



HOKKAIDO UNIVERSITY

Title	Research and development of diffusion bonding between high entropy alloys and stainless steel for nuclear application
Author(s)	SUN, Haotian
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第16115号
Issue Date	2024-09-25
DOI	https://doi.org/10.14943/doctoral.k16115
Doc URL	https://hdl.handle.net/2115/95930
Type	doctoral thesis
File Information	SUN_Haotian.pdf



Research and Development of Diffusion Bonding between High Entropy Alloys and Stainless Steel for Nuclear Application



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August 2024

Acknowledgements

Here, I would like to express my heartfelt gratitude to everyone who supported me during my long journey of study. Without their help, I could not have earned my Ph.D. and grown into a young researcher.

Firstly, I want to extend my sincere thanks to my supervisor, Professor Naoyuki Hashimoto. In 2021, I joined Prof. Hashimoto's group as a doctoral student. I am grateful for the opportunity to delve into high entropy alloys. I am especially thankful for the regular individual meetings and manuscript preparation guidance, as well as the numerous conference opportunities provided. This academic training significantly broadened my research perspectives and equipped me with the invaluable ability to think critically and solve problems independently—an indispensable asset in my academic journey.

Secondly, I would like to express my gratitude to my defense committee members, particularly the examiners: Professor Seiji Miura, Professor Munekazu Ohno, and Professor Shigehito Isobe. Their encouraging and constructive feedback, along with the invaluable discussions and advice, were instrumental in shaping my work.

I would also like to express my gratitude to the members of our research group. I extend my heartfelt appreciation to Professor Hiroshi Oka from the irradiation group for his enthusiastic discussions and unwavering technical support whenever I needed it. Additionally, special thanks to Professor Shigehito Isobe for his timely advice and encouragement. I am also grateful to our assistant, Ms. Kobayashi, for her efficient support in our daily routines, which significantly contributed to creating better research and living environment for all of us. I want to acknowledge our fellow group students and

alumni (OBs). I have learned immensely from each of you, gaining valuable insights into experimental techniques and ways of thinking. I will always cherish the kindness you showed me and the wonderful times we spent together.

Furthermore, I would like to extend my heartfelt thanks to all the professors and technical staff who have supported me throughout my studies. I am grateful for the exceptional technical support provided by Dr. Yongming Wang, Mr. Atsuki Sawa, Mr. Yu Uchida, and Ms. Yurika Yamanouchi from the Laboratory of Nano-Micro Material Analysis, and Ms. Yuko Mori from the Research Institute for Electronic Science. Their assistance has been instrumental in my research journey.

I also want to express my appreciation for the experiment support from Professor Shuai Wang at Southern University of Science and Technology and Professor Kenichi Ikeda at laboratory of materials strength modeling. Their expertise and guidance have significantly contributed to the success of my research endeavors. Furthermore, I extend my gratitude to the project foundations within our group and acknowledge the support from the China Scholarship Council, which enabled my overseas studies.

Lastly, I want to express my deepest gratitude to my parents for their unwavering support and care over the past three decades. I am determined to become stronger and make you proud of me. I also want to express my heartfelt gratitude to my wonderful and supportive friends: Peng Bi, Yukun Kong, Qingyan Xue, and Tian Liu. Thank you for your kindness and support in our daily lives, and for being there for me during times of difficulty. The moments we shared together during my doctoral studies have been truly joyful and memorable.

Abstract

To meet rapidly increasing global energy needs, safe, reliable, and economic operation of advanced fission and eventually fusion power plants is generally considered an important element of a lower carbon energy future. In the application of nuclear power plant and other fields, structural parts are mostly composed of multiple parts rather than a single part. Therefore, joining technology, as a processing method that can assemble parts into an integral structure, plays a vital role in promoting the engineering application of high entropy alloys (HEAs). However, compared with the studies on the design and performance of HEAs, the research on the joining of HEAs is relatively insufficient. Thus, suitable joining technologies for HEAs are needed to enlarge the application range for HEAs. Diffusion bonding has been applied in the field of nuclear power, such as first wall, which are manufactured with steel due to its outstanding oxidation resistance, mechanical properties and corrosion resistance at high temperatures. As a new material, HEAs also might be used in high temperature parts in the field of nuclear power. Therefore, it is necessary to investigate the diffusion bonding of HEAs to steels for further promoting the application of HEAs in nuclear power plant.

Firstly, equiatomic CoCrNi-based concentrated solid solution alloys (CSSAs) system (CoCrFeNiMn, CoCrFeNi, and CoCrNi) were successfully joined to 316 stainless steels by SPS diffusion bonding, and the effect of bonding temperature and concentration on diffusion behavior and tensile property of bonded joints were investigated. The tensile strength of the CSSAs/316SS joints were gradually increased with increasing bonding temperature. In addition, the tensile strength of the joints bonded at $0.8T_m$ were all exceeded 80% of that in 316SS. Meanwhile, the bonding at $0.8T_m$ seemed to have

sufficient diffusion and grain growth at the interface, resulted in the disappearance of voids and the increase in strength of joint. Furthermore, it suggests that the continuous FCC solid solution structure was generated in the diffusion zone, which was beneficial to the increase of tensile property in joints.

Secondly, this study explored the diffusion bonding of $\text{Cr}_{0.8}\text{FeMnNi}$ medium entropy alloy to 316SS with and without a Ni interlayer using spark plasma sintering. Direct bonding led to the formation of Cr_2O_3 and Mn_3O_4 oxides at the interface, resulting in stress concentration and reduced tensile strength. However, the introduction of a Ni interlayer effectively reduced oxide size and improved mechanical properties by accelerating diffusion and relieving stress concentrations. Optimal joints were achieved at $820\text{ }^\circ\text{C}$ / 60 min / 25 MPa, producing joints with tensile strength and elongation comparable to 316SS. Furthermore, diffusion behavior, growth kinetics of diffusion layers, and activation energy of diffusion in various atoms and layers were analyzed. The activation energy of each element in the joints with Ni interlayer was decreased compared to direct diffusion bonding.

Thirdly, this study focuses on analyzing the effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints. The joints cold-worked with different deformation rate and 316 stainless steels had similar grain sizes, but the dislocation density increased with the increase in deformation rate. In addition, Mn-O oxides and Cr-Mn-O oxides were recognized at the interface. Through line scanning of the interface, it was found that the diffusion distance of atoms through the joint increased with the increase in deformation rate, which probably due to the increase in dislocations as diffusion channels. As the secondary deformation rate increased from 0% to 20%, the diffusion distance through the joint increased from $4.796\text{ }\mu\text{m}$ to $8.309\text{ }\mu\text{m}$.

This result could suggest that the diffusion ability of atoms within the crystal structure may be enhanced in case a significant dislocation density was present in the HEA base metal, resulting in increased diffusion distances and higher tensile strength in diffusion bonded joints.

The HEA/316SS diffusion bonded joints shows good joining property, which could be candidate materials for advanced reactors.

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Chapter 1 Introduction

1.1 Materials and joining for advanced nuclear energy system

1.1.1 Materials for advanced nuclear energy system

The proportion of nuclear energy in global energy consumption has been increasing annually, evolving into a carbon-free alternative to fossil fuels [1]. The development of higher nuclear safety standards and advanced nuclear materials has become a significant challenge facing the nuclear industry. Nuclear materials, as the foundation of nuclear industry development, are also receiving increasing attention. Developing new nuclear power technologies is essential for promoting energy transition, environmental protection, enhancing energy supply security, and fostering economic development. With continuous technological advancements and widespread adoption, new nuclear power technologies will play an increasingly crucial role in contributing to sustainable development of human society.

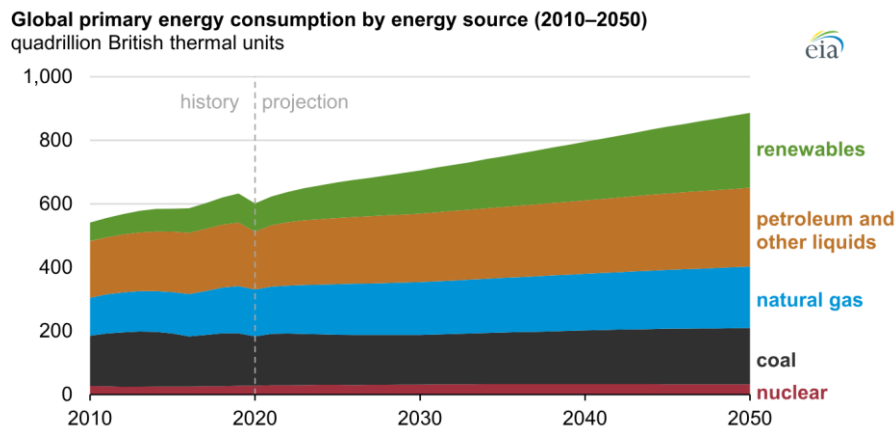


Fig. 1.1 Global primary energy consumption by energy source (2010-2050) [1].

Nuclear energy plays a crucial role in meeting global energy demands while reducing carbon emissions. However, traditional fission reactors, which currently dominate nuclear power generation, face challenges related to radioactive waste disposal, cost, and safety. To address these issues and advance nuclear energy technologies, significant efforts have been directed towards developing advanced

reactor concepts known as Generation IV (Gen IV) reactors (Fig. 1.2). Gen IV reactors offer the potential for improved efficiency, enhanced safety features, and reduced environmental impact compared to earlier reactor designs [2]. These next-generation reactors aim to optimize resource utilization, minimize waste production, and enhance overall safety. Key advancements in Gen IV reactor designs include innovative cooling systems, advanced fuel cycles, and enhanced proliferation resistance. Despite the promising attributes of Gen IV reactors, their deployment requires novel materials capable of withstanding more aggressive operational conditions and diverse coolant systems. The development of such advanced materials is essential to ensure the long-term viability and success of advanced nuclear reactor technologies. In parallel, nuclear fusion, the process that powers the sun and stars, holds tremendous promise as a sustainable and virtually limitless source of energy. As shown in Fig. 1.3, Fusion reactors, unlike fission reactors, generate minimal long-lived radioactive waste and pose inherently lower safety risks [3]. However, fusion also presents formidable materials challenges, such as extreme heat and neutron fluxes, necessitating the development of advanced materials capable of withstanding these conditions. High entropy alloys (HEAs), have emerged as a promising class of materials for nuclear applications. HEAs possess unique properties, including high entropy, sluggish diffusion, and cocktail effects, which can be tailored to meet the demanding requirements of both fission and fusion reactors. Therefore, it is necessary to design and study HEAs for nuclear power applications.

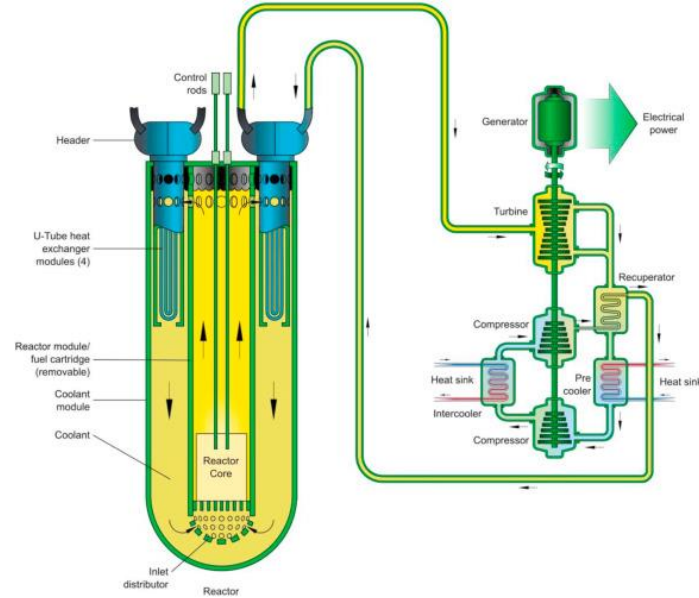


Fig. 1.2 Generation-IV reactors and nuclear hydrogen production.

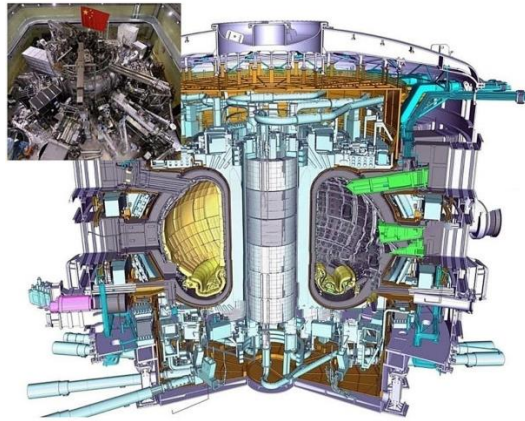


Fig. 1.3 Schematic diagram of the International Thermonuclear Experimental Reactor device [3].

1.1.2 Joining technology for advanced nuclear energy system

Joining technologies are fundamental technology used extensively throughout nuclear power plants, serving vital functions in reactor construction, piping systems, fuel assemblies, and auxiliary equipment. These joining play a crucial role in maintaining structural integrity and ensuring the safe and efficient operation of nuclear facilities. In nuclear power plants, joining technologies face unique challenges due to

the demanding operational environment characterized by high temperatures, varying pressure conditions, and exposure to radiation. The performance and reliability of joining are critical considerations to prevent structural failures and maintain operational safety over the plant's lifecycle. The application of joining technologies in nuclear power plants requires adherence to strict standards and procedures for material selection, joining techniques, quality control, and inspection. Specialized joining methods and advanced materials are often employed to meet the stringent requirements of nuclear applications and ensure joint integrity under extreme conditions.

The importance of joining technologies in nuclear power plants cannot be overstated, as they contribute directly to the overall safety, efficiency, and longevity of nuclear facilities. Understanding the role of joining technologies and the challenges associated with their application in nuclear environments is essential for advancing nuclear energy technologies and ensuring the continued success of nuclear power as a clean and sustainable energy source. There are a large number of dissimilar metal joints in the reactor. If the dissimilar materials could be reliably joined by suitable method, the respective advantages of both metals could be exploited without major changes to existing reactor design criteria. Diffusion bonding, which is a kind of solid-state joining technology with the advantages of small deformation and excellent welding quality, has been widely used for dissimilar metals joining. In nuclear power plants, diffusion bonding can be used to join the fuel cladding and structural components of nuclear reactors. Besides, stainless steel exhibited good mechanical properties and excellent weldability. Typically, as shown in Fig. 1.4, it is joined with other materials. In pressurized water reactors, the diffusion bonding between high entropy alloy and SS is a promising method for joining safe-end piping to the nozzle of the reactor pressure vessel [4].

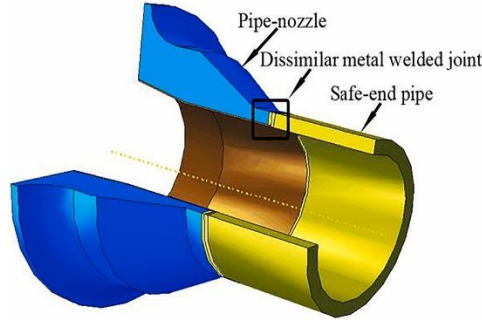


Fig. 1.4 The dissimilar metal weld joints structure for joining the pipe-nozzle of a reactor pressure vessel to safe-end pipe [4].

1.2 Research and development of high entropy alloys

1.2.1 Overview

In 2004, Professor Cantor from the University of Cambridge and Professor Ye from National Tsing Hua University in Taiwan separately reported research on multi-principal element alloys and HEAs [5, 6]. Their work introduced a groundbreaking concept in material design, where multiple principal elements form simple solid solution alloys, overcoming the traditional challenge of balancing strength and ductility in metals [7]. Over the past decade, research related to HEAs has evolved into a new field that is synthesizable, processable, and applicable, offering vast potential for development. Currently, the definition of HEAs can be known by entropy-based definition. Entropy, as a thermodynamic state function, represents the "intrinsic chaos" of a system [8]. According to Boltzmann's statistical thermodynamics, the quantitative relationship between entropy and system randomness can be expressed as:

$$\Delta S_{\text{conf}} = k \ln w \quad (1.1)$$

where w is the number of energy states that can be exchanged or mixed in the actual system, and k is the Boltzmann constant. The total mixing entropy can be divided into four categories: configurational entropy $\Delta S_{\text{mix}}^{\text{conf}}$, vibrational entropy $\Delta S_{\text{mix}}^{\text{vib}}$, magnetic

dipole entropy $\Delta S_{\text{mix}}^{\text{mag}}$, and electronic entropy $\Delta S_{\text{mix}}^{\text{elec}}$, with the relationship:

$$\Delta S_{\text{mix}} = \Delta S_{\text{mix}}^{\text{conf}} + \Delta S_{\text{mix}}^{\text{vib}} + \Delta S_{\text{mix}}^{\text{elec}} + \Delta S_{\text{mix}}^{\text{mag}} \quad (1.2)$$

Since configurational entropy dominates the total mixing entropy, configurational entropy is typically used to represent mixing entropy, avoiding complex calculations involving the other three entropies. For a solid solution composed of n component elements, assuming the molar fraction of its i -th component is X_i , the ideal molar configurational entropy is:

$$\Delta S_{\text{conf}} = -R \sum_{i=1}^n X_i \ln X_i \quad (1.3)$$

When an equiatomic alloy is in a liquid or ordered solid solution state, its molar configurational entropy can be calculated as:

$$\Delta S_{\text{conf}} = R \ln n \quad (1.4)$$

Therefore, regardless of whether it is single-phase or multiphase, the disordered solid solution configurational entropy formed by high entropy alloys at room temperature exceeds 1.5. This can be expressed by the formula:

$$\Delta S_{\text{conf}} > 1.5R \quad (1.5)$$

In addition, HEAs exhibit distinct effects stemming from Crystallographic Lattice Distortion Effect, Thermodynamic High Entropy Effect, sluggish diffusion kinetics, and a cocktail of elemental interactions that collectively influence their properties and performance.

(1) Thermodynamic High Entropy Effect:

This effect refers to the high configurational entropy exhibited by high entropy alloys due to their composition of multiple principal elements in nearly equiatomic proportions [9]. The high entropy promotes the stabilization of solid solution phases, contributing to the alloy's enhanced thermal stability and resistance to phase

transformations.

(2) Crystallographic Lattice Distortion Effect:

High entropy alloys experience significant crystallographic lattice distortion, primarily caused by the mismatch in atomic sizes and chemical properties of the alloying elements [10]. This lattice distortion influences the mechanical properties of the alloy, including strength, hardness, and ductility.

(3) Kinetic Sluggish Diffusion Effect:

The sluggish diffusion kinetics observed in high entropy alloys is attributed to the presence of multiple elements that impede atomic diffusion within the alloy's structure [11]. This effect promotes the formation of a stable solid solution phase and inhibits the segregation of alloying elements, contributing to the alloy's excellent phase stability and microstructural homogeneity.

(4) Performance Cocktail Effect:

The "cocktail effect" describes the collective impact of multiple alloying elements on the overall performance of HEAs. The diverse interactions among these elements result in tailored material properties, such as high strength, corrosion resistance, and thermal stability. This effect allows for the design of advanced alloys with customized performance characteristics suitable for specific engineering applications.

In summary, these four effects highlight the multifaceted nature of HEAs and underscore their potential for addressing challenges and advancing materials science in various industries.

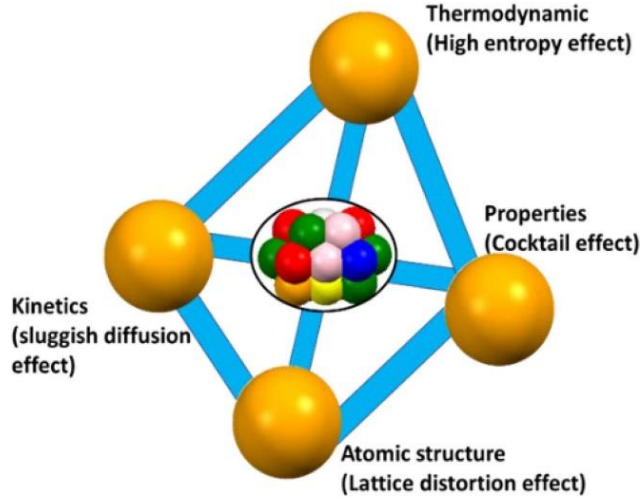


Fig. 1.5 Four core effects of HEAs.

1.2.2 Joining performance of HEAs

Studying the joining technology of HEAs is an important foundation for further expanding their potential application value. Currently, researchers have primarily investigated the connectivity performance of HEAs from three aspects: fusion welding, solid-state welding, and brazing.

Laser beam welding is a welding method that utilizes a laser beam as a concentrated heat source to melt and join workpieces, forming narrow and deep weld seams. Kashaev et al. [12] studied the laser welding of CoCrFeNiMn HEA. As shown in Figure 1.6(b), the microhardness in the weld zone increased to 208 HV compared to the base metal. Nam et al. [13] also found that the hardness of the weld zone and heat-affected zone in laser-welded joints of equiatomic $\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}$ increased compared to the base metal, with rolled joints exhibiting stronger work hardening performance as depicted in Figure 1.6(c). Specifically, the hardness increases in rolled HEA joints was limited, while that in cast joints exceeded 30% as shown in Figure 1.6(d). Additionally, Sokkalingam et al. [14] used tungsten inert gas (TIG) welding to join $\text{Al}_{0.5}\text{CoCrFeNi}$ HEAs, and the joint microstructure, hardness, and engineering

stress-strain curves are shown in Figure 1.7. The research indicated that the grain size significantly refined from 60 μm in the base metal to 8-12 μm in the fusion zone. However, compared to the base metal, the tensile strength and elongation decreased by approximately 6.4% and 16.5%, respectively.

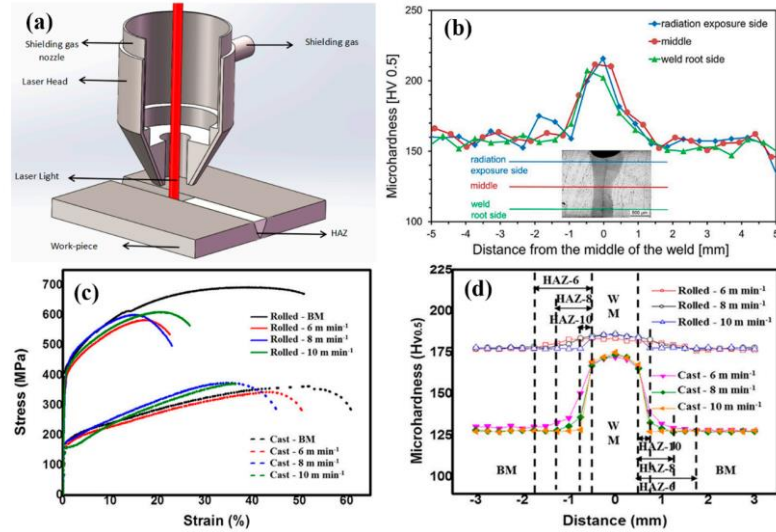


Fig. 1.6 Mechanical properties in laser welded joints for HEAs of (a) schematic diagram showing the laser welding process, (b) microhardness profile of a butt-joint, (c) stress-strain curves of BM at various welding velocities and (d) hardness distribution in the transverse welds of HEAs.

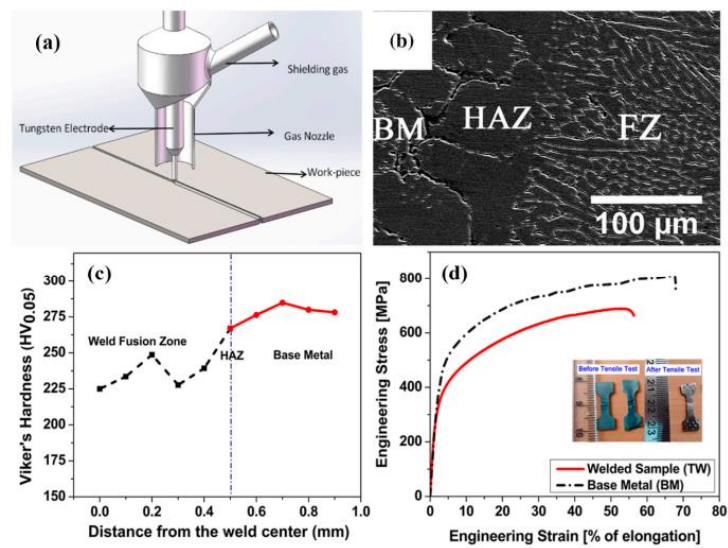


Fig. 1.7 Structure and hardness of the welded zones and engineering stress-strain curves of the welded samples of $\text{Al}_{0.5}\text{CoCrFeNi}$ high entropy alloy of (a) schematic of gas tungsten arc welding process, (b) scanning electron micrographs of base metal-heat affected zone-fusion zone interfaces, (c) microhardness profile on the surface of the welded sample and (d) engineering stress-engineering strain curve for the base metal and welded sample.

Friction welding, known for its high joint quality, efficiency in forming, and energy-saving advantages, finds widespread applications in aerospace, nuclear industries, automotive manufacturing, and other fields. Current research on friction welding of HEAs primarily focuses on friction stir welding. Jo et al. [15] employed friction stir welding to join CrMnFeCoNi and compared it with laser-welded joints. The study demonstrated that the friction stir welded samples exhibited higher tensile strength and elongation. Due to smaller grain sizes, the joint hardness surpassed that of the base metal. Zhu et al. [16] utilized friction stir welding to join $\text{CoCrFeNiAl}_{0.3}$ high entropy alloys and observed defect-free joints post-welding. As shown in Figure 1.8(a), under recrystallization, grain refinement occurred in the weld nugget zone, exhibiting the highest hardness. To further investigate the microstructural evolution and mechanical properties of friction stir welded high entropy alloys, Zhu et al. [17] applied friction stir welding to $\text{Co}_{16}\text{Fe}_{28}\text{Ni}_{28}\text{Cr}_{28}$ HEAs. The results showed that the welded joint retained an FCC crystal structure and achieved 70% of the elongation of the base metal. Tungsten and chromium-rich white bands appeared in the weld nugget zone due to tool wear during the welding process. Additionally, Li et al. [18] obtained high-quality joints of $\text{AlCoCrFeNi}_{2.1}$ eutectic high entropy alloys using rotary friction welding, as depicted in Figure 1.8(b). Although rotary friction welding and friction stir welding share the common use of friction heat and plastic deformation heat as welding

heat sources, rotary friction welding effectively avoids tool wear as it does not require a stirring tool. At a friction pressure of 200 MPa, the joint exhibited tensile strength and elongation of 913.5 MPa and 12.1%, respectively, surpassing that of the base metal. The joint fractured in the base metal region far from the weld seam center. However, joints fabricated using friction welding methods experience significant deformation, limiting their application in high-precision welding fields.

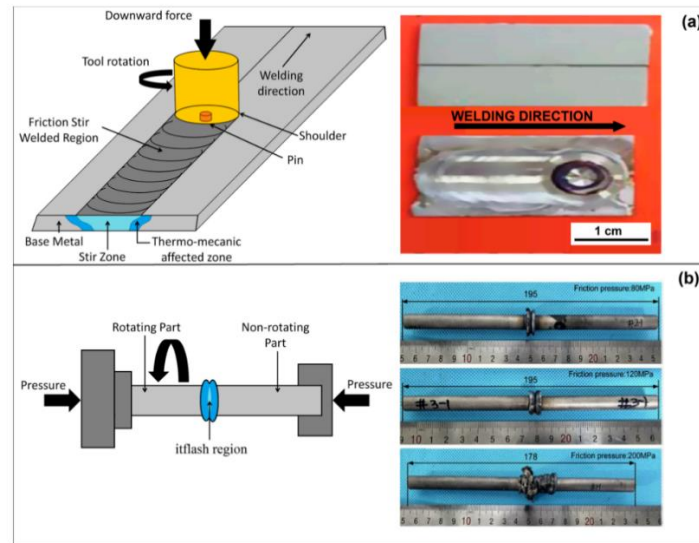


Fig. 1.8 Schematic illustration and produced specimens of (a) friction stir welding and (b) rotary friction welding.

Diffusion bonding, known for its high joint quality, minimal post-weld deformation, and broad applicability, is particularly suitable for joining dissimilar metals, heat-resistant alloys, ceramics, intermetallic compounds, and composite materials. It is especially advantageous for materials that are difficult to weld using fusion welding methods. Current research on diffusion bonding of HEAs primarily focuses on joining dissimilar materials, with limited studies on diffusion bonding of homogeneous HEAs. In fact, studying diffusion bonding of homogeneous HEAs plays a crucial role in understanding diffusion bonding mechanisms and interfacial diffusion behaviors. Zhang et al. [19] investigated vacuum diffusion bonding of

Co_{28.5}Cr_{21.5}Fe₂₀Ni₂₆Mo₄ HEA. At 1050 °C, the joint exhibited a maximum tensile strength of 597.13 MPa. They observed the formation of nano-scale Cr₃O₄ metal oxide film at the joint, which lowered the joint performance. However, with increasing welding temperature, the Cr₃O₄ metal oxide film gradually reduced and eventually fractured and disappeared at 1050 °C due to oxygen diffusion into the substrate. In nuclear power applications, diffusion bonding method ensures strong and reliable bonds critical for the safety and performance of nuclear power systems.

1.2.3 Joining between HEAs and stainless steel

The joining research between HEAs and stainless steels dissimilar metals has also been reported. Sokkalingam et al. [20] fabricated the dissimilar weld joint of Al_{0.1}CoCrFeNi HEA and 304 stainless steel using conventional tungsten inert gas welding, and the tensile test results indicated that the dissimilar weld joint showed significantly higher tensile strength than HEA base metal. Oliveira et al. [21] studied the laser welding of CoCrFeMnNi HEA to 316 stainless steel and significantly improved the joint fracture strain from 5% to 10 % by changing the base material condition from cold-rolled to annealed. Do et al. [22] used friction stir welding to join CoCrFeMnNi HEA and 304 stainless steel to avoid the occurrence of coarse grains and improve mechanical properties. Due to the remarkable martensitic transformation induced plasticity, it was found that the tensile properties of the joint at low temperature were better than those at room temperature. Although HEAs/stainless steels dissimilar metals joint could be obtained by these methods such as laser beam welding, the large deformation after joining limited the wide application of joints. Therefore, vacuum diffusion bonding method with low deformation and high precision should also be noticed and investigated.

Vacuum diffusion bonding method is quite suitable for joining dissimilar metals and has been widely used in the manufacture of reactor fuel elements, honeycomb panels, various blades and electronic components [23-24]. Samiuddin et al. [25] investigated the diffusion bonding of CoCrNi medium entropy alloy to 304 stainless steel and found that the bonding interface was almost free from IMCs and formed a solid solution, resulting in the enhancement of the joint's shear strength at the bonding temperature of 1075 °C. However, the traditional diffusion bonding still has the following two disadvantages: (I) Low efficiency. The diffusion bonding process usually takes more than ten hours to make one joint. (II) The sluggish diffusion effect of HEAs may affect the bonding quality. The sluggish diffusion effect reduces the diffusion distance of the joint, resulting in insufficient diffusion and decreased mechanical property. To overcome these two disadvantages, we first proposed the spark plasma sintering (SPS) diffusion bonding between HEAs and stainless steel. Because this method integrates plasma activation, thermal pressure, current and electric diffusion, it has the advantages of fast temperature rise and increased diffusion distance in joints [26].

In summary, researching diffusion bonding between HEAs and stainless steel holds significant importance for the future application of HEAs in the nuclear power sector. Evaluating the microstructure and mechanical properties of these joints and understanding the bonding mechanisms will contribute to improved alloy design and material reliability for practical implementation in next-generation nuclear power plants.

1.3 Objective and strategy

In order to meet rapidly increasing global energy needs, safe, reliable, and economic operation of advanced fission and eventually fusion power plants is generally considered an important element of a lower carbon energy future. One of the key challenges is how structural materials that are closest to the atomic fission and fusion reactions can retain the required performance under the associated extreme conditions that will involve higher temperatures, higher pressure, a higher irradiation dose and a more corrosive environment for longer periods than those experienced in current Gen II or Gen III fission reactors. There are a large number of critical requirements for reactor materials including good dimensional stability, favourable mechanical properties, acceptable resistance to radiation damage and high degree of chemical compatibility with the potentially corrosive environment. Fortunately, recent findings on the enhanced mechanical properties and radiation resistance in concentrated solid solution alloys, including HEAs, have attracted increasing attention from the nuclear materials community.

In the application of nuclear power plant and other fields, structural parts are mostly composed of multiple parts rather than a single part. Therefore, joining technology, as a processing method that can assemble parts into an integral structure, plays a vital role in promoting the engineering application of HEAs. However, compared with the studies on the design and performance of HEAs, the research on the joining of HEAs is relatively insufficient. Thus, suitable joining technologies for HEAs are needed to enlarge the application range for HEAs. Diffusion bonding has been applied in the field of nuclear power, such as first wall, which are manufactured with steel due to its outstanding oxidation resistance, mechanical properties and corrosion

resistance at high temperatures. As a new material, HEAs also might be used in high temperature parts in the field of nuclear power. Therefore, it is necessary to investigate the diffusion bonding of HEAs to steels for further promoting the application of HEAs in nuclear power plant.

1.4 Dissertation structure

In chapter 1, the materials and joining challenges and advantages of high entropy alloys for advanced nuclear energy system was introduced. Moreover, the background and objectives of this study were illustrated.

In chapter 2, fundamental theories of diffusion bonding were briefly introduced, and technical methods used in this study were identified.

In chapter 3, equiatomic CoCrNi-based concentrated solid solution alloys (CSSAs) system (CoCrFeNiMn, CoCrFeNi, and CoCrNi) were successfully joined to 316 stainless steels by SPS diffusion bonding, and the effect of bonding temperature and concentration on diffusion behavior and tensile property of bonded joints were investigated. The tensile strength of the CSSAs/316SS joints were gradually increased with increasing bonding temperature. In addition, the tensile strength of the joints bonded at $0.8T_m$ were all exceeded 80% of that in 316SS. Meanwhile, the bonding at $0.8T_m$ seemed to have sufficient diffusion and grain growth at the interface, resulted in the disappearance of voids and the increase in strength of joint. The tensile strength and elongation of diffusion bonded CSSAs/316SS joints were increased compared to laser beam welded joints.

In chapter 4, the diffusion bonding of $\text{Cr}_{0.8}\text{FeMnNi}$ medium entropy alloy to 316SS with and without a Ni interlayer using spark plasma sintering was studied. Direct bonding led to the formation of Cr_2O_3 and Mn_3O_4 oxides at the interface, resulting in stress concentration and reduced tensile strength. However, the introduction of a Ni interlayer effectively reduced oxide size and improved mechanical properties by accelerating diffusion and relieving stress concentrations. Optimal joints were achieved at $820\text{ }^\circ\text{C}$ / 60 min / 25 MPa, producing joints with tensile strength and elongation

comparable to 316SS. Furthermore, diffusion behavior, growth kinetics of diffusion layers, and activation energy of diffusion in various atoms and layers were analyzed. The activation energy of each element in the joints with Ni interlayer was decreased compared to direct diffusion bonding. This research highlights the significance of interlayer in enhancing diffusion bonding outcomes for nuclear power applications.

In chapter 5, we investigated the effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints. Dislocations can provide "channels" for pipe diffusion, making it easier for diffused atoms to move within the crystal lattice during diffusion bonding process. The diffusion bonding of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA to 316SS was conducted in a spark plasma sintering machine. The bonding temperatures of 900 °C were used. The result could suggest that the diffusion ability of atoms within the crystal structure may be enhanced in case a significant dislocation density was present in the HEA base metal, resulting in increased diffusion distances in diffusion bonded joints.

In chapter 6, the main conclusions and most relevant findings of this study are summarized.

Chapter 2 Fundamentals and Methodology

2.1 Diffusion bonding theory

The definition of diffusion bonding is the occurrence of atomic-scale mutual diffusion between material contact surfaces under certain pressure and temperature conditions, forming a new diffusion layer at the interface, thereby achieving high-quality joint welding technology. The solid-state diffusion theory serves as the theoretical foundation for diffusion bonding. It is an important method in the field of welding, opening up new paths for connecting metals, ceramics, and dissimilar materials.

The diffusion bonding process can be roughly divided into three stages, as shown in Figure 2.1. The first stage is the physical contact stage, where due to significant surface roughness, materials cannot completely conform, resulting in micro-protrusions. Under high temperature and pressure, the contact surfaces begin to yield and creep, causing localized plastic deformation [27]. With continued pressure, extensive interfacial bonding occurs. However, some voids still remain on the contact surface. In the second stage, there is interface migration and atomic diffusion. At this stage, atoms further diffuse under high temperature, and grain boundaries migrate away from the initial interface. The remaining voids from the first stage gradually close, forming a transition layer. In the third stage, atoms in the transition layer diffuse longitudinally towards the contact surface. During this stage, voids essentially disappear, and atomic diffusion reaches an equilibrium state.

It's important to note that these three stages do not strictly occur sequentially but instead alternate and continuously cycle, ultimately forming high-quality diffusion bonding joints.

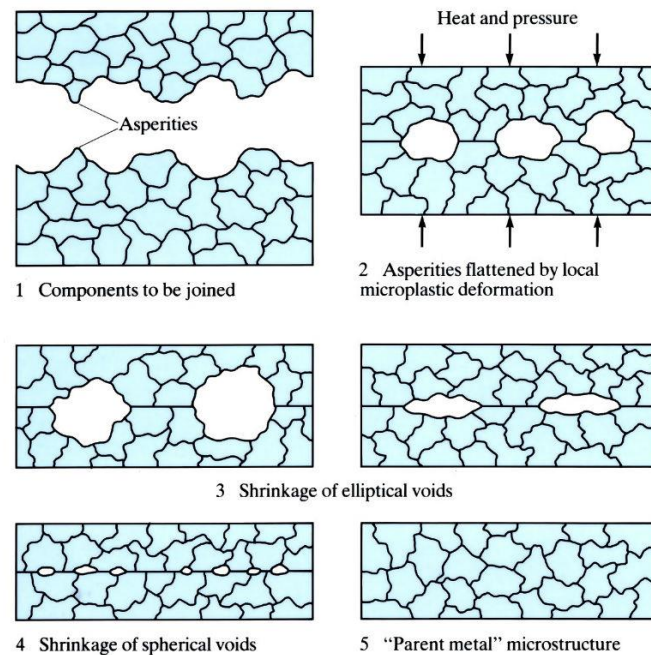


Fig. 2.1 Schematic diagram of diffusion bonding process.

Diffusion bonding is a type of solid-phase joining technique with several distinctive characteristics:

1. **No Overheating or Melting of Base Materials:** During welding, the base materials are not overheated or melted, allowing for the welding of metals or non-metals without compromising the properties of the welded components.
2. **High Joint Quality, Precision, and Minimal Deformation:** Diffusion bonding results in high-quality joints with high precision and minimal deformation.
3. **Ability to Weld Complex Structures and Parts with Large Variations in Thickness:** It is capable of welding complex structures and parts where joints are difficult to access or where there is a significant difference in thickness between the materials being joined.
4. **Simultaneous Welding of Multiple Joints in Assemblies:** Diffusion bonding can be used to simultaneously weld multiple joints within an assembly.

These characteristics make diffusion bonding a versatile and effective technique

for joining materials in applications where traditional fusion welding methods may not be suitable or desirable.

2.2 Experiment methodology

2.2.1 Vacuum melting

Arc melting and induction heating are commonly employed methods for producing alloys from various elements, particularly those requiring high melting temperatures. In arc melting, temperatures exceeding 3000°C can be achieved. Vacuum arc melting (VAM) has significantly advanced traditional metallurgical techniques, enabling precise control over materials crucial in biomedical, aviation, and aerospace applications. Compared to conventional methods, VAM offers several advantages. It allows for tight control over the solidification rate of molten material, effectively eliminating centerline porosity and segregation. Additionally, VAM reduces the concentration of elements with high vapor pressure, such as carbon, sulfur, and magnesium, which are often contaminants in alloys. Moreover, VAM enables the melting of certain metals and alloys like titanium that cannot be melted in open air furnaces due to their reactivity.

As depicted in Figure 2.2, the melting process occurs via an electrical arc between a tungsten electrode and metals contained within a crucible situated in a copper core. Throughout the melting process, the chamber is evacuated and then filled with argon gas. Argon, being an inert gas, does not react with molten metal. The evacuation of the chamber serves to prevent oxidation of the molten alloys.



Fig. 2.2 Arc melting furnace with an enclosed crucible.

In this study, to fabricate HEAs, pure Co, Cr, Fe, Ni, Mn (>99.9 percent purity) were used as raw elements material. All HEAs (CoCrFeNiMn, CoCrFeNi, CoCrNi, and $\text{Cr}_{0.8}\text{FeNi}_x\text{Mn}_y$) were made by arc-melting under a high vacuum, with the buttons turned and heated more than six times to achieve complete melting of all specimens.

2.2.2 Spark plasma sintering

Spark Plasma Sintering (SPS) is a specialized solid-state welding technique used for diffusion bonding, particularly for joining materials that are difficult to weld using conventional methods. In SPS diffusion welding, the process involves the application of a pulsed direct current (DC) through a graphite die that contains the materials to be joined. This high-energy electrical current generates heat primarily by joule heating, rapidly raising the temperature of the materials within the die.

During the SPS process, the localized heating near the interface of the materials causes them to reach a state of plasticity without melting. This is a key characteristic of solid-state welding methods like SPS — the materials are brought to a temperature where atomic diffusion can occur, facilitating the formation of metallurgical bonds between the surfaces to be joined.

The SPS process typically involves the following steps:

(1) Material Preparation: The materials to be joined are carefully prepared and positioned within the graphite die. Surface cleanliness and flatness are crucial to ensure proper bonding.

(2) Die Assembly: The materials are placed in the graphite die assembly, which includes the upper and lower punches necessary for applying pressure during the process.

(3) Pulse Current Application: A pulsed direct current (DC) is applied to the die assembly. This current passes through the graphite die and materials, generating intense heat primarily by joule heating. The pulse nature of the current allows for precise control over the heating and cooling rates.

(4) Pressure Application: Simultaneously with the heating, pressure is applied to the materials. The combination of heat and pressure promotes atomic diffusion across the interface, leading to the formation of a strong metallurgical bond.

(5) Cooling and Solidification: After the bonding process is complete, the assembly is allowed to cool down gradually under pressure. This cooling stage is critical for the solidification and strengthening of the joint.

The advantages of using SPS for diffusion bonding include:

(1) Low Processing Temperature: SPS allows for diffusion bonding at relatively lower temperatures compared to traditional welding methods, reducing the risk of thermal distortion and grain growth.

(2) Precise Control: The SPS process provides excellent control over temperature, pressure, and heating rate, allowing for the production of high-quality joints with minimal defects.

(3) Versatility: SPS can be used to bond a wide range of materials, including metals, ceramics, and composites, making it suitable for various applications across industries.

In summary, Spark Plasma Sintering (SPS) is an effective solid-state welding technique for diffusion bonding, offering precise control over the welding parameters and enabling the formation of strong joints between diverse materials without the need for melting. Its versatility and ability to produce high-quality bonds make it a valuable method in materials science and engineering applications.



Fig. 2.3 SPS diffusion bonding device.

2.2.3 Scanning electron microscopy

A scanning electron microscope (SEM) is an advanced tool used to capture high-resolution images of a sample's surface by scanning it with a focused beam of electrons. This analysis technique is instrumental in examining a material's microstructure, chemical composition, and surface morphology. Due to the fine electron beam used, SEM micrographs exhibit a broad depth of field, providing a typical three-dimensional appearance that aids in understanding the sample's surface structure.

Various signals generated within the SEM contribute to image formation,

including secondary electrons (SEs), characteristic X-rays and lights (CLs), backscattered electrons (BSEs), absorbed currents, and transmitted electrons. Energy Dispersive Spectroscopy (EDS) can be integrated with SEM to analyze the microstructure and elemental composition of the sample.

In this research on dissimilar joints, samples were examined using a scanning electron microscope (SEM, model JSM-6510LA) equipped with a 15 kV accelerating voltage and an energy dispersive spectrometer (EDS). This setup allowed for detailed analysis of the samples' microstructure and elemental composition, providing valuable insights into the properties and characteristics of the joints under study.

2.2.4 Transmission electron microscope (TEM)

Transmission electron microscopy (TEM) is an advanced microscopy technique where a beam of electrons is transmitted through a specimen to form an image. The specimen typically consists of an ultrathin section less than 100 nm thick or a suspension on a grid. Unlike scanning electron microscopy (SEM), which primarily provides details on the morphology of a specimen, TEM offers detailed information about a specimen's structure, morphology, crystallization, and stress.

TEM excels in imaging at extremely high resolution due to the smaller de Broglie wavelength of electrons compared to photons used in light microscopes. This capability allows TEM to capture fine details, including structures as small as a single column of atoms—thousands of times smaller than what can be resolved with a light microscope. Transmission electron microscopy is a vital analytical method used across physical, chemical, and biological sciences. TEM finds extensive applications in diverse fields such as cancer research, virology, materials science, pollution monitoring, nanotechnology, semiconductor research, paleontology, and palynology. In this

research, TEM images and diffraction patterns were obtained using a JEOL 2010F microscope operated at 200 kV.

Chapter 3 Vacuum diffusion bonding between equiatomic CoCrNi-based CSSAs/HEA system and 316 stainless steel by spark plasma sintering

3.1 Introduction

Concentrated solid solution alloys (CSSAs) have recently emerged as a new class of advanced metallic alloys promising for wide applications in nuclear power and aerospace field [28]. Among them, the most representative CSSAs are equiatomic CoCrNi-based alloys system, such as CoCrFeNiMn, CoCrFeNi, and CoCrNi [29-31]. Under the combined action of four core effects, CSSAs exhibit high strength and toughness, excellent corrosion resistance and good irradiation resistance [32-34]. However, current research on CSSAs mainly focuses on materials design and fabrication rather than materials processing. In fact, besides the design of CSSAs, it is also important to develop a suitable material processing technology for promoting the practical application of CSSAs in a short time and at low cost.

If the stainless steels and CSSAs could be reliably joined by suitable method, the respective advantages of both metals could be exploited without major changes to existing reactor design criteria. Actually, the joining of CSSAs has attracted extensive attention in recent years [35], and some researchers realized the joining of CSSAs using various methods, such as laser beam welding [36-38], friction stir welding [18], vacuum diffusion bonding [40-42], electron beam welding [43], rotary friction welding [18], etc. Furthermore, the joining research between CSSAs and stainless steels dissimilar metals has also been reported. Although CSSAs/stainless steels dissimilar metals joint could be obtained by these methods such as laser beam welding, the large deformation after joining limited the wide application of joints. Therefore, vacuum diffusion bonding method with low deformation and high precision should also be noticed and investigated.

Vacuum diffusion bonding method is quite suitable for joining dissimilar metals

and has been widely used in the manufacture of reactor fuel elements, honeycomb panels, various blades and electronic components [44-45]. Samiuddin et al. [46] investigated the diffusion bonding of CoCrNi medium entropy alloy to 304 stainless steel and found that the bonding interface was almost free from IMCs and formed a solid solution, resulting in the enhancement of the joint's shear strength at the bonding temperature of 1075 °C. However, the traditional diffusion bonding still has the following two disadvantages: (I) Low efficiency. The diffusion bonding process usually takes more than ten hours to make one joint. (II) The sluggish diffusion effect of CSSAs may affect the bonding quality. The sluggish diffusion effect reduces the diffusion distance of the joint, resulting in insufficient diffusion and decreased mechanical property. To overcome these two disadvantages, we first proposed the spark plasma sintering (SPS) diffusion bonding between CSSAs and stainless steel. Because this method integrates plasma activation, thermal pressure, current and electric diffusion, it has the advantages of fast temperature rise and increased diffusion distance in joints [47]. Due to differences in the composition of CSSAs, the concentration gradient in the diffusion zone can vary during the diffusion bonding process between different CSSAs and 316 stainless steel, impacting the diffusion rate and thus the strength of the joint. Therefore, this work selected three common equiatomic CSSAs that respectively represent ternary, quaternary, and quinary systems, and systematically studied the diffusion behavior and tensile property of different dissimilar metals joints (CoCrNi/316SS, CoCrFeNi/316SS and CoCrFeNiMn/316SS), in order to comprehensively assess the suitability and advantages for diffusion bonding of CSSAs to 316SS.

In this study, CoCrNi, CoCrFeNi, and CoCrFeNiMn CSSAs were joined to 316SS by SPS diffusion bonding technique in order to investigate the effect of bonding temperature and concentration on microstructure and tensile property of bonded joints.

The interfacial formation mechanism was analyzed, and the different diffusion distance of joint between SPS diffusion bonding and traditional diffusion bonding was compared.

3.2 Experimental method

The CoCrNi, CoCrFeNi, and CoCrFeNiMn CSSAs and commercially available 316 stainless steel were used as base metals, and their chemical composition is listed in Table 3.1. The CoCrNi, CoCrFeNi, and CoCrFeNiMn ingots were arc melted in argon atmosphere with a purity of more than 99.9 at.%. Then as-cast alloys were homogenized in vacuum at 1050 °C for 24 h. As shown in Fig. 3.1, the microstructure of CSSAs displayed single FCC phase, and the grain size decreased gradually with the increase of the number of components. The grain size of CoCrFeNiMn was smaller than that of CoCrNi, which was related to the difference of alloy composition. CoCrFeNiMn contained five elements in equimolar ratios, while CoCrNi contained only three elements. This means that CoCrFeNiMn had more types and quantities of atoms than CoCrNi, which may lead to more defects during arc melting. These defects could act as nucleation sites or increase the dislocation density, thereby restricting the growth of grain size. In addition, in CSSAs, twinning could appear without rolling. Heat treatment at high temperatures could also induce twinning due to the increased energy of atoms allowing them to move and form twins [48]. During high temperature heat treatment, the crystal structure of alloys underwent distortion, resulting in localized distortion regions that could trigger the formation of twinning.

Table 3.1 Chemical composition of CSSAs and 304SS base metals (wt. %).

Base Metals	Co	Cr	Fe	Ni	Mn	Mo	Si	S	P	C
CoCrNi	34.74	30.65	-	34.61	-	-	-	-	-	-
CoCrFeNi	26.14	23.06	24.77	26.03	-	-	-	-	-	-

CoCrFeNiMn	21.02	18.54	19.92	20.93	19.59	-	-	-	-	-
316 stainless steel	-	18.5	Bal	14.5	1.9	2.2	0.85	0.02	0.035	0.02

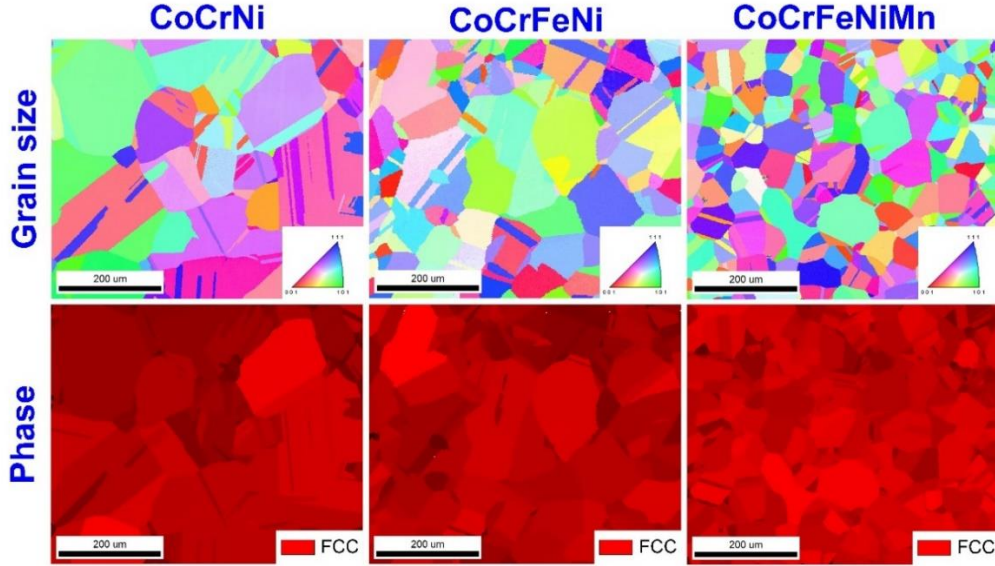


Fig. 3.1 Microstructures of CoCrNi, CoCrFeNi, and CoCrFeNiMn CSSAs.

Prior to diffusion bonding, the specimens were cut into blocks by wire cutting machine. Based on the references [49], all the specimens were ground with SiC sandpaper of various grit sizes (120, 240, 400, 800, 1000, 1500, 2000, 4000 and 5000 #) and then polished using 3 μm and 1 μm diamond pastes to ensure the same surface roughness. Finally, these specimens were ultrasonically cleaned to remove the dust and oil contamination in acetone. Then each two samples were placed in the graphite mold, and put into the SPS machine (DR.SINTER.LAB, SPS+510 L), as shown in Fig. 3.2(a). Fig. 3.2(b) illustrates the schematic of the process curve during the diffusion bonding. First, the temperature increased from 25 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$ at the speed of 100 $^{\circ}\text{C}/\text{min}$ and then stayed at 700 $^{\circ}\text{C}$ for 3 min under the pressure of 10 MPa to ensure the close contact of faying interfaces of samples. Second, the samples were heated up to diffusion bonding temperature and held for 60 min under the bonding pressure of 25 MPa. After

diffusion bonding, the bonding pressure was removed. According to the reference [50], generally, the bonding temperature range during diffusion bonding should be $0.6T_m$ - $0.8T_m$ (T_m is the melting point of the lower of two base metals (K)), while the melting points of 316SS, CoCrNi, CoCrFeNi, and CoCrFeNiMn are 1380 °C, 1417 °C, 1444 °C and 1330 °C, respectively [51-53]. Therefore, the bonding temperatures from 900 °C to 1050 °C were applied. The higher bonding temperature, such as 1100 °C, will deteriorate the properties of base metal, meanwhile, the excessive growth of brittle intermetallic compounds led to large residual stress, which caused cracks generation along the interface and reduced the tensile strength of joint. In fact, this temperature range has been widely used in the diffusion bonding between high entropy alloys and other traditional materials [54-55]. However, even at the same bonding temperature, comparing different bonded joints could be challenging due to the difference in base metals melting points. Additionally, determining a general temperature criterion for diffusion bonding of CoCrFe-based CSSAs to stainless steel is essential. As a result, this article has normalized bonding temperature at $0.75T_m$, $0.77T_m$, and $0.8T_m$, and the specific joining parameters of different joints are shown in Table 3.2. Due to the high bonding temperature, the sample bonded at $0.83T_m$ was deformed greatly, resulting in the failure of bonding experiment.

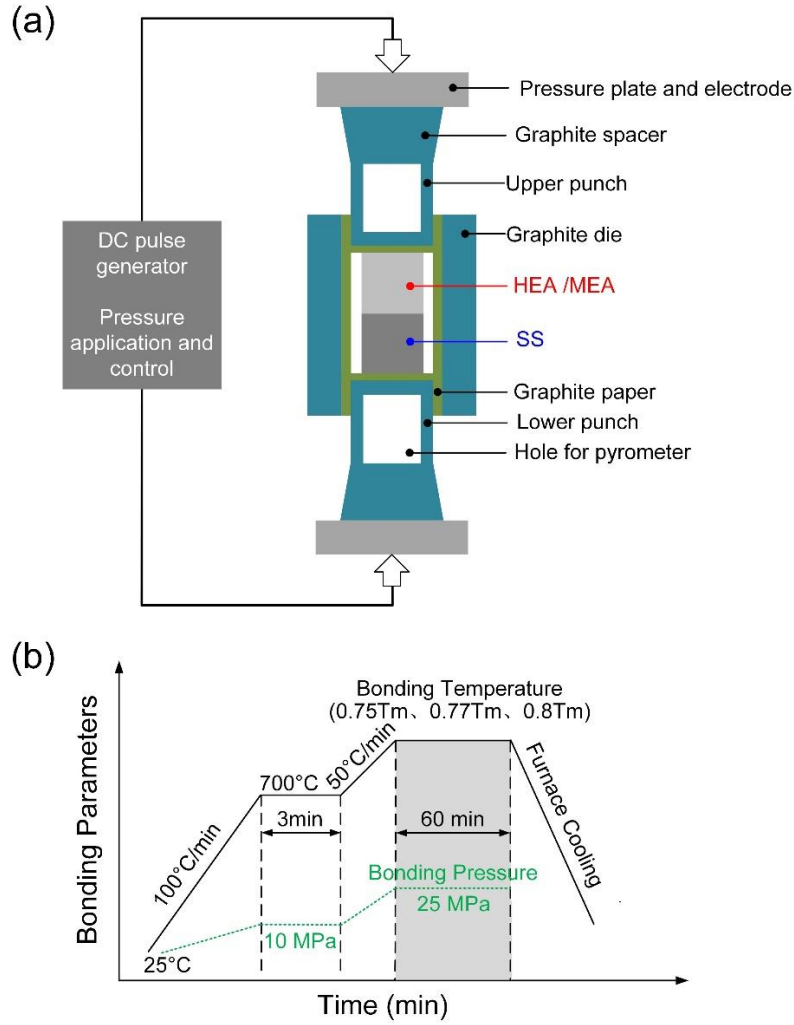


Fig. 3.2 (a) Schematic of SPS diffusion bonding process and (b) temperature profile.

Table 3.2 Diffusion bonding parameters of different joints.

Joints	Bonding temperature (°C)	Pressure (MPa)	Time (min)
CoCrNi / 316SS	0.77T _m (1000 °C)	25	60
	0.80T _m (1050 °C)		
CoCrFeNi / 316SS	0.77T _m (1000 °C)	25	60
	0.80T _m (1050 °C)		
CoCrFeNiMn / 316SS	0.75T _m (900 °C)	25	60
	0.77T _m (950 °C)		
	0.80T _m (1000 °C)		
	0.83T _m (failed)		

After joining, the samples were cut using abrasive cutter, ground with SiC paper and mechanically polished. The interfacial microstructure and diffusion behavior were investigated by electron probe micro-analyzer (EPMA, JEOL, JXA-8530 F). After

electropolishing in a solution composed of 8% perchloric acid and 92% alcohol, the grain size near the interface was measured from images taken by electron backscattered diffraction (EBSD, JEOL, JSM-6500F). The MTEX toolbox in MATLAB software was used based on EBSD results to estimate the density of geometrically necessary dislocations (GNDs). Tensile tests were conducted for mechanical properties of different joints by tensile tester (Instron-5564). Furthermore, the fracture surface was examined by scanning electron microscope (SEM, JEOL, JSM-6510LA) and energy dispersive spectroscopy (EDS, JEOL, JED-2300). For further analysis, the phase diagrams of diffusion zone were calculated with the CALPHAD methodology.

3.3 Results and discussion

3.3.1 *Typical microstructures of different joints*

Fig. 3.3 shows the microstructure of different joints. The left side was 316 stainless steel and the right side was CSSAs. In order to investigate the effect of bonding temperature on the joint, we selected CoCrFeNiMn and 316SS as representative base metals and conducted diffusion bonding on two base metals at three different bonding temperatures ($0.75T_m$, $0.77T_m$, $0.8T_m$). The results showed that insufficient diffusion led to the formation of numerous voids in the joint when using a bonding temperature of $0.75T_m$. Therefore, in order to obtain high-quality joints for CoCrNi/SS and CoCrFeNi/SS joints, we only conducted diffusion bonding under higher temperature conditions ($0.77T_m$ and $0.8T_m$). Then the effect of concentration on diffusion behavior and tensile property of different bonded joints were investigated. It could be seen that no cracks and intermetallic compounds formed at the interface, and only tiny voids with a size below 1 micron appeared. The number of voids gradually decreased with the

increase of bonding temperature, and the voids almost disappeared when the bonding temperature reached $0.8T_m$. Compared with other joints, the number of voids in CoCrNi/316SS joint was quite small at both $0.77T_m$ and $0.8T_m$, indicating that the joint had a large diffusion bonding process range. The difference in the number of voids may be related to different concentrations of CSSAs base metals. Therefore, the effects of bonding temperature and concentration on the microstructure and mechanical property of joints will be investigated in depth below.

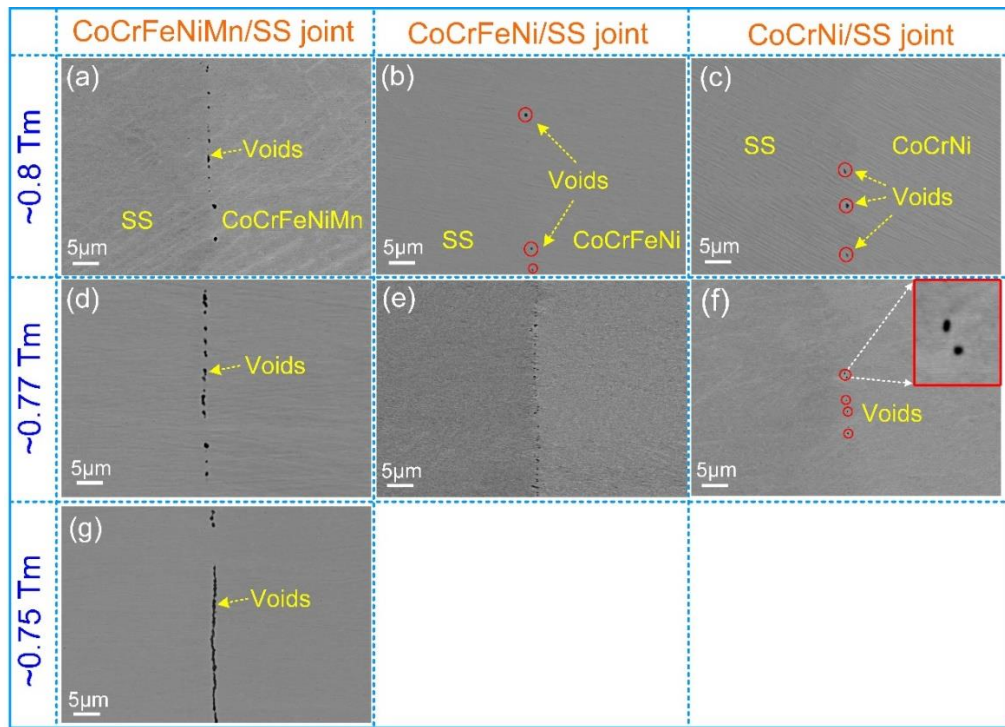


Fig. 3.3 Microstructure of joints at $0.8T_m$ of (a) CoCrFeNiMn/316SS, (b) CoCrFeNi/316SS, (c) CoCrNi/316SS, $0.77T_m$ of (d) CoCrFeNiMn/316SS, (e) CoCrFeNi/316SS, (f) CoCrNi/316SS and $0.75T_m$ of (g) CoCrFeNiMn/316SS.

3.3.2 Effect of bonding temperature on microstructure and tensile strength of CoCrFeNiMn/316SS joint

3.3.2.1 Elemental distribution of joints at different temperatures

Table 3.3 shows the bonding rate of CoCrFeNiMn / 316SS joints bonded at

different temperatures. The bonding rate was determined as a crucial indicator for evaluating the quality of diffusion bonding. A higher bonding rate indicated a better quality of the diffusion bonding. The length of voids was denoted by the sum of the entire void's length in the direction of bonding interface and given by the Eq. (3.1):

$$L' = L_1 + L_2 + L_3 + \cdots + L_n \quad (3.1)$$

where $L_1, L_2, \dots, L_n$ is the length of various voids. The calculated void length was further used to calculate the bonding rate using Eq. (3.2) [56]:

$$e_L = \frac{L-L'}{L} \times 100\% \quad (3.2)$$

where e_L is joint bonding rate, L is the length of the bonding interface, L' is the length of the unbonded and defective section. Furthermore, the map and line scanning analysis results of CoCrFeNiMn/316SS joint at different temperatures are illustrated in Fig. 3.4 and Fig. 3.5, and the definition of diffusion distance was established in this study. Specifically, the two endpoints of the diffusion distance were determined based on the starting and final positions of changes in element intensity observed in the line scan curve. The measurements indicated that the joints bonded at $0.75T_m$ and $0.77T_m$ had a large number of voids and a short diffusion distance, while the bonding rate increased to 80.19% and the diffusion distance increased to 22 μm with increasing bonding temperature to $0.80T_m$, as shown in Table 3.3 and Fig. 3.5(c). Li et al. [18] found that the number of voids in CSSAs joint decreased sharply at elevated temperatures. When the temperature reached 1000 °C, the voids could quickly disappear during the diffusion bonding process dominated by the viscoplastic deformation mechanism [18]. Furthermore, the increase in diffusion distance with temperature could be explained by Arrhenius formula [57]:

$$D = D_0 \exp(-Q/RT) \quad (3.3)$$

where Q is the activation energy of diffusion, D_0 is the diffusion constant (m^2/s), T is the bonding temperature (K), and R is the real gas constant ($8.314 \text{ J}/(\text{mol} \cdot \text{K})$). The elevated bonding temperature could improve the diffusion coefficient, leading to an increase in the diffusion distance. However, it should be noted that the increase in diffusion distance was not significant when the temperature rose from $0.75T_m$ to $0.77T_m$, possibly due to limited diffusion at lower temperature ranges. During the diffusion, Fe element diffused from stainless steel to CoCrFeNiMn side, while Co, Ni and Mn diffused from CoCrFeNiMn side to stainless steel side. Due to the similar concentration on both sides of the base metals, the diffusion of Cr element was not obvious. Furthermore, as shown in Fig. 3.5, the diffusion distances of Ni and Co elements were smaller than that of Mn element, which was attributed to the different activation energies of elements in CoCrFeNiMn. For CoCrFeNiMn CSSA, the sequence of element activation energy from the lowest to highest was reported by Tsai [58]: $\text{Mn} < \text{Cr} < \text{Co} < \text{Fe} < \text{Ni}$. Since the activation energies of Co and Ni elements were higher than that of Mn element, the elements of Co and Ni were difficult to diffuse during diffusion bonding process, resulting in a decrease of diffusion distance.

Table 3.3 The bonding rate of CoCrFeNiMn / 316SS joints at different bonding temperatures.

Bonding temperature	Bonding rate (%)
$0.75T_m$	21.92
$0.77T_m$	63.45
$0.80T_m$	80.19

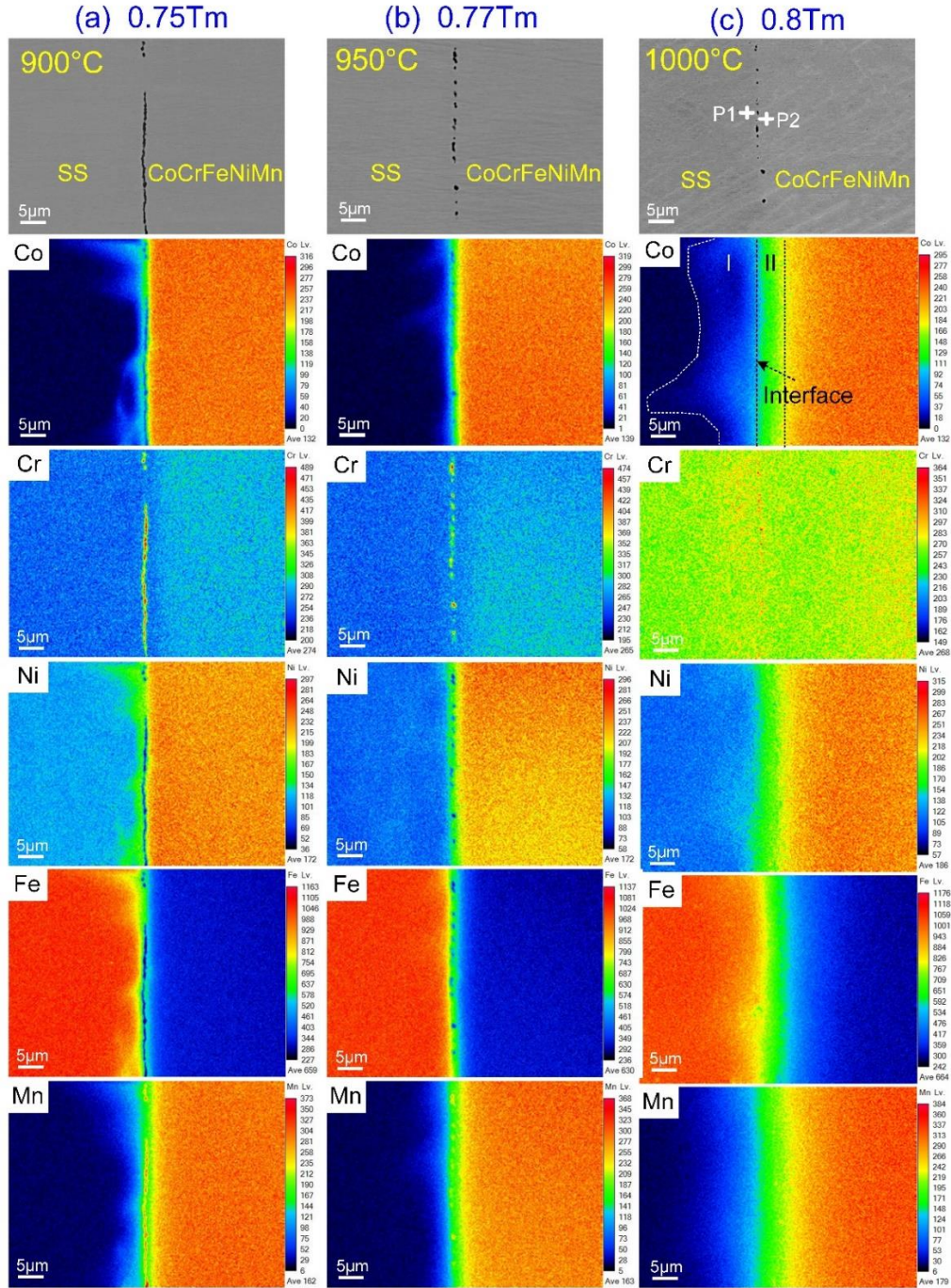


Fig. 3.4 Map scanning analysis results of CoCrFeNiMn/316SS joint at different temperatures of (a) 0.75 T_m , (b) 0.77 T_m and (c) 0.80 T_m .

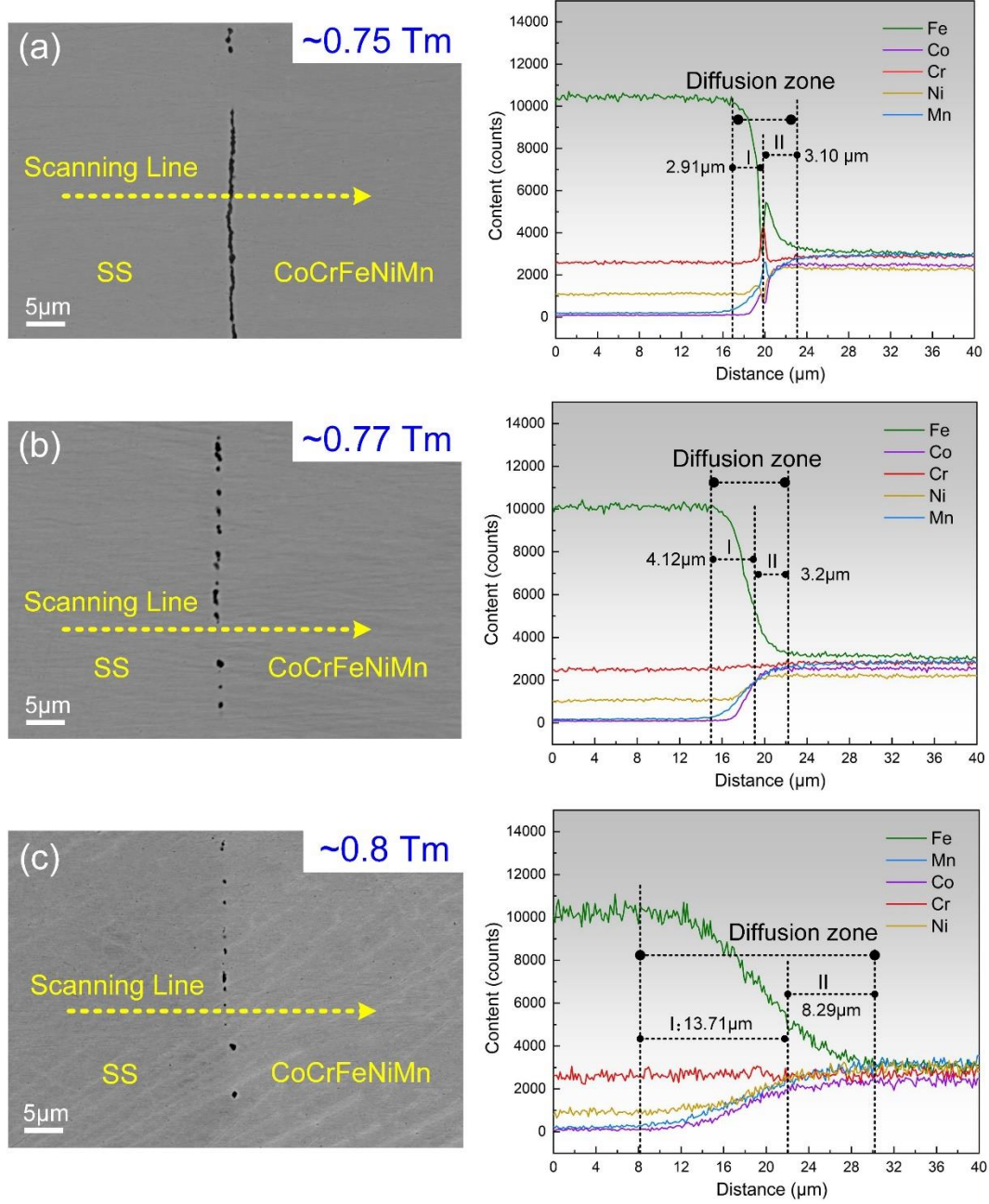


Fig. 3.5 Line scanning analysis results of CoCrFeNiMn/316SS joint at different temperatures of (a) $0.75T_m$, (b) $0.77T_m$ and (c) $0.80T_m$.

As shown in Fig. 3.4(c) and Table 4, the diffusion zone could be divided into zone I and zone II, where zone I was composed of Fe-rich solid solution and zone II was composed of Co-Cr-Fe-Ni-Mn solid solution. Further analysis of the two zones

illustrated that the average distance of zone I was greater than that of zone II, which may be related to lower activation energies of Mn and Cr elements in CSSAs than that of Fe in stainless steel. Under the dominance of Mn and Cr elements, the elements in CSSAs diffused more to the stainless steel side, resulting in an increase in the diffusion distance of zone I.

Table 3.4 Typical composition of diffusion zone in Fig. 3.4 (at. %).

Diffusion zone	Co	Cr	Fe	Ni	Mn	Structure
P1	6.4	19.6	54.6	11.9	7.5	Fe-rich solid solution
P2	19.8	20.8	24.4	18.6	16.4	Co-Cr-Fe-Ni-Mn solid solution

3.3.2.2 The diffusion behavior of atoms at interface

Due to the difference in elemental diffusion coefficients, the joint composed of CSSAs and stainless steel could be viewed as a one-dimensional semi-infinite diffusion couple. The diffusion of elements in the joint could be regarded as diffusion in a semi-infinite object, therefore the kinetic behavior of diffusion of Fe, Mn and other major elements in the joint could be calculated and quantitatively analyzed with Fick's second law of diffusion. Assuming that the diffusion direction was perpendicular to the joining interface, let $x = 0$ at the interface, the base metals was considered as a semi-infinite diffuser, the diffusion coefficient can be calculated according to the following formula:

$$C(x, t) = A - B \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad A = \left(\frac{C_1 + C_2}{2}\right) \quad B = \left(\frac{C_2 - C_1}{2}\right) \quad (3.4)$$

where the initial concentration of the element in both base metals was considered as C_1 and C_2 , x is the distance from interface, t is the bonding time, and D is diffusion coefficient. During the vacuum diffusion bonding of 4J29 kovar alloy and 316L stainless steel, Fang et al. [59] also used this formula to calculate the diffusion coefficients of Fe, Ni and Co in the joints. In this study, for a certain element, the distance from the interface and the element concentration were obtained by line scanning in EDS, and thus the diffusion coefficient could be calculated by the equation. Table 3.5 shows the diffusion coefficients of various atoms at diverse bonding temperatures. At relatively low temperatures, the diffusion coefficients of the elements were all small. While with increasing the temperature up to $0.8T_m$, the diffusion coefficients significantly increased, which further indicated that bonding temperature had a significant effect on the diffusion behavior during diffusion bonding.

Table 3.5 Diffusion coefficients (D) of various atoms at diverse bonding temperatures.

Sample	From CoCrFeNiMn into 316SS		From 316SS into CoCrFeNiMn
	$(\times 10^{-16} \text{ m}^2/\text{s})$		$(\times 10^{-16} \text{ m}^2/\text{s})$
	D_{Mn}	D_{Co}	D_{Fe}
$0.75T_m$	1.71	1.06	0.66
$0.77T_m$	1.31	0.75	0.79
$0.80T_m$	14.5	8.9	5.3

At $0.8T_m$, the diffusion coefficients of Mn and Co in joints were higher than those of Fe, which proved that the diffusion of Mn and Co elements from CoCrFeNiMn to stainless steel side was easier to occur. Despite the sluggish diffusion effect of CSSAs, the effectiveness of sluggish diffusion varied from element to element. According to Tsai's results [58], the sluggish diffusion effect of Mn and Co was relatively weak,

giving them higher diffusion coefficients than that of Fe diffusing from the stainless steel to the CoCrFeNiMn. In addition, Mn had a higher diffusion coefficient compared to Co, indicating that the Mn atoms could diffuse more easily in the joint. That further led to a longer diffusion distance in zone I due to the lower activation energy of Mn.

3.3.2.3 The grain size and dislocation density of joints

The thickness of the diffusion layer was not only related to the increased diffusion rate, but also to the grain size. Fine grains with more grain boundaries could provide more channels for atomic diffusion [60]. The inverse pole figures for CoCrFeNiMn/316SS joint bonded at $0.75T_m$ and $0.80T_m$ are shown in Fig. 3.6. As the bonding temperature increased, the grain growth would suppress the diffusion of atoms. However, the grain size was only increased by $11.3\ \mu\text{m}$ in this study, thus weakening the effect of grain growth on element diffusion. More importantly, there was a sharp interface in the joint at $0.75T_m$, while with increasing temperature to $0.8T_m$, the grains grew at the interface and the original interface disappeared. By ranking the grain orientation spread (GOS) [61], recrystallized and deformed grains were identified on the basis of whether their GOS was below or above 2° , respectively. Based on Fig. 3.5(b), it is evident that the joint bonded at $0.8T_m$ underwent grain boundary migration and recrystallization. During the bonding process, the pulsed current can significantly promote the recrystallization of the high-distortion grains near the interface [62]. Represented by the white dotted line in Fig. 3.6(b), the grains formed by recrystallization span the bonding interface and connect the two different base materials, thereby resulting in a high-strength SPS diffusion bonding at $0.8T_m$. Likewise, Li et al. [63] reported the occurrence of interfacial recrystallization during diffusion bonding of copper using SPS technique. The formation of complete grains at the interface due to

recrystallization during diffusion bonding was a crucial factor in the disappearance of interface and the improvement of mechanical properties. The results indicated that stronger metallurgical bonding and disappearance of interfacial voids could be achieved by controlling the bonding temperature to cause recrystallization and formation of complete grains at the interface.

Fig. 3.6 also shows the GNDs distribution for CoCrFeNiMn/316SS joint bonded at $0.75T_m$ and $0.80T_m$. The joints had similar GNDs density at different temperatures. In addition, at $0.75T_m$, the stress concentrations caused by dislocation entanglement at the interface appeared, which may decrease the tensile strength. By analyzing the grain size and GNDs density, it could be concluded that the effect of dislocation strengthening and grain boundary strengthening was not obvious. Instead, the main factors affecting the joint strength were the shrinkage and disappearance of voids at the interface and the formation of complete grains.

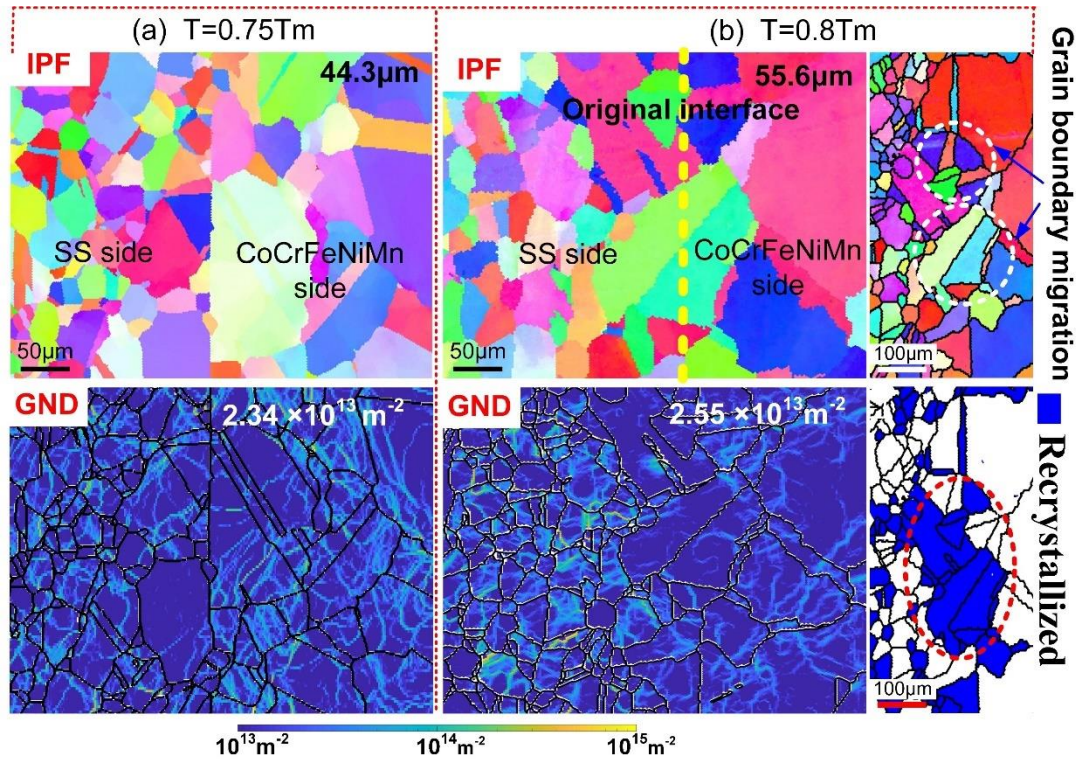


Fig. 3.6 Inverse pole figures, GND maps and recrystallization distribution map for

CoCrFeNiMn/316SS joint bonded at (a) $0.75T_m$ and (b) $0.80T_m$.

3.3.2.4 The grain size and dislocation density of joints

Fig. 3.7 illustrates the tensile strength, elongation, deformation rate and fracture morphology of CoCrFeNiMn/316SS joint. As shown in Fig. 3.7(a-b), the tensile strength and yield strength of joints increased with increasing bonding temperature, while the elongation was similar at all temperatures. Compared to the joint bonded at $0.75T_m$ and $0.77T_m$, the tensile strength of the joint increased by 55 MPa for temperature $0.8T_m$, which is $\sim 90\%$ of 316SS base metal. The reduction in the number of voids and the formation of complete grains at the interface were attributed as factors contributing to this phenomenon. Further analysis suggested that the reason for the high tensile strength of the joints at $0.8T_m$ was related to elevated temperature and high creep rate. On the one hand, the elevated temperature accelerated the diffusion of atoms in the diffusion zone, thus promoting the disappearance of voids. On the other hand, recrystallization and growth of new grains occurred under high creep rate, resulting in the formation of complete grains. In addition, the tensile strength and elongation of the joint bonded at $0.8T_m$ was higher than that obtained by laser beam welding, indicating that the mechanical properties of diffusion bonded joint exceeded the performance of fusion welded joints.

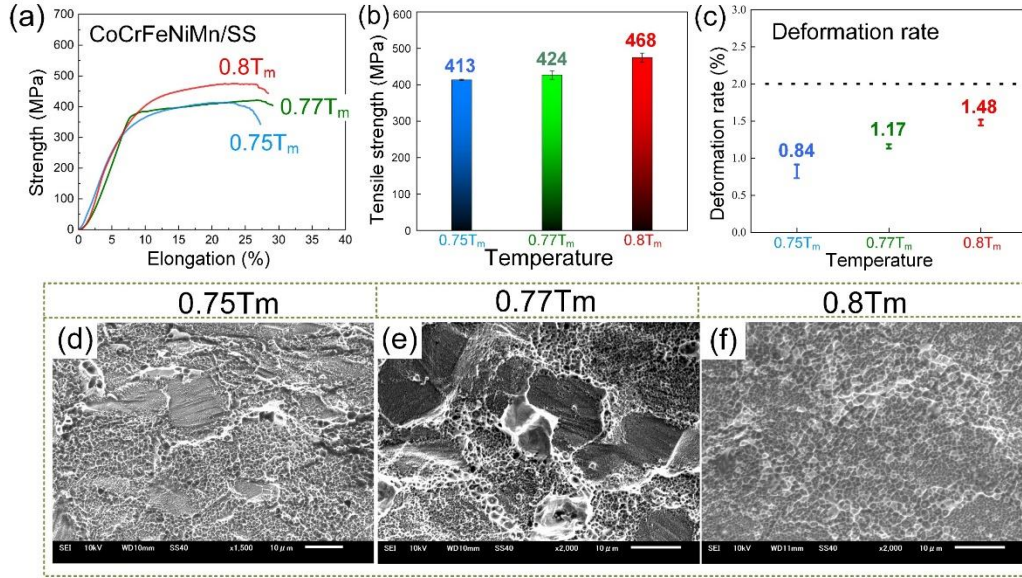


Fig. 3.7 (a) The stress-strain curve of CoCrFeNiMn/316SS joints, (b) the average tensile strength, (c) the deformation rate, the fracture morphology of CoCrFeNiMn/316SS joints bonded at diverse bonding temperatures: (d) 0.75T_m, (e) 0.77T_m and (f) 0.80T_m.

The deformation rate of joints is shown in Fig. 3.7(c). The deformation rate increased with increasing bonding temperature, while all the results were all below 1.5%, suggesting that the deformation of diffusion bonded joint was very small. Fig. 3.7(d-f) shows the fracture morphology of CoCrFeNiMn/316SS joints bonded at diverse bonding temperatures. The flat surface and dimples appeared at 0.75T_m and 0.77T_m, while a large number of dimples were observed at 0.8T_m, indicating that ductile fracture occurred.

3.3.3 Effect of concentration on microstructure and tensile strength of concentrated solid solution alloys /316SS joint

3.3.3.1 Elemental distribution of joints at 0.77T_m and 0.80T_m

The map scanning analysis results of joints at $0.77T_m$ are shown in Fig. 3.8. At $0.77T_m$, CoCrFeNiMn/SS and CoCrFeNi/SS joints contained many voids with short diffusion distance, while CoCrNi/SS joint had only few voids and a large diffusion distance. The difference in concentration of CSSAs base metals may be the main factor for the different diffusion distances. The sequence of the element concentration variation amplitudes in the diffusion zone of CoCrNi/SS joint was: Fe > Co > Cr > Ni. Besides, the Fe and Co elements concentration variation amplitudes in CoCrNi/SS joint was larger than that of CoCrFeNiMn/SS and CoCrFeNi/SS joints. The large concentration variation amplitudes of Fe and Co in the diffusion zone of CoCrNi/SS joint resulted in the rapid diffusion of atoms in joint.

Fig. 3.9 shows the map scanning analysis results of joints at $0.80T_m$. At $0.8T_m$, the number of voids in all joints was reduced and the diffusion distance was increased. The diffusion distances of different joints were similar, and the diffusion distances of zone I were all wider than zone II. The results showed that the effect of concentration could be diminished when the bonding temperature was high enough. At $0.8T_m$, sufficient diffusion reduced the number of voids and may contribute to the improvement of tensile strength.

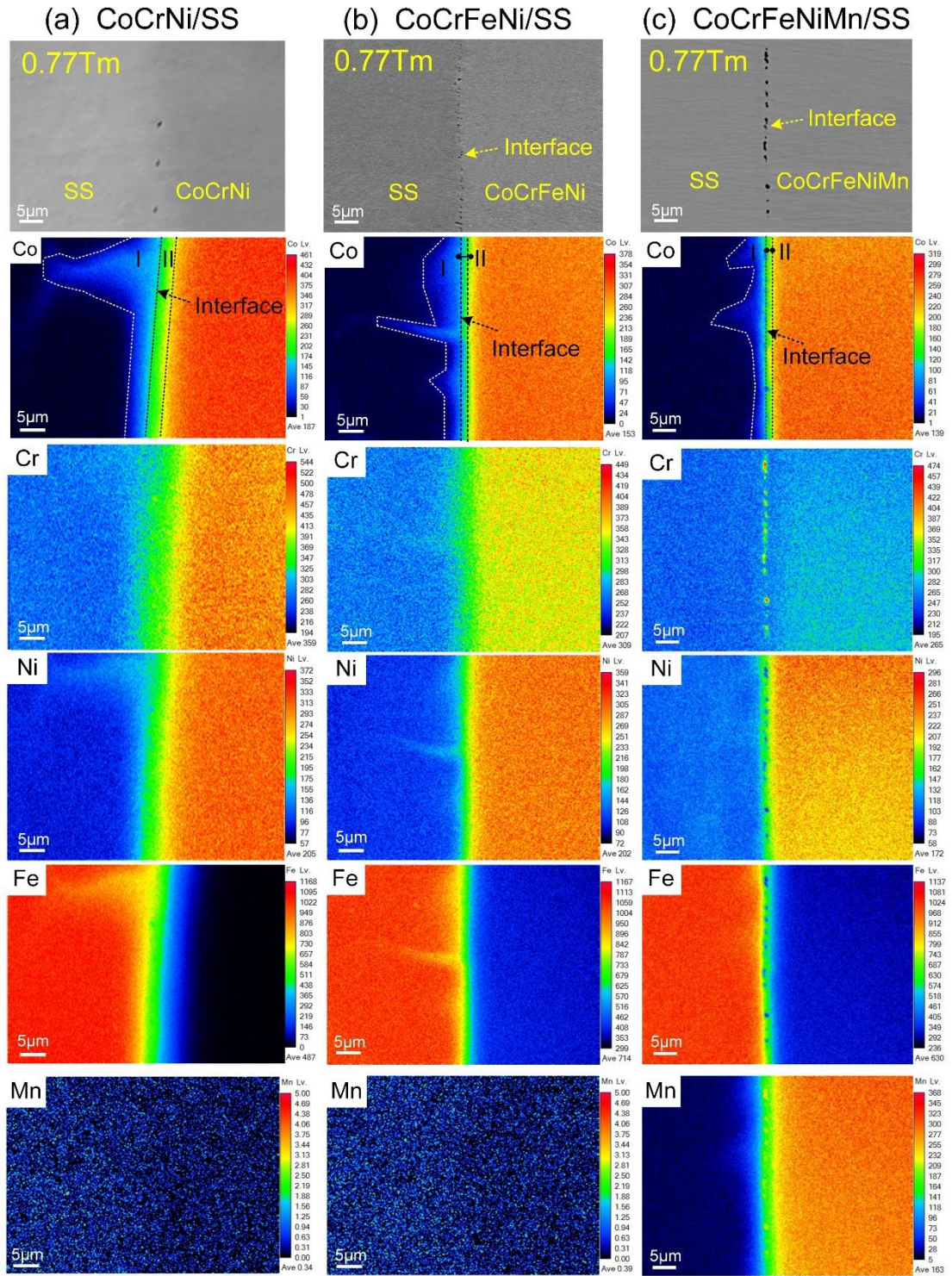


Fig. 3.8 Map scanning analysis results at $0.77T_m$ of (a) CoCrNi/316SS joint, (b) CoCrFeNi/316SS joint and (c) CoCrFeNiMn/316SS joint.

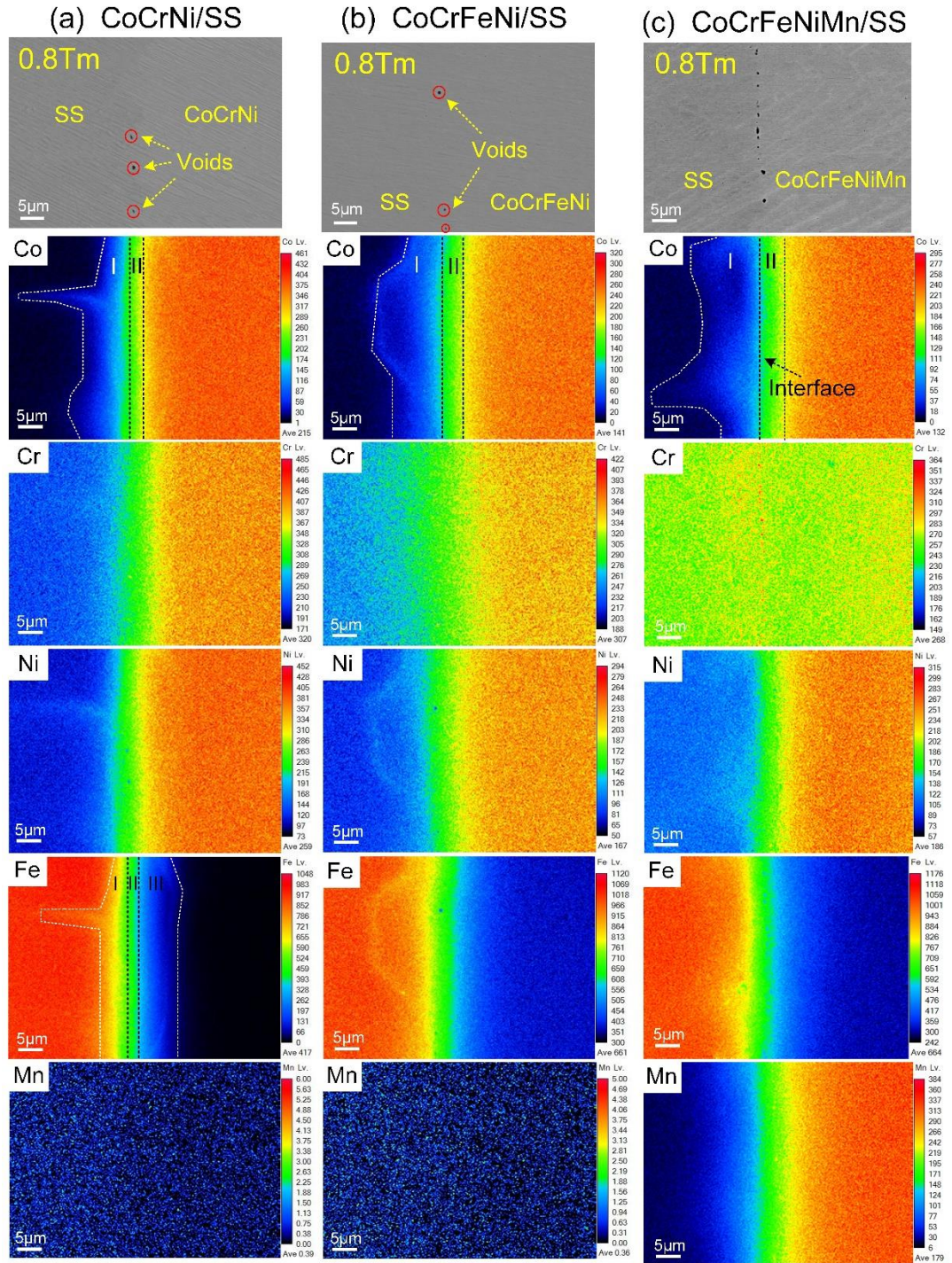


Fig. 3.9 Map scanning analysis results at $0.80T_m$ of (a) CoCrNi/316SS joint, (b) CoCrFeNi/316SS joint and (c) CoCrFeNiMn/316SS joint.

3.3.3.2 Tensile strength and fracture mechanism of different CSSAs/SS joints

Fig. 3.10 (a-c) shows the tensile strength of different CSSAs/SS joints and base

metals. It could be seen that the tensile strength of CoCrNi/SS joint was over than that of the 316 stainless steel base metal at both temperatures. Under the combined action of the high concentration difference of the elements and the high bonding temperature during diffusion bonding between CoCrNi and 316SS, fuller diffusion and higher creep rate may lead to the disappearance of the voids and the presence of complete grains. In addition, the tensile strength of all samples bonded at $0.8T_m$ exceeded 80% to the strength of 316SS base metal. Therefore, it could be inferred that the optimal bonding temperature of equiatomic CoCrNi-based CSSAs system/316SS was $0.8T_m$. Different joints had different tensile strengths and elongations may relate to the element concentration and the original base materials performance, and the performance of base materials may play a more important role. The tensile strengths of CoCrNi, CoCrFeNi and CoCrFeNiMn base materials were tested to be 757 MPa, 635 MPa and 644 MPa respectively, while the elongation was 32.3%, 29.1% and 38.7% respectively. The high performance of the CoCrNi base material may be the reason for the high tensile strength of the CoCrNi/SS joint. Besides, the high concentration difference of Co and Fe between two base materials promoted the atomic diffusion in the diffusion zone, thus improving the tensile strength of the CoCrNi/SS joint. Interestingly, the curve for CoCrNi/SS joint bonded at $0.8 T_m$ had a jump shift at initial stage in the elastic region, which could be attributed to the presence of residual stresses in the bonded joint. If residual stresses are present in the bonded joint and not fully relieved within the specimen, they will interact with the externally applied stress. This interaction can lead to a discontinuous or jump-like movement in the stress-strain curve's initial elastic region. Therefore, it is necessary to conduct the simulation and experimental research on residual stress of bonded joints in the future.

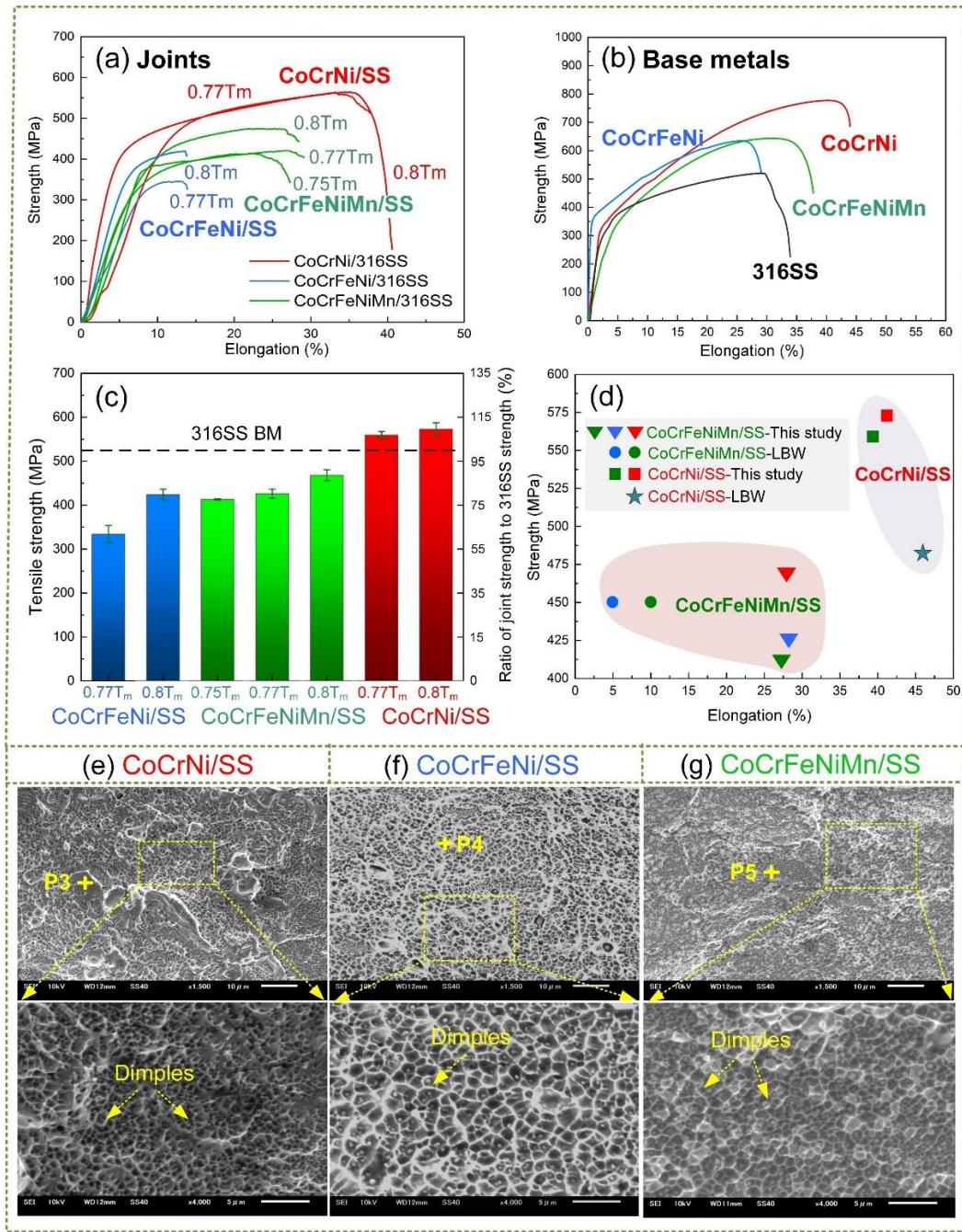


Fig. 3.10 The stress-strain curves of (a) different CSSAs/SS joints and (b) base metals; (c) the average tensile strength of joints; (d) comparison results of the UTS and ductility of our joints and previous reported joints [10, 20, 34]; and the fracture morphology of different CSSAs/SS joints bonded at 0.8T_m: (e) CoCrNi/316SS, (f) CoCrFeNi/316SS and (g) CoCrFeNiMn/316SS.

Table 3.6 The composition at the locations marked in Fig. 10 (at. %).

Locations	Co	Cr	Fe	Ni	Mn	Fracture location
P3	0.71	18.32	69.15	10.42	1.40	Stainless steel
P4	17.69	22.89	38.97	19.57	0.88	Interface
P5	12.58	20.24	37.34	15.97	13.87	Interface

The fracture morphology of different CSSAs/SS joints are shown in Fig. 3.10(e-g). The dimples were observed on the surface of all fractures, but the dimples of CoCrNi/316SS joint were larger and deeper. The appearance of a large number of dimples indicated that plastic deformation occurred during the fracture process, which improved the strength and toughness of the joint. Fig. 3.11 shows the element distribution of samples after tensile test, and based on this figure, the fracture path of different CSSAs/SS joints at $0.8T_m$ could be observed. From the point scanning results and fracture path in Fig. 3.10 and Fig. 3.11, the fracture of CoCrNi/316SS joint occurred on the stainless steel side, due to the tensile strength reaching the stainless steel base material. However, the CoCrFeNi/316SS joint and CoCrFeNiMn/316SS joint fractured at the interface because the joint strength was lower than that of stainless steel and CSSAs base materials. In summary, the CoCrNi/316SS joints with excellent joining quality could be obtained by the diffusion bonding method, while the other two joints could also achieve 80% of the tensile strength of the 316SS base material at the appropriate temperature.

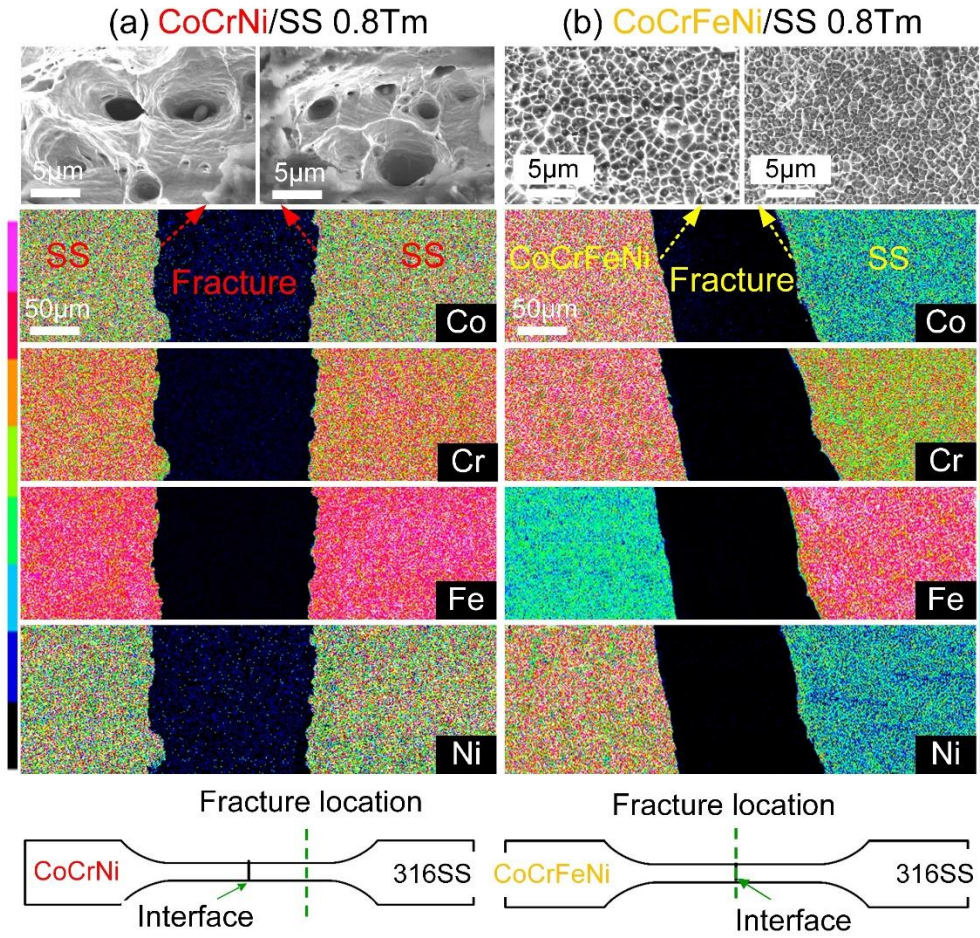


Fig. 3.11 Secondary electron images of fracture surface and the EDS elemental distribution maps of side surface in the fractured tensile specimens of the different CSSAs/SS joints bonded at 0.8T_m: (a) CoCrNi/316SS and (b) CoCrFeNi/316SS.

Fig. 3.10(d) shows the comparison results of the UTS and ductility of our joints and previous reported joints [64]. The CoCrFeNiMn/316SS joint obtained by diffusion bonding method have higher tensile strength and elongation than laser beam welded joints, especially the elongation seems to be increased by 18%. In addition, the tensile strength of diffusion bonded CoCrNi/316SS joint increased by 90 MPa with no significant reduction in elongation compared to the laser welded joint. The above results indicate that diffusion bonding seems to be a more suitable method than fusion welding

for the joining of CSSAs and stainless steels.

3.3.4 Composition and formation mechanism of the diffusion zone

3.3.4.1 Formation of solid solution phase in diffusion zone

To further analyze the phase structure of the diffusion zone, phase diagram predictions were performed. The phase diagram for diffusion zone was shown in Fig. 3.12. By analyzing the typical compositions of zone-I and zone-II in the diffusion zone of different joints, it was predicted that both diffusion zones contained FCC solid solution structure.

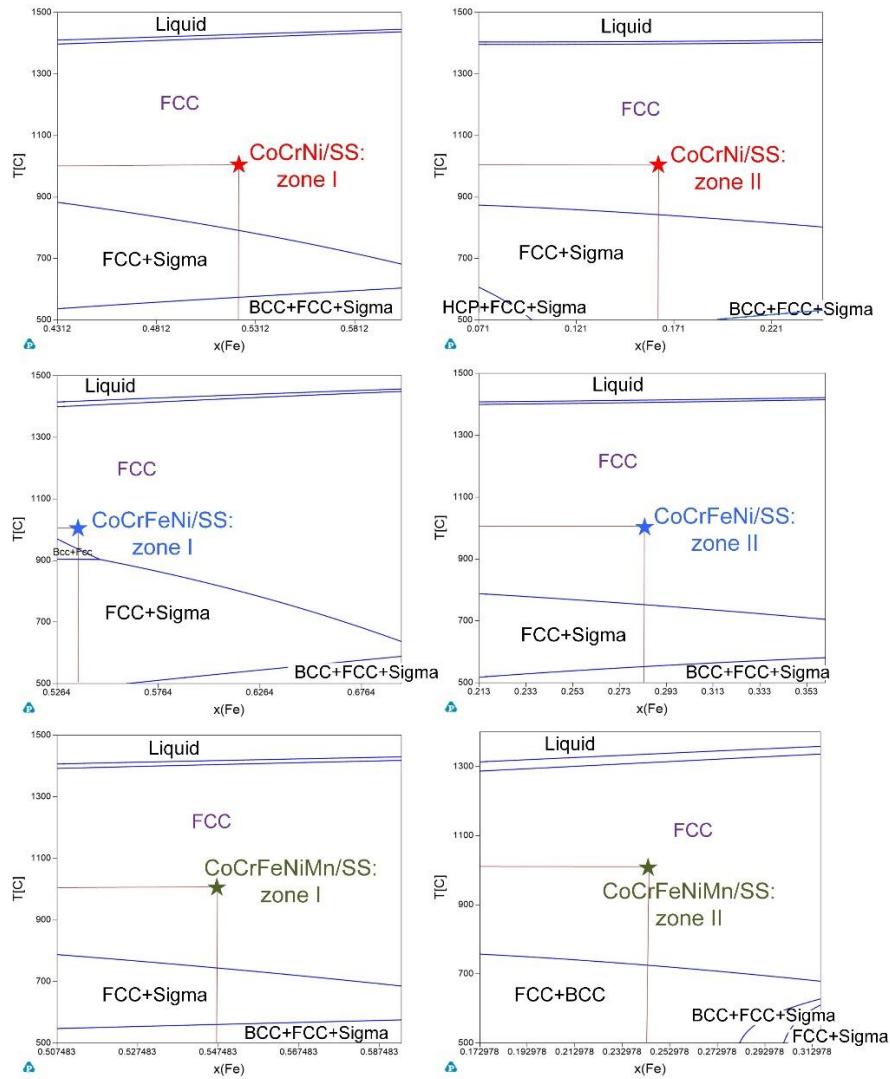


Fig. 3.12 Phase diagram for diffusion zone in bonded joints.

In addition, the high entropy alloy prediction model was also utilized to further verify the accuracy. The formation of solid solution phase during diffusion bonding was essentially a result of the reduction in mixed Gibbs free energy. Many scholars have studied the phase composition law of high entropy alloys, among which, considering the competing relationship between entropy and enthalpy, Yang et al. [65] proposed a new parameter Ω to predict the phase composition, which is defined as follows.

$$\Delta H_{mix} = \sum_n 4\Delta H_{ij}^{mix} C_i C_j \quad (3.5)$$

$$\Delta S_{mix} = -R \sum_{i=1}^n C_i \ln (C_i) \quad (3.6)$$

$$\Omega = \frac{T\Delta S_{mix}}{|\Delta H_{mix}|} \quad (3.7)$$

where C_i and C_j are the concentrations (at. %) of element i and j , respectively, in the diffusion zone. T and R represent the bonding temperature and universal gas constant, respectively. ΔH_{ij}^{mix} can be obtained using the Miedema model [66] and represents the mixing enthalpy between the elements i and j . Du et al. [67] used the similar method to analyze the phase composition of diffusion zone in $Al_5(TiZrHfNb)_{95}$ refractory high entropy alloy/ Ti_2AlNb alloy diffusion bonded joints. When $\Omega > 1$, the driving force for the formation of the solid solution (ΔS_{mix}) is higher than the resistance to the formation of the solid solution (ΔH_{mix}), and then the elements preferably form the solid solution phase. Fig. 3.13 illustrates the calculated results of Ω and VEC for the diffusion bonded joint at 1000 °C/25 MPa/1 h, and the red curve shows the variation of Ω with position. It could be seen that the Ω in the diffusion zone of all joints was greater than 1, indicating the formation of a continuous solid solution in the diffusion zone without the

appearance of intermetallic compounds.

The above results predicted the formation of the solid solution phase, but did not predict the crystal structure in the diffusion zone. Guo et al. [68] used *VEC* parameters to predict the phase structure of the high entropy alloy. The *VEC* of the diffusion zone could be calculated by the following equation:

$$VEC = \sum_{i=1}^n X_i(VEC)_i \quad (3.8)$$

where $(VEC)_i$ is the *VEC* value of the *i* element. It was found that the FCC phase exists stably when the average *VEC* of the alloy is greater than or equal to 7.84. The blue curves in Fig. 3.13 represent the *VEC* values at different locations, and the *VEC* values in the diffusion zone were all greater than 7.84, further confirming that the FCC solid solution phase was generated in the joint. Compared with intermetallic compounds, the FCC phase solid solution in the diffusion zone was consistent with the structure of the base materials on both sides, which was beneficial to improve the mechanical properties [14].

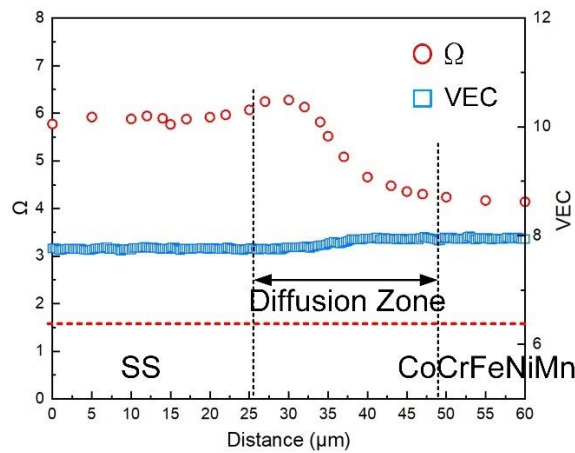


Fig. 3.13 Ω and *VEC* for the diffusion bonded CoCrFeNiMn/316SS joint at 1000

°C/25 MPa/1 h.

3.3.4.2 Elemental enrichment near the voids

Fig. 3.14 shows the distribution of elements near the interface in CoCrNi/SS joint and CoCrFeNiMn/SS joint. In CoCrFeNiMn/SS joint, Cr and Mn elements could be seen to accumulate around the voids, which may be related to the high diffusion rate of Cr and Mn. As mentioned above, the diffusion rates of Cr and Mn in the diffusion zone were higher than those of elements such as Fe and Co. As a result, migration of Cr and Mn from CoCrFeNiMn into 316 stainless steel substrates weakened the activity of other elements and made their diffusion slower. During the diffusion bonding process, Mn and Cr diffused first to the voids at the interface, and then a part of atoms were captured by the voids and gathered around the voids. However, in the CoCrNi/SS joint, Mn element was not enriched at the interface due to the low Mn content in base materials. In addition, it was evident that some oxides were present at the interface. In a vacuum environment, despite the minimal presence of oxygen, there might still exist trace quantities of impurities, including oxygen itself. These impurities had the potential to interact with metals and underwent chemical reactions. Zhang et al. [69] also found the chromium oxides during the diffusion bonding of CoCrFeNiMo medium entropy alloys. As shown in Fig. 3.15, the identification of oxides at the interface revealed the possible presence of Cr_2O_3 in the CoCrNi/SS joint, while Cr_2O_3 and Mn_3O_4 were appeared in the CoCrFeNiMn/SS joint. This may be attributed to two reasons. Firstly, the rapid diffusion of Cr and Mn in the base materials enables them to quickly diffuse to the interface. Secondly, Cr readily combines with oxygen to form Cr_2O_3 , while Mn readily combines with oxygen to form Mn_3O_4 , with the Gibbs free energy values following the order: $\text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4$ [70].

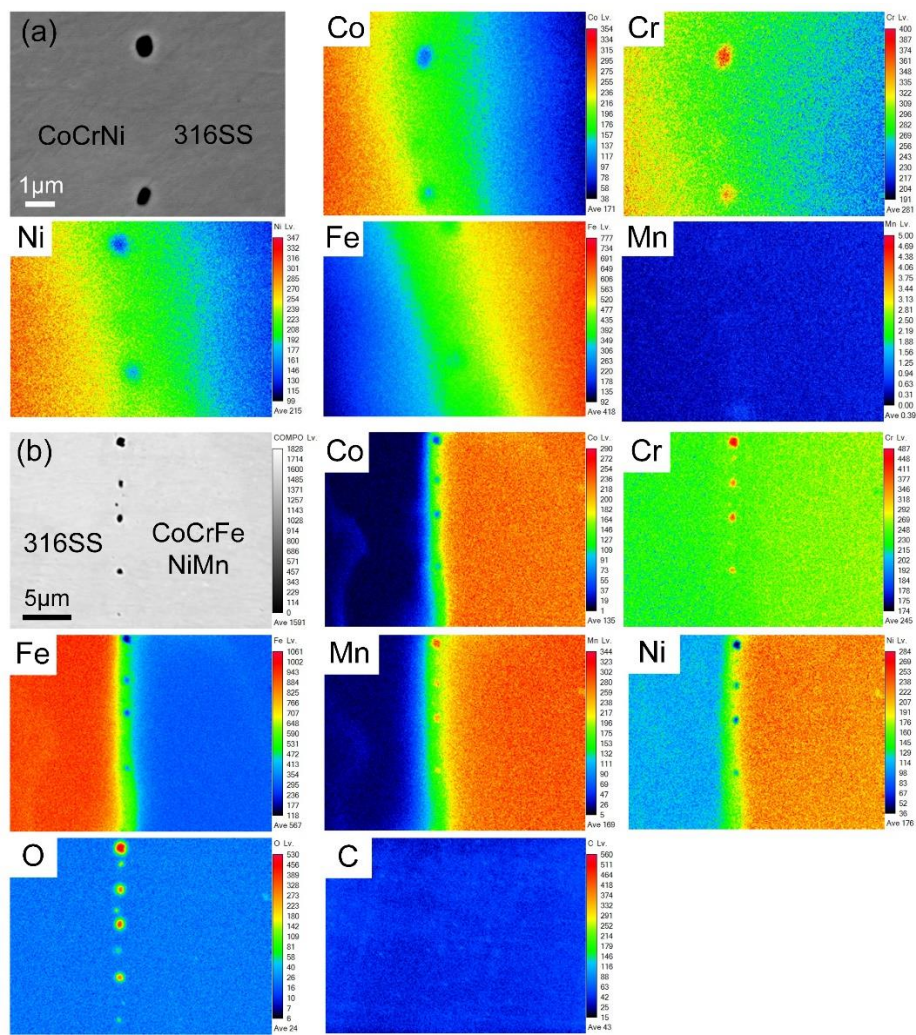


Fig. 3.14 Map scanning results near the interface of joints: (a) CoCrNi/SS and (b) CoCrFeNiMn/SS.

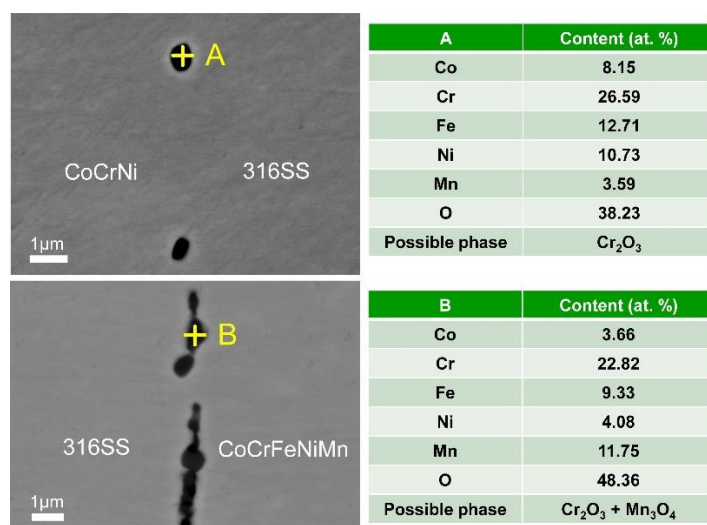


Fig. 3.15 Point scanning results near the interface of different joints bonded at $0.77T_m$.

3.3.4.3 Bonding mechanism of the joint

Fig. 3.16 illustrated a schematic of the bonding mechanism in CoCrFeNiMn/316SS joint. The bonding process could be divided into three stages. The first stage involved physical contact at the interface. The plastic deformation due to high bonding temperature and pressure resulted in an increase of the actual contact area. The second stage involved the interdiffusion of elements and the growth of grains at the interface. Under the action of elevated bonding temperature and large concentration variation amplitudes, Fe element diffused from the stainless steel side to the CoCrFeNiMn CSSA side, while Co, Cr, Mn and Ni elements diffused from the CoCrFeNiMn CSSA side to the stainless steel side. Furthermore, recrystallization and grain growth that caused by high bonding pressure occurred at the interface, and the voids gradually closed. Due to the high mixing entropy, a solid solution structure was formed in the diffusion zone instead of intermetallic compounds. In the third stage, the voids disappeared, and atomic diffusion reached an equilibrium state. With the further diffusion of atoms, the distance of the diffusion zone increased, while the width of zone I was wider than that of zone II because the diffusion rate of elements in CSSAs was greater than that of stainless steel. Besides, zone I was composed of Fe-rich solid solution and zone II was composed of Co-Cr-Fe-Ni-Mn solid solution. In this study, grain growth at the interface and sufficient diffusion were the key causal factors for the disappearance of voids and increased mechanical property.

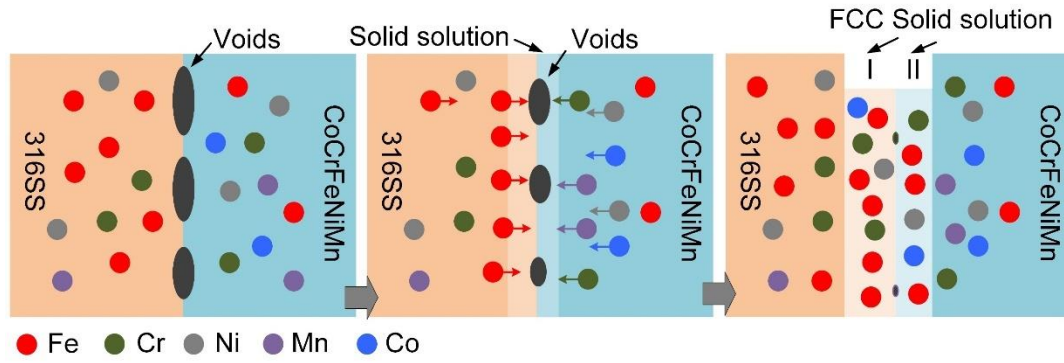


Fig. 3.16 Schematic of the bonding mechanism of CoCrFeNiMn/316SS joint.

3.3.4.4 Comparison of diffusion distance between SPS method and traditional method

The difference in the diffusion distances of the joints obtained by the traditional diffusion bonding method and the SPS method was compared. Samiuddin et al. [71] achieved the joining of CoCrNi CSSA and stainless steel using the traditional diffusion bonding method, where the distance of the diffusion zone was 10.14 μm at 1050 $^{\circ}\text{C}$. In contrast, the CoCrNi/SS joints obtained in this study at 1050 $^{\circ}\text{C}$ had a diffusion distance of 19.54 μm , which was about twice the result of Samiuddin et al. The increase in diffusion distance indicated that more adequate diffusion occurred, which resulted in fewer voids and higher tensile strength. For diffusion bonding of bulk materials, the main difference between spark plasma assisted diffusion bonding and traditional vacuum diffusion bonding is the acceleration of atomic diffusion by electric fields. To explain the physical phenomenon of accelerated atomic diffusion by electric field, Conrad [72] proposed the theory of electromigration, which shows that metal ions have a scattering effect on electrons, and the electron momentum tends to transfer to ions, and the electron wind force formed at this time drives the atomic migration and diffusion. In addition, Garay et al. [73] suggested that the applied electric field has an effect on the vacancy mobility, which means that the electric field causes an increase in

mobility and accelerates the atomic diffusion process.

In general, compared with traditional diffusion bonding, the advantages of spark plasma assisted diffusion bonding are mainly reflected in the following three points: (I) fast heating rate, solving the problem of high energy consumption during traditional diffusion bonding; (II) low required bonding pressure and higher dimensional accuracy; (III) the electric field is introduced in addition to the temperature and stress fields required for traditional diffusion bonding, and the electromigration effect under the action of the electric field accelerates the diffusion of joints.

3.4 Summary

Using SPS diffusion bonding method, CoCrNi, CoCrFeNi, and CoCrFeNiMn CSSAs were respectively joined to 316 stainless steel. The effect of bonding temperature and concentration on microstructure and tensile property of bonded joints were investigated. The results were summarized as follows.

(1) Sound joints of equiatomic CoCrNi-based CSSAs/316SS were obtained by SPS diffusion bonding. The tensile strength of CoCrFeNiMn/316SS joint was gradually increased with increasing bonding temperature, and the maximum value of 468 MPa was obtained at $0.8T_m$. Meanwhile, the bonding at $0.8T_m$ seemed to have sufficient diffusion and grain growth at the interface of the joint, resulted in the disappearance of voids and the increase in strength of joint.

(2) The optimal bonding temperature for equiatomic CoCrNi-based CSSAs system/316SS joint was $0.8T_m$, and the tensile strength of the joints were all exceeded 80% of the 316 stainless steel base material. In CoCrNi/316SS joint, large element concentration variation would amplitude in the diffusion zone, could result in rapid diffusion of atoms and large diffusion distance.

(3) Continuous FCC solid solution structure was generated in the diffusion zone of joints, which was beneficial to the increase of tensile property. Compared to laser beam welded joints, the tensile strength of diffusion bonded CoCrNi/316SS joint increased by 90 MPa and the elongation of diffusion bonded CoCrFeNiMn/316SS joint increased by 18%.

**Chapter 4 Effect of Ni interlayer on
diffusion bonded reduced activation
Cr_{0.8}FeMnNi medium entropy alloy /
316 stainless steel joint: interfacial
microstructure, diffusion behavior
and mechanical properties**

4.1 Introduction

Medium entropy alloys (MEAs) are a class of metallic materials that contain three or more elements in roughly equal proportions. Due to the high degree of atomic disorder, MEAs possess unique mechanical, physical, and chemical properties [74]. MEAs can be tailored for specific applications (such as nuclear power plants), but also have challenges such as processing difficulties. Considering about the long-term stable operation of nuclear power plants, the content of high radioactive elements (such as ^{60}Co) in structural materials needs to be effectively controlled [33]. Given that ^{60}Co is a high-energy radioactive isotope with a relatively short half-life of about 5.27 years, its production elevates the radiation levels within the reactor. Consequently, minimizing the utilization of alloys containing cobalt can mitigate issues arising from irradiation damage. Reduced activation MEAs, especially Co-free MEAs should be well developed. Hashimoto et al. [75] found that $\text{Cr}_{0.8}\text{FeMnNi}$ -based MEAs had the potential to be developed as high irradiation resistant materials. The $\text{Cr}_{0.8}\text{FeMnNi}$ MEA exhibited the Frank loops number density of $2.9 \times 10^{21} \text{ m}^{-3}$ and the Frank loops average diameter of 48 nm after electron irradiation at 400 °C, utilizing the Multi-beam High Voltage Electron Microscope (HVEM) operated at 1.25 MeV. However, MEAs used in nuclear power plants require not only outstanding irradiation resistance, but also good joining properties, because joining is necessary for many components in the construction, operation, and maintenance of nuclear power plants [76]. The joining quality directly affects the service life and safety of MEAs used. Therefore, it is also necessary to investigate the joining of $\text{Cr}_{0.8}\text{FeMnNi}$ -based MEAs to expand their application in nuclear power plants.

Diffusion bonding, which is a kind of solid-state joining technology with the

advantages of small deformation and excellent welding quality, has been widely used for dissimilar metals joining [77]. In nuclear power plants, diffusion bonding can be used to join the fuel cladding and structural components of nuclear reactors [78]. Besides, stainless steel (SS) exhibited good mechanical properties and excellent weldability. Typically, it is joined with other materials [79-80]. In pressurized water reactors, the diffusion bonding between $\text{Cr}_{0.8}\text{FeMnNi}$ -based MEAs and SS is a promising method for joining safe-end piping to the nozzle of the reactor pressure vessel. Furthermore, since $\text{Cr}_{0.8}\text{FeMnNi}$ MEA and SS share common constituent elements, namely Fe, Cr, and Ni, this similarity can reduce the formation of intermetallic compounds [81]. Several researchers have investigated diffusion bonding between high entropy alloy (HEA)/MEA and SS. Gao et al. [82] studied the diffusion bonding between CoCrFeMnNi HEA and 304SS and found that HEA/SS joint could achieve a useable strength of 320 MPa at relative lower temperature of 850 °C ($\sim 0.63 T_m$, T_m , Temperature of melting) by surface nano-crystallization treatment. Samiuddin et al. [83] investigated the diffusion bonding of CoCrNi MEA to 304SS and found that the bonding interface was almost free from IMCs and formed a solid solution, resulting in the enhancement of joint strength at the bonding temperature of 1075 °C. It was clear that sound HEA (MEA)/SS joints could be obtained by diffusion bonding, but the radioactivity of the Co element in MEAs limits their application in nuclear power. Consequently, it is crucial to investigate the dissimilar diffusion bonded joints between $\text{Cr}_{0.8}\text{FeMnNi}$ MEA and SS.

The critical problem associated with $\text{Cr}_{0.8}\text{FeMnNi}$ MEA/SS diffusion bonded joint is that the triggering of atomic diffusion at the interface needs higher bonding temperatures, pressures, and times because of lower concentration gradient between $\text{Cr}_{0.8}\text{FeMnNi}$ MEA and SS [84-85]; and this may degrade the performance of joints.

Numerous published papers have demonstrated the feasibility of reducing bonding temperature and preventing the formation of harmful products by introducing a suitable interlayer. Among the various types of interlayers, Ni has been extensively utilized as an interlayer during the diffusion bonding process because of its plastic deformation capability and its good compatibility with other alloys [86-87]. He et al. [88] found that incorporating a Ni interlayer between titanium alloy and stainless steel prevented the production of hard and brittle phases, resulting in the highest shear strength. To alleviate the coarsening of γ' precipitates resulting from the high bonding temperature, Yang et al. [89] utilized a pure Ni foil to reduce the bonding temperature. The incorporation of this Ni foil interlayer significantly increased the shear strength of the joints bonded at 950 °C and 1000 °C. Overall, the Ni interlayer is expected to improve the strength of diffusion bonded joints and decrease the bonding temperature.

In this study, the diffusion bonding of Cr_{0.8}FeMnNi MEA to 316SS was studied with and without the use of Ni interlayer. Microstructure evolution and mechanical properties of diffusion bonded joints at different bonding temperatures were studied, and the diffusion kinetics and diffusion coefficient of various elements as well as the growth kinetics of diffusion layers were analyzed.

4.2 Experimental

The Cr_{0.8}FeMnNi MEA and commercially available 316 stainless steel were used as base metals. The Cr_{0.8}FeMnNi MEA ingots were arc melted in argon atmosphere with high purity metal powders (>99.9 wt% purity). The ingots were flipped at least 7 times to make them homogeneous. Then as-cast alloys were homogenized in vacuum at 1160 °C for 24 h. The chemical compositions of Cr_{0.8}FeMnNi and 316 stainless steel are listed in Table 4.1. As shown in Fig. 4.1, Cr_{0.8}FeMnNi displayed single FCC phase

with uniform composition distribution. The high entropy effect in Cr_{0.8}FeMnNi alloys favors the formation of random solid solutions over intermetallic compounds. Several criteria have been proposed by Guo et al. [90] and Zhang et al. [91] to assess the formation of phases in multi-principal systems. It has been observed that certain factors, including the atomic radial difference (δ), mixing enthalpy (ΔH_{mix}), and entropy of mixing (ΔS_{mix}), play significant roles in phase formation. The values of δ , ΔH_{mix} , and ΔS_{mix} can be calculated using the following formulas, respectively:

$$\Delta H_{mix} = 4 \sum_{i=1, i \neq j}^n c_i c_j \Delta H_{mix}^{AB} \quad (4.1)$$

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (4.2)$$

$$\Delta S_{mix} = -R \sum_{i=1}^n c_i \ln c_i \quad (4.3)$$

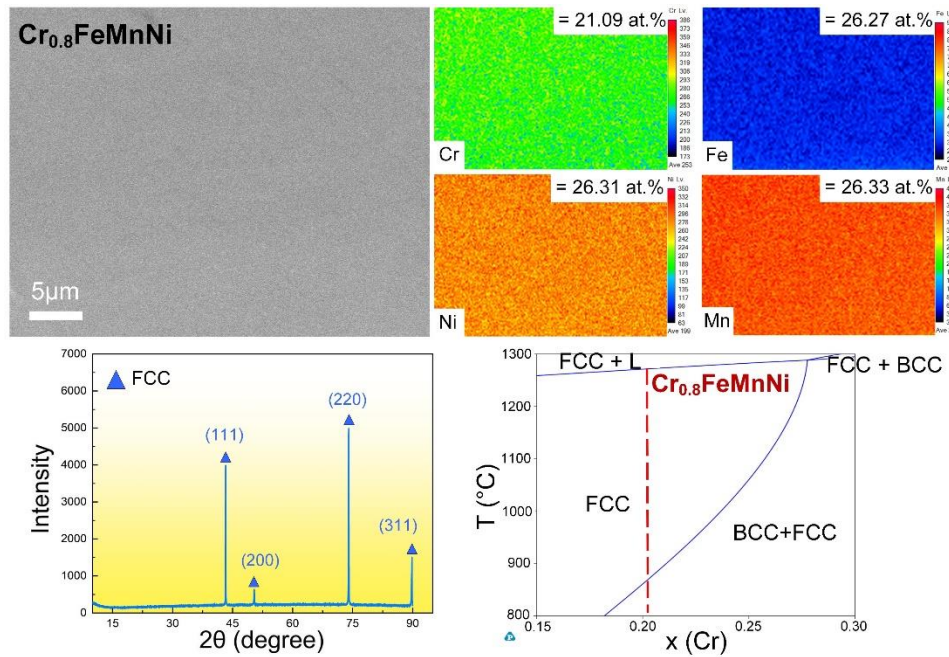
where n is the number of principal elements, r_i and c_i are the atomic radius and atomic percentage of i_{th} element, respectively, $\bar{r}$ is the average atomic radius, ΔH_{mix}^{AB} is the mixing enthalpy of binary A-B system, and R is the gas constant. Based on the formation rules [92], solid solution will form if $0 \leq \delta \leq 8.5 \%$, and $-22 \leq \Delta H_{mix} \leq 7$ kJ/mol, $11 \leq \Delta S_{mix} \leq 19.5$ J/(K·mol). The parameters for Cr_{0.8}FeMnNi MEA in this work are listed in Table 1. All the parameters satisfy the rules proposed by Guo et al. Besides, the mechanical properties of the base metals are shown in Table 4.2. The Cr_{0.8}FeMnNi MEA exhibited comparable tensile strength and elongation to that of 316 stainless steel. In addition, as shown in Fig. 4.1, the phase diagram of Cr_{0.8}FeMnNi MEA was calculated with the CALPHAD methodology, and the melting point of Cr_{0.8}FeMnNi is 1280 °C.

Table 4.1 Parameters of Cr_{0.8}FeMnNi MEA.

Material	δ (%)	ΔS_{mix}	ΔH_{mix}
		J/(K·mol)	(kJ/mol)
Cr _{0.8} FeMnNi	0.25	11.49	-17.69

Table 4.2 The mechanical properties of the base metals.

Base metals	Tensile strength	Elongation (%)
	(MPa)	
Cr _{0.8} FeMnNi MEA	506	39.8
316SS	498	33.7

**Fig. 4.1** Microstructure, element distribution, crystal structure and phase diagram of Cr_{0.8}FeMnNi.

Before diffusion bonding, the samples were cut into blocks by abrasive cutter, and

the base metals were grounded with up to 5000 grit sandpaper and then polished using up to 0.1 μm diamond pastes to ensure the same surface roughness. Pure Ni foils with a thickness of 30 μm were utilized to diffusion bond $\text{Cr}_{0.8}\text{FeMnNi}$ and 316SS. As shown in Fig. 4.2(a), the Ni foils were sandwiched between two base metals, and the diffusion bonding of $\text{Cr}_{0.8}\text{FeMnNi}$ MEA to 316SS was conducted with and without the use of Ni interlayers in a spark plasma sintering machine (DR.SINTER.LAB, SPS+510 L). Fig. 4.2(b) shows the schematic of the process curve during the diffusion bonding.

According to reference [50], generally, the bonding temperature range during diffusion bonding should be $0.6 T_m - 0.8 T_m$ (T_m is the melting point of the lower of two base metals (K)), while the melting points of 316SS and $\text{Cr}_{0.8}\text{FeMnNi}$ are 1370 $^{\circ}\text{C}$ and 1280 $^{\circ}\text{C}$, respectively [93]. Therefore, the bonding temperatures from 660 $^{\circ}\text{C}$ to 970 $^{\circ}\text{C}$ should be selected. However, too low a temperature could lead to insufficient diffusion and decrease the mechanical properties of the joint. The higher bonding temperature, such as 1000 $^{\circ}\text{C}$, will deteriorate the properties of base metal, meanwhile, the excessive growth of brittle intermetallic compounds led to large residual stress, which caused cracks generation along the interface and reduced the tensile strength of joint. Therefore, in this study, the bonding temperatures from 750 $^{\circ}\text{C}$ to 970 $^{\circ}\text{C}$ were applied. Due to the large deformation of the joint at 970 $^{\circ}\text{C}$ in Fig. 4.2(d), the bonding temperatures of 750 $^{\circ}\text{C}$, 820 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$ were used. The holding time at bonding temperatures was 60 min and the bonding pressure was 25 MPa. Due to the presence of undesirable substances such as oxides on the surfaces of base metals before bonding, applying higher pressure can ensure a tight fit between the bonding surfaces, facilitating the diffusion bonding process. Elevated pressure levels help overcome these irregularities, ensuring uniformity and enhancing the overall bonding quality. In contrast, lower pressures, such as 10 MPa, may result in uneven diffusion, leading to irregularities in

the bonding interface. Such irregularities could introduce minute cracks or defects, consequently compromising the mechanical properties of the bonded joint. Previous studies have also indicated that high / medium entropy alloys require bonding pressures exceeding 20 MPa during diffusion bonding to achieve optimal joints [77]. Besides, during the diffusion bonding, a vacuum level below 7×10^{-2} Pa and a peak value of pulse current around 780 A were applied.

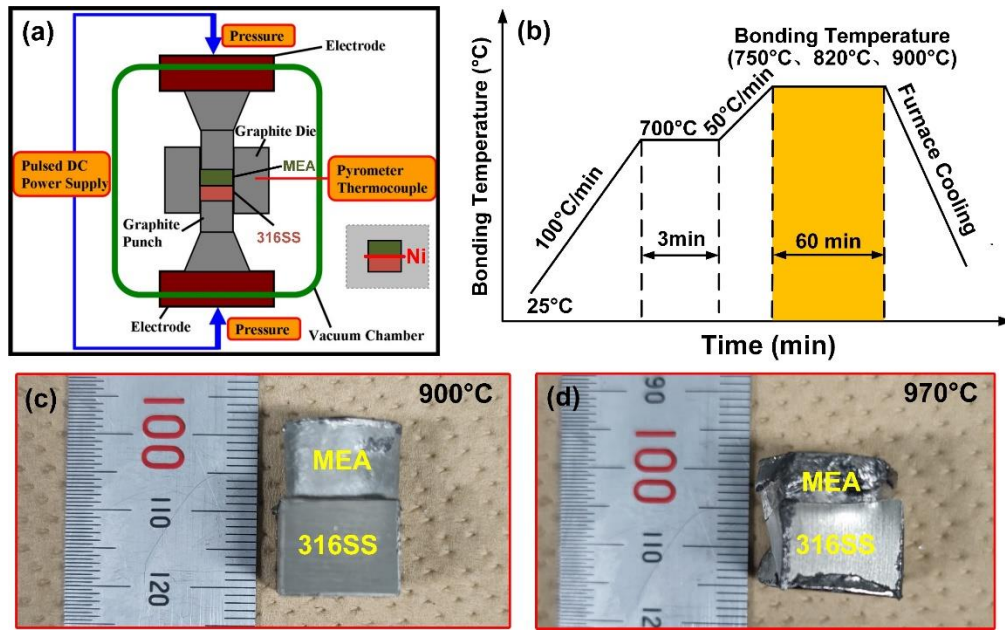


Fig. 4.2 (a) Schematic of SPS diffusion bonding process, (b) temperature profile, and appearance of the joints bonded at different bonding temperatures of (c) 900 °C, (d) 970 °C.

Based on the result, The interfacial microstructures and diffusion behavior were studied by scanning electron microscope (SEM, JEOL, JSM-6510LA) and electron probe micro-analyzer (EPMA, JEOL, JXA-8530 F). Transmission electron microscopy (TEM, JEOL JEM-2010) was employed to further investigate the microstructure and chemical composition of the specimens. TEM samples were picked up by focused ion beam system (FIB, Hitachi FB-2100) and milled to a thickness of approximately 100

nm. The joint block was machined into thin plate, then small sheet-type tensile specimens with the gauge section of 5 mm long, 1.2 mm wide and 0.25 mm thick (SS-J type) were punched out from the joint center. Tensile tests were conducted to investigate the mechanical properties of different joints by using tensile tester (Instron-5564) with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ at room temperature. The microhardness of joint was tested by a nanoindentation tester (Hysitron TI 950) with a Berkovich-type indentation tip. Depth-control indentations were performed with a constant penetration depth of 300 nm. Furthermore, the fracture morphology of the tensile specimen was examined by SEM and energy dispersive spectroscopy (EDS, JEOL, JED-2300).

4.3 Results

4.3.1 Interfacial microstructures of the joints

Fig. 4.3 shows the microstructures of joints bonded at various temperatures. In Fig. 4.3(a-b), a black interface layer was observed, while the bonded joint with a Ni interlayer did not exhibit such a layer obviously. Instead, a continuous solid solution structure was formed near the interface. Moreover, as the bonding temperature increased from 820°C to 900°C, the black interface layer in the direct diffusion bonded joint became discontinuous. Fig. 4.4 presents the EPMA map scanning analysis results of the $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint at various temperatures, aiming to investigate the composition of the black interface layer in greater detail. In the black interface layer, there was an enrichment of Cr, Mn, and O, suggesting the formation of oxides. The origin of these oxides is thought to be the residual oxide film on the surface of the base metal. When the base metals near the voids area was subjected to heating and pressure, it could lead to partial or complete rupture of the residual oxide film, resulting in the

appearance of oxide inclusions. These oxide inclusions typically accumulated along the base metals surface surrounding the voids, filling the space around them. The details will be discussed in section 4.4.1. Table 4.3 shows the point scanning results in the different positions of Fig. 4(c). It suggested the presence of two types of oxides, namely Cr_2O_3 and Mn_3O_4 , while the diffusion regions on both sides of the interface exhibited a solid solution structure enriched with Fe element. The formation of a solid solution in the diffusion region was accomplished through the process of atomic diffusion and mutual dissolution. When two base metals came into contact and were heated, atoms started to diffuse from one material into the other. This atomic diffusion resulted in the rearrangement of atoms at the interface and the formation of solid solution structure. Furthermore, with the increase in bonding temperature, the width of the diffusion region also increased. This was attributed to the higher temperature providing a greater amount of thermal energy, which accelerated the diffusion rate of atoms. Fig. 4.4(d) shows the thermodynamic data for MnO_2 , Mn_2O_3 , Mn_3O_4 . Jacob et al [93] found that the order of manganese oxide from highest to lowest at different temperatures is MnO_2 , Mn_2O_3 , Mn_3O_4 . Therefore, during diffusion bonding in the temperature range of 750-900°C, Mn_3O_4 will appear due to its lowest Gibbs free energy. In addition, the Cr_2O_3 oxide could originate from the residual oxide film on the base materials, and the reaction at high temperature in furnace. The interface oxides primarily stem from the Cr_2O_3 oxide film on the surface of the base material. Even after polishing with 0.1 μm diamond paste before diffusion bonding, it was unavoidable that residual oxide films remained on the base materials. In addition, diffusion bonding typically takes place under high-temperature conditions. At elevated temperatures, metal surfaces are more prone to react with oxygen, leading to the formation of oxides. Chromium elements readily form Cr_2O_3 oxides at high temperatures. According to the study by Tsai et al. [58], the

activation energy (in $\text{kJ}\cdot\text{mol}^{-1}$) in Cantor alloy follows the order from largest to smallest: Ni, Fe, Co, Cr, Mn. It can be observed that Cr and Mn exhibit lower activation energies, allowing them to swiftly migrate to the interface at high temperatures and react with oxygen to form oxides, such as Cr_2O_3 and Mn_3O_4 .

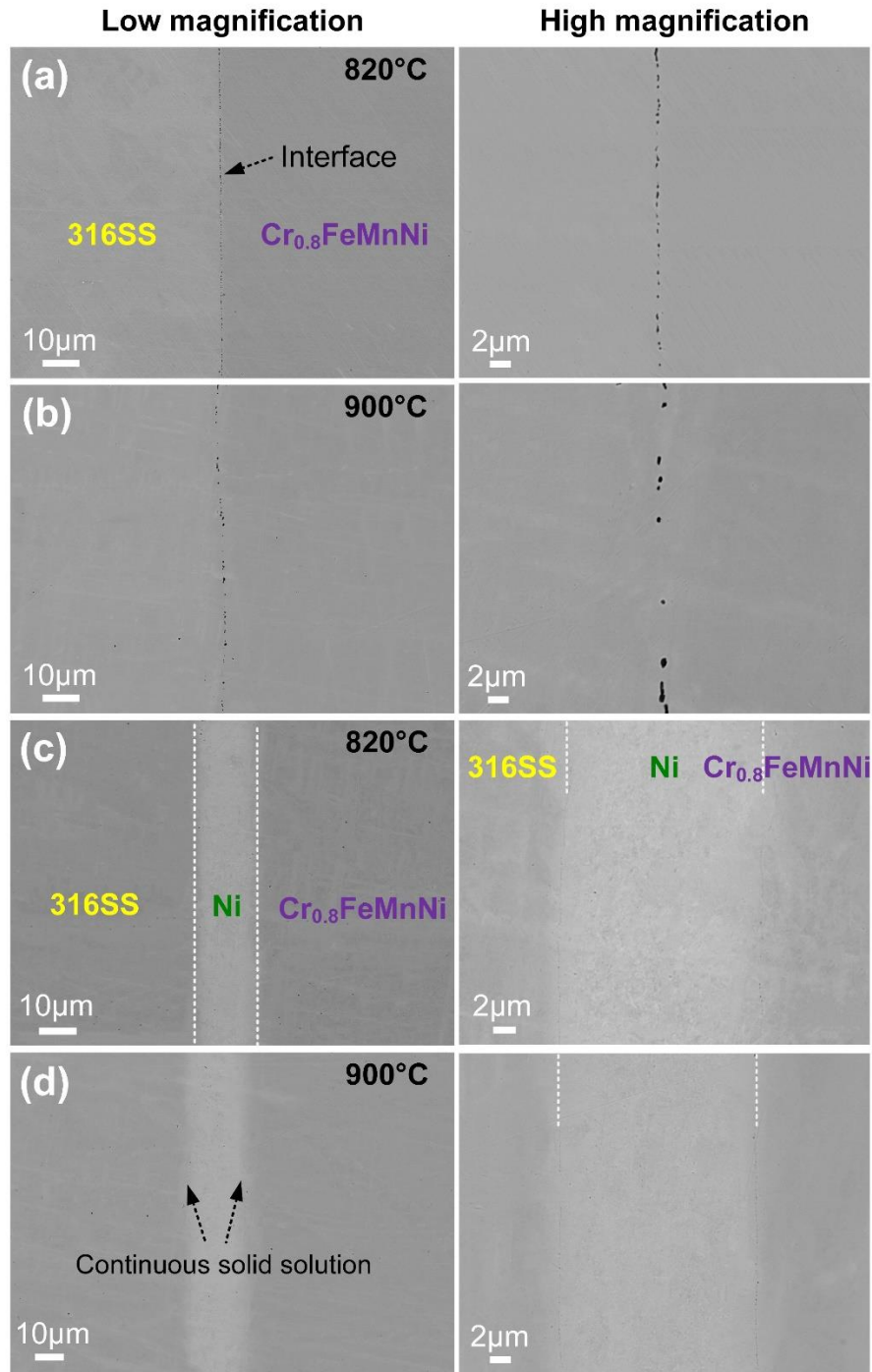


Fig. 4.3 Microstructure of $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joints bonded at (a) 820°C , (b)

900 °C, and $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}/316\text{SS}$ joints bonded at (c) 820 °C, (d) 900 °C.

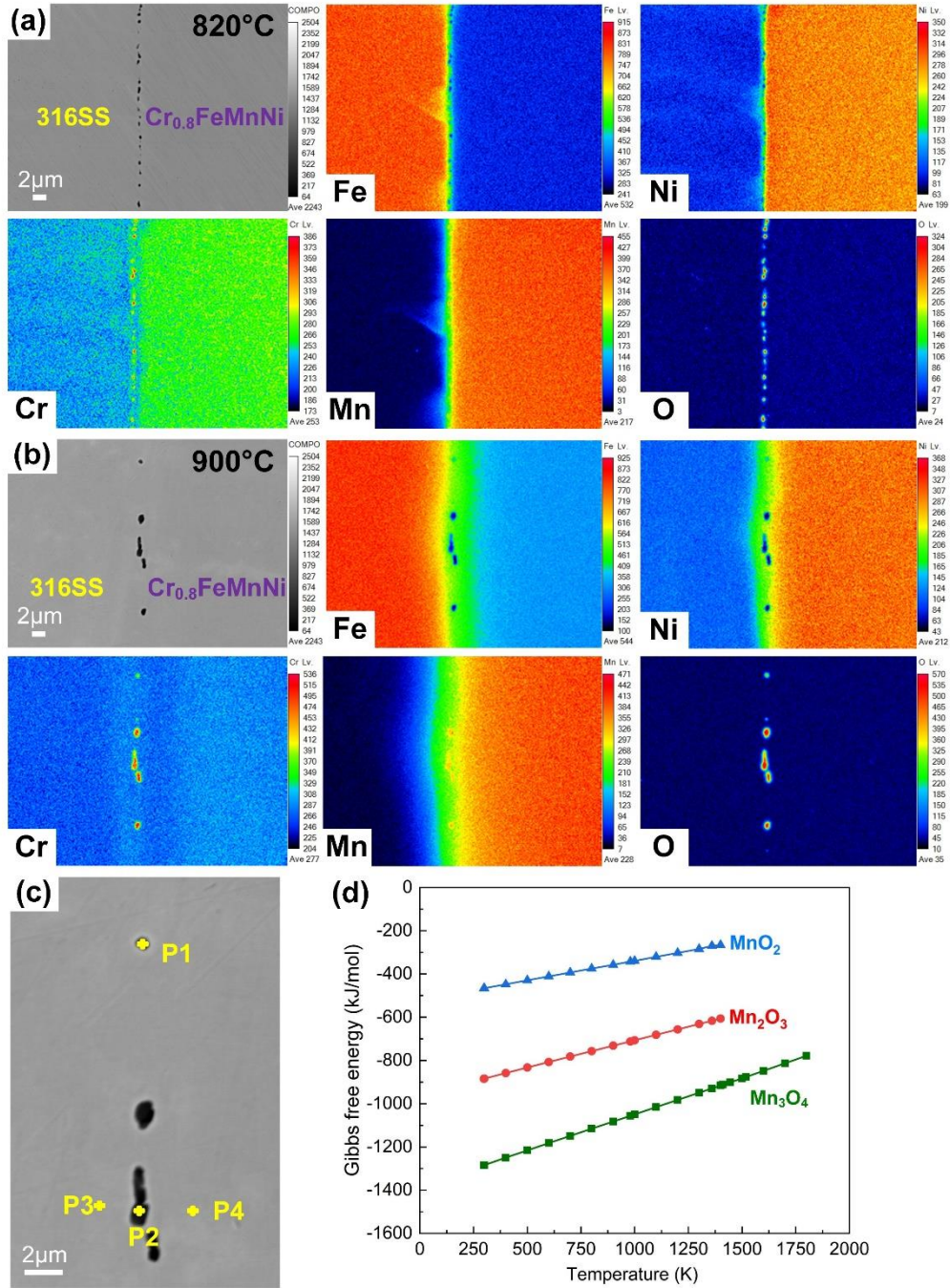


Fig. 4.4 Map scanning analysis results of $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint at different temperatures of 820 °C, (b) 900 °C, (c) the position of point scanning analysis for $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint at 900 °C, and (d) thermodynamic data for MnO_2 , Mn_2O_3 ,

Table 4.3 The elemental composition in Figs. 4.4 and 4.5 (at. %).

Diffusion zone	O	Cr	Fe	Ni	Mn	Possible phase
P1	49.15	32.88	10.72	-	7.25	Cr ₂ O ₃
P2	57.22	20.89	3.05	-	18.84	Cr ₂ O ₃ + Mn ₃ O ₄
P3	-	23.02	54.17	8.37	14.44	Fe-rich solid solution
P4	-	24.54	43.22	11.94	20.30	Fe-rich solid solution
P5	57.4	0.7	1.4	0.3	40.2	Mn ₃ O ₄
P6	3.4	16.5	42.8	19.7	17.6	Fe-rich solid solution
P7	3.7	16.9	37.8	20.7	20.9	Fe-rich solid solution
P8	-	21.8	25.5	26.1	26.6	Cr _{0.8} FeMnNi
P9	-	18.7	70.2	9.8	1.3	Stainless steel

The microstructure of Cr_{0.8}FeMnNi/316SS joint bonded at 820 °C is further observed by TEM, as shown in Fig. 4.5(a). The left side was 316SS and the right side was Cr_{0.8}FeMnNi, while oval and elongated oxides appeared at the interface area. By diffraction analysis in Fig. 4.5(b) and point scan analysis in Table 4.3, the oxide was mainly composed of Mn₃O₄, which verified the previous result. There was a diffusion zone near the interface, and point scans performed at P6 and P7 revealed that the diffusion zone primarily consists of a Fe-rich solid solution, which was consistent with the results obtained from EMPA. Additionally, as shown in Fig. 4.5(c), some voids could be observed at the interface, which were common defects during diffusion bonding. At the beginning of bonding process, numerous voids were typically present

at the interface, the concentrated stress exerted on the surrounding metal of the voids could induce the fracture, deformation, or detachment of the initial oxide film, thereby leading to the formation of oxide inclusions. Typically, these oxide inclusions aggregated along the metal surface near the voids area, occupying the void space. The presence of oxides usually reduces the mechanical properties of the joints. Zhang et al [94] studied the vacuum diffusion bonding of non-equiatomic CoCrFeNiMo medium entropy alloys and found the Cr-rich oxide at the interface. However, with the increase of bonding temperature, they found that the Cr-rich oxide gradually decreased and disappeared at 1050 °C. Therefore, similarly, this study also attempted to reduce the oxides quantity by increasing the diffusion bonding temperature, such as 970 °C. Unfortunately, as shown in Fig. 4.2(d), the sample experienced severe deformation, resulting in the failure of the bonding experiment. This deformation is attributed to the relatively low melting point of Cr_{0.8}FeMnNi MEA, which may induce metal softening at temperatures close to 1000 °C. Consequently, this study further aimed to reduce the oxide quantity by introducing a Ni interlayer between the two base metals.

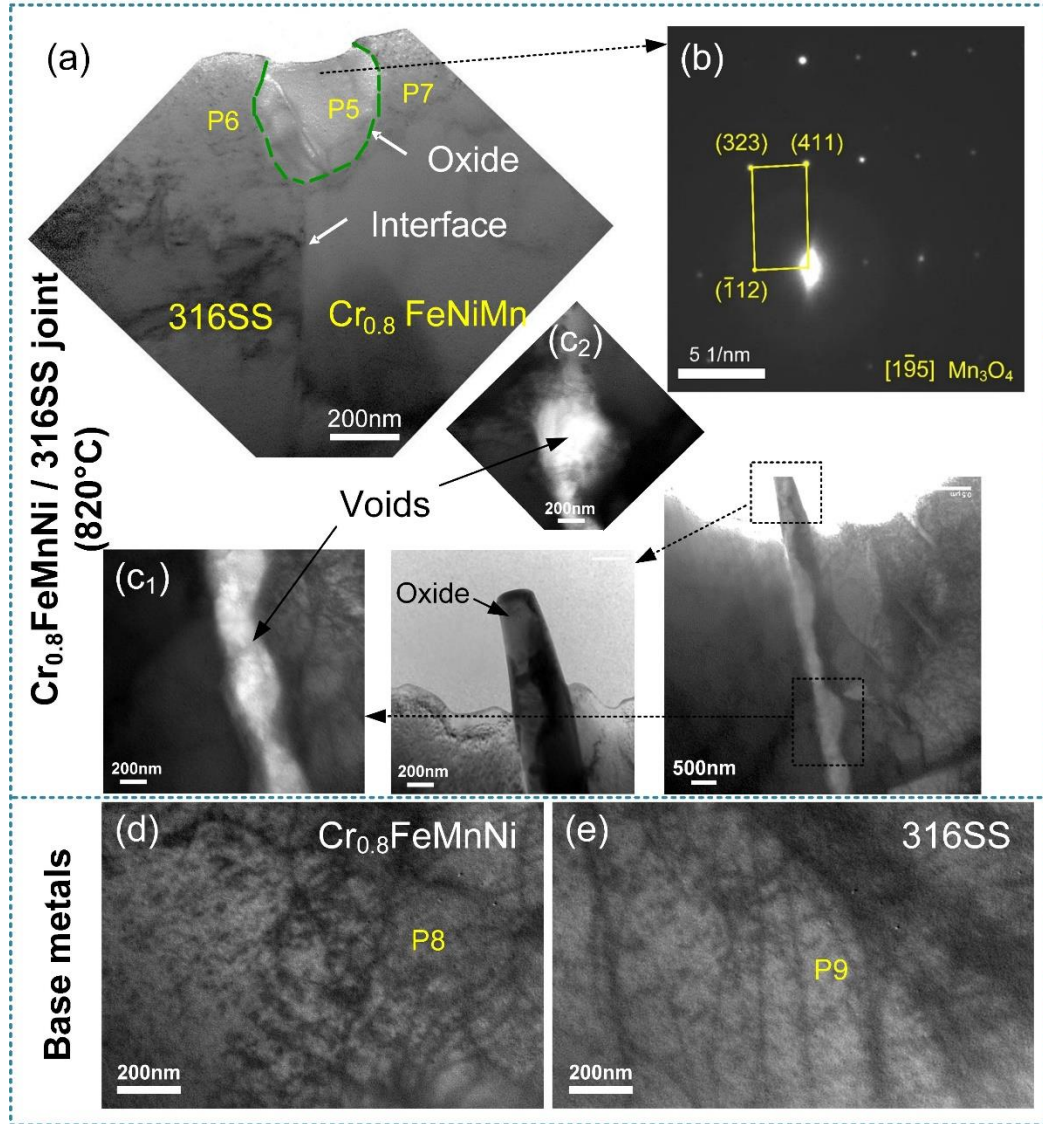


Fig. 4.5 (a) TEM bright field image of the $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint bonded at 820°C , (b) diffraction pattern taken at P5 position; (c₁-c₂) voids at the interface; and TEM bright field images of base metals in (d) $\text{Cr}_{0.8}\text{FeMnNi}$ and (e) 316SS.

Fig. 4.6 and Fig. 4.7 show the results of the map scanning analysis of the $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint with a Ni interlayer at various bonding temperatures. Table 4.4 shows the average oxide size at the interface. The oxide size was measured in the secondary electron images by using ImageJ software, which employs techniques such as thresholding and edge detection for shape extraction. The acquired data is then

subjected to quantitative analysis, involving specific mathematical formulas customized for different oxide shapes. The formula $D = 2 \times \sqrt{A/\pi}$ is applicable to calculate the oxides diameter (D), where A represents the oxide area. Finally, average the oxide diameters to obtain the oxide size. As shown in Fig. 4.6 and Fig. 4.7, with increasing bonding temperature, the diffusion zone near the interface exhibited a gradual widening. Additionally, the previously prominent dark oxide layer on the interface became less prominent, and the average oxide size at the interface was significantly reduced in joints with a Ni interlayer, as demonstrated in Table 4.4. The reduction of oxide size in the presence of the Ni interlayer could be attributed to three key factors: the shielding effect of the Ni interlayer, accelerated diffusion, and the excellent plasticity of Ni. These factors will be elaborated upon in the subsequent discussion section.

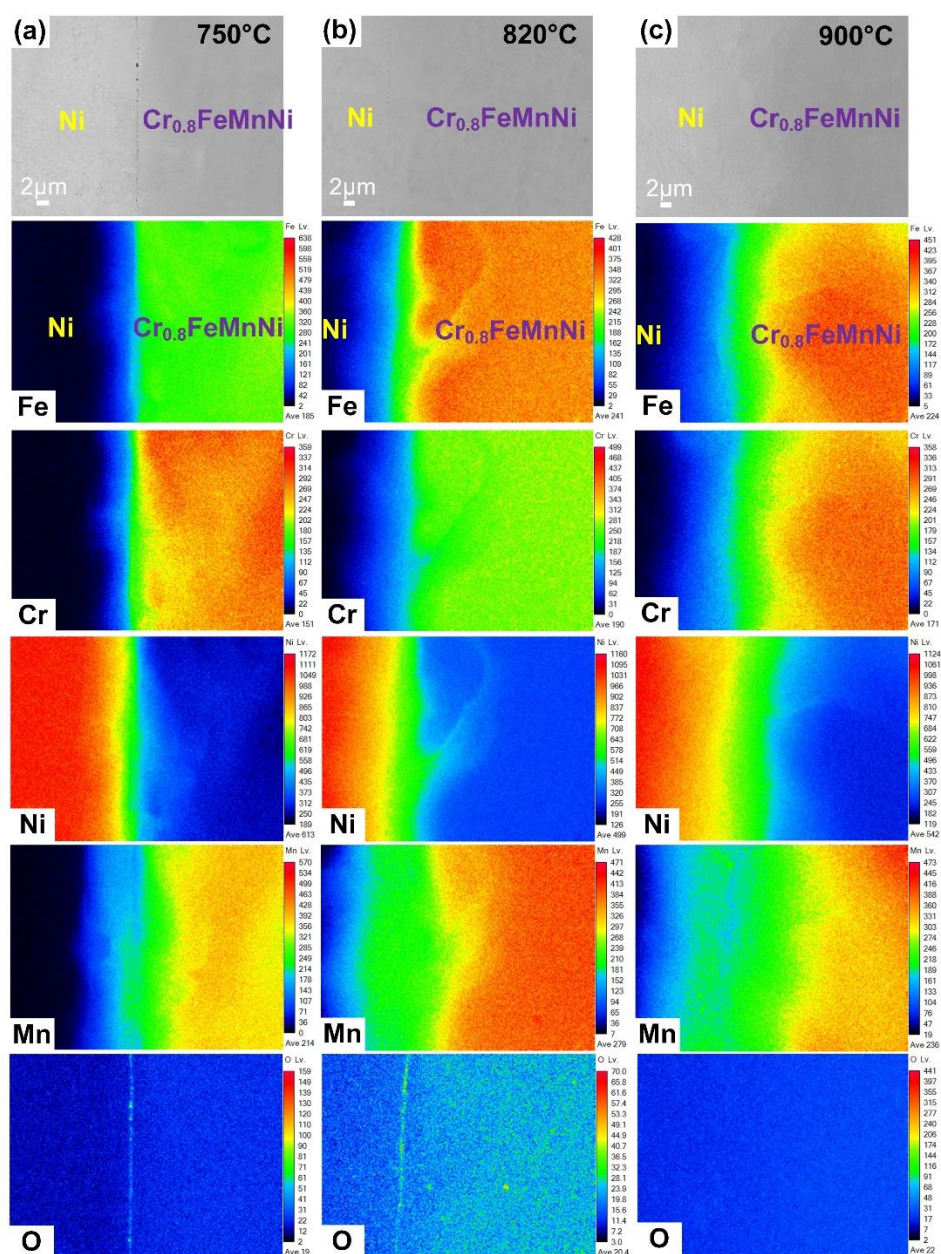


Fig. 4.6 EPMA map scanning analysis results of $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}/316\text{SS}$ joint on the $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}$ side at different temperatures of (a) 750 °C, (b) 820 °C, and (c) 900 °C.

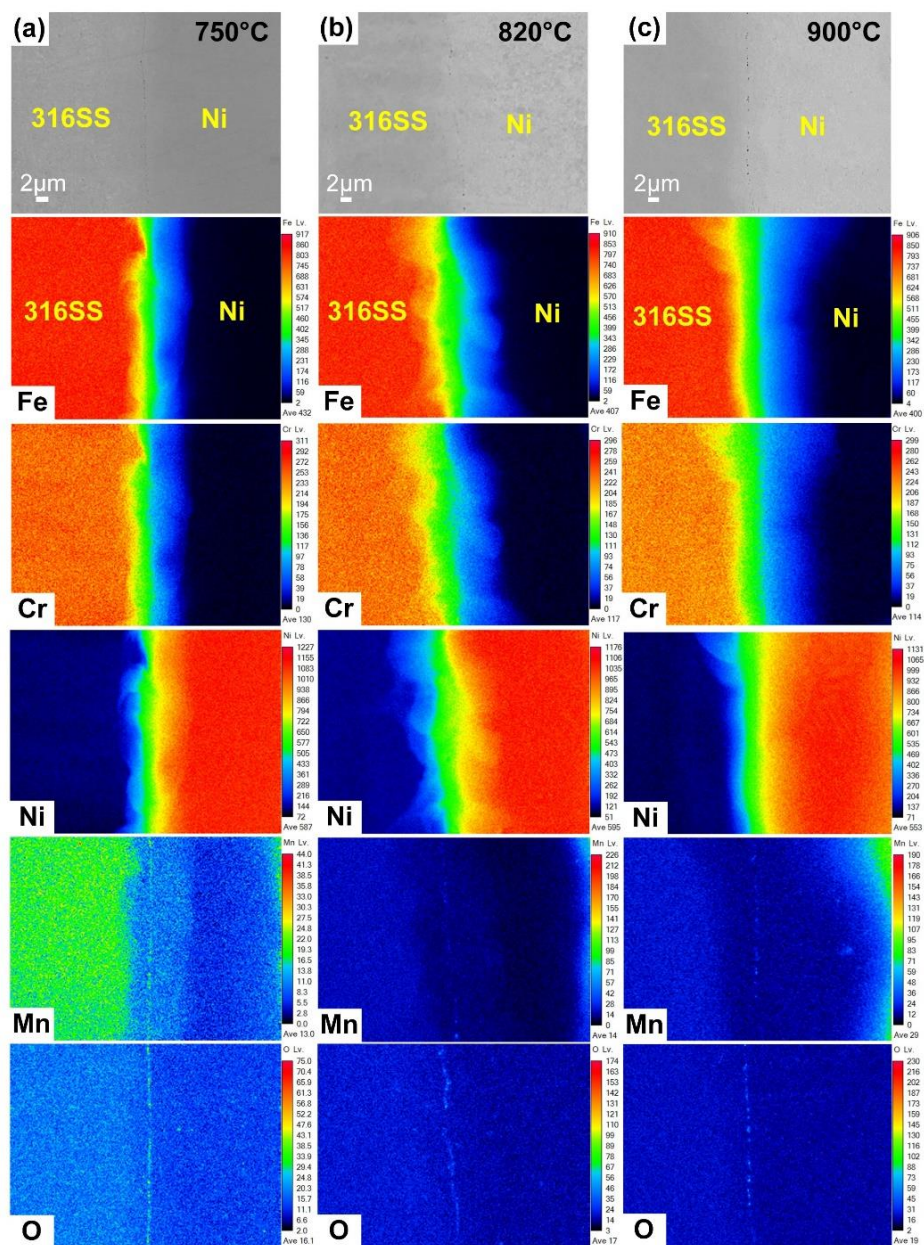


Fig. 4.7 EPMA map scanning analysis results of $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}/316\text{SS}$ joint on the Ni/316SS side at different temperatures of (a) 750 °C, (b) 820 °C, and (c) 900 °C.

Table 4.4 The average oxide size at the interface.

	Direct diffusion bonding		With Ni interlayer	
Temperature	820 °C	900 °C	820 °C	900 °C

Average Size	359 nm	655 nm	72 nm	80 nm
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4.3.2 Diffusion behavior of atoms at interface

The line scanning analysis results of Cr_{0.8}FeMnNi/316SS joint bonded at 820 °C are shown in Fig. 4.8. Among them, Fig. 4.8(a) illustrates the line scanning result of direct diffusion bonding. It is evident that the diffusion distance near the interface measured 3.78 μm, and there was an enrichment of Cr and O elements at the interface. However, with the incorporation of the Ni interlayer, the diffusion distance exhibited a significant increase, as depicted in Figs. 4.8(b) and 4.8(c). This notable improvement could be attributed to the introduction of Ni, which led to an increased concentration difference of elements on both sides of the interface, thereby facilitating the diffusion process of elements.

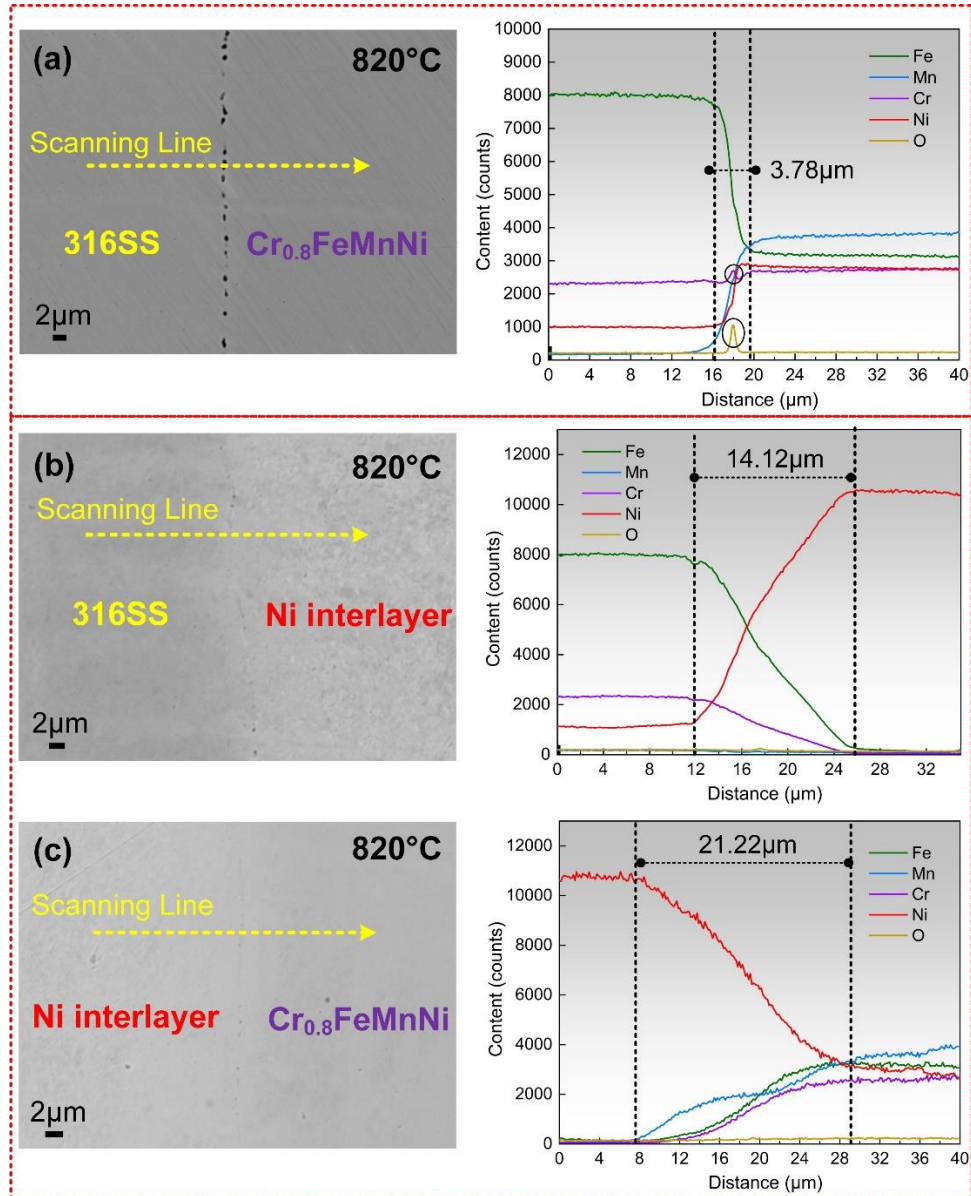


Fig. 4.8 Line scanning analysis results of $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint bonded at 820°C

C: (a) without Ni interlayer, (b) 316SS/Ni side with Ni interlayer and (c)

$\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}$ side with Ni interlayer.

Further calculations were conducted on the diffusion coefficient of different elements to study the diffusion behavior. The joint consisting of $\text{Cr}_{0.8}\text{FeMnNi}$ and stainless steel can be treated as a one-dimensional semi-infinite diffusion couple. The diffusion process of elements within the joint can be regarded as diffusion in a semi-

infinite object. Therefore, the quantitative analysis of the diffusion kinetics can be conducted using Fick's second law of diffusion. Assuming that the diffusion occurs perpendicular to the joining interface, with $x = 0$ representing the interface, and considering the base metals as semi-infinite diffusers, the diffusion coefficient can be calculated using the following formula:

$$C(x, t) = A - B \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad A = \left(\frac{C_1 + C_2}{2}\right) \quad B = \left(\frac{C_2 - C_1}{2}\right) \quad (4.4)$$

where the initial concentration of the element in both base metals was considered as C_1 and C_2 , D is diffusion coefficient, x is the distance from interface, and t is the bonding time. During the vacuum diffusion bonding process between 4J29 Kovar alloy and 316L stainless steel, Fang et al. [59] applied the aforementioned formula to determine the diffusion coefficients of Fe, Ni, and Co within the bonded joints. In this study, for a certain element, the distance from the interface and the element concentration were obtained by line scanning in EDS, and thus the diffusion coefficient could be calculated by the equation. Table 4.5 shows the diffusion coefficients of various atoms in direct diffusion bonding, while Table 4.6 shows the diffusion coefficients of various atoms in diffusion bonding with Ni interlayer. With increasing bonding temperature, the diffusion coefficients of various elements also increased. According to the Arrhenius equation, higher bonding temperatures could effectively enhance the diffusion coefficients of elements. Compared to direct diffusion bonding process, the addition of a Ni interlayer could effectively increase the diffusion coefficients, thereby extending the diffusion distance of elements. In particular, the diffusion coefficients of Cr and Ni elements exhibited a significant increase due to the enhanced concentration gradient of

these elements on both sides of the interface. Additionally, in the presence of a Ni interlayer, elements could diffuse more rapidly through the Ni interlayer, thereby shortening the diffusion time. Consequently, introducing a Ni interlayer could increase the diffusion coefficients of elements during diffusion bonding by enhancing concentration gradients, providing fast diffusion pathways, and eliminating interface defects to facilitate element diffusion.

Table 4.5 Diffusion coefficients (D) of various elements in direct diffusion bonding ($\times 10^{-16} \text{ m}^2/\text{s}$).

Sample	From MEA into 316SS			From 316SS into MEA
	D_{Mn}	D_{Cr}	D_{Ni}	D_{Fe}
750 °C	0.35	0.28	0.18	0.28
820 °C	1.52	1.43	1.33	1.24
900 °C	2.78	2.65	2.56	2.29

Table 4.6 Diffusion coefficients (D) of various elements in diffusion bonding with Ni interlayer ($\times 10^{-16} \text{ m}^2/\text{s}$).

Sample	From MEA into Ni			From Ni into MEA	From 316SS into Ni		From Ni into 316SS
	D_{Mn}	D_{Cr}	D_{Fe}	D_{Ni}	D_{Cr}	D_{Fe}	D_{Ni}
750	0.63	0.56	0.45	1.12	0.87	0.89	1.19
820	1.71	1.63	1.53	2.07	1.92	1.94	2.15
900	2.89	2.78	2.66	3.09	3.15	3.02	3.05

4.3.3 Mechanical properties of the bonded joints

Fig. 4.9(a) shows the tensile strength of different joints. It was observed that the tensile strength of joints by direct diffusion bonding ranged from 320 MPa to 380 MPa, with the strength at 900 °C being higher than at 820 °C. The elongation of the joints was similar at both bonding temperatures, approximately around 18%. However, with the addition of a Ni interlayer, the joint strength significantly improved, surpassing the strength of the 316SS base metal. Due to the inclusion of the Ni interlayer, the interface oxides size reduced, and a continuous solid solution structure formed at the interface, thereby enhancing the mechanical property of the joint. The joint with Ni interlayer also reached the elongation of 316SS base metal, which could be explained by matching thermal expansion coefficient and facilitating atomic diffusion during the diffusion bonding process. On the one hand, the base metals undergo thermal expansion during temperature changes, and materials with different thermal expansion coefficients are prone to stress concentration at the joint. By adding a Ni interlayer between the MEA and 316SS, the difference in thermal expansion coefficients can be effectively adjusted, reducing stress concentration at the joint and thereby improving the joint's elongation. On the other hand, the addition of a Ni interlayer provides more diffusion paths, facilitating atomic diffusion between the MEA and 316SS, resulting in a stronger bond at the joint. Overall, the addition of a Ni interlayer effectively improved the tensile strength and elongation of the joint.

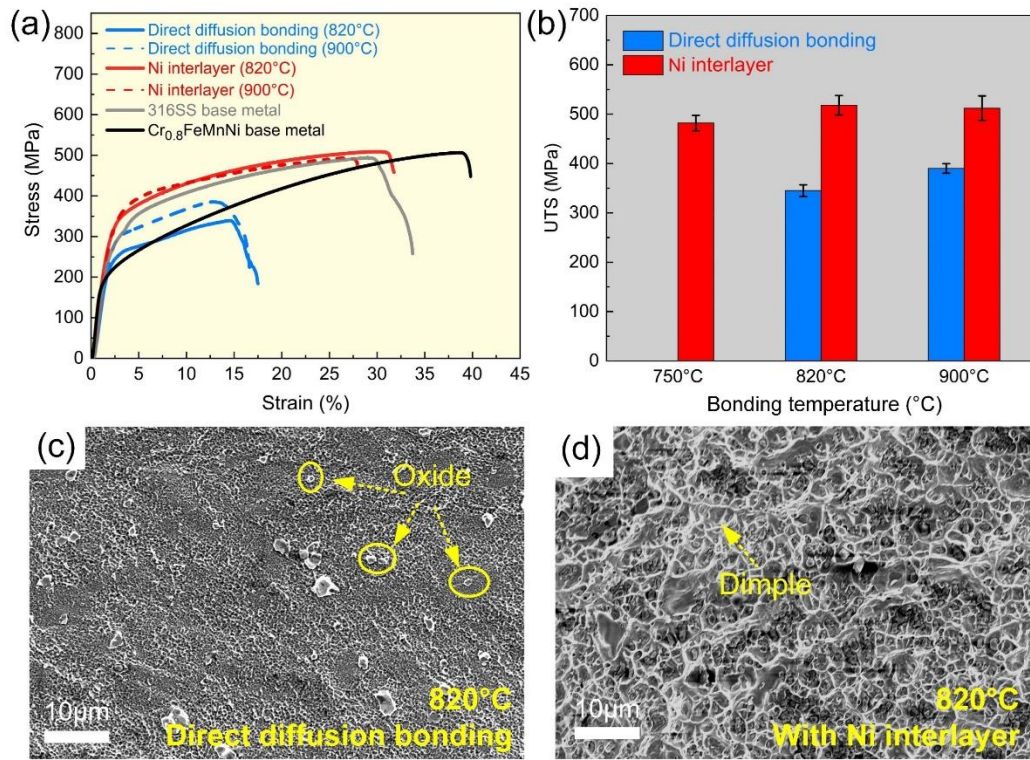


Fig. 4.9 (a) The stress-strain curves of different joints, (b) the average ultimate tensile strength of joints; and the fracture morphology of different joints bonded at 820 °C: (c) direct bonding, (d) with Ni interlayer.

The fracture morphology of different joints bonded at 820 °C are shown in Fig. 4.9(c-d). The dimples were observed on the surface in Fig. 4.9(d), indicating the occurrence of ductile fracture. However, in Fig. 4.9(c), the fracture surface was flat and accompanied by oxide peeling, indicating that the fracture mode was brittle fracture along the interface. Fig. 4.10 shows the Fe element distribution of samples after tensile test, and based on this figure, the fracture path of different joints at 820 °C could be observed. The fracture of Cr_{0.8}FeMnNi/Ni/316SS joint occurred on the 316SS side, primarily due to the tensile strength reaching the level of the 316SS base material. However, in the case of the Cr_{0.8}FeMnNi/316SS joint, the fractures occurred at the

interface since the joint strength was lower than that of the stainless steel and $\text{Cr}_{0.8}\text{FeMnNi}$ base metals.

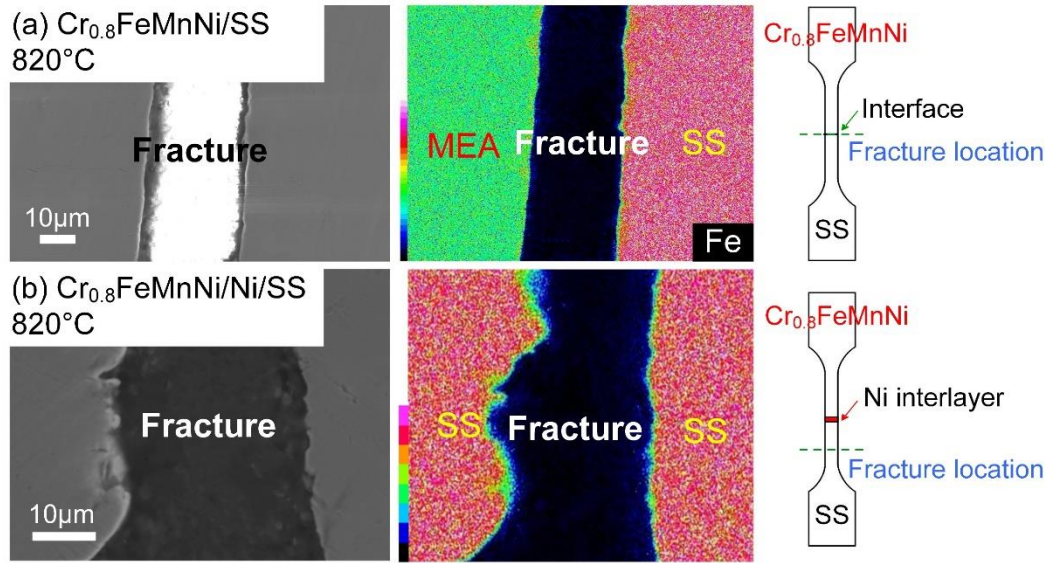


Fig. 4.10 Secondary electron images of fracture surface and the EDS elemental distribution maps of side surface in the fractured tensile specimens of the different joints bonded at 820 °C: (a) $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ and (b) $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}/316\text{SS}$.

Fig. 4.11 illustrates the nanoindentation results of the different areas in the $\text{Cr}_{0.8}\text{FeMnNi}/316\text{SS}$ joint and $\text{Cr}_{0.8}\text{FeMnNi}/\text{Ni}/316\text{SS}$ joint. As shown in Fig. 4.11(b), the microhardness of $\text{Cr}_{0.8}\text{FeMnNi}$ and 316SS base metals kept steady, while the value of oxide layer at the interface increased suddenly and reached the peak of 4.37 GPa. As a result, this significant variation in local properties among the bonded zones will impact the deformation behavior of the joints under load, as evidenced by the elastic recovery ratio (ERR). According to the reference [95-96], the ERR was defined as the ratio of the elastic recovery displacement to the total displacement observed during the loading-unloading process. This ratio directly served as an indicator of the deformation response of materials under external forces. The ERR is given by:

$$\text{ERR} = h_e / h_{\max} \quad (4.5)$$

where h_e is the elastic recovery, and $h_{\max}$ is maximum penetration depth shown in Fig. 4.11(c). The results indicated that the ERR values of both base metals almost unchanged, while the ERR at the interface abruptly increased to a maximum of 33.03%. This observed variation in ERR essentially reflected the deformation process and resulted in inadequate coordination between the two base metals [97]. Consequently, the interface became potential locations for crack initiation. However, as shown in Fig. 4.11(f), the addition of a Ni interlayer resulted in a relatively uniform distribution of microhardness in the joint, effectively avoiding stress concentration and enhancing the mechanical property of the joint.

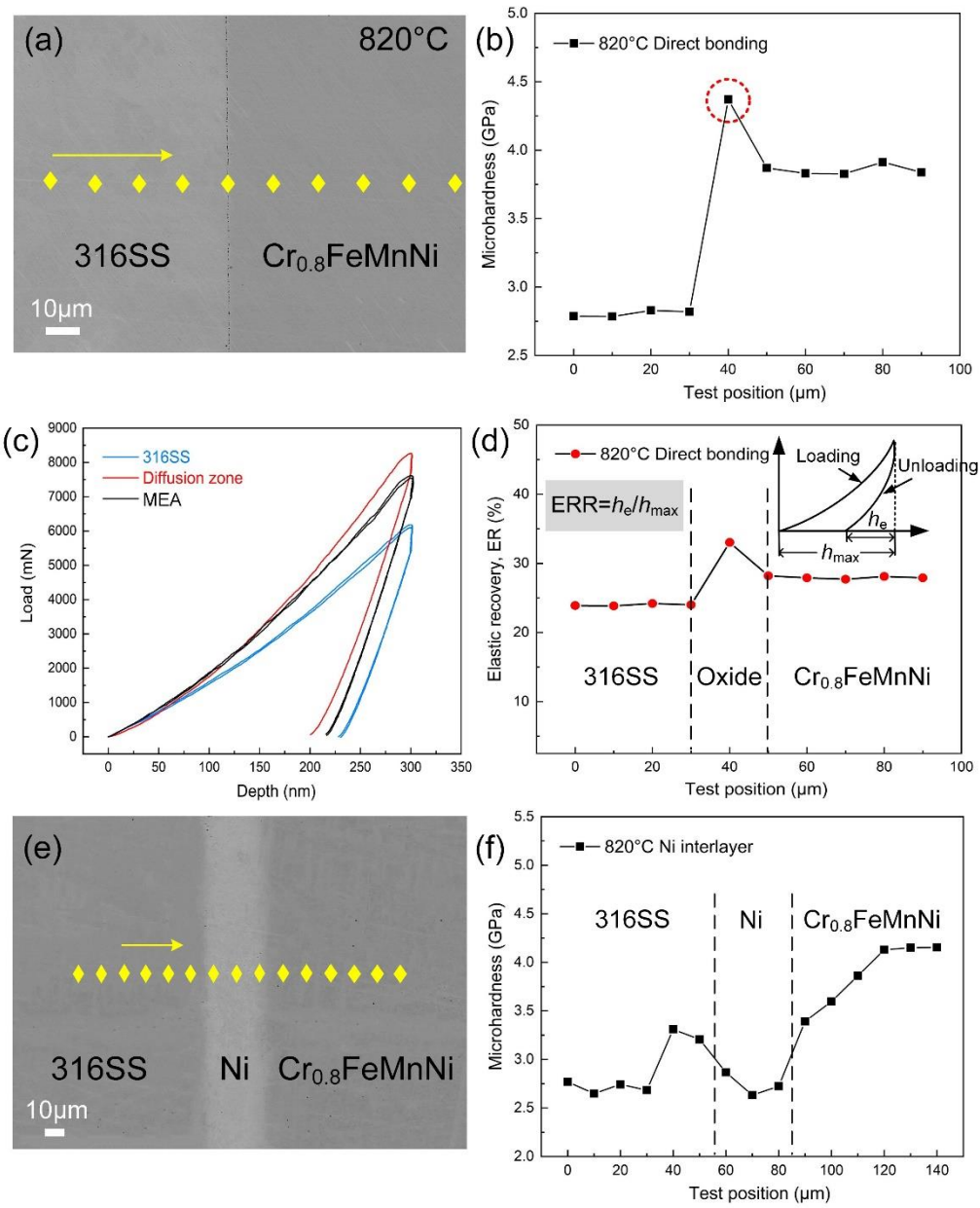


Fig. 4.11 Nanoindentation results of Cr_{0.8}FeMnNi/316SS joint and Cr_{0.8}FeMnNi/Ni/316SS joint at 820 °C: (a) test locations for Cr_{0.8}FeMnNi/316SS joint, (b) microhardness variation at different test points for Cr_{0.8}FeMnNi/316SS joint, (c) load versus depth curves for Cr_{0.8}FeMnNi/316SS joint, (d) elastic recovery of different areas in Cr_{0.8}FeMnNi/316SS joint; (e) test locations for Cr_{0.8}FeMnNi/Ni/316SS joint, (f) microhardness variation at different test points for Cr_{0.8}FeMnNi/Ni/316SS joint.

4.4 Discussion

4.4.1 Origin of oxides at the interface

To clarify the origin of the oxide, we further carried out a supplementary experiment of diffusion bonding. Li et al. [98] also observed the presence of oxides at the interface during the vacuum diffusion bonding of Inconel 617 superalloy. They postulated that these oxides could originate from the residual oxide film on the base material, the furnace atmosphere, and impurities in the materials. Even after using 0.1 μm diamond pastes for polishing before diffusion bonding, it was inevitable that residual oxide films remained on the base materials. To investigate the source of the oxides, we conducted a comparative experiment between pre-treatment and non-pre-treatment of the base materials prior to bonding. Among them, the non-pre-treated sample refers to the sample without grinding and polishing, and the pretreated sample refers to the sample polished using up to 0.1 μm diamond pastes. In cases where non-pre-treatment was applied to the base materials before diffusion bonding, the original oxide film was found to be present at the interface. If the width of interface oxides layer increased when compared to pre-treated samples, it could be inferred that the original oxide film was the primary source. Conversely, if the amount of interface oxides formed was similar to that of pre-treated samples, it could be deduced that trace oxidation during bonding was the primary source. Fig. 4.12 displays the microstructure and interfacial element distribution of the non-pre-treated joint after diffusion bonding at 820 °C. An evident oxide layer with a width of 1.342 μm was observed, predominantly containing Cr and O elements, along with a small amount of Mn elements. Thus, it can be inferred that in the untreated joints, the interface oxides mainly originate from the Cr_2O_3 oxide film on the base material surface.

Furthermore, to further validate this inference, we subjected the pre-treated joints bonded at 820 °C to vacuum heat treatment. The joints were sealed in tubes and kept at 820 °C for 24 hours to simulate the conditions during diffusion bonding. If the width of the oxide layer significantly increased after heat treatment, it would indicate that trace oxidation during high-temperature bonding was the primary source of the oxides. Fig. 4.13 displays the microstructure and interfacial element distribution of the joints after heat treatment. In this case, there was no significant change in the size and width of the interface oxides compared to joints before the heat treatment. Elemental analysis revealed the presence of two types of oxides at the interface, rich in Cr and Mn, rather than predominantly Cr oxide as observed in Fig. 4.12. Based on the previous analysis, the interface primarily consisted of Cr_2O_3 and Mn_3O_4 oxides. These results demonstrate that trace oxidation during high-temperature bonding is not the main source of the oxides; instead, as mentioned earlier, the primary source of the interface oxides is the original oxide film. Additionally, the residual oxide films mainly composed of Cr_2O_3 , acted as a favorable position for nucleation of the Mn_3O_4 , because the Cr_2O_3 provides the source of O for the formation of Mn_3O_4 .

Overall, the oxides at the interface primarily originate from the residual oxide film. Therefore, pre-bonding treatments such as cleaning and oxide layer removal are crucial. However, even with pre-grinding and polishing of the base material before bonding, it is challenging to completely eliminate surface oxide films, and practical pre-bonding procedures in production require significant time and cost. Nevertheless, this study has discovered that the addition of a Ni interlayer significantly reduces the interface oxide layer and improves the mechanical properties. This finding provides a promising reference for the practical industrial application of diffusion bonded H/MEAs and 316SS joints.

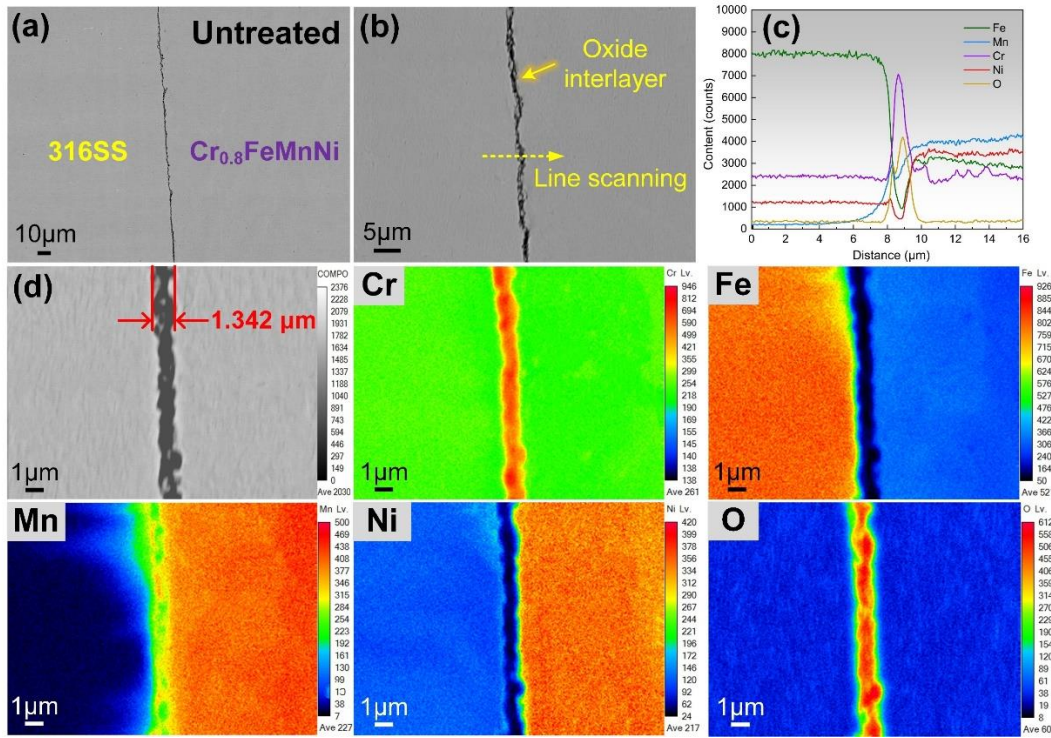


Fig. 4.12 The non-pre-treated joint after diffusion bonding at 820 °C: (a-b) microstructure, (c) line scanning analysis results, and (d) map scanning analysis results.

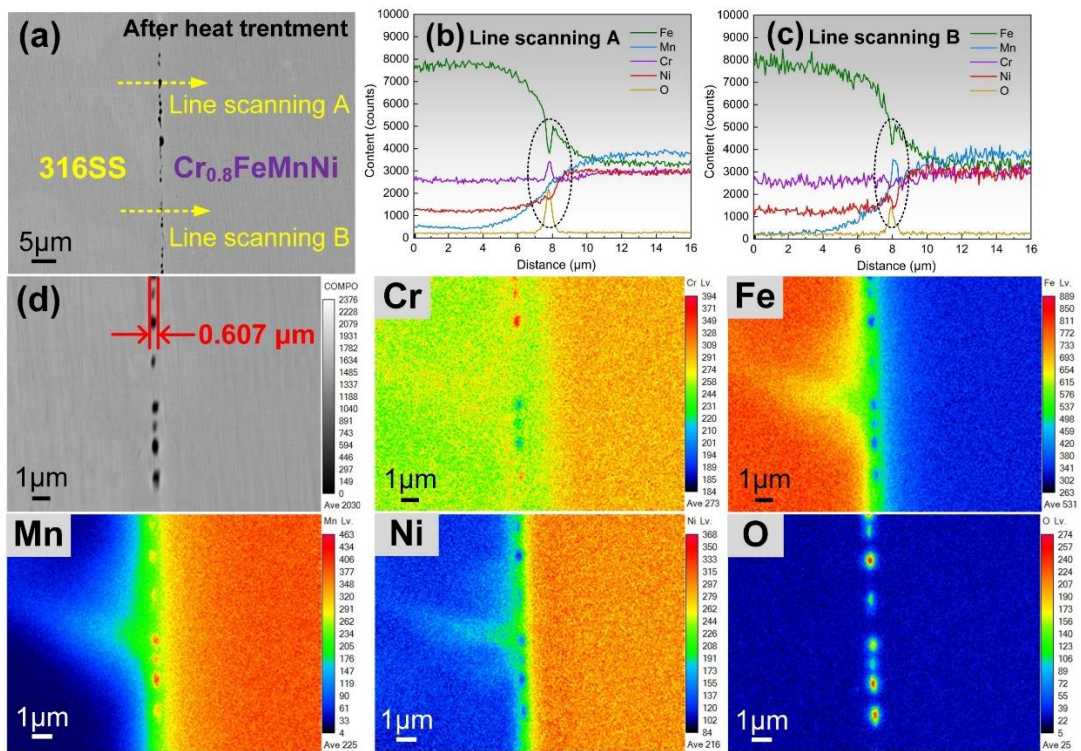


Fig. 4.13 The pre-treated joint after heat treatment at 820 °C: (a) microstructure, (b-c) line scanning analysis results, and (d) map scanning analysis results.

4.4.2 Effect of Ni interlayer on mechanical properties

The improvement of mechanical properties in diffusion bonded joints with Ni interlayer could be explained by the following three mechanisms. (1) Shielding effect [22]. The formation of oxides at the interface will decrease the mechanical properties of the bonded joint. However, by inserting a Ni interlayer, direct contact between two base metals is restricted, reducing the oxides size and relieving the stress concentration at the interface. Consequently, the mechanical properties of the bonded joint are improved. (2) Accelerated diffusion effect. During the bonding process, the interfaces are formed between the Ni interlayer and the MEA and stainless steel, respectively, leading to an increase in concentration gradients of elements. This increased concentration gradient facilitates the rapid diffusion of elements at the interface, promoting atomic exchange and rearrangement and improving the joint strength [99]. (3) Deformation-induced oxide fragmentation. During the bonding process, the high temperature softens the Ni interlayer, while the applied pressure provides additional force. Under these conditions, the Ni interlayer can force the oxide to break, thereby reducing the oxide size and improving the joint strength. In summary, the Ni interlayer improves the mechanical property of diffusion bonded joints between MEA and stainless steel through shielding effect, accelerated diffusion effect, and deformation-induced oxide fragmentation. These mechanisms interact synergistically, resulting in bonded joints with high tensile strength and excellent ductility.

4.4.3 Growth kinetics of diffusion layers

Table 4.7 shows the widths of diffusion layers formed at the interface under different bonding temperatures. The thickness of the diffusion layers increases with an increase in the bonding temperature. In comparison to the 316SS side, diffusion layer II exhibits a relatively wider width, and the maximum thickness of diffusion layer II is observed at a bonding temperature of 900°C. Assuming that the growth of the diffusion layers between the Ni interlayer and the two base materials follows the parabolic law, the growth rate value (K) of the diffusion layer can be calculated using Equation (4.8-4.10) [100]:

$$X^2 = Kt \quad (4.8)$$

$$\ln K = \ln K_0 - Q/RT \quad (4.9)$$

$$\text{Slope} = (-Q/R) \quad (4.10)$$

where X is the width of diffusion layers (m), K_0 is the growth constant (m^2/s), K is the growth velocity of diffusion layers (m^2/s), t is the bonding time (s), Q is the activation energy of growth of diffusion layers (10^3 J/mol), R is the real gas constant (8.314 J/mol/K) and T is the bonding temperature (K). According to Equation (4.9), the curves of the growth velocity of diffusion layer (K) vs. bonding temperature (T) are shown in Fig. 4.14. Therefore, the activation energy (Q) for the growth of diffusion layers can be determined using Equation (4.10) and the slopes of the plots. Besides, the growth constant (K_0) can be calculated using the intercepts of the plots. The activation energy values obtained for the growth of diffusion layer I and diffusion layer II are 51.38 kJ/mol and 51.88 kJ/mol, respectively. However, compared with diffusion layer I, since diffusion layer II possesses a higher growth constant, the width of diffusion layer II is

relatively wider [101]. In addition, it could be seen that diffusion layer II on the MEA side was wider than the diffusion layer I on the SS side. Despite the high activation energy of certain atoms in MEA side and the potential influence of sluggish diffusion effect, the activation energy of atoms in diffusion bonding only represents the energy barrier that must be overcome to initiate diffusion. It dictates the ease with which atoms commence their diffusion. Nevertheless, beyond these considerations, the diffusion width is also governed by a multitude of factors, encompassing variations in temperature, as well as the structural characteristics and defect states of the base materials. Defects within the lattice, such as dislocations, could serve as channels for atomic diffusion. Dislocations may instigate atomic migration along dislocation lines, which are frequently non-linear and may exhibit curved or irregular profiles, thereby introducing complexity to the diffusion path and width. Furthermore, the crystal structure and compositional variances inherent in MEAs may induce disparities in defect energetics when contrasted with conventional materials like stainless steel. For instance, the high dislocation density in the Cr_{0.8}FeMnNi MEA may lead to faster layer growth and wider diffusion width. Consequently, our future research endeavors will be primarily directed toward elucidating the effect of dislocations on the diffusion distance and behavior in the diffusion bonding process.

Table 4.7 Width of diffusion layers across the diffusion zone (μm).

Bonding Temperature (°C)	Diffusion layer I (316SS alloy side)	Diffusion layer II (MEA side)
750	11.57 ± 0.27	17.52 ± 0.76
820	14.12 ± 0.49	21.22 ± 0.54

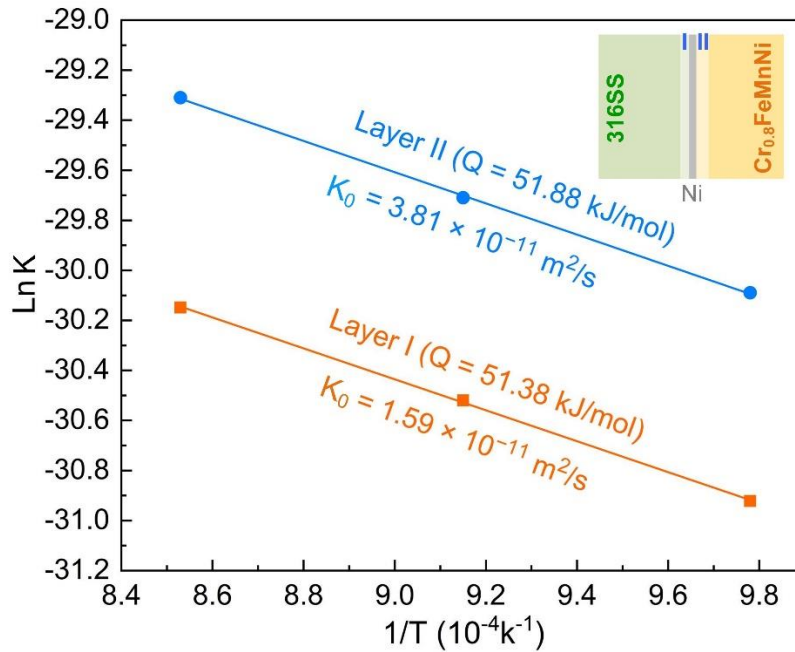


Fig. 4.14 The plot of the growth velocity of diffusion layer vs. bonding temperature.

4.4.4 Bonding mechanism of the joints

The schematic diagram of the MEA/316SS diffusion bonded joint with and without Ni interlayer is shown in Fig. 4.15. At the onset of diffusion bonding, physical contact is established at the interface. Under specific pressure and temperature conditions, the actual contact area of the MEA/316SS joint increases due to plastic deformation. Element diffusion is initially constrained and does not form a diffusion zone. As elements continue to diffuse, a diffusion zone forms near the interface and gradually widens. In direct diffusion bonding, the atomic diffusion is limited due to the small concentration gradient on both sides of the interface, resulting in a relatively small diffusion distance. Additionally, larger-sized oxides develop at the interface, leading to joint failure at the interface position during tensile tests. In joints with a Ni interlayer, the inclusion of Ni increases the concentration gradient on both sides of the interface

and alters the diffusion path, significantly increasing the diffusion distance. Moreover, the larger growth constant of the diffusion layer on the MEA side widens its diffusion width compared to the stainless steel side. Due to the barrier effect of Ni, the size of oxide particles at the interface significantly decreases, and stress concentration at the interface is mitigated. As a result, the joint fractures on the stainless steel side, leading to an increase in the tensile strength of the joint.

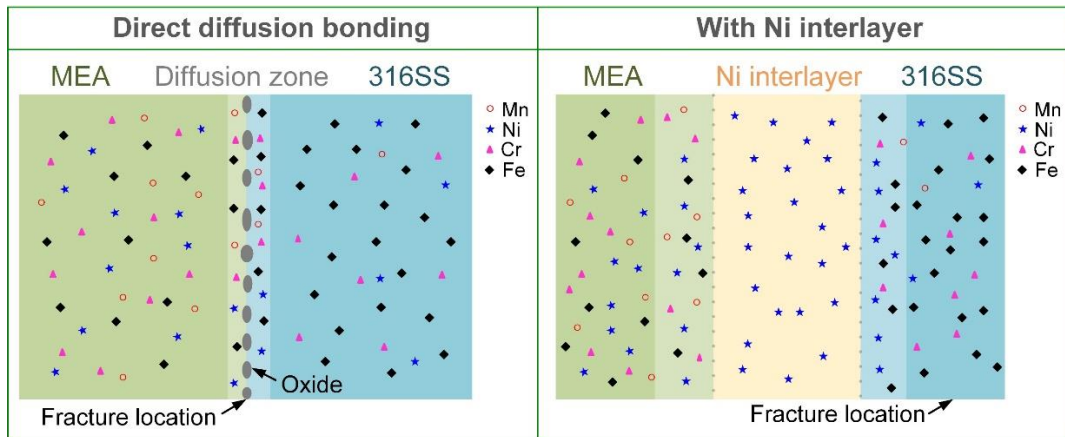


Fig. 4.15 Schematic diagram of the MEA/316SS diffusion bonded joint with and without Ni interlayer.

4.5 Summary

(1) The dissimilar joining of $\text{Cr}_{0.8}\text{FeMnNi}$ medium entropy alloy to 316 stainless steel was successfully achieved by inserting a Ni interlayer. When bonded at $820\text{ }^{\circ}\text{C}$ / 60 min / 25 MPa with a Ni interlayer, the tensile strength and elongation of joint reached the level of the 316SS base metal. The fracture morphology was characterized primarily by ductile fracture.

(2) During the direct diffusion bonding, Cr_2O_3 and Mn_3O_4 oxides appeared at the interface. However, the incorporation of a Ni interlayer in the joint effectively reduced the oxide size at the interface, and improved the mechanical properties due to shielding

effect, accelerated diffusion, and reduced stress concentrations.

(3) The diffusion coefficient and activation energy of atoms were evaluated by Fick's law and Arrhenius relationship. In comparison to diffusion layer on the 316SS side, diffusion layer on the $\text{Cr}_{0.8}\text{FeMnNi}$ side had a higher growth constant, resulting in a relatively wider width.

Chapter 5 Effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints

5.1 Introduction

Based on the previous research, we know that in addition to process parameters, there are also concentration gradients that affect the quality of diffusion bonding. If the concentration difference between the base metal elements on both sides of the interface is larger, the diffusion is more thorough. Therefore, in order to further increase the concentration difference, we selected Cr_{0.8}FeMn_{1.3}Ni_{1.3} HEA developed by Hashimoto et al. [34] in this part. This alloy exhibits excellent radiation resistance and is a material with broad prospects in the field of nuclear power. Additionally, dislocations can provide "channels" for pipe diffusion, making it easier for diffused atoms to move within the crystal lattice during diffusion bonding process. Therefore, this study focuses on analyzing the effect of dislocations on diffusion behavior in diffusion bonded Cr_{0.8}FeMn_{1.3}Ni_{1.3} HEA/316SS joints.

5.2 Experimental

In order to determine the stability of this HEA, we conducted an aging study on Cr_{0.8}FeMn_{1.3}Ni_{1.3} before conducting joining experiments. A HEA with a chemical composition of Cr_{0.8}FeMn_{1.3}Ni_{1.3} (18at%Cr-24at%Fe-30at%Mn-30at%Ni) was produced by arc melting under a pure Ar atmosphere. The ingots were flipped and remelted at least five times to minimize macroscopic inhomogeneity in composition and microstructure. The as-cast ingots were initially solution treated for 24 hours at 1160 °C, followed by longitudinal cold rolling to reduce the total thickness by approximately 90%, then recrystallized for 4 hours at 1000 °C. Subsequently, these samples were subjected to isothermal aging treatments at 300, 500, and 700°C for varying durations (4 to 1500 hrs). All heat treatment experiments in this study were

conducted by individually encapsulating the samples in evacuated quartz tubes.

Then HEA base material for diffusion bonding was prepared. As shown in Fig. 5.1, the $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEAs ingots were arc-melted in argon atmosphere. The as-cast HEAs were homogenized at 1160 °C for 24 h, and then further recrystallization was achieved through cold-rolling to a 50% thickness reduction and subsequent 1000 °C annealing for 4 h. To fabricate HEAs with different dislocation densities, the alloys were second cold rolled with different deformations of 0%, 5%, 10%, and 20%. The diffusion bonding of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA to 316SS was conducted in a spark plasma sintering machine. The bonding temperatures of 900 °C were used. Then the interfacial microstructures and diffusion behavior were investigated by using electron probe micro-analyzer (EPMA) and scanning electron microscope (SEM). The grain size and dislocation density were recognized by electron back-scatter diffraction (EBSD) method. The MTEX toolbox in MATLAB software was used based on EBSD results to estimate the density of geometrically necessary dislocations (GNDs). The microhardness of joints was measured by a nanoindentation tester.

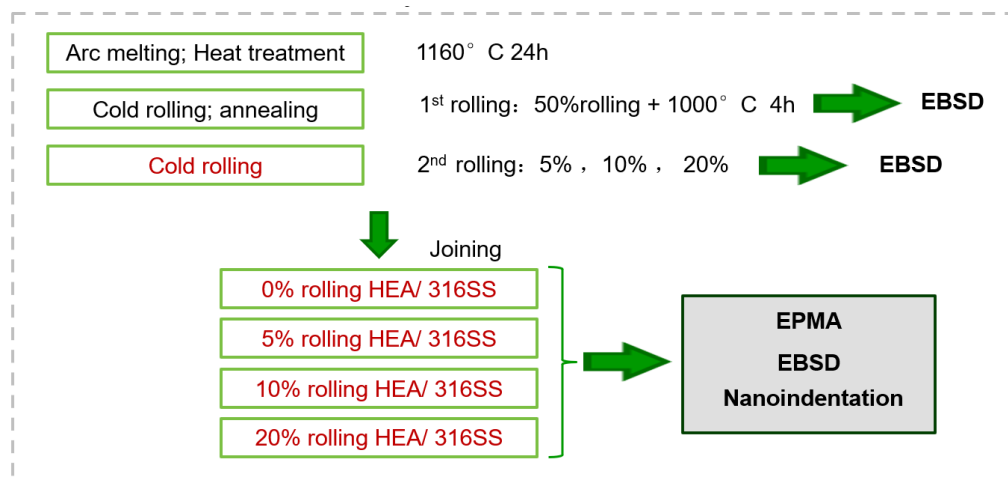


Fig. 5.1 Experimental flowchart.

5.3 Results and discussion

5.3.1 Aging of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA

5.3.1.1 Recrystallized annealed state

Fig. 5.2 shows the representative backscattered electron (BSE) images and corresponding elemental distribution maps of the alloy after recrystallization annealing. After annealing at 1000°C, no intermetallic compound particles were observed solely attributed to the HEA constituent elements. In fact, in Fig. 5.2(a), the constituent elements of the HEA are uniformly distributed, and there is no evidence of segregation or clustering at the length scale of these images. The inset in Fig. 1b displays the XRD results of the annealed alloy, where only peaks corresponding to the FCC phase are detected, indicating that the $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA remains a single FCC phase solid solution after severe plastic deformation and subsequent recrystallization annealing. Regarding the indexing of low-intensity peaks in XRD patterns, small peaks at low angles may represent impurities. In addition, the XRD peaks of the samples aged at different temperatures for 300 hours also show that the alloy is still dominated by the FCC phase, but there are more heterogeneous peaks after aging at 500°C for 300 hours.

The inverse pole figure (IPF) and phase distribution map shown in Fig. 1c exhibit a typical FCC equiaxed grain microstructure with numerous twin boundaries traversing the grains. As depicted in Fig. 5.2(e), the grain size distribution indicates an average grain size (d_{avg}) of 54.98 μm .

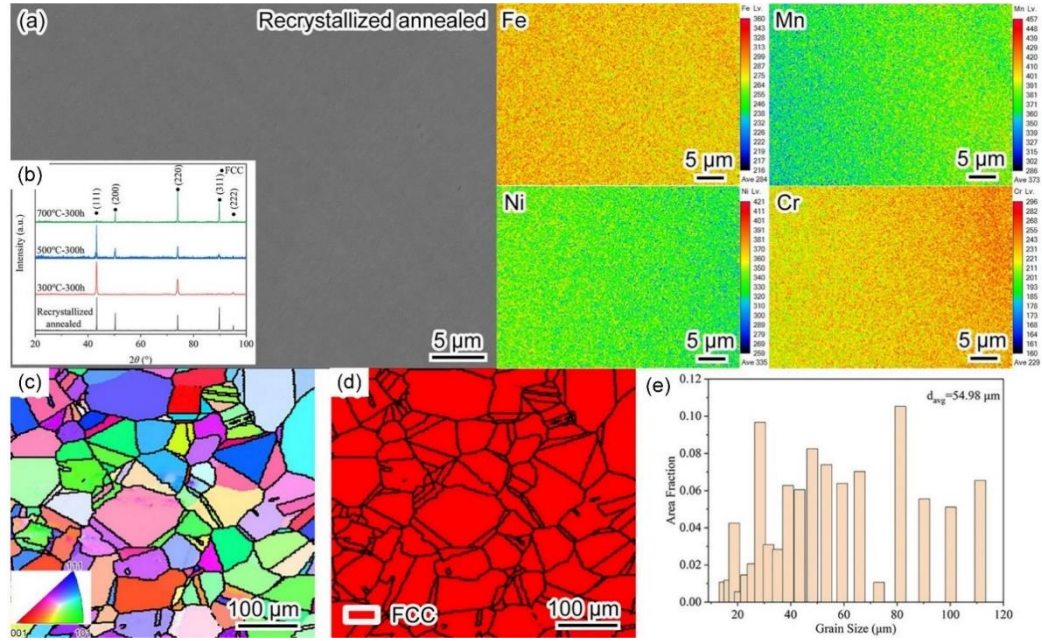


Fig. 5.2 Microstructure of the $Cr_{0.8}FeMn_{1.3}Ni_{1.3}$ HEA after recrystallized annealed: (a) BSE image and elemental maps, (b) XRD patterns, (c) IPF map, (d) phase distribution, (e) grain size distribution.

5.3.1.2 Tensile property evolution

The room temperature tensile properties of the specimens after various temperature aging treatments were measured, and the tensile curves are shown in Fig. 5.3(a).

The quantitative data of the tensile test results are shown in Table 5.1. Compared to the recrystallized annealed samples, the tensile strength and elongation exhibit slight improvements after aging at 300 °C. However, after aging for 300 and 1500 hours, the properties show little change, indicating that the alloy may have approached an equilibrium state. After aging at 700 °C, there is a significant increase in the tensile strength, but the elongation undergoes a considerable decrease, which becomes more pronounced with longer aging times. Most notably, the samples aged for 300 and 1500 hours at 500 °C exhibit severe brittle fracture in the elastic region before achieving

plastic yield during the tensile process. This brittle behavior is a cause for concern as it can lead to unexpected failures and reduced mechanical performance of the alloy.

Table 5.1 Tensile properties of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA under different aging conditions.

Aging conditions.	Yield strength/MPa	Ultimate tensile strength/MPa	Elongation/%
Recrystallized annealed	171±3	487±13	54±4
300°C-300h	167±10	501±26	58±3
300°C-1500h	175±2	492±15	59±2
500°C-300h	/	317±22	4±0.3
500°C-1500h	/	562±24	6±1
700°C-300h	194±13	534±31	45±5
700°C-1500h	234±41	637±10	33±3

The differences in fracture modes are further substantiated by more comprehensive evidence on the fracture surfaces (Fig. 5.3(b)). The tensile fracture surface of the 300 °C-300h sample exhibits a significant presence of dimples, indicative of ductile fracture. The fracture surface of the 700 °C-300h sample displays dimples along with features of intergranular fracture. In contrast, the tensile fracture surface of the 500 °C-300h sample lacks any ductile fracture characteristics and is characterized by prominent brittle fracture. Therefore, during the diffusion bonding process, the sample should avoid staying in the medium temperature range (~500 °C).

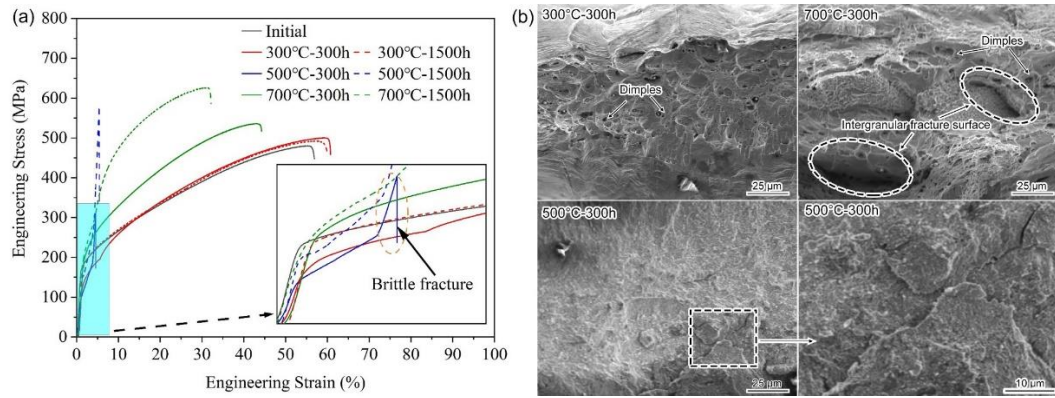


Fig. 5.3 (a) Uniaxial tensile curves of the investigated HEAs tested at room temperature, (b) Fracture surface morphology.

5.3.2 Grain size and dislocation density of HEA base metal

Fig. 5.4 presents the IPF maps of joints subjected to different deformation rate. As the deformation rate of the HEA base metal increases from 0% to 20%, the grain sizes sequentially measure 89.3 μm, 88.1 μm, 87.2 μm, and 85.5 μm. It can be observed that the grain sizes did not undergo significant changes, laying the groundwork for studying the influence of dislocations on diffusion. Since grain boundaries also affect diffusion, varying grain sizes can lead to different diffusion behaviors. However, in this study, there was no significant change in grain size, thereby minimizing the influence of grain boundaries.

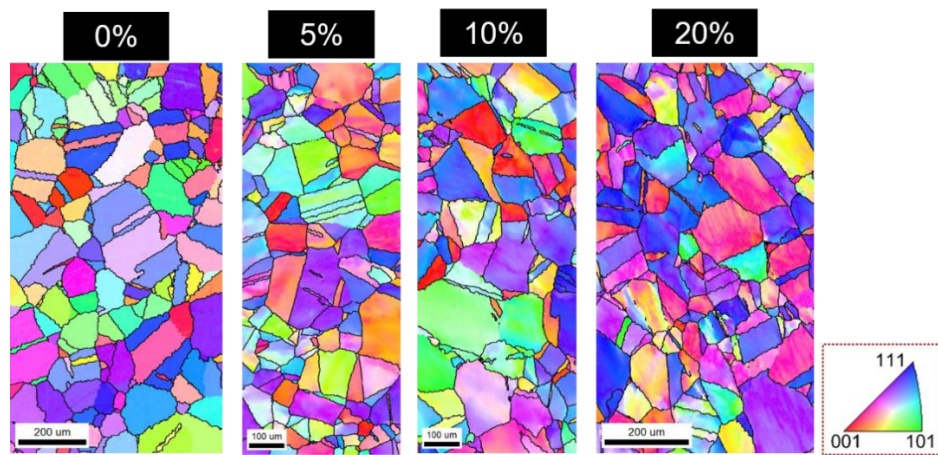


Fig. 5.4 Inverse pole figures for Cr_{0.8}FeMn_{1.3}Ni_{1.3}/316SS joint.

Fig. 5.5 presents the geometrically necessary dislocation (GND) density maps of different joints. Although statistical storage dislocations (SSDs) may also exist in the alloy, their distribution cannot be discerned from kernel average misorientation (KAM) maps, as they do not accumulate influences from local orientation errors. Most SSDs may annihilate under cyclic heating, leaving GNDs potentially predominant among the residual dislocations, thus warranting more attention towards GNDs. As depicted in Fig. 5.5, the GND density of the HEA gradually increases with increasing deformation. This is attributed to the generation, accumulation, and proliferation of dislocations within the crystal lattice during the plastic deformation process. Cold rolling, involving material compression and elongation to alter shape and reduce thickness, induces atomic slip and rearrangement within the crystal lattice, thereby introducing dislocations. Notably, at a cold rolling deformation of 20%, the GND density reaches $7.8 \times 10^{13} \text{ m}^{-2}$.

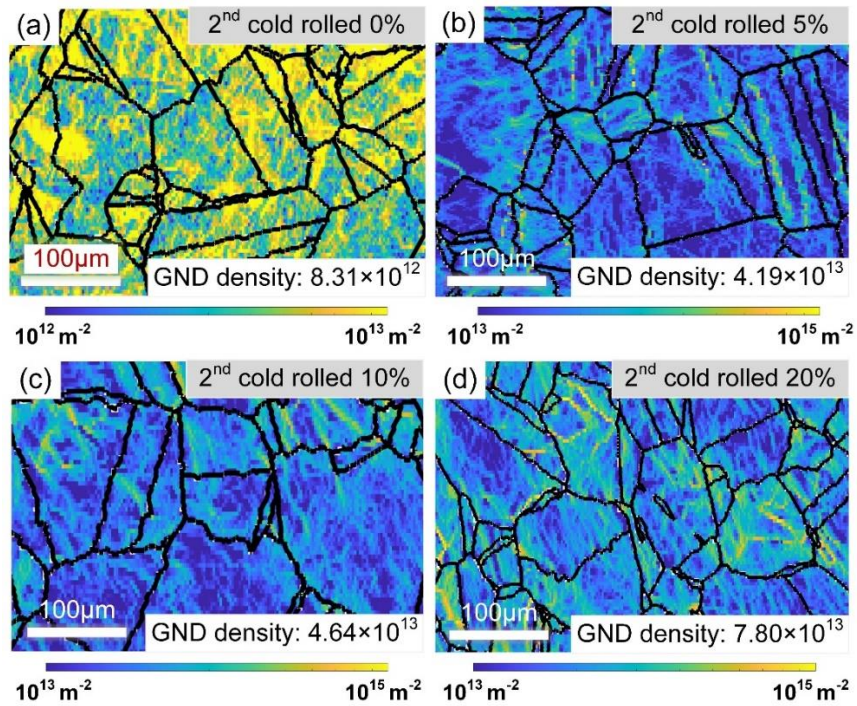


Fig. 5.5 GND maps for $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}/316\text{SS}$ joint.

5.3.3 Diffusion behavior of joints

The line scan results of joints subjected to different deformation rates of HEA are illustrated in Fig. 5.6. Fe diffuses from the stainless steel side towards the HEA side, while Ni and Mn elements diffuse from the HEA side towards the stainless steel side. Notably, the line scan results demonstrate a significant increase in the diffusion distance of Fe with increasing deformation. Specifically, the diffusion distances of Fe from the interface to the HEA side in samples with 0%, 5%, 10%, and 20% deformation are 4.796 μm , 5.078 μm , 5.921 μm , and 8.309 μm , respectively. Clearly, the diffusion distance of Fe atoms notably increases with increasing deformation. Regions with high dislocation densities can form special channel structures, attributed to the effects of dislocations within the crystal. Dislocations represent defects in the crystal lattice, indicating deviations in atomic arrangements. In areas of high dislocation density, dislocation lines and networks cause local structural distortions and strains, creating relatively loose regions or channels. The local strains and relaxations around dislocations lead to the formation of vacancies or defects within the crystal, thus establishing effective pathways for atomic movement. Due to the relatively loose structure in dislocation-rich regions, atoms can move more freely within the crystal, thereby accelerating the diffusion process. The arrangement of dislocation lines and networks can also contribute to the directional guidance of channels, facilitating atomic movement along specific pathways. Therefore, the special channel structures formed in regions of high dislocation density provide convenient and effective pathways for atomic diffusion within the crystal, consequently increasing the diffusion distances observed.

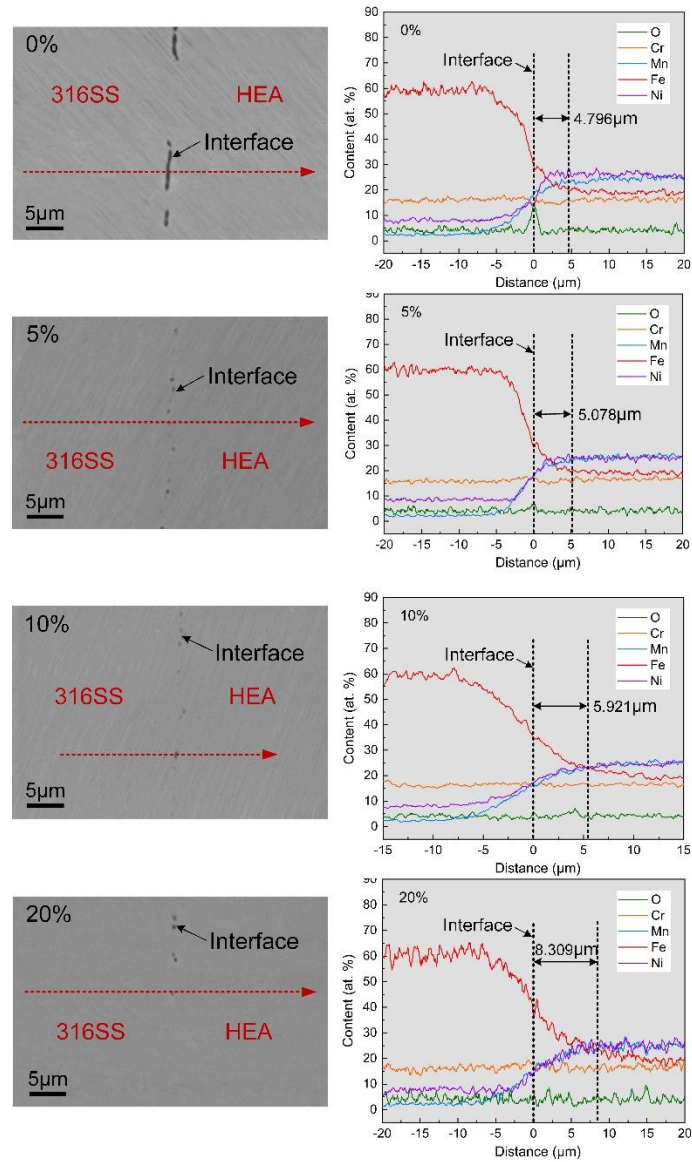


Fig. 5.6 Line scanning analysis results of joints.

Fig. 5.7 shows the relationship between dislocation density and diffusion distance. It can be observed that with the increase of dislocation density, the diffusion distance of Fe atoms in HEAs also gradually increases. In the joints, two fundamental types of diffusion mechanisms are lattice diffusion and pipe diffusion, each characterized by distinct mechanisms and behaviors. Lattice diffusion occurs when atoms diffuse through a crystalline lattice by occupying lattice vacancies or interstitial sites. This diffusion mechanism relies on the availability of lattice defects such as vacancies and

is influenced by thermal vibrations that facilitate atomic movement within the crystal structure. Lattice diffusion typically proceeds at a relatively slow rate due to limitations imposed by the density and mobility of lattice defects. In contrast, pipe diffusion involves atoms moving along specific pathways or channels within the crystal structure. These pathways are determined by the arrangement of crystal lattice planes, grain boundaries, or other crystallographic features that create favorable diffusion routes. Pipe diffusion generally occurs more rapidly compared to lattice diffusion because atoms can traverse these well-defined and direct paths with less hindrance. The distinction between lattice diffusion and pipe diffusion lies in their respective mechanisms of atomic movement within materials. Lattice diffusion relies on random vacancies and interstitial spaces in the crystal lattice, whereas pipe diffusion exploits pre-existing channels or pathways that guide atomic migration. In the case of a deformation rate of 0%, atomic diffusion primarily occurs through lattice diffusion. However, as the deformation increases, pipe diffusion gradually becomes dominant, thereby accelerating the diffusion process. When the deformation rate reaches 20%, the combined effect of pipe diffusion and lattice diffusion leads to an increase in diffusion distance. Furthermore, this experiment proves that controlling dislocation density by changing the amount of deformation can effectively enhance diffusion distance, like the effect of surface nano-crystallization treatment method. Gao et al. [82] demonstrated an increase in diffusion distance in HEA/stainless steel joints by surface nano-crystallization treatment of HEA. After 2 hours treatment of HEA, the diffusion distance increased to 5.2 micrometers, thereby enhancing shear strength. Therefore, comparing these findings, it can be inferred that controlling dislocation density through the methods explored in this study can achieve a greater diffusion distance under a 20% deformation rate.

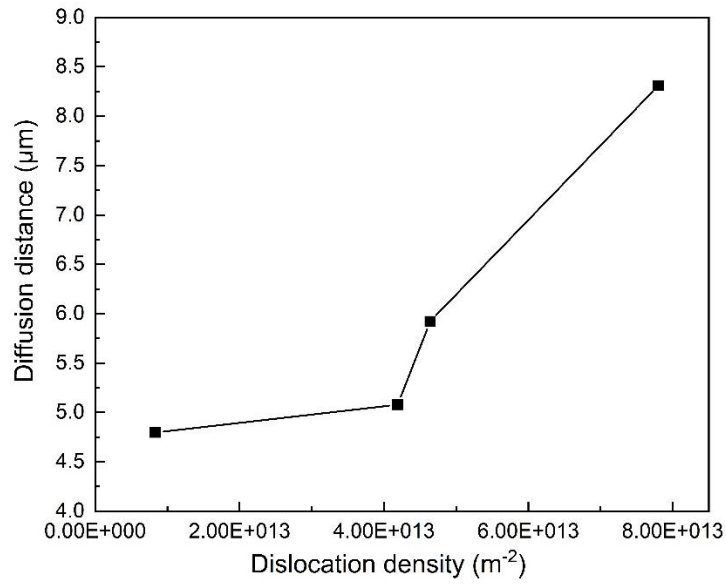


Fig. 5.7 Relationship between dislocation density and diffusion distance.

The EPMA map scanning analysis results of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}/316\text{SS}$ joint at $900\text{ }^{\circ}\text{C}$ is shown in Fig. 5.8. At the interface, the formation of Mn-O and Cr-Mn-O oxides was observed. Additionally, in the diffusion zones adjacent to the stainless-steel side, a Fe-rich solid solution was present, whereas closer to the HEA side, a high-entropy solid solution was identified.

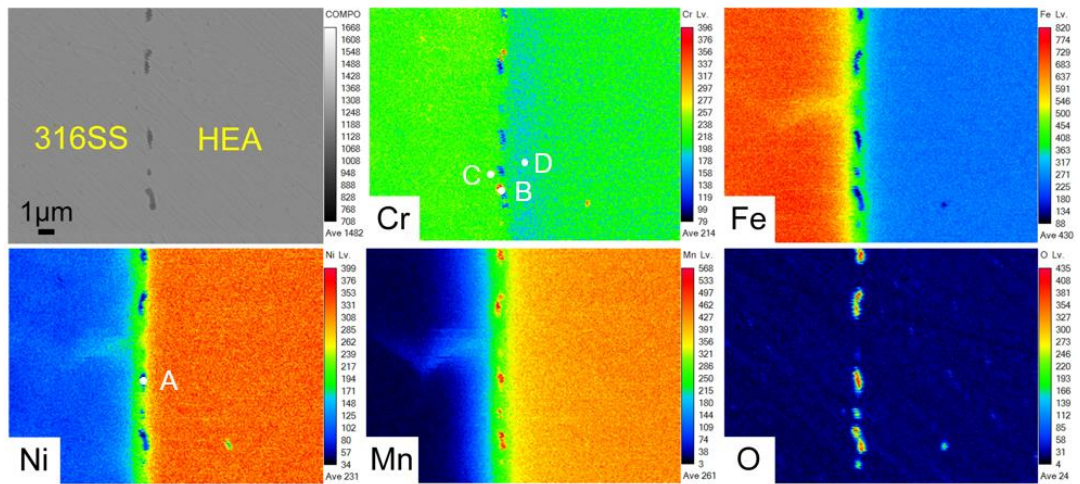


Fig. 5.8 EPMA map scanning analysis results of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}/316\text{SS}$ joint at $900\text{ }^{\circ}\text{C}$.

Table 5.2 The elemental composition in Fig. 5.8 (at. %).

	Cr	Fe	Ni	Mn	O	Possible phase
A	10.35	12.30	6.19	42.83	28.33	Mn-O
B	29.65	13.13	6.84	23.58	26.80	Cr-Mn-O
C	21.18	50.79	11.16	15.11	1.76	Fe rich solid solution
D	16.00	28.85	25.36	27.74	2.04	High entropy solid solution

5.3.4 Mechanical properties of joints

The nanoindentation test results under different deformation rate are shown in Fig. 5.9. The hardness of the 316 stainless steel base metal remains stable, while the hardness of the HEA substrate gradually increases due to the increase in dislocation density. When the deformation reaches 20%, the hardness of the diffusion zone reaches 3.69, which is 12% higher than the hardness of the joint at 0% deformation. During the cold rolling deformation processes, the dislocation density within the HEA crystal structure will increase significantly. These dislocations can hinder the slip and movement of crystal atoms and increase the hardness of the material. The hardness similarity between the diffusion zone and the base metal at 20% deformation rate helps reduce local stress concentrations in the joint, thereby contributing to improved mechanical performance of the joint.

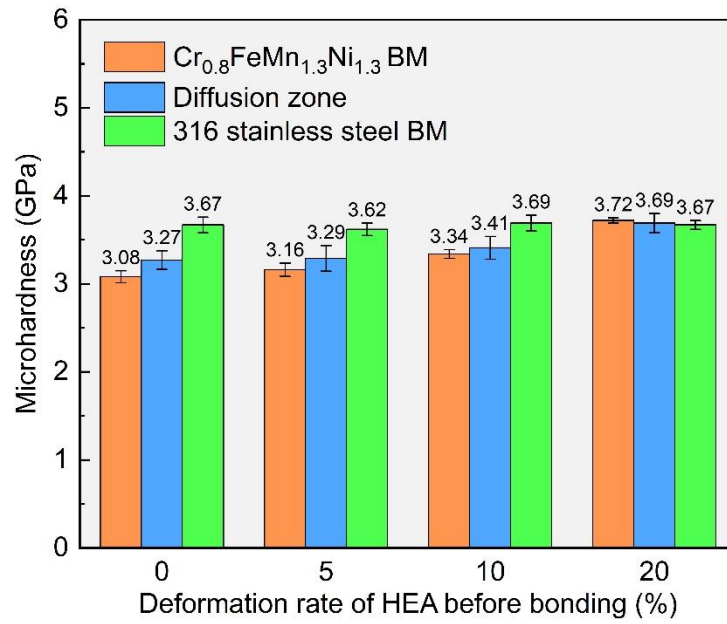


Fig. 5.9 Nanoindentation test results.

The tensile curve is shown in Fig. 5.10. It can be clearly observed that the tensile strength of the joints increased with the increase of deformation rate. The above results indicate that the cold rolling not only increase the deformation rate, but also introduces more dislocation density as diffusion channels to enhance the joint strength after bonding.

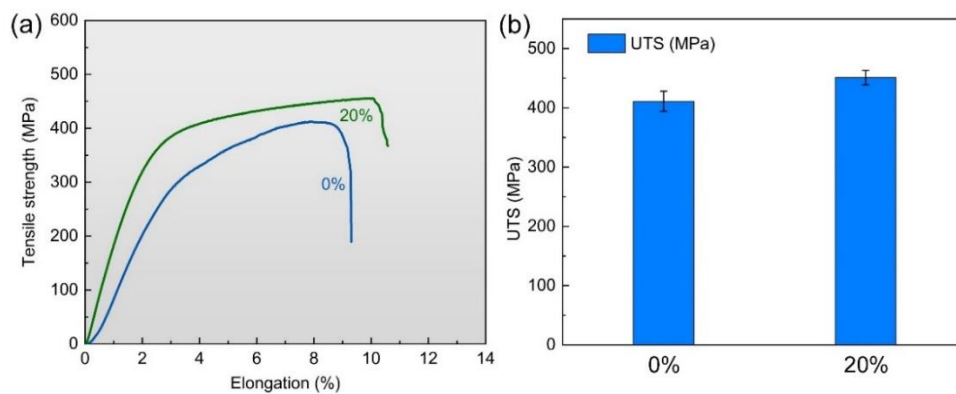


Fig. 5.10 (a) Tensile curve and (b) ultimate tensile strength.

5.4 Summary

This study focuses on analyzing the effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints. The $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEAs ingots were arc-melted in argon atmosphere. The as-cast HEAs were homogenized at 1160 °C for 24 h, and then further recrystallization was achieved through cold-rolling to a 50% thickness reduction and subsequent 1000 °C annealing for 4 h. To fabricate HEAs with different dislocation densities, the alloys were second cold rolled with different deformations of 0%, 5%, 10%, and 20%. The diffusion bonding of $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA to 316SS was conducted in a spark plasma sintering machine. The bonding temperatures of 900 °C were used. Then the interfacial microstructures and diffusion behavior were investigated by using electron probe micro-analyzer (EPMA) and scanning electron microscope (SEM). The grain size and dislocation density were recognized by electron back-scatter diffraction (EBSD) method. The MTEX toolbox in MATLAB software was used based on EBSD results to estimate the density of geometrically necessary dislocations (GNDs). The microhardness of joints was measured by a nanoindentation tester. The joints cold-worked with different deformation rate and 316 stainless steels had similar grain sizes, but the dislocation density increased with the increase in deformation rate. In addition, Mn-O oxides and Cr-Mn-O oxides were recognized at the interface. Through line scanning of the interface, it was found that the diffusion distance of atoms through the joint increased with the increase in deformation rate, which probably due to the increase in dislocations as diffusion channels. As the secondary deformation rate increased from 0% to 20%, the diffusion distance through the joint increased from 4.796 μm to 8.309 μm . This result could suggest that the diffusion ability of atoms within the crystal structure may

be enhanced in case a significant dislocation density was present in the HEA base metal, resulting in increased diffusion distances and higher tensile strength in diffusion bonded joints.

Chapter 6 Conclusions

Conclusions

To explore dissimilar joints for advanced nuclear reactors application, the diffusion bonding of high entropy alloys (HEAs) to stainless steels were evaluated. The experimental results can be concluded as follows:

- (1) Diffusion bonding between equiatomic CoCrNi-based HEAs system and 316 stainless steels

Equiatomic CoCrNi-based concentrated solid solution alloys (CSSAs) system (CoCrFeNiMn, CoCrFeNi, and CoCrNi) were successfully joined to 316 stainless steels by SPS diffusion bonding, and the effect of bonding temperature and concentration on diffusion behavior and tensile property of bonded joints were investigated. The tensile strength of the CSSAs/316SS joints were gradually increased with increasing bonding temperature. In addition, the tensile strength of the joints bonded at $0.8T_m$ were all exceeded 80% of that in 316SS. Meanwhile, the bonding at $0.8T_m$ seemed to have sufficient diffusion and grain growth at the interface, resulted in the disappearance of voids and the increase in strength of joint.

In CoCrNi/316SS joint, large element concentration variation would amplitude in the diffusion zone, could result in rapid diffusion of atoms and large diffusion distance. The diffusion distance of diffusion zone in the CoCrNi/SS joint was increased by nearly two times compared to traditional diffusion bonding. Furthermore, it suggests that the continuous FCC solid solution structure was generated in the diffusion zone, which was beneficial to the increase of tensile property in joints. The tensile strength and elongation of diffusion bonded CSSAs/316SS joints were increased compared to laser beam welded joints.

- (2) Effect of Ni interlayer on diffusion bonded reduced activation Cr_{0.8}FeMnNi MEA / 316 stainless steel joint

This study explored the diffusion bonding of Cr_{0.8}FeMnNi medium entropy alloy to 316SS with and without a Ni interlayer using spark plasma sintering. Direct bonding led to the formation of Cr₂O₃ and Mn₃O₄ oxides at the interface, resulting in stress concentration and reduced tensile strength. However, the introduction of a Ni interlayer effectively reduced oxide size and improved mechanical properties by accelerating diffusion and relieving stress concentrations. Optimal joints were achieved at 820 °C / 60 min / 25 MPa, producing joints with tensile strength and elongation comparable to

316SS. Furthermore, diffusion behavior, growth kinetics of diffusion layers, and activation energy of diffusion in various atoms and layers were analyzed. The activation energy of each element in the joints with Ni interlayer was decreased compared to direct diffusion bonding. This research highlights the significance of interlayer in enhancing diffusion bonding outcomes for nuclear power applications.

(3) Effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints

This study focuses on analyzing the effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ HEA/316SS joints. The joints cold-worked with different deformation rate and 316 stainless steels had similar grain sizes, but the dislocation density increased with the increase in deformation rate. In addition, Mn-O oxides and Cr-Mn-O oxides were recognized at the interface. Through line scanning of the interface, it was found that the diffusion distance of atoms through the joint increased with the increase in deformation rate, which probably due to the increase in dislocations as diffusion channels. As the secondary deformation rate increased from 0% to 20%, the diffusion distance through the joint increased from 4.796 μm to 8.309 μm . This result could suggest that the diffusion ability of atoms within the crystal structure may be enhanced in case a significant dislocation density was present in the HEA base metal, resulting in increased diffusion distances and higher tensile strength in diffusion bonded joints.

In conclusion, the HEA/316SS diffusion bonded joints shows good joining property, which could be candidate materials for advanced reactors.

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Academic Achievements

Journal Articles

1. **Haotian Sun***, Naoyuki Hashimoto, Hiroshi Oka. Vacuum diffusion bonding between equiatomic CoCrNi-based concentrated solid solution alloys system and 316 stainless steel by spark plasma sintering. *Materials Science & Engineering A*. 879 (2023) 145297.
2. **Haotian Sun***, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe, Tian Liu. Unveiling the effect of Ni interlayer on diffusion bonded reduced activation Cr_{0.8}FeMnNi medium entropy alloy / 316 stainless steel joint: interfacial microstructure, diffusion behavior and mechanical properties. *Materials Characterization*. 206 (2023) 113443.
3. **Haotian Sun**, Tian Liu*, Hiroshi Oka*, Naoyuki Hashimoto. Role of aging temperature on thermal stability and tensile properties of reduced activation Cr_{0.8}FeMn_{1.3}Ni_{1.3} high-entropy alloy. *Materials Characterization*. 210 (2024) 113804.
4. **Haotian Sun***, Tian Liu, Naoyuki Hashimoto, Hiroshi Oka. Effect of vacuum heat treatment on novel Co-free Al_{0.9}Cr_{0.8}FeMn_{0.8}Ni_{2.0} eutectic high entropy alloy: microstructure evolution and mechanical properties. *Vacuum*. 222 (2024) 113038.
5. **Haotian Sun***, Zairan Luo, Shuai Wang*, Naoyuki Hashimoto, Hiroshi Oka, Qian Liu, Shigehito Isobe. Overcoming strength-ductility trade-off in CoCrNi medium entropy alloy by forming fine crescent grains in laser powder-bed fusion. *Materials Letters*. 347 (2023) 134644.

Presentations on conferences

- [1] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Solid-state diffusion bonding between CoCrNi-based high entropy alloys system and 316 stainless steels by spark plasma sintering. PRICM11 (The 11th Pacific Rim International Conference on Advanced Materials and Processing), Jeju, Korea, 2023.11.19-23. Oral presentation (Best poster award).
- [2] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Improving

- mechanical properties in diffusion bonded joints between reduced activation $\text{Cr}_{0.8}\text{FeMnNi}$ MEA and 316SS by adding Ni interlayer. 日本金属学会 2023 年秋期(第 173 回)講演大会. 富山・富山大学, 2023.9.19-22. Oral presentation.
- [3] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Diffusion bonding between CoCrNi-based H/MEAs and 316SS by spark plasma sintering. 日本金属学会 2023 年春期(第 172 回)講演大会. 東京・東京大学, 2023.3.7-10, Oral presentation.
- [4] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Study on additive manufacturing of CoCrNi medium entropy alloy by selective laser melting. 日本金属学会 2022 年秋期(第 171 回)講演大会. 福岡・福岡工業大学, 2022.9.20-23, Oral presentation.
- [5] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Study on microstructure and mechanical property of CoCrNi medium entropy alloy fabricated by selective laser melting and arc melting. 日本顕微鏡学会 2022 年北海道支部学術講演会. 札幌・北海道大学, 2022.11.19, Oral presentation.
- [6] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Effect of Ni interlayer on microstructure and mechanical properties of $\text{Cr}_{0.8}\text{FeNiMn}$ MEA/316SS diffusion bonded joint. 2023 年度日本鉄鋼協会・日本金属学会両北海道支部合同サマーセッション. 室蘭・室蘭工業大学, 2023.07.14, Poster presentation.
- [7] **Haotian Sun**, Naoyuki Hashimoto, Hiroshi Oka, Shigehito Isobe. Effect of dislocations on diffusion behavior in diffusion bonded $\text{Cr}_{0.8}\text{FeMn}_{1.3}\text{Ni}_{1.3}$ /316SS joints. 日本金属学会 2024 年春期(第 174 回)講演大会. 東京・東京理科大学, 2024.3.12-15, Poster presentation.