to be lower than that of Ni₃(Si,Ti). The pit was formed and distributed on the two phase mixture region of L1₂ and fcc Ni_{ss}, but not in the single L1₂ phase region. Therefore, the pitting resistance of a homogenized Ni₃(Si,Ti) with 2Mo was lower than that of Ni₃(Si,Ti), but higher than that of pure nickel. On the other hand, the pitting potentials of homogenized Ni₃Al/Ni₃V two-phase intermetallic compounds with and without minor elements such as Nb, Co, Cr, Ta and W decreased with increasing test temperature and chloride concentration. The critical chloride concentration was found to be about 0.004 kmol/m³ for those compounds. The pitting potentials were found to be higher than those of Ni₃(Si,Ti) and Ni₃(Si,Ti) with 2Mo. The addition of minor elements such as Cr, W, Ta and Nb enhanced the pitting corrosion resistance of the Ni₃Al/Ni₃V two-phase intermetallic compounds.

In chapter 5, the EIC of as cold-rolled $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo intermetallic compounds has been investigated as functions of applied stress, Cl^- ion concentration, test temperature, and pH in NaCl solutions. From the applied stress dependence of the three parameters: (1). time to failure (t_f); (2). steady state elongation rate (l_{ss}); (3). transition time (t_{ss}); the relations between applied stress and three parameters were divided into three regions; the stress-dominated, EIC -dominated and corrosion-dominated regions, respectively. Whenever EIC occurred, the ratio of t_{ss}/t_f in the EIC-dominated region kept constant with a value of 0.98 independent of applied stress, test temperature, Cl^- ion concentration, and pH. The EIC susceptibility of both intermetallic compounds increased with increasing Cl^- ion concentration and test temperature; and increased with decreasing pH. Both compounds had the same transgranular appearance and the relationship between $\log t_f$ and $\log l_{ss}$ became the identical straight line irrespective of the above factors, which means that l_{ss} becomes a relevant parameter for predicting t_f . The EIC susceptibility of as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ with 2Mo was lower than that of as-cold rolled $\text{Ni}_3(\text{Si,Ti})$, which showed the beneficial effect of Mo. On the basis of the results obtained, it was presumed that those intermetallic compounds had a HE susceptibility. Furthermore, the EIC behavior of as-annealed $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo intermetallic compounds was similar to that of the EIC of as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ with 2Mo. However, the fracture appearances of both as-annealed $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo was predominantly intergranular. The EIC susceptibility increased with increasing Cl^- ion concentration and test temperature; and increased with decreasing pH. The EIC susceptibility of as-annealed $\text{Ni}_3(\text{Si,Ti})$ with 2Mo was lower than that of $\text{Ni}_3(\text{Si,Ti})$, which showed the beneficial effect of Mo. The EIC susceptibility of both as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo was higher than that of both as-annealed $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo. From the results obtained, it was also presumed that as-annealed $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo would have the HE susceptibility as well as as-cold rolled $\text{Ni}_3(\text{Si,Ti})$ and $\text{Ni}_3(\text{Si,Ti})$ with 2Mo.

Finally, the conclusions of this thesis were summarized in chapter 6.

審査結果の要旨

Ni 基金属間化合物は高温耐熱材料として有望であると考えられている。しかしながら、腐食環境下での **Ni** 基金属間化合物の腐食挙動および環境誘起割れはほとんどなされていないため、広範囲な応用・適用に関して疑問視されている。それゆえ、**Ni** 基金属間化合物の腐食現象を明らかにすることは、金属間化合物の利用・応用において新たな領域を拓くものである。本論文は、**Ni** 基金属間化合物(**Ni₃(Si,Ti)**, **Ni₃Al/Ni₃V** 等)の腐食挙動および環境誘起割れを腐食損失法、電気化学的方法、定荷重法などを用いて、腐食現象の基礎的な知見を得るとともにさらなる耐食性金属間化合物の開発に資することを目的として実施した研究をまとめたものであり、以下のような成果を得ている。

- (1) **Ni** 基金属間化合物の構造・組織を **XRD** と **SEM** で調べ、**Ni₃(Si,Ti)**は **L1₂**相の単層構造、添加元素 (**Mo,Cr and Al**)を含有する **Ni₃(Si,Ti)**は **L1₂**相と **Ni** 固溶体の2相構造、**Ni₃Al/Ni₃V** は添加元素の有無にかかわらず **L1₂**相と(**L1₂+D0₂₂**)相の2相構造であることを明らかにした。
- (2) 酸性溶液(塩酸、硫酸、硝酸)中における **Ni** 基金属間化合物の腐食特性を腐食損失法と電気化学的方法で調べた結果、**Ni₃(Si,Ti)**と添加元素 (**Mo,Cr and Al**)を含有する **Ni₃(Si,Ti)**は硝酸で腐食抵抗が最も小さくなり、**Ni₃Al/Ni₃V**等は塩酸で腐食抵抗が最小になることを明らかにした、さらに、添加元素(**Mo,Cr and Al**)を含有する **Ni₃(Si,Ti)**は **L1₂**相で、**Ni₃Al/Ni₃V**は(**L1₂+D0₂₂**)相で優先溶解することを見出した。
- (3) 塩化物溶液における **Ni** 基金属間化合物の孔食特性電位を温度および塩化物濃度の関数と調べた結果、**Ni₃(Si,Ti)**の孔食電位は **Mo**を含有する **Ni₃(Si,Ti)**のものより大きくなるが、孔食を起こさない臨界塩化物濃度は逆に **Ni₃(Si,Ti)**より **Mo**を含有する **Ni₃(Si,Ti)**の方が高くなることが分かった。**Ni₃Al/Ni₃V**の孔食電位は添加元素(**Cr,W,Ta and Nb**)により、孔食電位が大きくなることを見出した。
- (4) 塩化物溶液における冷間圧延および焼鈍された **Ni₃(Si,Ti)**と **Mo**を含有する **Ni₃(Si,Ti)**の環境誘起割れ特性を定荷重法により負荷応力、**pH**,温度および塩化物濃度の関数と調べた結果、腐食伸び曲線から得られる定常伸び速度が負荷応力、**pH**,温度および塩化物濃度に関係なく、破断寿命予測パラメーターになることを明らかにした。また、これら金属間化合物の環境誘起割れは水素脆性で起こると推測した。

以上の研究成果は、金属間化合物の金属学的アプローチと腐食科学を横断する学際領域において重要な基礎的な知見を与えるものである。また、金属間化合物の構造・組織と腐食現象の理解が、金属間化合物の新たな分野の開拓と開発への指針を提供するものであり、マテリアル工学分野の学術的・産業的な発展に貢献するところ大である。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。