

Article

Temperature-Dependent Sigma (σ) Phase Evolution and Transformation Kinetics in 24Cr–14Ni Stainless Steel Aged at 700–1000 °C

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Abstract

This study investigated the temperature-dependent σ phase transformation behavior of 24Cr–14Ni stainless steel subjected to aging at 700–1000 °C for 1–8 h. At 700 °C, the σ phase mainly retained the original dendritic morphology, whereas at 800 °C, the $\delta \rightarrow \sigma + \gamma_2$ eutectoid decomposition became most pronounced. The σ phase begins to decompose from the dendrite arms. XRD analysis confirmed that σ phase precipitation was most significant at 800 °C, while only weak σ peaks were detected at 900 and 1000 °C, indicating suppressed precipitation and partial σ phase dissolution at higher temperatures. EPMA/WDS analysis showed that σ phase preferentially formed in Cr-rich δ -ferrite regions, while Ni was mainly enriched in the γ -phase. At 1000 °C, the more homogeneous Ni distribution suggested that δ -ferrite dissolution and $\delta \rightarrow \gamma$ transformation became dominant. JMAK analysis revealed two distinct kinetic regimes: diffusion-controlled σ phase precipitation at 700–800 °C, with Avrami exponents of 0.4327–0.4606, and σ phase dissolution at 900–1000 °C, with higher Avrami exponents of 0.7932–0.8671. The apparent activation energies for precipitation and dissolution were 37.18 and 122.95 kJ·mol^{−1}, respectively. These findings indicate that σ phase transformation in 24Cr–14Ni stainless steel changes from precipitation-dominated behavior at 700–800 °C to dissolution-dominated behavior at 900–1000 °C.

Keywords: σ phase; precipitation; dissolution; JMAK kinetics; Arrhenius plot

1. Introduction

Fe–Cr–Ni austenitic stainless steels are widely used in demanding engineering environments because they offer a favorable combination of corrosion resistance, strength, and thermal stability [1–6]. However, their solidification behavior is strongly affected by alloy composition. In some grades, a certain amount of δ -ferrite can remain after solidification or subsequent thermal processing, which may alter the phase stability and make the microstructural evolution during high-temperature exposure more complex [7–9]. The 24Cr–14Ni stainless steel is widely applied in welding electrode core wires and industrial furnace components due to its high chromium and silicon contents [10,11]. This stainless steel is a high-Cr, Si-containing alloy. Because Si is a δ -ferrite stabilizer, it promotes the formation and retention of δ -ferrite in the microstructure [12–15]. With an increasing

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amount of δ -ferrite, more potential sites become available for σ phase precipitation, thereby increasing the likelihood of the $\delta \rightarrow \sigma$ phase transformation.

During aging at intermediate temperatures, retained δ -ferrite may lose its stability and undergo decomposition. This process often produces σ phase and secondary austenite, γ_2 , through a eutectoid-like transformation [16–19]. Since the reaction requires redistribution of alloying elements, its kinetics are strongly influenced by diffusion behavior, chemical partitioning, and local compositional variations within the microstructure [20–22].

The σ phase is regarded as a critical secondary phase in stainless steels because its formation can seriously impair material performance. In high-Cr stainless steels, σ phase tends to form preferentially at δ/γ interfaces and within retained δ -ferrite, where local enrichment of ferrite-stabilizing elements, particularly Cr and Si, facilitates nucleation and growth [23–27]. Its precipitation is controlled by the combined effects of alloy composition, aging temperature, and holding time. In general, σ phase forms during thermal exposure within the range of about 600–1000 °C, with more pronounced precipitation occurring when diffusion-assisted elemental redistribution becomes sufficiently active [24,25].

Aging-induced microstructural evolution can markedly change the mechanical and corrosion performance of stainless steels. Although σ phase precipitation may raise hardness, the brittle character of this phase usually reduces ductility and toughness [28–30]. At the same time, Cr consumption during σ phase formation can locally deplete the surrounding matrix, thereby lowering corrosion resistance, especially against pitting and intergranular corrosion [31–33]. For this reason, the kinetics of σ phase formation and its spatial distribution are important factors in understanding the degradation behavior of aged stainless steels [34].

Although σ phase precipitation in stainless steels has been widely reported [28–34], the temperature-dependent transition between σ phase precipitation and dissolution remains insufficiently understood, particularly in 24Cr–14Ni stainless steel. Most previous studies [28–34] have emphasized σ phase formation within a limited aging temperature range, while less attention has been given to how σ phase stability changes when the aging temperature is increased from the precipitation regime to the dissolution regime. Therefore, the novelty of this study lies in systematically clarifying the σ phase evolution over 700–1000 °C and linking the observed precipitation/dissolution behavior with JMAK kinetic parameters and apparent activation energy. This approach provides a more comprehensive understanding of the temperature-dependent transformation mechanism of σ phase in 24Cr–14Ni stainless steel.

This study investigates σ phase precipitation and the associated phase transformations in 24Cr–14Ni stainless steel, a material used for welding electrode cores, during aging at 700–1000 °C. This temperature range is relevant to the thermal exposure that may occur during the heating and cooling stages of welding. In the as-cast condition, the alloy contains retained δ -ferrite and dendritic elemental segregation, both of which can provide favorable regions for σ phase formation during subsequent thermal exposure. However, σ phase stability may change considerably with aging temperature. At intermediate temperatures, σ phase precipitation is expected to occur preferentially in δ -ferrite-containing regions, whereas at higher temperatures the σ phase may lose stability and gradually dissolve into the surrounding matrix. Therefore, σ phase evolution in 24Cr–14Ni stainless steel is hypothesized to proceed through two temperature-dependent regimes rather than a single continuous pathway: precipitation-dominated behavior at 700–800 °C and dissolution-dominated behavior at 900–1000 °C. To test this hypothesis, σ phase fraction, microstructural evolution, JMAK kinetics, and apparent activation energy were examined over the aging temperature range of 700–1000 °C. The results are expected to provide a

basis for predicting the post-welding microstructure and related properties of this welding electrode core material.

2. Experimental Procedures

2.1. Material Preparation and Isothermal Heat Treatment

The chemical composition of the 24Cr–14Ni stainless steel used as the welding electrode core material in this study is presented in Table 1. The material was examined in the as-cast condition to focus on the σ phase transformation associated with the original solidification microstructure. Although 24Cr–14Ni stainless steels are generally used after hot working, the as-cast structure contains dendritic segregation and retained δ -ferrite, both of which are closely related to σ phase formation during aging. Therefore, studying the as-cast material allows the influence of the initial solidification structure on σ phase precipitation and dissolution to be examined more directly.

Table 1. Chemical composition of the 24Cr–14Ni stainless steel used in this study.

Material		Element (wt.%)								
24Cr-14Ni	Cr	Ni	C	Si	Mn	P	S	Mo	Cu	Fe
Stainless Steel	24.59	14.34	0.03	0.75	1.70	0.01	0.01	0.15	0.22	Bal.

The specimens were sectioned from the outermost region of the as-cast ingot using a metallographic cutting machine. Coolant was applied during cutting to reduce local heating and cutting-induced deformation. This region was selected because it showed a clear dendritic structure and retained δ -ferrite, making it suitable for tracking the subsequent δ -ferrite to σ phase transformation. Since the initial microstructure may vary within the ingot, all specimens were taken from the same region to minimize position-related microstructural differences. This sampling strategy allowed the effects of aging temperature and time to be compared under a consistent initial microstructural condition. The specimens used for isothermal aging were prepared with dimensions of approximately 10 mm $\times$ 10 mm $\times$ 5 mm.

The isothermal aging treatments were carried out under an Ar atmosphere to reduce oxidation during heat treatment. The prepared specimens were aged at 700, 800, 900, and 1000 °C for 1, 2, 4, and 8 h, respectively, followed by rapid water quenching to room temperature to retain the high-temperature microstructural features. These heat-treatment conditions were designed to evaluate the temperature- and time-dependent transformation behavior of the σ phase. Figure 1 presents the experimental procedure used in this study.

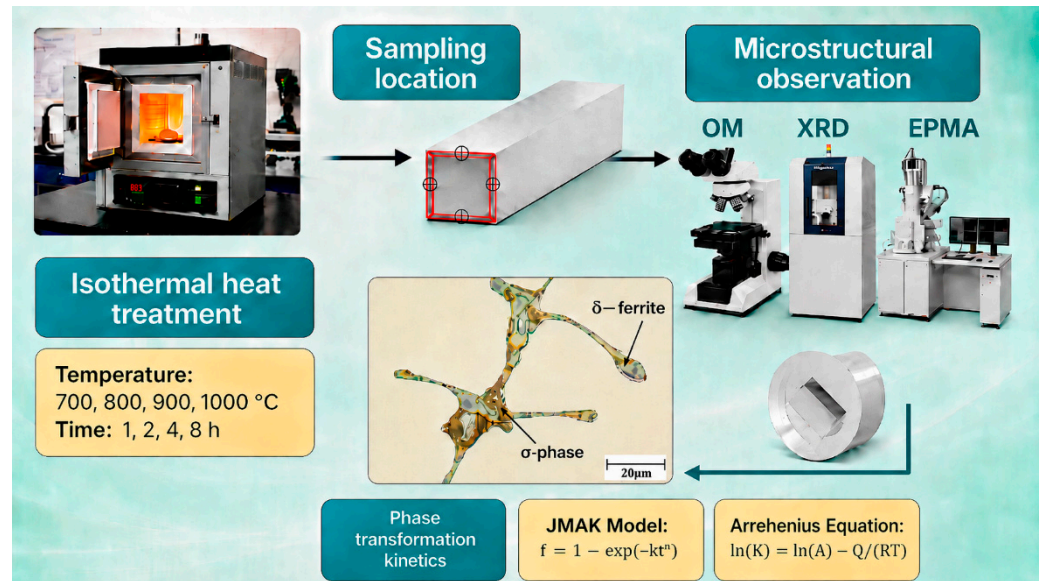


Figure 1. Schematic illustration of the experimental procedure used in this study. Note: The red rectangle marks the sampling location in the 24Cr–14Ni stainless steel billet.

2.2. Metallographic Observation and Quantitative Image Analysis

Following the isothermal heat treatments, the samples were prepared using standard metallographic techniques, which included grinding with silicon carbide (SiC) papers up to 2000 grit and subsequent polishing with a 1-micron diamond suspension. For metallographic examination, the polished specimens were etched with Groesbeck’s reagent prepared from 4 g KMnO_4 , 4 g NaOH , and 100 mL deionized water. The etched microstructures were observed using an optical microscope (OM, ZEISS Axioskop 2 MAT, Carl Zeiss, Göttingen, Germany). To determine the quantitative evolution of the σ phase, a digital image analysis method was implemented. For each heat-treated condition, a minimum of ten representative, non-overlapping microstructural fields were captured at appropriate magnifications. The volume fractions of the σ phase were statistically evaluated through threshold-based segmentation using specialized digital imaging software (Image-Pro plus 6.0, Media Cybernetics, Rockville, MD, USA), with the average values recorded as the absolute phase fractions for kinetic modeling.

2.3. Phase Constitution and Identification

The phase constitution of the 24Cr–14Ni stainless steel aged at 700, 800, 900, and 1000 °C was examined by X-ray diffraction (XRD, SIEMENS D5000, Siemens AG, Karlsruhe, Germany) using $\text{Cu K}\alpha$ radiation with a wavelength of 1.5409 Å. The diffraction patterns were collected over a 2θ range of 20–80° at a scanning rate of 4° min^{-1} . The XRD analysis was used to identify the phases formed after aging and to evaluate the temperature-dependent precipitation behavior of the σ phase.

Elemental mapping was performed using an electron probe micro-analyzer (EPMA, JXA-8900R, JEOL Ltd., Akishima, Tokyo, Japan) to examine the distribution of Cr and Ni in specimens aged at 800 and 1000 °C. Quantitative compositional analysis was further conducted using wavelength dispersive spectroscopy (WDS). The WDS results were used to support phase identification and to clarify the elemental partitioning among the σ , δ , and γ phases.

2.4. Kinetic Evaluation of σ Phase Precipitation

The σ phase fractions obtained after aging at 700–1000 °C were analyzed as a function of holding time to evaluate the transformation behavior of 24Cr–14Ni stainless steel. The

phase-fraction data at each aging temperature were fitted with time-dependent kinetic functions to describe the precipitation or reduction in the σ phase during aging. The fitting results were used to determine the rate-related parameters and to compare the transformation tendency under different thermal conditions.

The extracted rate constants were subsequently used to estimate the apparent activation energy of the σ phase transformation. The calculated kinetic parameters and activation energies were used to support the mechanistic discussion presented in the Sections 3.4 and 3.5.

3. Results and Discussion

3.1. Microstructural Evolution of σ Phase with Different Temperatures and Times

Figure 2 shows the microstructural evolution of 24Cr–14Ni stainless steel aged at 700, 800, 900, and 1000 °C for 1, 2, 4, and 8 h. At 700 °C, the σ phase mostly retained a well-developed dendritic morphology. This feature is closely related to the sampling position in this study, which was taken from the outer region of the 24Cr–14Ni stainless steel billet. As a result, the initial microstructure already contained a relatively coarse cast dendritic structure. During aging at 700 °C, the $\delta \rightarrow \sigma$ transformation gradually proceeded as the aging time increased from 1 to 8 h. Nevertheless, the overall morphology remained largely unchanged, and most of the transformed regions still followed the original interconnected dendritic network.

At 800 °C, the $\delta \rightarrow \sigma + \gamma_2$ eutectoid decomposition becomes more pronounced. This indicates that 800 °C is a favorable temperature for the precipitation of the σ phase in this alloy. With prolonged aging, the δ -ferrite-containing inter-dendritic regions are progressively transformed into σ phase. The σ phase is mainly formed along the original inter-dendritic network, and its morphology becomes increasingly fragmented with increasing aging time. Similar the $\delta \rightarrow \sigma + \gamma_2$ eutectoid decomposition has been reported in previous studies [35,36], where the precipitation of the σ phase in stainless steel is faster near 800 °C than at other heat treatment or hot working temperatures.

When the aging temperature was increased to 900 °C, the morphology of the σ phase changed noticeably. After aging for 1 h, the σ phase no longer showed a complete network structure, but instead appeared as an incomplete network consisting of ribbon-like features and a small amount of globular morphology. As the aging time was further extended, the dissolution of the σ phase into the γ matrix became more apparent, suggesting that the stability of the σ phase decreased at this temperature.

At 1000 °C, the network-like σ phase was hardly observed after aging for 1 h, and the remaining σ phase mainly exhibited a lacy morphology. When the aging time exceeded 2 h, the σ phase gradually changed into elongated and partially globular features, while its overall amount continued to decrease. This behavior is mainly because 1000 °C is close to the solution-treatment temperature range of stainless steels. Under this condition, the $\delta \rightarrow \gamma$ transformation becomes more dominant, which promotes the dissolution of σ phase into the γ matrix. Therefore, σ phase dissolution is the main reaction at 1000 °C, whereas the $\delta \rightarrow \sigma$ transformation becomes difficult and limited.

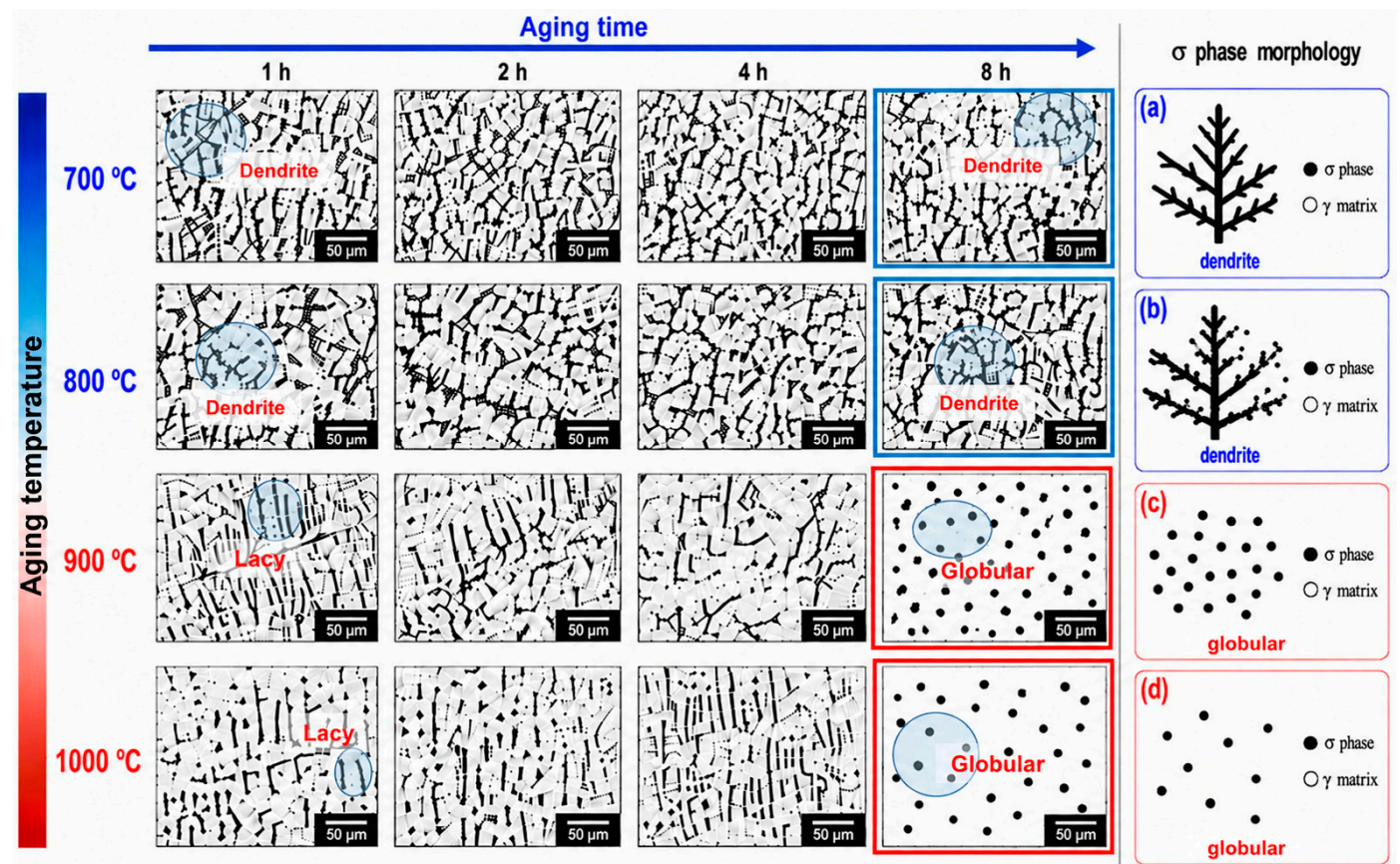


Figure 2. Morphological development of σ phase at different aging temperatures and times (a,b): dendritic morphology; (c,d): globular morphology.

3.2. Phase Precipitation via the XRD Analysis in 24Cr-14Ni Stainless Steels with Different Temperatures

Based on the metallographic observations presented in Section 3.1, the $\delta \rightarrow \sigma$ phase transformation can be observed over the investigated temperature range. However, σ phase precipitation is more pronounced at 700 and 800 °C, whereas at 900 and 1000 °C the σ phase tends to dissolve back into the γ -phase matrix. To further verify these microstructural observations, XRD analysis was carried out to identify the phase constituents of the specimens aged at 700, 800, 900, and 1000 °C, with particular emphasis on the transformation and precipitation behavior of the σ phase, as shown in Figure 3.

The XRD results show that the $\delta(110)$ diffraction peak is present at all aging temperatures. This is mainly because 24Cr-14Ni stainless steel is a Cr-Ni austenitic stainless steel, in which δ -ferrite and γ phase are the principal constituent phases. In addition, a $\gamma_2(111)$ diffraction peak appears near the $\delta(110)$ peak, confirming the occurrence of the eutectoid decomposition reaction $\delta \rightarrow \sigma + \gamma_2$ in the present alloy.

Regarding σ phase precipitation, the $\sigma(110)$ diffraction peak can be clearly identified at both 700 and 800 °C. Among all aging temperatures, the σ phase peak intensity is highest at 800 °C, indicating that the largest amount of σ phase precipitates at this temperature. The formation of σ phase can be attributed to two possible transformation routes: the direct $\delta \rightarrow \sigma$ transformation and the eutectoid-type $\delta \rightarrow \sigma + \gamma_2$ decomposition. In general, both transformation mechanisms may occur during aging treatment, and regardless of the dominant route, the final result is the precipitation of σ phase.

By contrast, at 900 and 1000 °C, only weak σ phase diffraction peaks are detected, suggesting that σ phase precipitation is suppressed in this temperature range. This result

indicates that the σ phase tends to dissolve into the γ -phase matrix at higher aging temperatures, leading to a lower precipitation rate and the smallest amount of σ phase. Moreover, the $\gamma(220)$ diffraction peak exhibits the highest intensity at 1000 °C, suggesting an increased γ -phase fraction at this temperature. This implies that the $\delta \rightarrow \gamma$ transformation becomes more favorable at higher temperatures. In stainless steels, when the $\delta \rightarrow \gamma$ transformation is more pronounced, the tendency for $\delta \rightarrow \sigma$ transformation is significantly reduced.

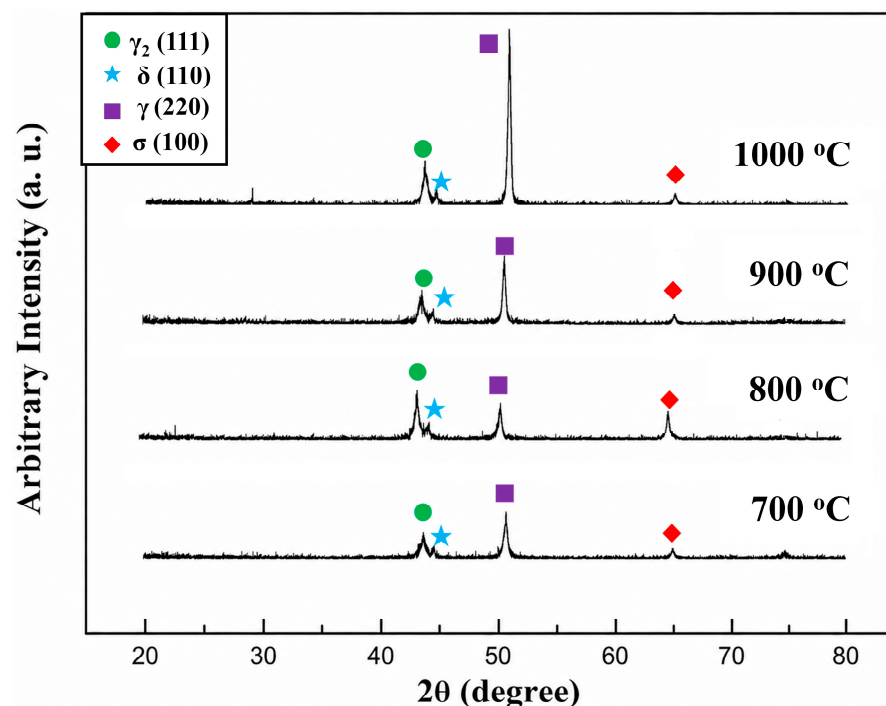


Figure 3. XRD analysis of constituent phases in 24Cr-14Ni stainless steels at different aging temperatures for 4 h.

3.3. Concentration Profiles and WDS Analysis of δ , σ , and γ Phases in 24Cr-14Ni Stainless Steel Aged at 800 and 1000 °C

EPMA elemental mapping and WDS quantitative analysis were performed on the specimens aged for 4 h at 800 and 1000 °C. The 4 h condition was selected as a representative intermediate aging time to compare the temperature-dependent phase constitution and elemental partitioning under a fixed aging duration. The purpose of this analysis was to support phase identification and to distinguish the elemental characteristics of the σ , δ , and γ phases, rather than to describe the complete time-dependent microstructural evolution at each aging temperature. To further compare the elemental diffusion and enrichment behavior of 24Cr-14Ni stainless steel aged at 800 °C and 1000 °C, EPMA elemental mapping of Cr and Ni was performed for the δ , σ , and γ phases, as shown in Figure 4. Figure 4a,d present the secondary electron images of the specimens aged at 800 °C and 1000 °C, respectively. As shown in Figure 4a, σ phase precipitates within the network-like δ -ferrite at 800 °C, indicating that the $\delta \rightarrow \sigma$ transformation occurs during aging. In contrast, no obvious σ phase precipitation is observed at 1000 °C, and the microstructure mainly consists of δ -ferrite and γ phase. This suggests that the phase transformation at this temperature is dominated by the $\delta \rightarrow \gamma$ transformation.

For the specimen aged at 800 °C for 4 h, the σ phase region exhibits pronounced Cr enrichment. This result suggests that σ phase preferentially precipitates in retained δ -ferrite regions where Cr is locally enriched. Once σ phase forms, its Cr content becomes higher than that of the surrounding δ -ferrite, as supported by the Cr mapping in Figure

4b. By contrast, after aging at 1000 °C for 4 h, the Cr distribution between δ -ferrite and γ phase becomes more homogeneous. This behavior indicates that σ phase precipitation is largely suppressed at this temperature, while partial dissolution of δ -ferrite and the $\delta \rightarrow \gamma$ transformation become more dominant. Accordingly, the microstructural evolution at 1000 °C is mainly governed by the $\delta \rightarrow \gamma$ transformation rather than by continued σ phase precipitation, as shown in Figure 4e.

The Ni mapping at 800 °C, shown in Figure 4c, reveals that Ni is not enriched in either δ -ferrite or σ phase. This is because both δ and σ phases are Cr-rich and Ni-depleted phases. Instead, Ni enrichment is mainly observed around the δ and σ phases, indicating that these surrounding regions correspond to the γ phase. This result is consistent with the fact that austenite is the primary Ni-rich and relatively Cr-depleted phase in austenitic stainless steels. A similar trend is observed in the Ni mapping at 1000 °C. However, the Ni distribution in the γ phase becomes more homogeneous than that at 800 °C, which is associated with the higher aging temperature approaching the solution-treatment range of stainless steel. Under this condition, δ -ferrite becomes less stable and tends to dissolve into the γ matrix, while σ phase precipitation is effectively suppressed, as shown in Figure 4f. Therefore, the EPMA mapping results clearly indicate that aging at 800 °C promotes Cr enrichment and σ phase precipitation within δ -ferrite, whereas aging at 1000 °C leads to a more homogeneous Cr and Ni distribution and favors the $\delta \rightarrow \gamma$ transformation rather than σ phase formation.

Table 2 summarizes the WDS quantitative analyses of points 1–5 marked in the SEI images of Figure 4a,d. The δ -ferrite phase is characterized by relatively high Cr and Si contents, as indicated by the measurements at points 1 and 4. In particular, the σ phase shows the highest Cr concentration among the examined phases, with a Cr content of approximately 40.59 wt.% at point 2. This result implies that σ precipitation occurs preferentially in the Cr-enriched regions of δ -ferrite during the $\delta \rightarrow \sigma$ transformation. By contrast, the γ phase, serving as the matrix phase of the 24Cr–14Ni austenitic stainless steel, contains the highest Ni content, as observed at points 3 and 5.

The difference between the specimens aged at 800 and 1000 °C provides useful evidence for the temperature-dependent change in transformation behavior. At 800 °C, σ phase is clearly present in the retained δ -ferrite/inter-dendritic regions, where a marked Cr enrichment is observed. This suggests that the δ -ferrite to σ phase transformation is favored at this temperature. After aging at 1000 °C, however, σ phase precipitation becomes much less apparent, and the Cr distribution between δ -ferrite and γ phase is more homogeneous. This indicates that the stability of σ phase is reduced at 1000 °C, while partial dissolution of δ -ferrite and the $\delta \rightarrow \gamma$ transformation become more prominent. These observations support the view that the dominant transformation changes from σ phase precipitation at 800 °C to σ phase suppression and δ/γ -related transformation at 1000 °C.

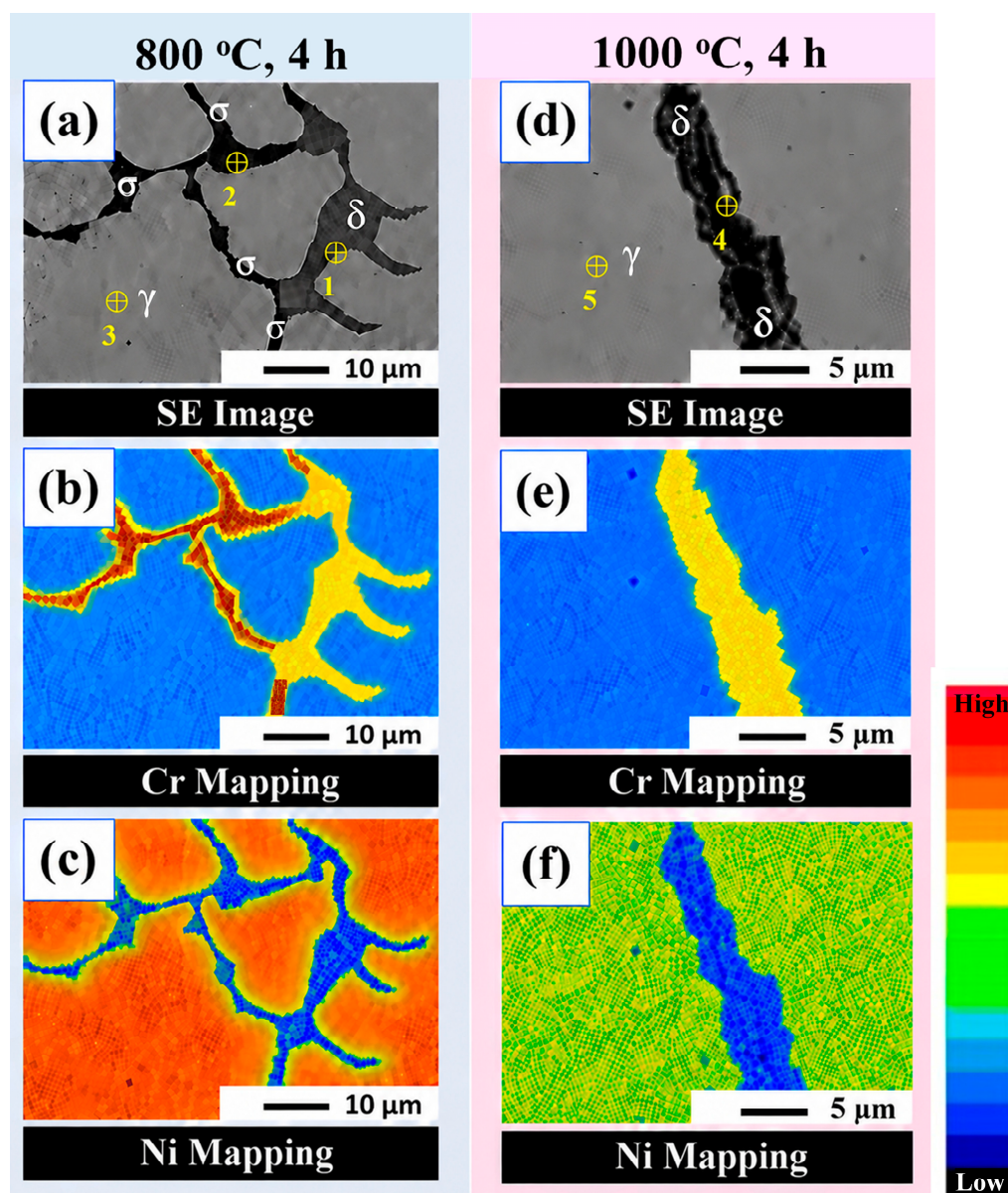


Figure 4. EPMA mapping and WDS analyses of δ , σ , and γ phases in 24Cr-14Ni stainless steels (a,d): SE image (b,e): Cr mapping, (c,f): Ni mapping at 800 °C (light blue rectangle) and 1000 °C (light purple rectangle), respectively, for 4 h. Note: δ : ferrite; σ : sigma phase; γ : austenite; $\oplus$: Elemental analysis point.

Table 2. WDS quantitative analysis of the δ , σ , and γ phases in 24Cr-14Ni stainless steel after aging at 800 and 1000 °C for 4 h.

Temperature (°C)	Point	Element (wt.%)	Cr	Ni	Si	Mo	Mn	C	Cu	Fe
		Phase								
800 °C	1	δ	34.70	5.12	0.56	0.36	1.34	0.06	0.01	57.85
	2	σ	40.59	5.09	0.30	0.42	1.24	0.06	0.01	52.29
	3	γ	19.86	14.21	0.38	0.10	1.61	0.05	0.26	63.53
1000 °C	4	δ	31.18	7.12	0.85	0.17	1.71	0.55	0.10	58.32
	5	γ	22.88	12.63	0.72	0.10	1.83	0.71	0.15	60.98

3.4. Isothermal Transformation Kinetics and JMAK Modeling of σ Phase

The isothermal transformation kinetics of the σ phase in the 24Cr-14Ni stainless steel were systematically quantified utilizing the classic Johnson–Mehl–Avrami–Kolmogorov (JMAK) phenomenological framework. Figure 5 delineates the instantaneous σ phase fraction (f) as a function of aging time across the investigated temperature spectrum (700–1000 °C), where two opposite thermodynamic tendencies are explicitly captured. At lower aging temperatures (700 and 800 °C), the volume fraction of the σ phase increases monotonically over time, signifying a conventional precipitation and growth process. In stark contrast, when the aging temperature transitions to higher regimes (900 and 1000 °C), the σ phase exhibits a progressive decay, revealing a high-temperature diffusion-controlled dissolution back into the austenite matrix.

To mathematically correlate these concurrent phenomena, the non-linear regression curves were successfully constructed and superimposed on the experimental data points (Figure 5). For the precipitation regime (700 and 800 °C), the growth kinetics were successfully tracked by the standardized JMAK equation, as illustrated by Equation (1) [37,38]:

$$f(t) = f_{\sigma,\max} \cdot [1 - \exp(-kt^n)] \quad (1)$$

while the high-temperature dissolution kinetics (900 and 1000 °C) were fitted via the exponential decay formulation, as indicated in Equation (2):

$$f(t) = f_{\sigma,0} \cdot \exp(kt^n) \quad (2)$$

where $f(t)$ denotes the volume fraction of the sigma phase at a given isothermal holding time t (s). The parameters $f_{\sigma,\max}$ and $f_{\sigma,0}$ represent the maximum equilibrium volume fraction and the initial volume fraction of the σ phase, respectively. The term k is the kinetic rate constant (s^{-n}) dependent on the transformation temperature, while n is the dimensionless Avrami exponent associated with the specific nucleation and growth mechanisms.

The reliability of the JMAK fitting is shown by the linear regression results in Figure 6. Here, X denotes the transformed fraction of the σ phase, calculated from the normalized σ phase fraction obtained by metallographic image analysis. For the linearized JMAK plot, y is defined as $\ln[-\ln(1 - X)]$, while x is defined as $\ln(t)$, where t is the aging time. With this definition, the slope of the fitted line gives the Avrami exponent n , and the intercept is related to the rate constant k . The linearized plots exhibit good fitting linearity, with coefficients of determination R^2 higher than 0.98. In the precipitation regime at 700–800 °C, the n values are 0.4327 and 0.4606, respectively, both close to 0.5. This suggests that σ phase precipitation is mainly controlled by diffusion-assisted growth, with nucleation sites being limited or rapidly consumed at the early stage of aging. After this stage, the growth of σ phase is mainly restricted by the diffusion of ferrite-stabilizing elements, especially Cr, toward the σ phase region.

Conversely, upon entering the dissolution regime (900–1000 °C), the Avrami exponent undergoes a significant inflation, reaching 0.7932 at 900 °C and stabilizing at 0.8671 at 1000 °C. This near-unity value ($n \approx 1.0$) underscores a fundamental mechanistic shift. Above the σ -solvus temperature, the tetragonal lattice of the σ phase becomes thermodynamically unstable, prompting its collapse. The near-unity exponent strongly implies that the dissolution kinetics are no longer constrained by conventional multi-directional impingement but are instead controlled by interfacial reaction kinetics or one-dimensional boundary-controlled atomic retraction back into the face-centered cubic (FCC) austenite matrix.

The linearized JMAK fitting further clarifies the kinetic origin of the temperature-dependent sigma phase transformation. In the plots of $\ln[-\ln(1 - X)]$ against $\ln(t)$, the slope represents the Avrami exponent n , while the intercept corresponds to $\ln k$. The fitted equations for the precipitation regime were $y = 0.4327x - 0.8226$ at 700 °C and $y = 0.4606x -$

0.3944 at 800 °C, where $y = \ln[-\ln(1 - X)]$ and $x = \ln(t)$. The relatively low n values at these two temperatures suggest that σ phase precipitation is mainly controlled by diffusion-assisted growth rather than continuous nucleation. This is consistent with the microstructural observation that σ phase preferentially develops from δ -ferrite regions, where nucleation sites are likely limited or rapidly consumed during the early stage of aging. The larger k value at 800 °C further indicates that the precipitation reaction is accelerated by enhanced atomic mobility.

At higher aging temperatures, the fitting equations changed to $y = 0.7932x - 1.5210$ at 900 °C and $y = 0.8671x - 1.5887$ at 1000 °C. These parameters were obtained from the modified JMAK-type expression used for the dissolution regime; therefore, they should be interpreted as apparent dissolution kinetics rather than σ phase growth kinetics. The decrease in σ phase fraction with increasing aging time, together with the higher n values and lower apparent k values, indicates that the dominant transformation process shifts from diffusion-controlled precipitation to diffusion-assisted dissolution. These kinetic features support the proposed mechanism that σ phase formation is favored at 700–800 °C, whereas σ phase becomes unstable and gradually dissolves at 900–1000 °C.

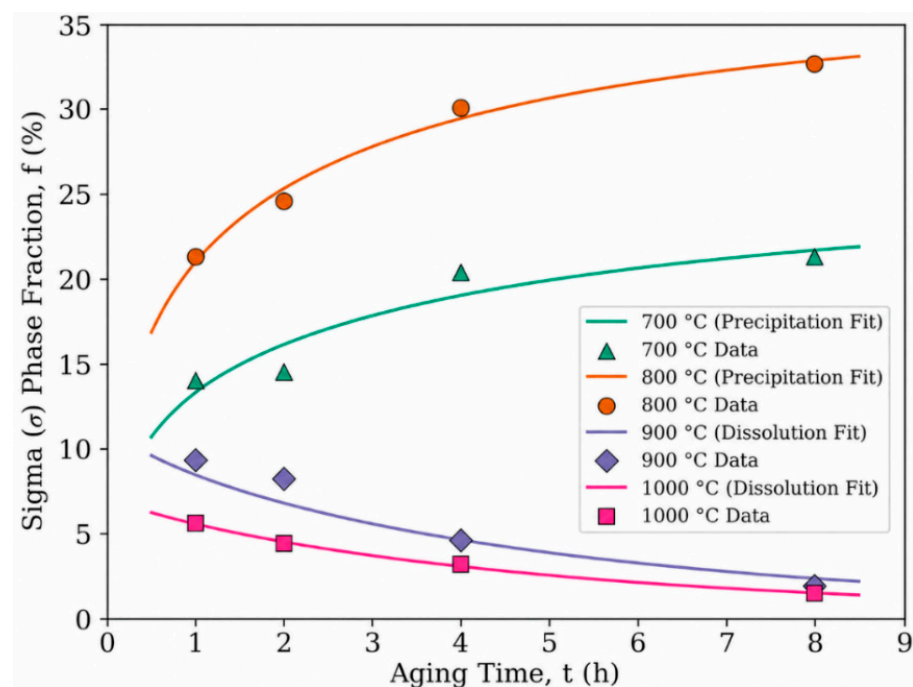


Figure 5. Isothermal evolution curves of the σ phase fraction in 24Cr–14Ni stainless steel at different aging temperatures. The solid lines represent the non-linear JMAK mathematical fitting curves tracking low-temperature precipitation growth (700 °C, 800 °C) and high-temperature structural dissolution (900 °C, 1000 °C).

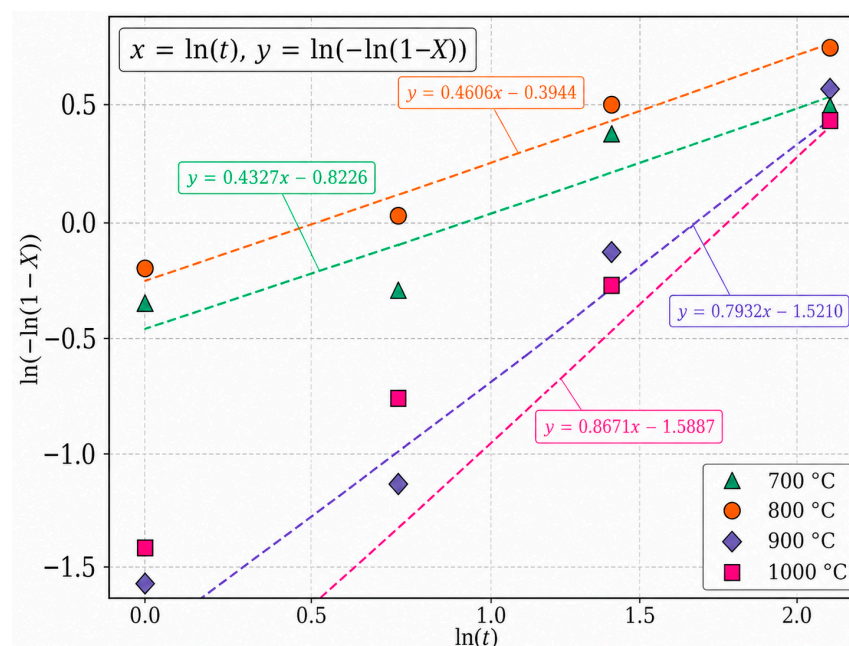


Figure 6. Standardized JMAK linearized plots of $\ln(-\ln(1-X))$ versus $\ln(t)$ for the σ phase transformation in 24Cr–14Ni stainless steel. The dashed lines demonstrate the linear regression segments utilized for extracting the Avrami exponents (n) and global kinetic rate constants (K).

3.5. Quantitative Evaluation of Apparent Activation Energies via Arrhenius Relationship

To further quantify the energetic barriers dominating the dual regimes of σ phase transformation, the apparent activation energies (Q) for both precipitation and dissolution were individually evaluated. By utilizing the temperature dependence of the standardized global rate constants (K) summarized in Figure 7, the classic Arrhenius relationship was applied as Equation (3) [39–42]:

$$Q = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \left(\frac{k_2}{k_1} \right) \quad (3)$$

where R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and k_1 and k_2 denote the standardized rate constants at absolute temperatures T_1 and T_2 , respectively. It is theoretically imperative to underscore that a combined cross-regime Arrhenius regression encompassing both 800–900 °C data points yields physically invalid energy values. This limitation arises from the radical reversal of the chemical driving force (ΔG) across the s - σ solvus boundary, which transitions the system from a precipitation-driven state to a dissolution-driven state. Consequently, separate thermodynamic treatments were executed for each discrete mechanism. For the lower-temperature precipitation stage (700–800 °C), the apparent activation energy (Q_{prec}) was calculated to be 37.18 kJ/mol.

This empirical value is markedly lower than the reported activation energy for the lattice self-diffusion of substitutional Cr atoms within a fully recrystallized austenite matrix, which typically ranges from 240 to 280 kJ/mol. This significant energetic deficit firmly demonstrates that the isothermal precipitation of the σ phase in the 24Cr–14Ni stainless steel does not rely on conventional bulk lattice diffusion. Instead, short-circuit diffusion pathways—principally grain boundary pipe diffusion—act as the primary vehicle for atomic transport. The high-angle grain boundaries and high-density dislocation networks localized at the intergranular zones dramatically lower the kinetic barrier, allowing ferrite-stabilizing elements (Cr and Ni) to rapidly aggregate and accelerate the nucleation of the tetragonal s lattice even within relatively brief aging windows.

Conversely, within the high-temperature dissolution stage (900–1000 °C), the apparent activation energy (Q_{diss}) was determined to be 122.95 kJ/mol. The substantial inflation of Q_{diss} relative to Q_{prep} indicates a fundamentally more sluggish atomic restructuring during the high-temperature solutionization process. Once the temperature exceeds the stability limit, the chemical driving force prompts the dissolution of the pre-existing σ phase. The liberated Cr and Ni atoms must overcome a significantly higher energetic threshold to escape the collapsing σ boundaries and re-dissolve back into the face-centered cubic (FCC) austenite lattice. This elevated energy barrier aligns with the observed shift in the Avrami exponent ($n \rightarrow 1.0$), confirming a transitional mixed-control mechanism wherein lattice bulk diffusion begins to heavily penalize and dictate the overall dissolution velocity.

Table 3 summarizes the JMAK kinetic parameters, apparent activation energies, and dominant kinetic mechanisms for σ phase transformation in 24Cr–14Ni stainless steel. The data show that σ phase evolution does not follow a single continuous kinetic pathway throughout the investigated temperature range. At 700–800 °C, σ phase precipitation is favored, together with relatively high σ phase fractions and low Avrami exponents. These low n values indicate that σ phase formation is mainly governed by diffusion-controlled growth, with nucleation sites likely being limited or rapidly saturated during the early stage of aging. At 900–1000 °C, the transformation behavior shifts to σ phase dissolution, as evidenced by the reduced σ phase fraction and the different kinetic response. Accordingly, the dominant mechanism changes from diffusion-controlled precipitation growth to diffusion-assisted dissolution at higher temperatures. Thus, Table 3 links the fitted JMAK parameters with the underlying transformation mechanism and confirms that σ phase stability in 24Cr–14Ni stainless steel is highly sensitive to aging temperature.

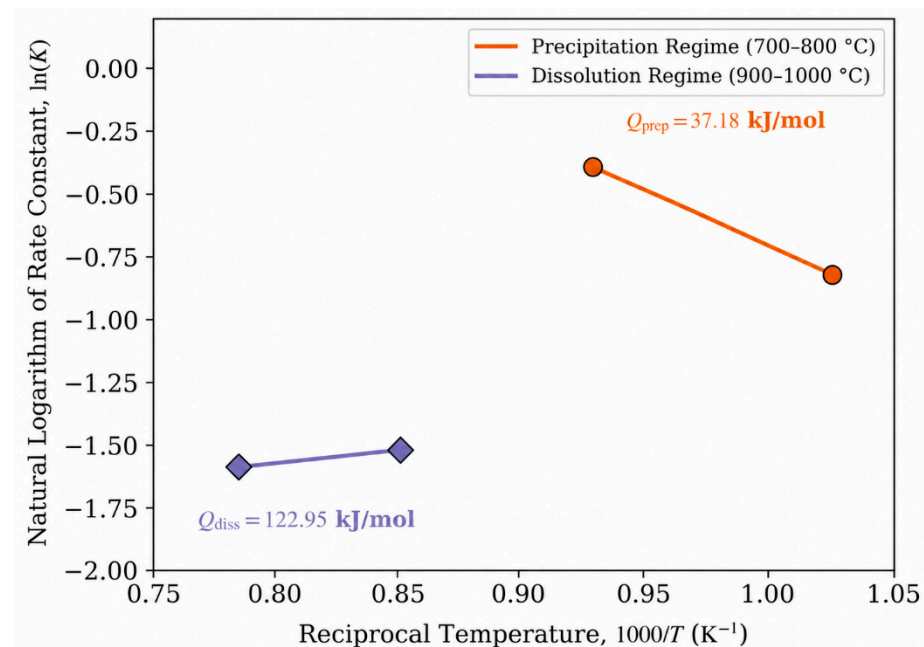


Figure 7. Arrhenius plots of $\ln(K)$ versus $1000/T$ for the σ phase transformation in 24Cr–14Ni stainless steel, showing distinct linear regression segments and calculated apparent activation energies (Q) for the low-temperature precipitation growth regime (700–800 °C) and high-temperature dissolution regime (900–1000 °C).

Table 3. Summary of the JMAK kinetic parameters, apparent activation energies, and dominant kinetic mechanisms of σ phase precipitation and dissolution in 24Cr–14Ni stainless steel aged at 700–1000 °C.

Temperature (°C)	Maximum/Initial σ Phase Fraction, $f_{\sigma,max}/f_{\sigma,0}$ (%)	^[a] Rate Constant, k (h ^{−1})	^[a] Avrami Exponent, n	^[b] Apparent Activation Energy, Q (kJ/mol)	Transformation Behavior	Dominant Kinetic Mechanism
700	26.41	0.4393	0.4327	37.18	Precipitation	Diffusion-controlled σ phase growth with limited nucleation
800	37.12	0.6741	0.4606	37.18	Precipitation	Diffusion-controlled σ phase growth with enhanced atomic mobility
900	11.39	0.2185	0.7932	122.95	Dissolution	Diffusion-assisted σ phase dissolution
1000	7.15	0.2042	0.8671	122.95	Dissolution	Thermally activated σ phase dissolution

Note: ^[a] The rate constant k was obtained from JMAK-type equations with a consistent unit of h^{−1}. The precipitation regime was fitted using $f(t) = f_{\sigma,max} [1 - \exp(-kt^n)]$, while the dissolution regime was fitted using $f(t) = f_{\sigma,0} \exp(-kt^n)$. ^[b] The apparent activation energy Q was calculated using $\ln k = \ln A - Q/RT$. Q_{prec} and Q_{diss} correspond to the 700–800 °C precipitation regime and the 900–1000 °C dissolution regime, respectively.

4. Conclusions

This study investigated the σ phase transformation behavior of 24Cr–14Ni stainless steel used as a welding electrode core material during aging at 700–1000 °C. The investigation combined microstructural characterization, XRD, EPMA/WDS, JMAK kinetic modeling, and Arrhenius analysis. The main conclusions are summarized as follows:

1. The σ phase precipitation at 700 °C mainly followed the original dendritic network, whereas aging at 800 °C promoted pronounced $\delta \rightarrow \sigma + \gamma_2$ eutectoid decomposition and led to the progressive breakdown of the dendritic structure;
2. XRD analysis confirmed that σ phase precipitation was most significant at 800 °C, as evidenced by the strongest σ diffraction peak. In contrast, σ phase peaks became weak at 900 and 1000 °C, indicating that σ phase precipitation was suppressed and partial dissolution occurred at higher temperatures;
3. EPMA elemental mapping and WDS analysis showed that σ phase preferentially precipitated in Cr-rich δ -ferrite regions at 800 °C, while Ni was mainly enriched in the γ phase. At 1000 °C, the Cr and Ni distributions became more homogeneous, suggesting that δ -ferrite dissolution and $\delta \rightarrow \gamma$ transformation became dominant;
4. JMAK analysis revealed two distinct kinetic regimes for σ phase evolution. At 700–800 °C, σ phase precipitation was governed by diffusion-controlled growth with low Avrami exponents of approximately 0.43–0.46, indicating rapid saturation of nucleation sites during the early stage of aging. At 900–1000 °C, the transformation shifted to σ phase dissolution, with higher Avrami exponents of approximately 0.79–0.87;
5. The apparent activation energy for σ phase precipitation was 37.18 kJ/mol, suggesting that short-circuit diffusion paths promoted σ phase formation at 700–800 °C. In contrast, the activation energy for σ phase dissolution increased to 122.95 kJ/mol at 900–1000 °C, reflecting a higher energy barrier for atomic redistribution during dissolution. These results confirm that σ phase evolution changes from precipitation-dominated behavior at 700–800 °C to dissolution-dominated behavior at 900–1000 °C.

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