

Article

Low-Temperature EMF Stability of Mineral-Insulated Thermocouples for Pressurized Water Reactor Core Outlet Temperature Measurement

Jie Chen ^{1,2,3,*}, Xiaodong Peng ², Min Liu ³, Anzhong Zhao ³, Meiliang Huang ⁴ and Shuzhi Chen ⁴

¹ School of Intelligent Manufacturing and Automobile, Chongqing Polytechnic University of Electronic Technology, Chongqing 401331, China

² Department of Material Science and Engineering, Chongqing University, Chongqing 400044, China; pxd@cqu.edu.cn

³ Chongqing Material Research Institute Co., Ltd., Chongqing 400707, China; ccliumin@139.com (M.L.); ncfma06@126.com (A.Z.)

⁴ China Nuclear Power Engineering Co., Ltd., Shenzhen 518116, China; huangmeiliang@cgnpc.com.cn (M.H.); chenshuzhi@cgnpc.com.cn (S.C.)

* Correspondence: 202324001@cqu.edu.cn; Tel.: +86-023-65926118

Featured Application

The stability of the electromotive force (EMF) of K-type thermocouples used for measuring the core outlet temperature in PWRs is studied. The selection of optimized materials, the preparation of pre-oxidized wires, and the implementation of a stabilization treatment effectively suppress EMF drift under abnormal temperature conditions. The results can be directly applied to the design, manufacturing, and qualification of nuclear-grade thermocouples to improve the accuracy and reliability of temperature monitoring of instruments and control systems in nuclear power plants.

Abstract

The core outlet temperature is an important safety parameter for pressurized water reactors (PWRs), and its accurate determination depends on highly reliable thermocouple sensors. In this study, two typical commercial K-type thermocouple alloys (de1 and de2) were used to fabricate mineral-insulated metal-sheathed (MIMS) thermocouples. A comparative severe accelerated aging test at 500 °C for 168 h was performed to investigate electromotive force (EMF) stability under high-temperature exposure conditions. After aging, both alloy types exhibited obvious positive EMF drift, and the maximum drift magnitude appeared at the calibration temperature of 400 °C. The measured irreversible EMF drift of de2 thermocouples was lower than that of de1 thermocouples. For the same de2 alloy, thermocouples fabricated with pre-oxidized thermoelement wires presented smaller irreversible drift than those made of bright wires. Reversible EMF drift and heating–cooling calibration hysteresis were more significant for de1 specimens. Stabilization treatment at 570 °C for 2 h followed by furnace cooling effectively reduced the thermal hysteresis of both alloys during temperature cycling. This study provides straightforward experimental data and practical processing references for optimizing the manufacturing route of nuclear-grade MIMS thermocouples with improved high-temperature EMF stability.

Keywords: thermocouple; electromotive force (EMF) drift; stability

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1. Introduction

Continuous monitoring of the core outlet temperature is essential for reactor safety because this temperature is a key indicator of core cooling conditions [1,2]. Due to the non-uniform neutron fluence and cooling across the core, fuel assembly outlets tend to register the highest temperature under both normal and accident operating modes. Mineral-insulated metal-sheathed (MIMS) thermocouples are installed at the core outlet to display its temperature distribution. Monitoring the core cooling state involves calculating the saturation margin. At the Daya Bay Nuclear Power Plant, an alarm RIC701/702AA will be activated when the temperature difference between the maximum and minimum thermocouple readings at the core outlet surpasses 20 °C [2]. Thus, the reliability of these thermocouple sensors is very important for the nuclear power instrumentation and control system.

Thermocouple alloys exhibit differences in chemical composition, metallurgical structure, and physical state, and these variations can directly degrade reliability [3–8]. Notably, prolonged service alters the composition and physical state of thermocouple wires, inducing an appreciable electromotive force (EMF) drift [5–15]. The long-term stability of thermocouples is more important than absolute accuracy. Below 800 °C, the stability of K-type armored thermocouples depends primarily on alloy composition and physical state, rather than on the sheath outer diameter [16–18]. Previous research found that, when aged for 200 h between 200 °C and 800 °C, the positive KP alloy showed the most significant variation in Seebeck coefficient at 450 °C, with a value of approximately +0.5 $\mu\text{V/K}$. Variations in trace elements such as Cr and Fe shifted this peak temperature to 350 °C. After aging, the negative KN alloy presented two distinct Seebeck coefficient peaks at 350 °C and 600 °C. Due to these compositional differences, the drift at 600 °C ranged from −0.04 $\mu\text{V/K}$ to −0.25 $\mu\text{V/K}$ [16]. It is generally accepted that thermocouples exhibit no reversible EMF drift when aged below 200 °C [19–21]. However, Webster et al. [22] observed a positive Seebeck coefficient drift of 0.3% after 20 min of aging at 200 °C, and the drift increased to roughly 0.6% after 200 h of treatment. Although these results confirm a close correlation between alloy composition and thermocouple stability, further research is still needed to clarify thermocouple behaviors in certain low-temperature ranges.

The current nuclear industry standards do not specify technical requirements or performance evaluation methods for the long-term stability of thermocouples under abnormal operating conditions. For example, ASTM E235 and IEC 62651 do not specify technical requirements or performance evaluation methods for long-term thermocouple stability under abnormal operating conditions. This omission poses potential risks regarding the safe operation of nuclear power plants and assessments of equipment availability. Modern commercial K-type thermocouple alloys have been substantially optimized compared with conventional materials, yet systematic comparisons and engineering validation of EMF drift for different compositions under abnormal PWR conditions (e.g., core outlet temperatures exceeding 350 °C) remain insufficient.

To address these research gaps, this study selected two commercial K-type thermocouple alloys (denoted de1 and de2) and conducted a comparative severe accelerated aging test at 500 °C for 168 h to evaluate EMF stability under prolonged elevated-temperature exposure. The 500 °C test temperature is an elevated thermal level far above the routine steady-state core outlet temperature of PWRs. The internal drift mechanism was revealed by comparatively analyzing the EMF drift behaviors of the two alloys. On this basis, an optimized thermocouple fabrication process was proposed for improving the high-temperature EMF stability of MIMS thermocouples.

The results offer engineering suggestions for improving the selection and manufacturing process of sheathed thermocouples at the core outlet, which can enhance the reliability and stability of temperature measurements in nuclear plant instrumentation

and control systems after accidents and provide technical assistance for the safe and economical operation of nuclear power plants.

2. Materials and Methods

Thermocouple wires, as the key material in MIMS thermocouples, are a principal determinant of measurement accuracy. Two typical NiCr–NiAl thermocouple alloys (denoted de1 and de2) were selected for the study, and their chemical compositions are shown in Table 1. The EMF characteristics of these wires meet the accuracy grade requirements specified in ASTM E230 and are presented in Table 2.

Table 1. The nominal compositions of the thermocouple alloys used in this study (wt%).

Elements	Thermocouple Alloy—de1		Thermocouple Alloy—de2	
	KP (de1-KP)	KN (de1-KN)	KP (de2-KP)	KN (de2-KN)
Si	0.5	1.5	0.5	1.5
Cr	10.5	/	9.7	/
Al	/	0.8	/	1.7
Mn	/	2.1	/	1.6
Co	0.7	0.8	/	0.6
Fe	/	/	0.5	0.12
Ni	Balance			

Table 2. The calibration characteristics of the two thermocouple wires.

Thermocouple Alloy	EMF (μ V)							
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	800 °C	1000 °C
de1	4114	8178	12,168	16,432	20,619	24,989	33,349	41,354
de2	4117	8186	12,166	16,425	20,620	24,981	33,337	41,343

The thermocouple wires, MgO powder, and 316L stainless-steel tube (chemical compositions shown in Tables 3 and 4) were assembled and then subjected to multiple drawing and stress-relief annealing to produce a mineral-insulated thermocouple cable with an outer diameter of Φ 2.5 mm. The cable was baked at 120 °C for 5 h to remove residual water vapor from the MgO powder, ensuring that the insulation resistance between the thermocouple wires and the metal sheath exceeded 1000 M Ω (100 VDC). The hot junction was welded and insulated from the sheath. The cold junction was sealed with epoxy to prevent moisture and air ingress.

Table 3. The weight percent of MgO powder and its impurity (wt%).

Elements	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	C	S	B	Cd	B + Cd
Content%	99.56	0.072	0.12	0.018	0.040	0.026	0.0035	0.0010	<0.00005	0.0010

Table 4. The nominal compositions of 316L sheath alloys (wt%).

Elements	Si	Cr	Al	Mn	Fe	Mo	Ni
Content%	≤1.0	16~18	/	≤2	Balance	2.2	10~14

The comparison method was employed to measure the calibration characteristics of the thermocouples. The tested sheathed thermocouples were evenly bound around an S-type standard thermocouple using Nichrome wire, with all measuring junctions kept on the same plane. The assembly was then placed in a GL-4 tube furnace, where the measuring junctions were positioned in the central maximum temperature zone of the

furnace with an insertion depth of approximately 300 mm. The cold junctions of the thermocouples were placed in an ice-point thermostat with a reserved wire length of about 220 mm.

The tube furnace featured a uniform temperature zone whose center deviated from the geometric center along the axis by no more than 10 mm. Within this zone, which extended at least 60 mm in length and had a radius of 14 mm, the maximum temperature variation did not exceed 1 °C.

The standard calibration tests were conducted at a metrology institute, in compliance with the requirements of national metrological verification regulations for base-metal thermocouples. The measurement uncertainty mainly arose from the inherent uncertainty of the standard reference thermocouple, measurement repeatability, electronic measuring equipment, parasitic thermoelectric potentials, and furnace temperature fluctuations. All calibration results are expressed as expanded uncertainties (U) with a coverage factor of $k = 2$. During measurement, the furnace temperature was controlled within ± 2 °C and the temperature fluctuation was less than 0.2 °C/min. At each calibration temperature point, the EMF was measured four times and the average value was taken. The expanded uncertainty was estimated to range from approximately 0.05 °C to 0.15 °C, corresponding to a thermoelectric voltage interval of roughly 2 μ V to 6 μ V.

All heating–cooling hysteresis tests were performed inside a GL-4 tube furnace following standard thermocouple calibration procedures. The thermocouple assembly (including an S-type standard thermocouple) was positioned with a 300 mm insertion depth. The test temperature sequence covered 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, and 550 °C. Starting from room temperature (~25 °C), the furnace was heated at a controlled rate of 5–10 °C/min. At each target temperature, the furnace was stabilized until the temperature fluctuation was less than 0.2 °C/min before the EMF data were recorded. During the heating stage, the EMF data were collected sequentially from the lowest to the highest calibration point.

After completing measurements at the maximum temperature of 550 °C, the cooling-phase test was initiated. The furnace was cooled at a natural furnace cooling rate. When the furnace temperature dropped to each target calibration point (450, 400, 350, 300 °C), an isothermal hold was implemented at each temperature. The EMF values of the cooling branch were only collected after the temperature fluctuation had stabilized below 0.2 °C/min. The identical holding and stabilization criteria were applied for all cooling measurement points. It is important to note that the cooling branch data were measured after the sample had been exposed to the maximum temperature (550 °C). Thus, the EMF values obtained during cooling reflect the material state after high-temperature exposure and should not be interpreted as independent low-temperature measurements.

An aging test was performed in the same GL-4 tube furnace. The sheathed thermocouples were inserted to a depth of 300 mm and exposed to 500 °C for 168 h. All specimens adopted unified 1070 °C/15 min air-cooled annealing for the separation of reversible and irreversible EMF drift; potential consistent minor oxidation during annealing is acknowledged as a limitation of the comparative testing scheme.

Cross-sections of the aged thermocouples were prepared using standard metallographic procedures (grinding, polishing, and etching with a solution consisting of CuCl_2 (10 g), CH_3OH (200 mL), and HCl (200 mL)). The microstructures and composition of the thermoelements were characterized by electron probe microanalysis (EPMA-1720, SHIMADZU, Kyoto, Japan). All EPMA line scans were operated at a 15 kV accelerating voltage and a 50 nA beam current. The oxide layer thickness was used to estimate the apparent thickness of the oxidized region formed on the thermoelement surfaces. The scanning step size was fixed at 0.1 μm , corresponding to the minimum thickness resolution of the test.

All performance tests were conducted with two duplicate specimen sets per test group to ensure data reliability. For the aging test at 500 °C for 168 h to compare the EMF stability of de1 and de2 alloys, three identical thermocouples were fabricated for each alloy. One specimen from each group was used for post-aging metallographic characterization and elemental diffusion analysis. The remaining two intact parallel specimens were subjected to aging and subsequent annealing to acquire irreversible EMF drift data for the statistical calculation of mean values and standard deviations.

For comparison of the influence of thermoelement surface conditions on irreversible EMF drift, four bright de2 thermocouples and four pre-oxidized de2 thermocouples were fabricated. Within each type (de2-bright and de2-oxidized), two parallel specimens were subjected to initial baseline calibration to investigate the influence of thermoelement surface conditions on intrinsic EMF–temperature characteristics. The other two parallel specimens underwent the 500 °C aging procedure for post-aging EMF drift measurement. Then, the specimens were subsequently subjected to annealing treatment to quantify irreversible drift.

For the stabilization process experiment, six thermocouples of de1 alloy and six thermocouples of de2 alloy were separately split into three groups—untreated, furnace-cooled, and water-quenched—with two parallel replicates allocated to each subgroup. All specimens were subjected to heating–cooling calibration tests for characterization.

3. Results and Discussion

3.1. EMF Drift After Aging at 500 °C

Exposure to elevated temperatures significantly exceeding normal in core operating conditions will result in a marked drift in the EMF of MIMS thermocouples. In commercial pressurized water reactors (PWRs), the core outlet temperatures are typically kept below 330 °C during normal operation. If the reactor coolant's heat removal is impaired or the core power becomes unbalanced, the reactor outlet temperature will exceed 330 °C, thus entering an abnormal operating condition. In this study, a test temperature of 500 °C was selected to induce substantial thermoelectric drift, thereby enabling a comparative analysis of the stability differences among alloys subjected to severe thermal exposure in the laboratory.

It is important to recognize that establishing a precise quantitative correlation between laboratory aging conditions and real reactor abnormal transients using the Arrhenius model is not feasible. MIMS thermocouple sensors are composite assemblies composed of metallic alloys, oxide ceramics, and insulating materials. However, the lack of universally acknowledged activation energy parameters for the entire multi-material sensor assembly in engineering applications hinders the accurate extrapolation of temperature-time aging equivalences. This partly explains the absence of dedicated standards for evaluating the EMF stability of the thermocouple.

The aging temperature of 500 °C was selected as a significantly elevated thermal level, well above the normal operating temperatures of pressurized water reactors (PWRs). The holding duration of 168 h was chosen to generate discernible and measurable EMF drift within a manageable laboratory timeframe, thereby enabling a direct quantitative comparison of thermoelectric stability between the two alloys and the various surface pretreatment methods. This thermal treatment (500 °C for 168 h) is characterized as a comparative severe accelerated aging condition for laboratory investigation. It is not designed to quantitatively replicate the cumulative thermal loads experienced during in-reactor transient events, and the results obtained cannot be directly extrapolated to predict the long-term performance of thermocouples in actual nuclear reactors.

Figure 1 shows the variations in the calibration properties of de1 and de2 thermocouples after aging at 500 °C for 168 h. The EMF drift at each testing time point is

defined as the deviation from the initial measured value, expressed as $\Delta E = E - E_0$. After aging, the EMF drifts of the thermocouples increased within the temperature range of 300 °C to 1000 °C, and the largest change in EMF was found at 400 °C. The EMF drifts for de1 and de2 were 89 μV and 42 μV , respectively, which approximately corresponded to increases of 2.2 °C and 1.1 °C.

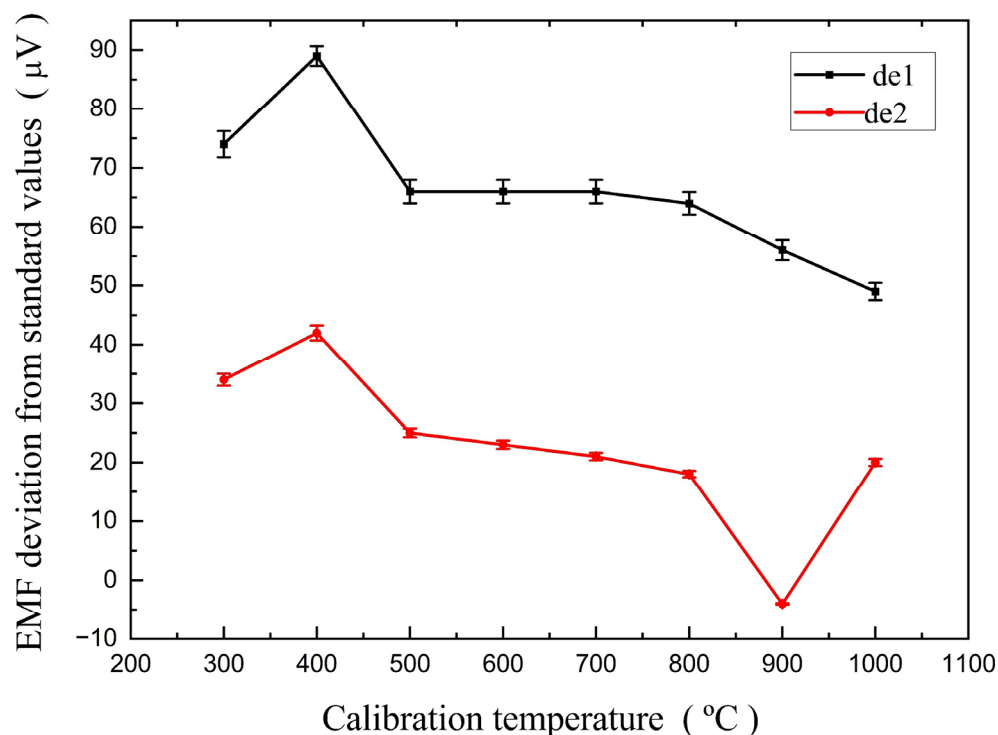


Figure 1. The calibration characteristics of de1 and de2 thermocouple alloys after aging for 168 h at 500 °C. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

The EMF drift of the aged de1 thermocouple was consistently higher than that of the aged de2 thermocouple. Within the temperature range of 300 °C to 800 °C, the EMF drift of de1 was about 44 μV higher than that of de2. At temperatures of 900 °C and 1000 °C, the EMF drift of de1 was higher by 60 μV and 29 μV , respectively. The overall drift generated during 500 °C aging stemmed from reversible and irreversible drift. To clarify the fundamental mechanism behind such performance changes, an annealing treatment was performed to separate these two drift components for further analysis.

3.2. Irreversible EMF Drift After Aging

The aged thermocouples were further annealed at 1070 °C for 15 min and cooled in air to room temperature. This annealing protocol follows the standardized industrial heat treatment for MIMS K-type thermocouples to eliminate Ni–Cr short-range ordering and separate ordering-associated reversible drift from irreversible drift. All specimens of de1 and de2 alloys were subjected to an identical annealing atmosphere, temperature and holding time. While targeted characterization verifying zero oxidation or compositional shift pre- and post-annealing was not conducted in this study, any minor uniform surface oxidation induced during annealing constitutes identical systematic interference across all test groups and does not alter the comparative drift trends between the two alloys. The remaining EMF changes in the thermocouples arose from irreversible drift. The cumulative irreversible EMF drift curves for the two thermocouple alloys are illustrated

in Figure 2. After aging, the de1 thermocouple exhibited a minimum irreversible EMF variation of approximately $-13\ \mu\text{V}$ at $500\ ^\circ\text{C}$, while the maximum drift reached about $+47\ \mu\text{V}$ at $800\ ^\circ\text{C}$. In contrast, the de2 thermocouple displayed a minimum irreversible EMF variation of roughly $-2\ \mu\text{V}$ at $900\ ^\circ\text{C}$, with the maximum EMF variation of approximately $+33\ \mu\text{V}$ occurring at $600\ ^\circ\text{C}$.

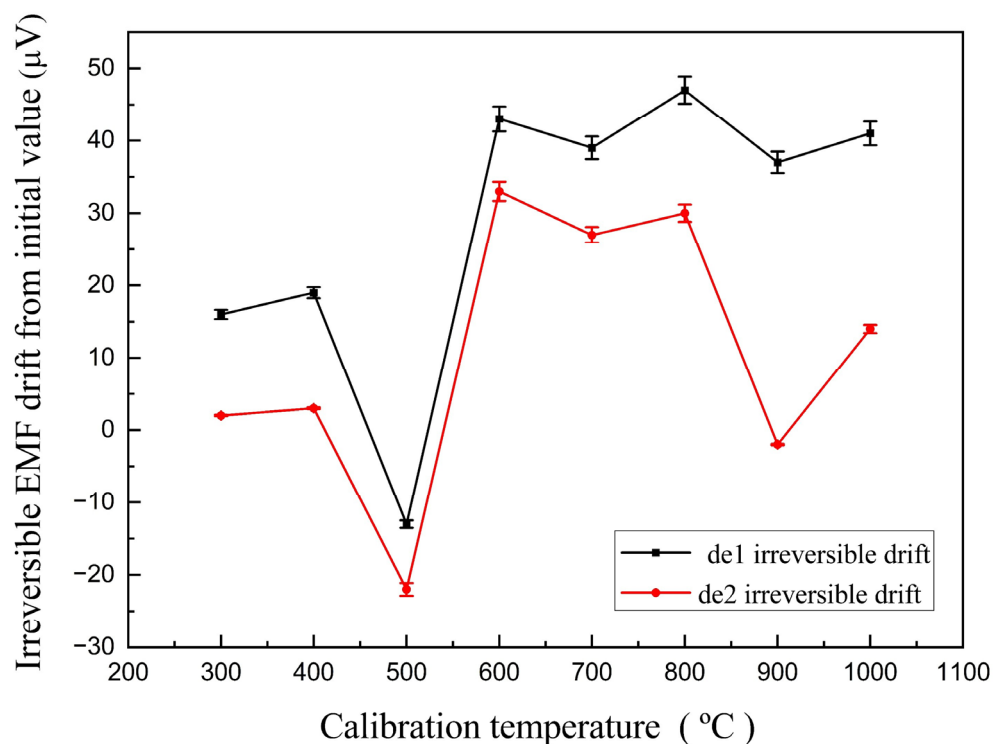


Figure 2. The irreversible EMF drifts of the two thermocouple alloys after annealing. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

After aging, the two thermocouple alloys exhibited similar irreversible drift curves. Between $300\ ^\circ\text{C}$ and $800\ ^\circ\text{C}$, the EMF drift of the de1 thermocouple was approximately ten microvolts ($0.4\ ^\circ\text{C}$) higher than that of de2. At $900\ ^\circ\text{C}$ and $1000\ ^\circ\text{C}$, the discrepancies in EMF drift between the two alloys rose to $39\ \mu\text{V}$ and $27\ \mu\text{V}$, respectively.

Irreversible EMF drift is typically related to compositional changes caused by oxidation. After multiple cold drawing processes, the compaction density of MgO powder was not fully achieved, leaving about 24% trapped air inside the metal sheath. Residual oxygen reacted with thermoelement surfaces, leading to irreversible EMF drift. Metallographic cross-sections of the sheathed thermocouples were prepared, and electron probe microanalysis (EPMA) line scans were conducted across the MgO–thermoelement interface to analyze elemental distribution, as depicted in Figure 3.

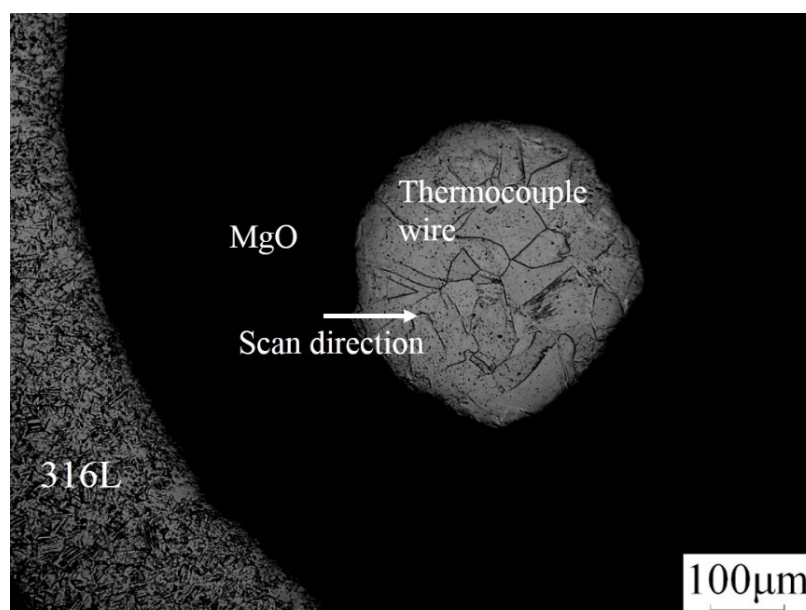
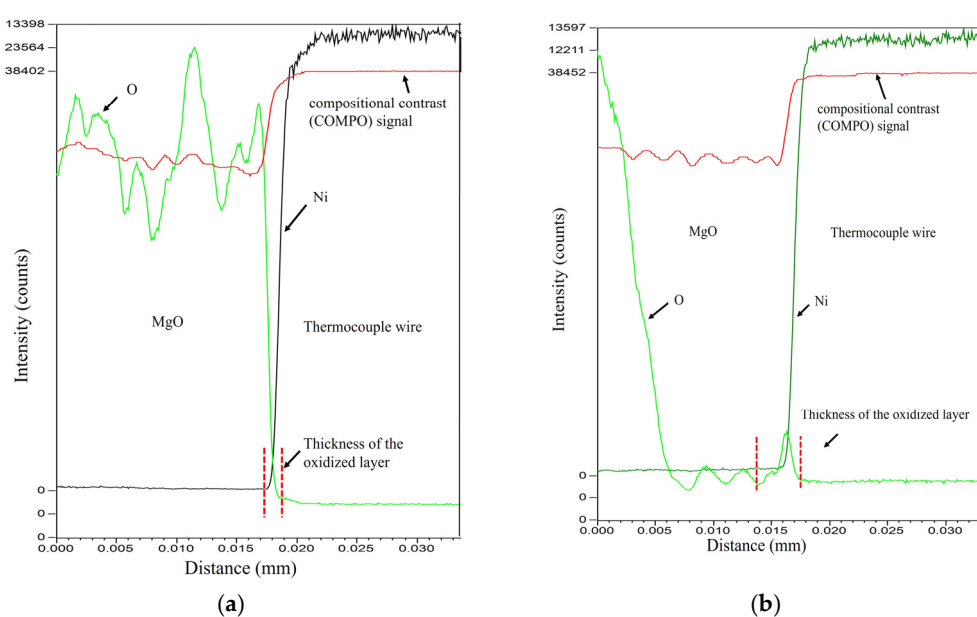
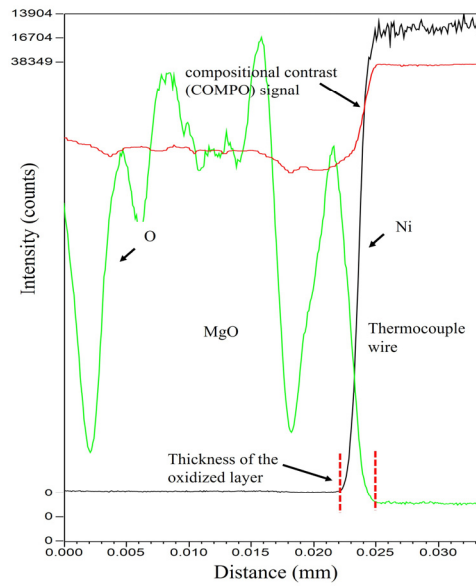


Figure 3. An EPMA line-scan diagram of the MgO powder and thermocouple wires.

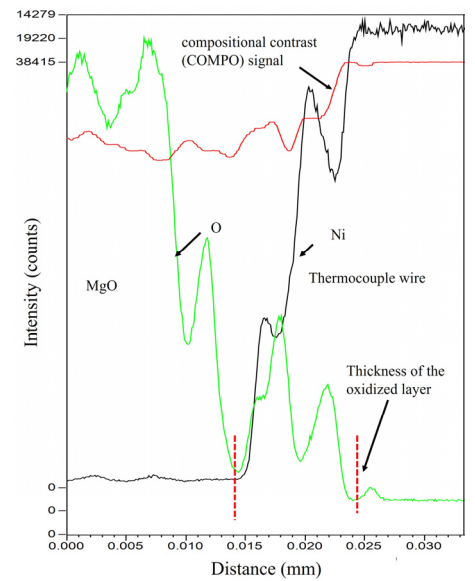
Figure 4 illustrates the distribution profiles of Ni and O elements at the interface between MgO powder and thermoelements on the thermocouple cross-sections. The O concentration reached its maximum within the MgO powder layer. As the scanning path extended toward the thermoelements, the O content gradually declined, while the Ni content gradually rose. Accordingly, the distance between the abrupt transition zones of the two element curves can be used to determine the thickness of the oxide layer formed on the thermoelement surfaces.

Before aging, the oxide layer thicknesses of the positive and negative thermoelements in de1 were approximately 1 μm and 3 μm (0.001 mm and 0.003 mm, consistent with the horizontal unit in Figure 4), respectively. After aging, these values increased to 3.5 μm and 10 μm . For the de2 thermocouple, the oxide layer thickness of the KP also increased from 3 μm to 9 μm after aging. These results confirm that the irreversible EMF drift after aging was mainly caused by surface oxidation of the thermoelements, with all oxide layers maintained at the micrometer scale.

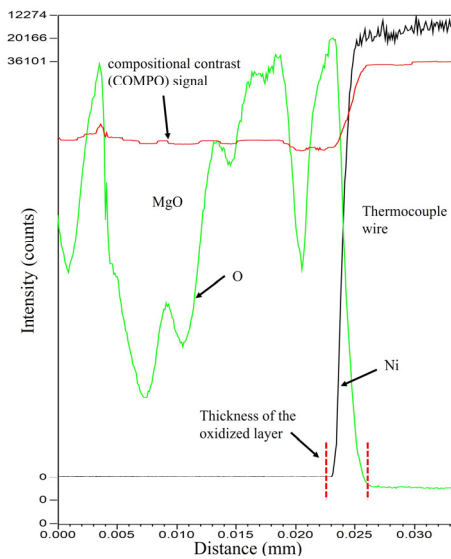




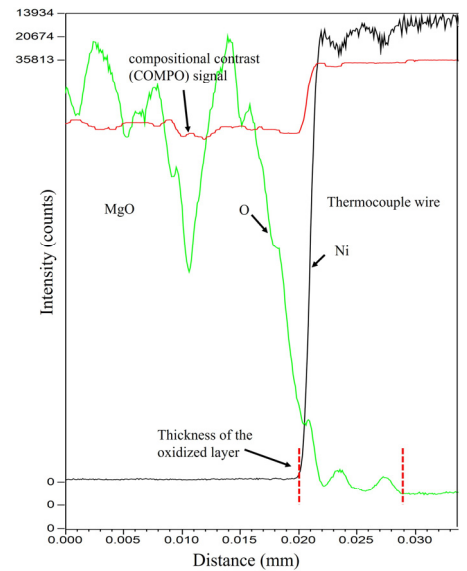
(c)



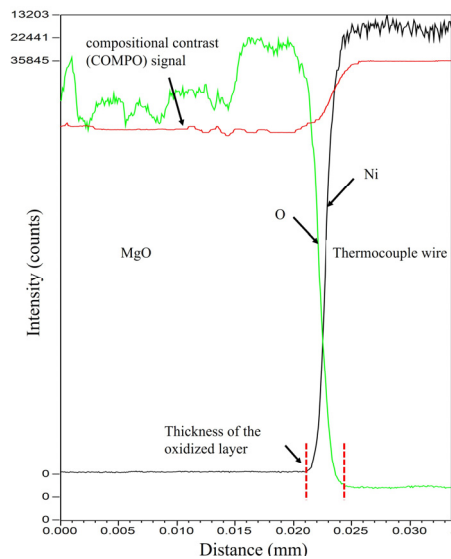
(d)



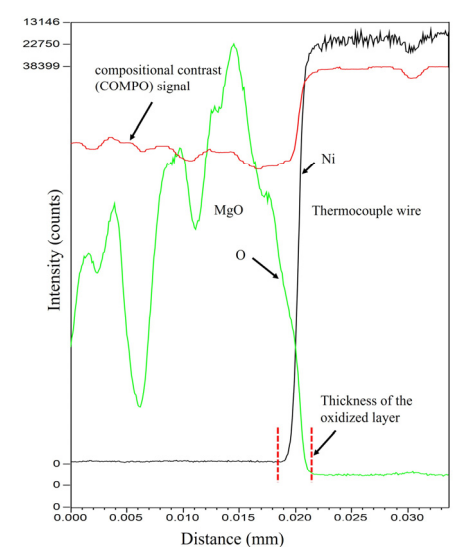
(e)



(f)



(g)



(h)

Figure 4. The distribution of Ni and O elements in EPMA line scans: (a) de1-KP before aging; (b) aged de1-KP; (c) de1-KN before aging; (d) aged de1-KN; (e) de2-KP before aging; (f) aged de2-KP; (g) de2-KN before aging; (h) aged de2-KN.

According to the EPMA point scan results obtained on the aged thermoelement surfaces (Table 5), both the positive and negative alloys experienced surface oxidation to a different extent, and their oxygen mass fractions varied between 1.92 wt% and 4.51 wt%. This compositional trend agreed with the line-scan data. Meanwhile, the contents of alloying elements, such as Si, Cr, Al, Mn, and Fe, exhibited significant differences compared with those before aging.

Table 5. The surface compositions of the thermoelements after aging, as measured by EPMA (wt%).

Elements	de1-KP	de1-KN	de2-KP	de2-KN
O	4.44	3.56	1.92	4.51
Si	0.71	1.38	0.23	1.43
Cr	10.14	/	10.98	/
Al	/	0.23	/	0.19
Mn	/	2.18	/	1.86
Co	0.77	0.33	/	0.82
Fe	/	/	0.53	/
Ni	Balance			

Bentley et al. verified that the addition of Al and Mn can improve the EMF stability of thermocouple alloys [20]. In this work, the de1 thermocouple alloy contained approximately 0.8 wt% Al and 2.1 wt% Mn, while the de2 thermocouple alloy had 1.7 wt% Al and 1.6 wt% Mn. From a thermodynamic perspective, alloy elements with a lower standard Gibbs free energy ΔG^0 exhibit a stronger tendency toward oxidation [23]. When Al and Mn coexist, Al is preferentially oxidized [23]. The present EPMA elemental line-scan data cannot independently confirm the formation of discrete Al-containing oxide phases or separate the individual contributions of Al, Mn, and Cr to drift behavior due to simultaneous compositional differences between de1 and de2 alloys. Wang et al. further reported that variations in Al concentration exert a much weaker influence on EMF compared with Mn when the Mn content is below 2 wt% [24]. As indicated by the compositional data, the Mn fraction of de2 fell below 2 wt%. It is tentatively hypothesized that Al acts as the primary oxidizable constituent during thermal aging. If this hypothesis is valid, the relatively weak EMF disturbance induced by Al oxidation could partially suppress the overall drift in de2, whereas the pronounced oxidation of Mn in de1 may amplify EMF fluctuations. This proposed elemental oxidation mechanism only provides qualitative consistency with measured oxide layer thickness and EPMA elemental distribution results, and remains an unvalidated hypothesis without complementary XRD, XPS or cross-sectional EDS phase identification. The de2 thermocouple exhibited a smaller irreversible drift, which is consistent with the tentative hypothesis that the higher Al content in the KN alloy might promote the preferential oxidation of Al, thereby alleviating thermoelectric degradation. However, definitive validation of this mechanism requires additional phase characterization experiments.

3.3. Effect of Surface Condition on Irreversible EMF Drift

The irreversible EMF drift of the sheathed thermocouples after aging at 500 °C was caused by oxidation. Commercially available thermocouple wires typically exist in two states: bright and pre-oxidized. This study investigated the impact of thermoelement surface condition on the irreversible EMF drift during aging at 500 °C.

A bright de2 thermocouple wire, initially $\Phi 2.2$ mm in outer diameter, was reduced to $\Phi 2.0$ mm through drawing, and then subjected to stress relief annealing in an ammonia decomposition furnace at 1070 °C for 15 min. Subsequently, the wire underwent a secondary drawing to $\Phi 1.8$ mm, followed by a second stress relief annealing process to create a thermocouple wire with a slightly oxidized state.

Subsequently, two types of sheathed thermocouples (de2-bright and de2-oxidized) were fabricated to investigate the influence of the thermoelement surface condition on the oxidation rate following aging at 500 °C.

The EMF–temperature characteristics of the de2-bright and de2-oxidized sheathed thermocouples in the temperature range of 300 °C to 1000 °C are illustrated in Figure 5. The two thermocouples satisfied the Grade I accuracy criteria defined in the ASTM E230 standard. Specifically, the maximum standard deviations of the bright and oxidized thermocouples were 0.14%t and 0.21%t, respectively. The EMF of the de2-bright thermocouple was consistently higher than that of the de2-oxidized thermocouple. After multiple drawing and heat treatment processes, a thin oxide film formed on the surface of the de2 thermoelements, which induced slight compositional changes in the alloy. This effect led to a deviation from the standard EMF for the oxidized samples. Nevertheless, the EMF difference between the two thermocouples remained nearly constant at approximately 30 μ V across all calibration points. As a result, oxidation was limited to a thin surface layer and the alloy composition in the inner region of the thermocouples remained homogenous. The oxidized wires retained almost the same calibration characteristics as the original bright samples.

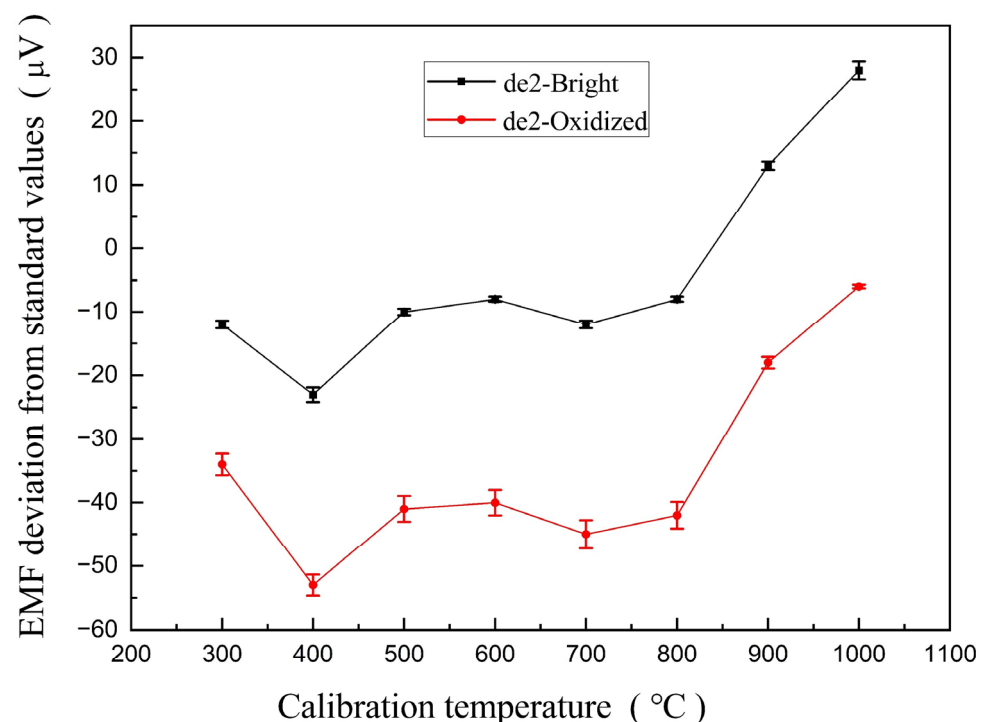


Figure 5. EMF deviations from standard values of de2-bright and de2-oxidized thermocouple alloys ($\Delta E = E - E_{std}$). All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

Figure 6 illustrates the EMF drift trends of the de2-bright and de2-oxidized thermocouple alloys after aging at 500 °C for 168 h. Both samples exhibited positive EMF drift after aging, with the maximum EMF deviation observed at 300 °C. The drift

magnitude gradually declined as the calibration temperature rose. For the de2-bright thermocouple, the EMF drift was approximately $103\text{ }\mu\text{V}$ ($\sim 2.6\text{ }^{\circ}\text{C}$) within the temperature range of $300\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$, and it reached the minimum value of $+63\text{ }\mu\text{V}$ ($\sim 1.57\text{ }^{\circ}\text{C}$) at $1000\text{ }^{\circ}\text{C}$. In comparison, the de2-oxidized thermocouple recorded an EMF increase of $82\text{ }\mu\text{V}$ ($\sim 2.05\text{ }^{\circ}\text{C}$) at $300\text{ }^{\circ}\text{C}$ and a shift of $+30\text{ }\mu\text{V}$ ($\sim 0.75\text{ }^{\circ}\text{C}$) at $1000\text{ }^{\circ}\text{C}$. The cumulative EMF drift of the de2-oxidized thermocouple remained consistently lower than that of the de2-bright thermocouple after aging.

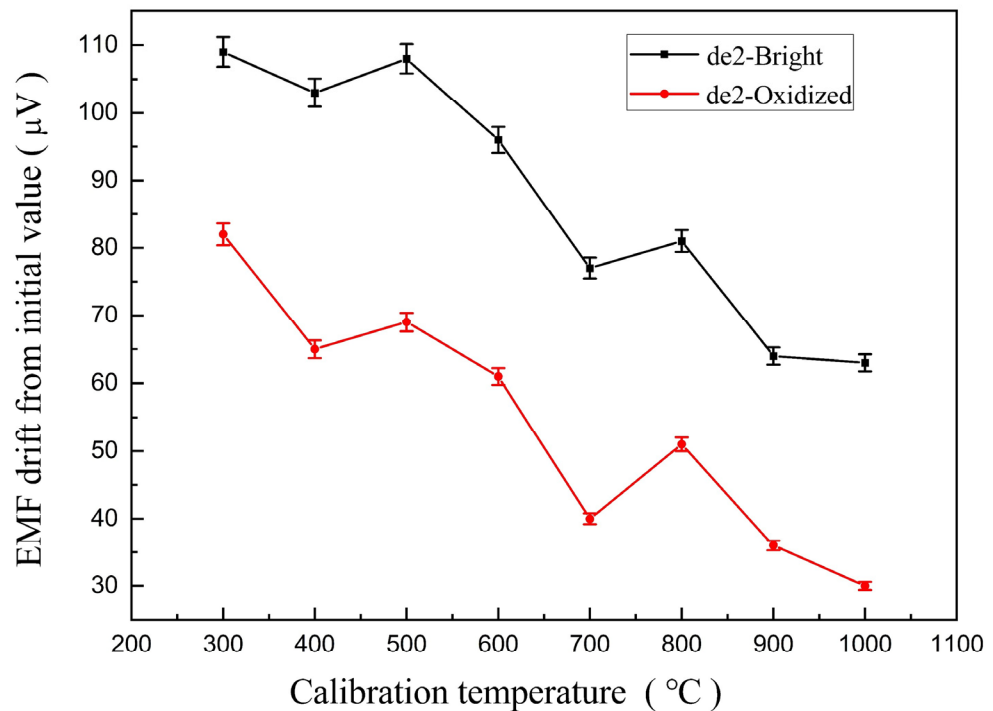


Figure 6. EMFs drifts of de2-bright and de2-oxidized thermocouple alloys after aging for 168 h at $500\text{ }^{\circ}\text{C}$. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

The aged de2-bright and de2-oxidized thermocouples were annealed at $1070\text{ }^{\circ}\text{C}$, and the irreversible EMF drift was measured, as depicted in Figure 7. The de2-bright thermocouple showed cumulative negative irreversible drift, and the EMF variation increased with the calibration temperature, ranging from $-4\text{ }\mu\text{V}$ to $-59\text{ }\mu\text{V}$ ($\sim 0.1\text{ }^{\circ}\text{C}$ to $\sim 1.97\text{ }^{\circ}\text{C}$). In contrast, the de2-oxidized thermocouple exhibited a maximum positive EMF drift of $18\text{ }\mu\text{V}$ at $600\text{ }^{\circ}\text{C}$ and a maximum negative drift of $-24\text{ }\mu\text{V}$ at $1000\text{ }^{\circ}\text{C}$. At all other calibration points, the irreversible EMF change was only a few microvolts.

The oxide present on the surface of the thermoelement provides sufficient oxygen partial pressure during aging at temperatures ranging from $800\text{ }^{\circ}\text{C}$ to $1100\text{ }^{\circ}\text{C}$. This condition leads to the selective internal oxidation of Cr in the positive KP alloy, resulting in the formation of Cr_2O_3 and a degradation of thermoelectric stability [25]. Nevertheless, metallic elements are oxidized only when the ambient oxygen partial pressure equals or exceeds the corresponding equilibrium partial pressure of oxide [23]. According to the Ellingham diagram, the critical oxygen potential for forming Cr_2O_3 at $500\text{ }^{\circ}\text{C}$ is far lower than that at $800\text{ }^{\circ}\text{C}$ [23]. Under the confined oxygen environment inside mineral-insulated thermocouples, the low oxygen partial pressure at aging temperature ($500\text{ }^{\circ}\text{C}$) might fail to sustain the continuous internal oxidation of Cr, which could account for the protective effect conferred by pre-oxidized surface films. A tentative hypothesis is proposed

whereby the thin pre-formed oxide film acts as an oxygen diffusion barrier, thereby retarding the continuous internal oxidation of the thermoelements. However, neither can the present EPMA line-scan results verify that this oxide layer constitutes a continuous, fully protective barrier, nor can the confounding effects of multi-element co-oxidation be excluded. Consequently, this protective pre-oxidation mechanism remains an unconfirmed hypothesis, pending supplementary phase and cross-sectional microstructural evidence.

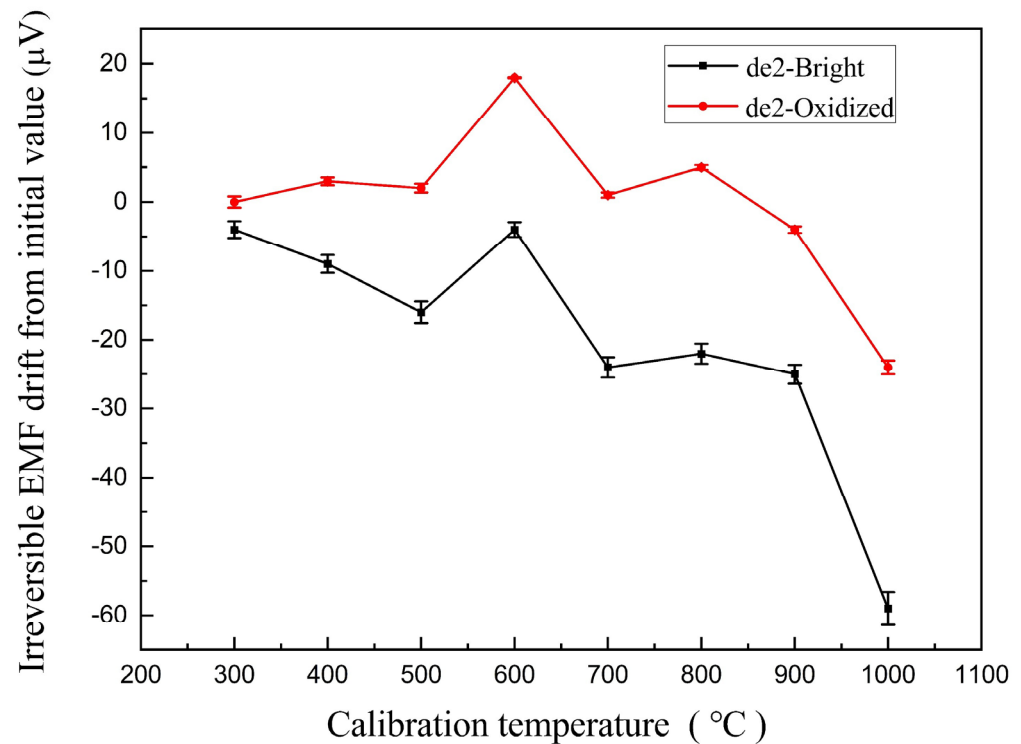


Figure 7. The irreversible EMF drifts of the de2-bright and de2-oxidized thermocouple alloys after aging for 168 h at 500 °C. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

3.4. Reversible EMF Drift After Aging

Reversible EMF drift is defined as the cumulative EMF change of aged thermocouples that can be removed by annealing at 1070 °C. It therefore equals the total EMF change minus the irreversible EMF change. Figure 8 presents the reversible EMF drift curves of the de1 and de2 thermocouple alloys after aging at 500 °C for 168 h. Both alloys exhibited similar reversible EMF drift profiles over the temperature range of 300 °C to 800 °C.

For the aged de1 thermocouple alloy, the reversible EMF drift was positive across the entire temperature range and showed larger magnitudes than those of de2. Specifically, the EMF increased by 58–79 μV (1.45–1.97 °C) at the calibration points from 300 °C to 500 °C, whereas the increase was only 23–8 μV (0.57–0.20 °C) between 600 °C and 1000 °C. For the de2 thermocouple alloy, the EMF varied by 32–47 μV (0.80–1.17 °C) between 300 °C and 500 °C, which was smaller than that of de1. By contrast, a negative EMF drift of –10 to –2 μV (0.25–0.05 °C) occurred between 600 °C and 900 °C.

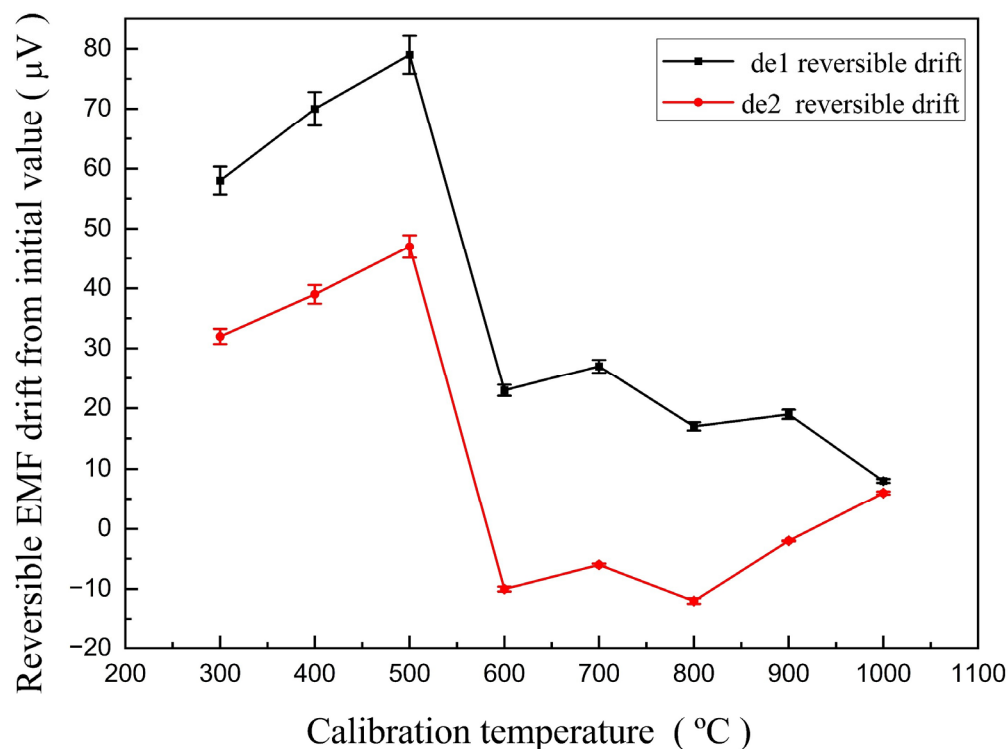


Figure 8. The reversible EMF drifts of the two thermocouple alloys after aging for 168 h at 500 °C. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

When thermocouples are aged below 600 °C, the reversible EMF drift is mainly caused by short-range ordering in the positive KP alloy and the magnitude of EMF drift is related to the number of NiCr lattices undergoing ordering transformation [26,27]. The reversible EMF drift of the de1 thermocouple was greater than that of the de2 thermocouple. This observed disparity could potentially be ascribed to their differing Cr contents (10.5 wt% Cr for de1-KP, 9.7 wt% Cr for de2-KP), which might lead to minor variations in the quantity of ordered lattices formed during aging. To further evaluate the effect of order–disorder transformation, heating–cooling calibration was performed on unaged de1 and de2 thermocouples over the temperature range of 300 °C to 550 °C.

Figure 9 presents the deviation curves ($\Delta E = E - E_{std}$) from the standard EMF during heating–cooling calibration tests for the de1 and de2 thermocouples. Both thermocouples satisfied the ASTM E230 Class I accuracy requirement of 0.4%t during heating and cooling. However, the EMF values during cooling were consistently higher than during heating, producing hysteresis loops. The maximum EMF difference between heating and cooling was 46 μ V (1.15 °C) for the de1 thermocouple at 300 °C, and 37 μ V (0.68 °C) for the de2 thermocouple at 400 °C, as reported in Table 6.

Table 6. The EMF hysteresis of the de1 and de2 thermocouples during the heating and cooling process.

Calibration Temperature, °C	ΔE (Mean $\pm 1\sigma$, μ V)	
	de1	de2
300	46 (1.41)	36 (1.41)
350	31 (2.12)	21 (0.71)
400	41 (2.83)	37 (1.41)
450	24 (2.83)	21(1.41)
500	13 (2.42)	9 (2.12)

Note: ΔE denotes the EMF hysteresis value calculated as the difference between EMF values measured at the same temperature during heating and cooling ramps. Each value was obtained from repeated tests on two identical thermocouple specimens; the value in parentheses represents the one standard deviation (1σ) measurement uncertainty of parallel samples.

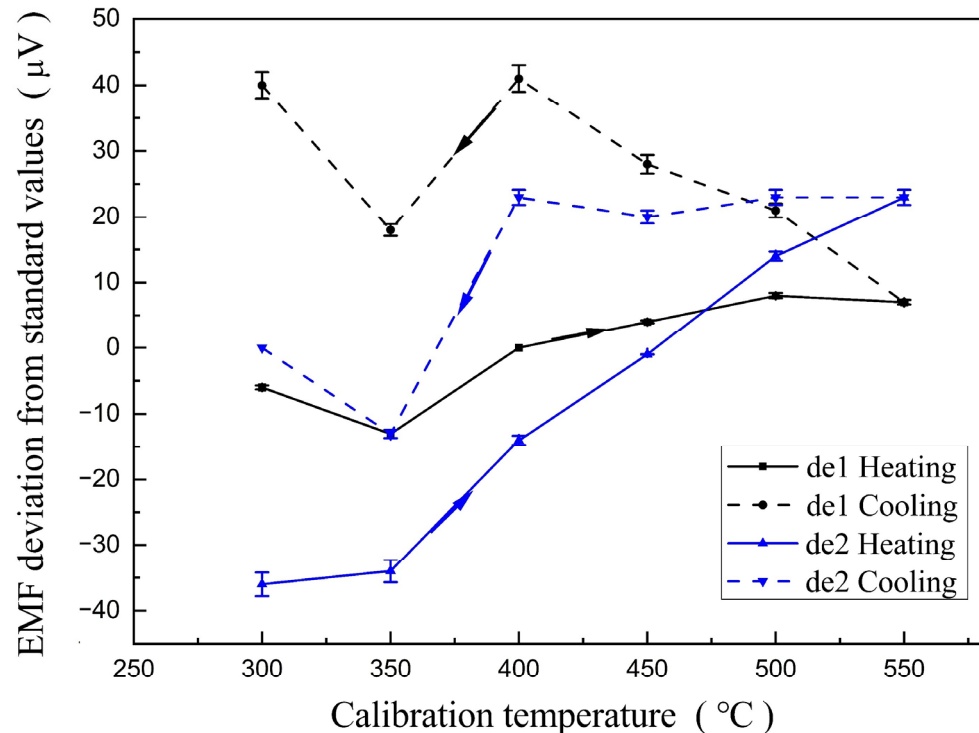


Figure 9. The calibration characteristics of the de1 and de2 thermocouples during the heating and cooling process. All plotted data are averaged results calculated from two parallel thermocouple specimens. The error bars represent one standard deviation (1σ) of these parallel samples.

This behavior is likely associated with the disorder–order transformation of NiCr atoms in the positive KP alloy during cooling. At calibration points from 300 °C to 500 °C, the EMF hysteresis of the de1 thermocouple was consistently greater than that of de2. This trend appears consistent with the reversible EMF changes observed after aging at 500 °C (Figure 8). Compared with de2-KP (9.7 wt% Cr), de1-KP contained a higher Cr concentration (10.5 wt%), which tends to facilitate the formation of abundant Ni–Cr ordered domains. However, no ordering-sensitive characterization has been performed to directly identify Ni–Cr ordered domains in the alloy matrix. It is tentatively hypothesized that the slightly higher Cr content in de1-KP may promote a greater extent of Ni–Cr short-range ordering, thereby enlarging the reversible EMF drift and thermal hysteresis. This ordering mechanism remains an unvalidated hypothesis pending targeted microstructural testing.

Appropriate heat treatment can generate an optimal number of ordered Ni–Cr lattices in the positive KP alloy of K-type thermocouples, which greatly diminishes the EMF hysteresis between heating and cooling calibration [27]. This treatment effectively suppresses reversible EMF drift during thermal aging.

In this study, the de1 and de2 thermocouples were stabilized at 570 °C for 2 h, followed by furnace cooling or water quenching. Their EMF hysteresis characteristics were then evaluated after the stabilization treatments.

The de1 and de2 thermocouples were placed within a tube furnace with an insertion depth of 400 mm. Subsequently, the furnace was heated to 570 °C at a ramp rate of 10 °C/min, and the specimens were maintained at this temperature for 2 h. Following the heat holding period, two distinct cooling procedures were employed.

- (1) Furnace cooling: The tube furnace power supply was cut off, and specimens were cooled inside the furnace at an average cooling rate of approximately 3 °C/min until the temperature dropped to 100 °C, followed by air cooling to ambient temperature.
- (2) Water quenching: Specimens were rapidly withdrawn from the furnace and fully submerged in room-temperature deionized water for rapid quenching.

Table 7 summarizes the heating–cooling EMF hysteresis after stabilization treatments. The hysteresis of both alloys was greatly reduced. For the furnace-cooled de1 thermocouple, the maximum hysteresis fell to 18 µV (~0.45 °C), while at 350 °C (~normal operating temperature of pressurized water reactor cores), the hysteresis was only 8 µV (~0.2 °C). Under identical stabilization procedures, de1 consistently exhibited smaller EMF differences between heating and cooling stages than de2.

Table 7. The EMF hysteresis differences for the de1 and de2 thermocouples during heating–cooling calibration after different stabilization treatments.

Calibration Temperature (°C)	ΔE (Mean $\pm$ 1 σ , µV)			
	Furnace-Cooled de1	Water-Quenched de1	Furnace-Cooled de2	Water-Quenched de2
300	18 (1.41)	22 (2.83)	27 (2.83)	23 (3.54)
350	8 (2.83)	14 (1.41)	13 (0.71)	10 (2.83)
400	4 (2.12)	24 (0.71)	12 (3.54)	20 (3.54)
450	1 (1.41)	7 (1.41)	4 (2.83)	6 (2.12)
500	3 (1.41)	4 (0.71)	1 (1.41)	0 (2.12)

Although the EMF stability of the de1 thermocouple alloy, which was affected by ordering transformation, was inferior to that of the de2 thermocouple alloy, an appropriate stabilization treatment could effectively reduce the reversible EMF drift during aging. For wires of identical composition, different cooling rates after stabilization produce substantial differences in heating–cooling EMF hysteresis; therefore, the cooling method is also a critical factor in the stabilization process. For wires with different compositions, the effect of the cooling rate after stabilization should be considered carefully.

4. Conclusions

This study systematically evaluated the EMF stability of two commercial K-type MIMS thermocouples (de1 and de2) under a comparative severe accelerated aging condition at an elevated test temperature of 500 °C with a 168 h holding time, and offers potential optimized fabrication strategies for improving the high-temperature EMF stability of nuclear-grade thermocouples.

After aging, both the de1 and de2 thermocouples exhibited substantial positive EMF drifts, which peaked at 400 °C. The de2 thermocouple showed a smaller irreversible drift. Fabrication using pre-oxidized thermoelement wires reduced the overall irreversible EMF drift compared with bright-surface wires of the same de2 alloy.

Under identical aging treatment, de1 thermocouples exhibited larger reversible EMF drift and wider heating–cooling hysteresis loops relative to de2 thermocouples. Stabilization treatment at 570 °C for 2 h followed by furnace cooling effectively narrowed the EMF hysteresis range for both alloy systems, demonstrating that post-processing

thermal schedules can mitigate reversible measurement deviation during temperature cycling.

It is worth noting that this study has certain limitations. The drift statistics are derived from only two parallel specimens for each test condition, which restricts the statistical robustness of the measured drift values. The 500 °C/168 h scheme is merely a laboratory comparative severe aging setup using an elevated test temperature and cannot be applied to quantitatively assess thermocouple degradation under real reactor transient thermal loads. Moreover, only thermal aging under atmospheric conditions is considered, while irradiation, high pressure and coolant chemistry effects relevant to practical PWR operation are not included.

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