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In-situ reactive synthesis of the Ni_3Al intermetallic compound and subsequent diffusion bonding with different steels for surface coating

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The Ni_3Al intermetallic compound has been *in situ* reaction synthesized from elemental powders to form a surface coating material and then diffusion bonded with three representative steels, i.e. a carbon steel, a stainless steel and a tool steel, in order to improve the high-temperature corrosion and wear resistance of these conventional materials. The as-reaction-formed intermetallic has been found to have an unstable crystalline structure. Diffusion-induced recrystallization takes place in the region close to the interface during subsequent diffusion bonding. A conformable contact between the as-reaction-formed intermetallic and the steel substrate is essential for subsequent interfacial bonding, which can be achieved by heating the as-reaction-formed intermetallic up to a high temperature to allow local melting to wet the interface prior to diffusion bonding. During diffusion bonding *via* an annealing step, an interdiffusion zone is formed and its thickness depends mainly on annealing temperature and duration. As a result of the microstructural development at the interface during annealing, different interfacial properties, i.e. a hardened interface or a softened one, can be obtained. The current success in coating the steels with the intermetallic opens up a new way to broaden the applications and prolong the service life of a wide range of conventional materials.

1. Introduction

In recent years, intermetallic compounds, especially those based on aluminides, have received lots of attention in view of their great potential to be used as structural materials, thanks to their low density, excellent oxidation resistance and high strength at elevated temperatures [1–3]. Many efforts have been made to characterize these materials in microstructures and mechanical properties and also to search for cost-effective techniques to fabricate the materials into end products [4, 5]. Due to the high melting points of these intermetallics, powder metallurgy (PM) techniques become favourable ones to prepare these materials with conventional sintering or reactive sintering or self-propagating temperature synthesis (SHS) [6–10]. Among these processes, reactive sintering is of more interest, which starts with mixed and compacted elemental powders and ends up with a synthesized intermetallic compound or even an intermetallic matrix composite. Furthermore, it is possible to apply an external pressure to aid in the densification of the reaction-formed product. In comparison with the conventional sintering process starting with prealloyed powders, the major advantage of reactive sintering is the flexibility in adjusting the end composition of the reacted product to meet the requirements of properties. Another advantage is that the sintering temperature needed to initiate the reaction is much lower and the sintering time much shorter than for conventional sintering, thereby cutting processing costs. SHS is actually similar to reactive sintering and the only difference lies in that only a limited part of a green compact is heated to initiate the reaction.

While a lot of work has been done to understand the possibilities and the mechanisms of the *in-situ* reactive synthesis of intermetallics and intermetallic matrix composites to prepare bulk materials for structural applications, little has been known on the *in-situ* reactive synthesis as applied to coat the conventional materials for the applications where both high-temperature corrosion resistance and wear resistance are required.

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The advantages of intermetallic coating are obvious, just considering the broadened possibilities to use the conventional materials in harsher environments and the prolonged service life of the existing components. There are however two main challenges lying on the way to the success in intermetallic coating on the conventional materials such as steels: one being process development and another being the design of material systems to ensure strong bonding between the reaction-formed surface layer and the substrate materials.

The present work is part of a study to explore the possibilities to *in-situ* synthesize intermetallic compounds from gas-atomized elemental powders for surface coating and to control the microstructures and mechanical properties across the interface between the reaction-formed intermetallic compounds and various substrate materials. The initial consideration has been confined to the *in-situ* synthesis of the monolithic Ni_3Al intermetallic and diffusion bonding with different types of steels, *i.e.* a carbon steel, a stainless steel and a tool steel. Focus has been placed on the understanding of the microstructural development of the reaction-formed intermetallic, the compatibility between the intermetallic and the substrates, and the interfacial microstructure and mechanical properties of the diffusion couples. It is hoped that the results of the present work are of use in laying a solid basis on which a complete set of fabrication procedures can later on be developed for a wide range of intermetallic coatings on various substrate materials.

2. Experimental details

2.1. Characterization of starting materials

In the present work, a nickel powder and an aluminium powder, supplied by Sherritt in Canada and Metalloys in the UK, respectively, were used as the starting materials for the coating. The as-received powders were first subjected to the analyses of oxygen, hydrogen and nitrogen concentrations, since these gases adsorbed on the powder particle surfaces would be released during heating prior to the combustion reaction between nickel and aluminium. Ströhlein OSA-MAT, H-MAT and NSA-MAT gas analyzers were used to measure the contents of oxygen, hydrogen and nitrogen in the powders, respectively. The results of the analyses are presented in Table I. The sizes and size distributions of the elemental powders were measured with a Malvern 2600 master particle sizer. The mean sizes of the powders are included in Table I. The powder particles were all spherically shaped.

Three commercially available steels, namely a carbon steel, a stainless steel and a tool steel, were used in the present investigation as the substrate materials for diffusion bonding with the intermetallic. Their nominal compositions are given in Table II.

TABLE I Concentrations of oxygen, hydrogen and nitrogen, as well as the mean particle sizes of the elemental powders used as the starting materials for the coating in the present work

Powder	Oxygen (ppm)	Hydrogen (ppm)	Nitrogen (ppm)	Mean particle size (μm)
Ni	5900	28.0	400	5.0
Al	2700	24.5	50	7.7

TABLE II Chemical compositions of the substrate materials used in the present work

Substrate material	C	Si	Mn	Cr	Ni	Mo	V	Fe
Carbons steel ST.37	0.4	—	1.0	—	—	—	—	bal.
Stainless steel 316	0.03	1.0	2.0	17.5	13	2.5	—	bal.
Tool steel PG3-2365	0.32	0.3	0.3	3.0	—	2.8	0.5	bal.

2.2. Mixing and compaction of the powders

The elemental powders were loaded in a cylindrical container to half full by volume and mixed with a Turbula mixer for 60 min. For the experiments of pressureless reactive synthesis/diffusion bonding, the mixed powders were poured onto groove-shaped steel substrates and cold compacted with an Amsler press at a pressure of 420 MPa for 2 min. For the experiments of diffusion bonding aided with external pressure, the mixed powders were compacted into tablet-shaped samples with a diameter of 8 mm and a thickness of 5–6 mm under a pressure of 400 MPa.

2.3. Reactive synthesis and diffusion bonding

2.3.1. Without external pressure

The experiments of reactive synthesis and diffusion bonding without external pressure were performed in a Vacuum Industries Systems VII furnace at a vacuum level of 6×10^{-7} mbar. Two heating schemes were applied: (i) continuous heating across the reaction temperature zone (620–650 °C) up to an annealing temperature for diffusion bonding, and (ii) heating across the reaction temperature zone up to a temperature slightly above the melting point of the intermetallic, soaking for a short time and cooling down to an annealing temperature for diffusion bonding. It was found that the scheme (ii) provided a better contact between the reaction-formed intermetallic and the steel substrates. In all the experiments, the samples were first heated at a rate of 20 °C/min to 300 °C, soaked for 15 min to remove a zinc Seferate lubricant (which had been mixed in the powders for the convenience of cold compaction), and then heated at a rate of 30 °C to higher temperatures. In the experiments with the scheme (ii), the intermetallic samples on the carbon steel, stainless steel and tool steel substrates were heated to 1400, 1380 and 1400 °C, respectively, and soaked for 5 min for local melting. It should be noted that the heating temperature of the Ni_3Al-stainless steel couple (1380 °C) was actually lower than the melting point of Ni_3Al. However, a good interfacial contact was created probably due to the relatively low melting temperature of the stainless steel. In addition, the experiments of the diffusion bonding between the reaction-formed Ni_3Al intermetallic and the tool-steel substrate were performed at an annealing temperature of 1200 °C for 0.5, 2, 4, 8 and 18 h to determine the kinetics of the diffusion process. Also the annealing at 1000, 1100, 1200 and 1300 °C for 4 h was applied in an attempt to establish the diffusion mechanism and the relationship between temperature and diffusion rate.

2.3.2. With external pressure

The tablet-shaped Ni-Al compacts were first placed in zirconium oxide containers and heated in the vacuum furnace across the reaction temperature zone up to 700 °C for reactive synthesis and immediately cooled down. The reaction-formed intermetallic was then homogenized at 1100 °C for 5 h. Diffusion bonding with the carbon steel was carried out at 1000 °C for 100 h in a vacuum furnace at a vacuum level of 3×10^{-6} mbar under an external pressure of 2 MPa. The process temperatures were controlled within ±2 °C. Heating and cooling rates were 300 and 600 °C/h, respectively.

2.4. Microstructural analyses

An X-ray diffractometer with a cylindrical texture camera was used to characterize the crystalline thin films of the reaction-formed intermetallic. A Neophot-2 optical microscope (OM) with differential interference contrast was employed to examine the cross-sections of the reaction-formed samples at different processing steps and under different treatment conditions. The OM samples were either just polished or subsequently etched with a solution consisting of 75% HCl and 25% HNO_3. The as-reaction-formed intermetallic as well as the diffusion couples of the Ni_3Al-carbon steel, Ni_3Al-stainless steel and Ni_3Al-tool steel after diffusion bonding at 1200 °C for 2 h were also examined with a Jeol JSM 840A scanning electron microscope (SEM) after a gold-deposition procedure.

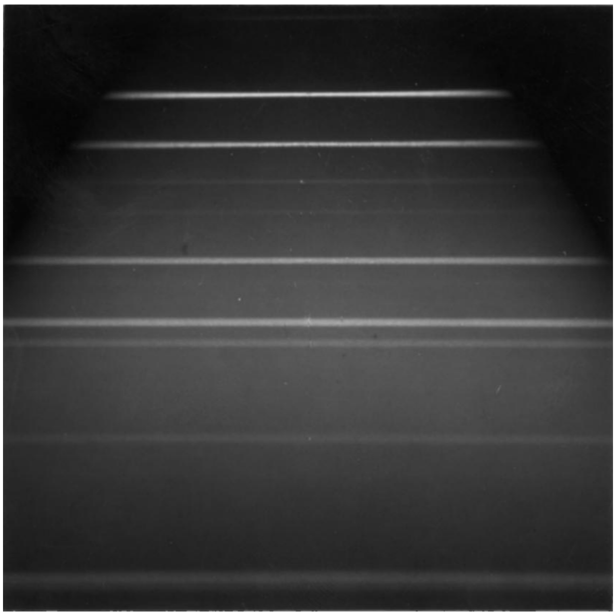


Figure 1 X-ray diffraction pattern with superdiffraction lines, indicating the reaction-formed intermetallic with the ordered γ'-Ni_3Al structure.

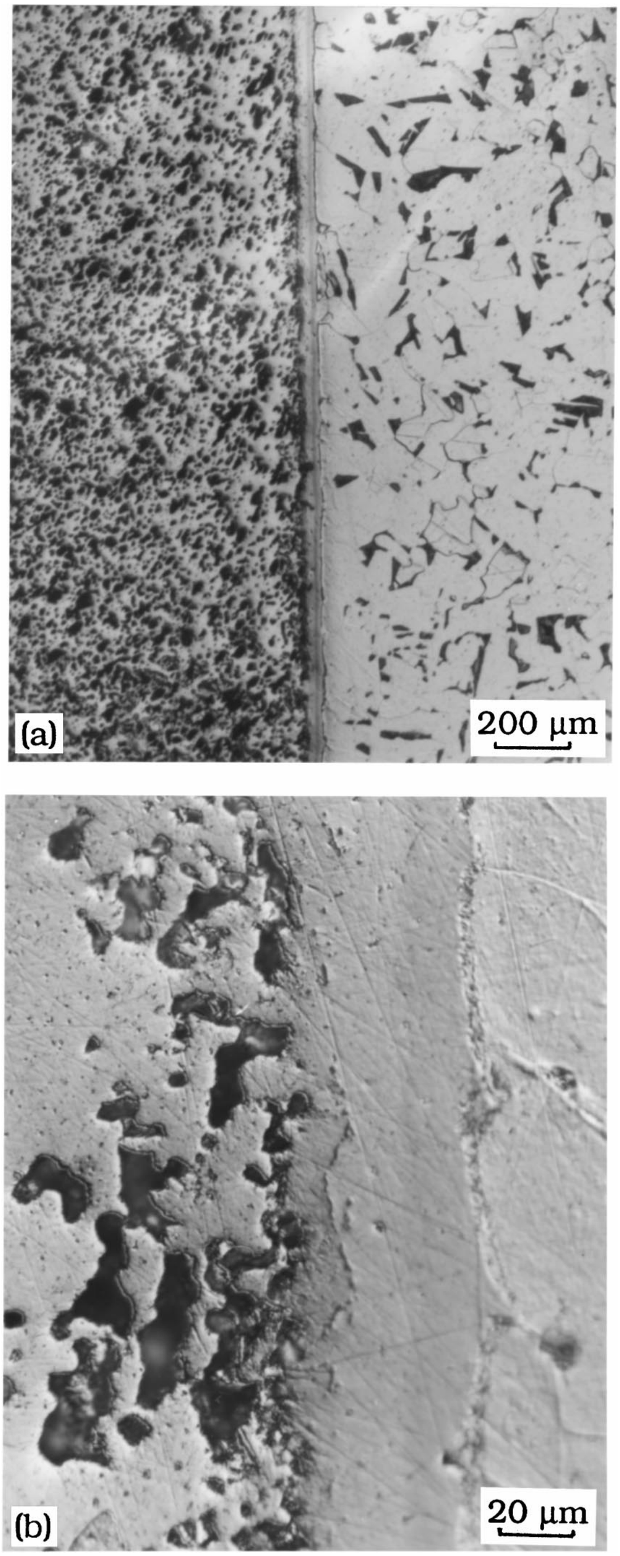


Figure 2 Optical micrographs taken from the diffusion couple (Ni_3Al-carbon steel) following continuous heating to 1300 °C and holding for 2 h, showing the locally bonded interface.

2.5. Microhardness testing

Microhardness measurements were made of the reaction-formed Ni_3Al intermetallic, the substrate steels and the interfaces of the diffusion couples after diffusion bonding to obtain hardness profiles across the interface and to assist in understanding the diffusion process in these diffusion couples.

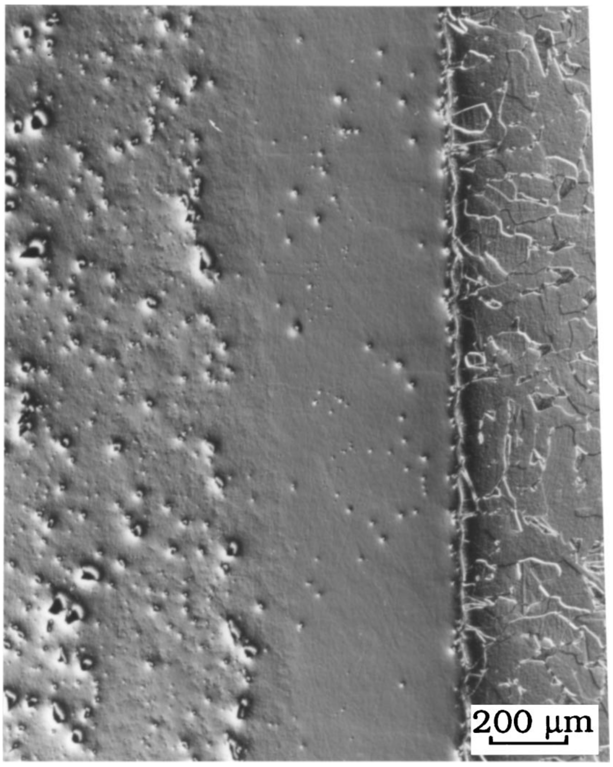


Figure 3 Optical micrograph taken from the diffusion couple (Ni_3Al-carbon steel) following 1400 °C/5 min and 1200 °C/2 h, showing the bonded and densified interface.

2.6. Interface thickness measurement and electron probe microanalysis

The thicknesses of the diffusion layers on both sides of the interface were measured with OM and described as a function of the temperature and time of diffusion bonding *via* an annealing step. At least twenty measurements at randomly chosen positions across the interface were taken to yield an average value. The chemical concentration profiles of the principle elements at the interface were determined with SEM plus a Tracor EDS (energy dispersion spectroscopy) microprobe and used to estimate the interface thickness.

3. Results and discussion

3.1. Microstructural development in the reaction-formed intermetallic and at the intermetallic/substrate interface

X-ray diffractometry showed that the as-*in-situ*-reaction-synthesized Ni_3Al intermetallic from the elemental powders did not have the exact microstructures or phases in accordance with the phase diagram. This non-equilibrium state was however changed during subsequent annealing for a long time in order to create proper diffusion bonding at the interface between the intermetallic and the substrate. Furthermore, the as-reaction-formed intermetallic had an unstable crystalline structure with pores, which was modified through recrystallization occurring also during subsequent annealing.

Fig. 1 shows an X-ray diffraction pattern obtained from a reaction-formed Ni_3Al sample after annealing at 1100 °C for 5 h. The superdiffraction lines indicate the presence of the ordered γ'-Ni_3Al structure. No other intermediate phases or residual elemental powders could be detected in the reacted and annealed Ni_3Al sample.

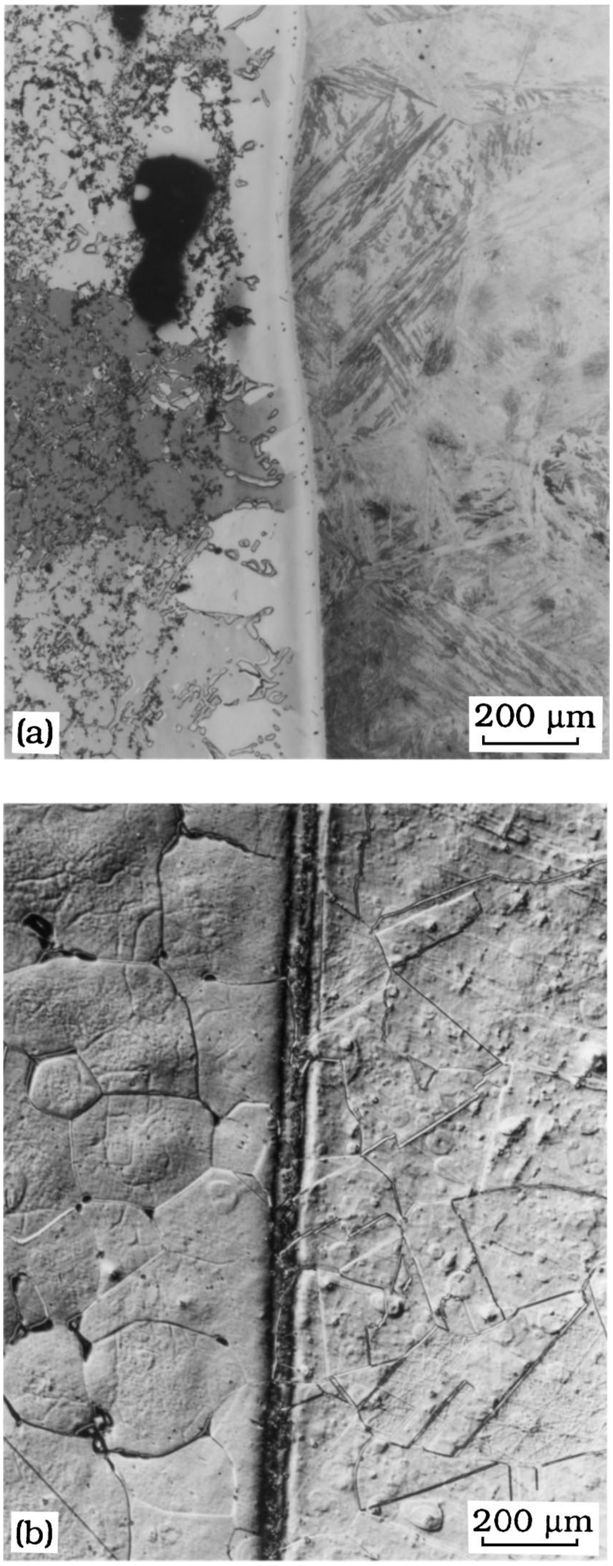


Figure 4 Optical micrographs taken from the diffusion couples of (a) the Ni_3Al-tool steel following 1400 °C/5 min and 1200 °C/2 h, and (b) the Ni_3Al-stainless steel following 1380 °C/5 min and 1200 °C/2 h, showing the interfacial bonding.

To obtain strong interfacial bonding and the desired mechanical properties of a diffusion couple, it is important to have a completely conformable contact between the substrate and the Ni_3Al intermetallic which is *in-situ* formed through the combustion reaction at a relatively low temperature, i.e. between 620 and 650 °C. It was found that right after the intermetallic formation the interfacial contact was usually not good because of the volume changes involved in the reaction. In some cases, there was even no contact at all so that the whole piece of the reaction-formed intermetallic sample could easily be separated from the substrate. Subsequent annealing for diffusion bonding, as applied in the heating scheme (i) could not yield any improvement in the interfacial contact. Nevertheless, for the reaction-formed samples having local, direct contacts with the substrates, good diffusion bonding with the steels could be achieved. Fig. 2 presents the optical micrographs taken from the diffusion couple (Ni_3Al-carbon steel) prepared through continuous heating up to 1300 °C and annealing for 2 h for diffusion bonding, i.e. the heating scheme (i). After such a treatment, only a small part of the reacted Ni_3Al sample had a good contact with the substrate and at such a location a fully densified interfacial layer was developed, as can be seen in Fig. 2. This densified interfacial layer appeared to have been built up by pushing pores to its front on the intermetallic side, see Fig. 2b. The thickness of the interfacial layer as a function of annealing temperature and time will be discussed later.

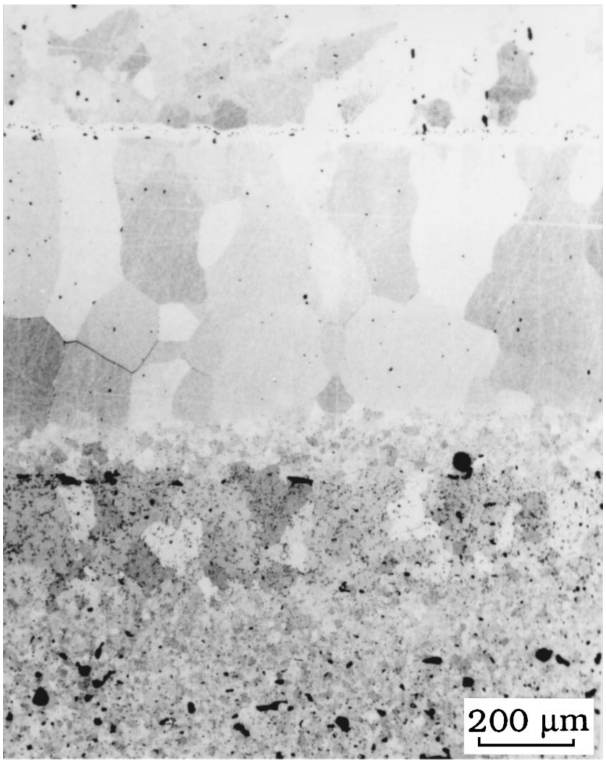


Figure 5 SEM micrograph showing the variations in grain size and density at the interface as a result of the diffusion-induced recrystallization.

In order to ensure a conformable contact over the whole interface between the reaction-formed Ni_3Al intermetallic and the substrate prior to diffusion bonding, a special heating scheme was developed, consisting of continuous heating passing the reaction temperature zone up to a temperature slightly above the melting point of Ni_3Al, holding there for a short time (5 min) and then cooling down to an annealing temperature, i.e. the heating scheme (ii) as detailed in Section 2.3.1. of this communication. In such a way, a good wetting and contact between the newly formed intermetallic and the substrate throughout the interface could be achieved. Due to the short holding time at the high temperature (5 min), the local melting of the intermetallic was yet quite limited and could not exert a marked influence on the thickness of the interfacial layer. As will be shown later, this thickness is controlled mainly by the parameters of annealing for diffusion bonding, i.e. temperature and time. An interfacial layer with a thickness of 2–4 μm was observed in the samples after heating up to 1400 °C and holding there for 5 min without subsequent annealing.

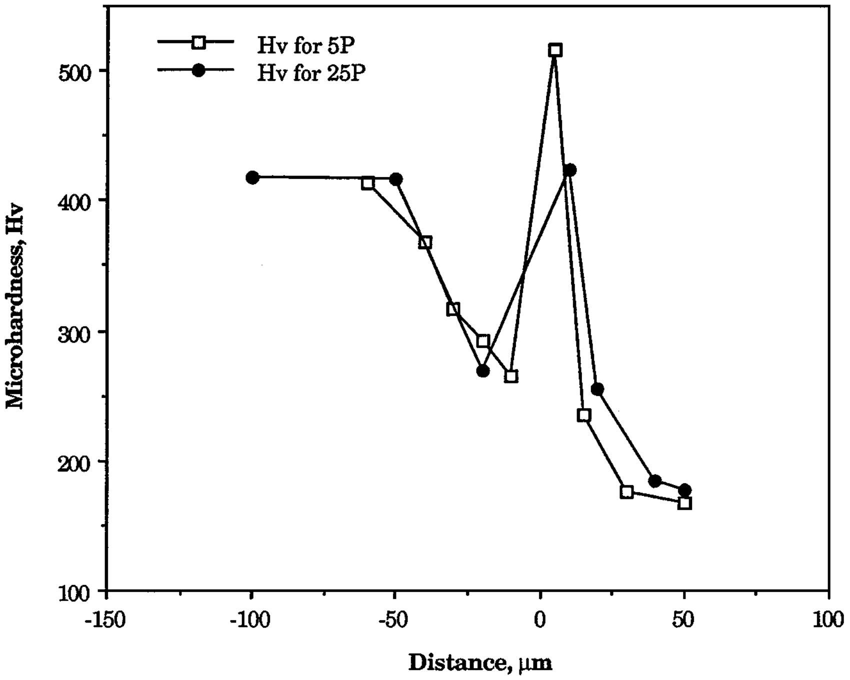


Figure 6 Microhardness profile across the interface of the Ni_3Al-carbon steel couple following 1400 °C/5 min and 1200 °C/2 h.

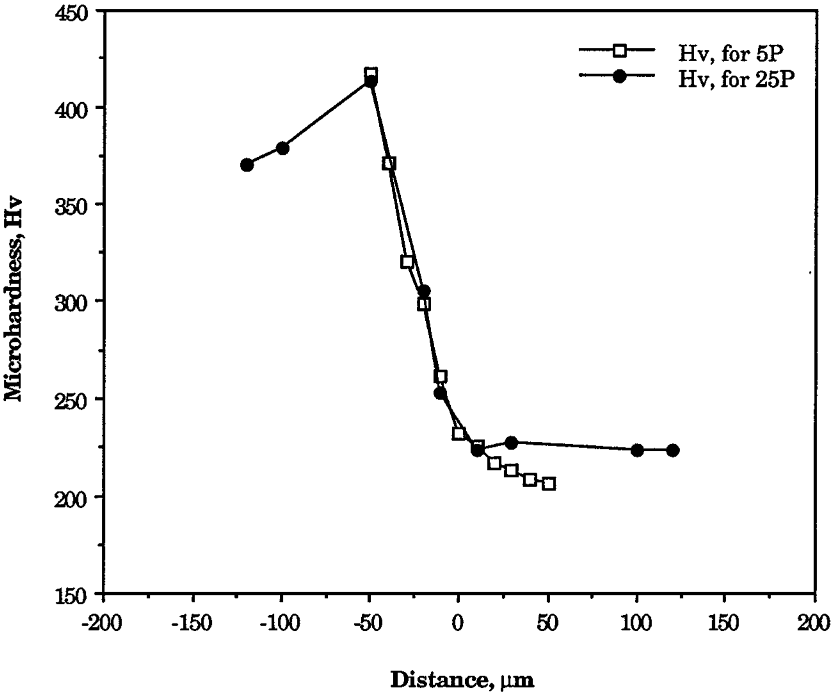


Figure 7 Microhardness profile across the interface of the Ni_3Al-stainless steel couple following 1380 °C/5 min and 1200 °C/2 h.

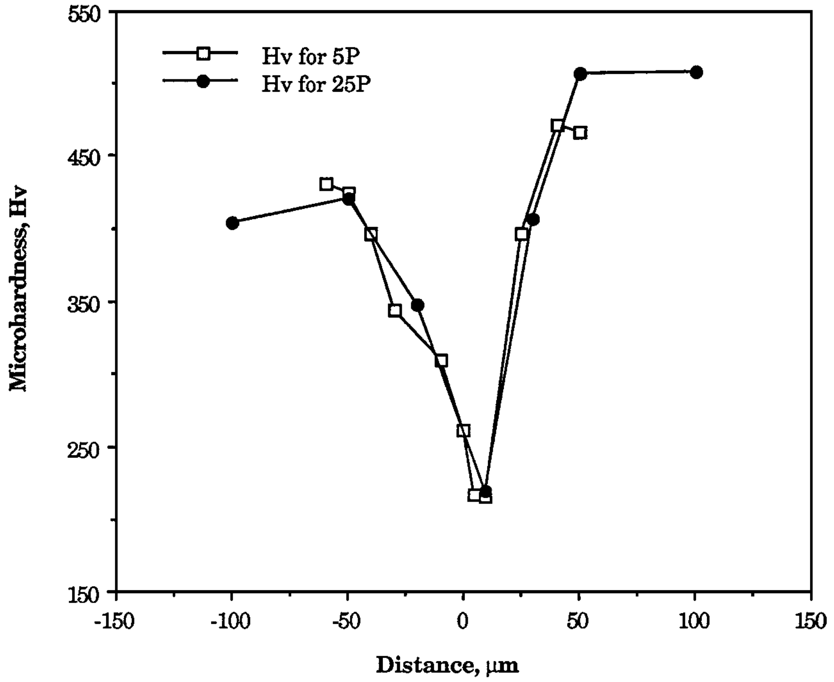


Figure 8 Microhardness profile across the interface of the Ni_3Al-tool steel couple following 1400 °C/5 min and 1200 °C/2 h.

However, such a heating scheme could have an influence on the microstructure in the vicinity of the interface, especially on recrystallization and densification there. The interface between the Ni_3Al intermetallic and the carbon steel following the heating scheme (ii) involving annealing at 1200 °C for 2 h is shown in Fig. 3. In comparison with Fig. 2b, we can see a much higher overall density of the reaction-formed Ni_3Al compound than that of the intermetallic without experiencing local melting. Moreover, the thickness of the fully densified layer at the interface is much larger. It should be noted that the annealing temperature of the sample shown in Fig. 3 was 1200 °C while that shown in Fig. 2b was 1300 °C. This difference in annealing temperature is responsible for the observable difference in the thickness of the interfacial layer. It is thus clear that the heating up to the high temperature before diffusion bonding can lead to a higher overall density of the reaction-formed intermetallic and furthermore the resultant local melting can facilitate further densification of the material near the interface, which is related to recrystallization occurring during subsequent annealing. With the heating scheme (ii), good interfacial bonding, similar to that in the Ni_3Al-carbon steel couple, was achieved with the other substrate materials. Fig. 4a shows the interfacial bonding of the Ni_3Al-tool steel

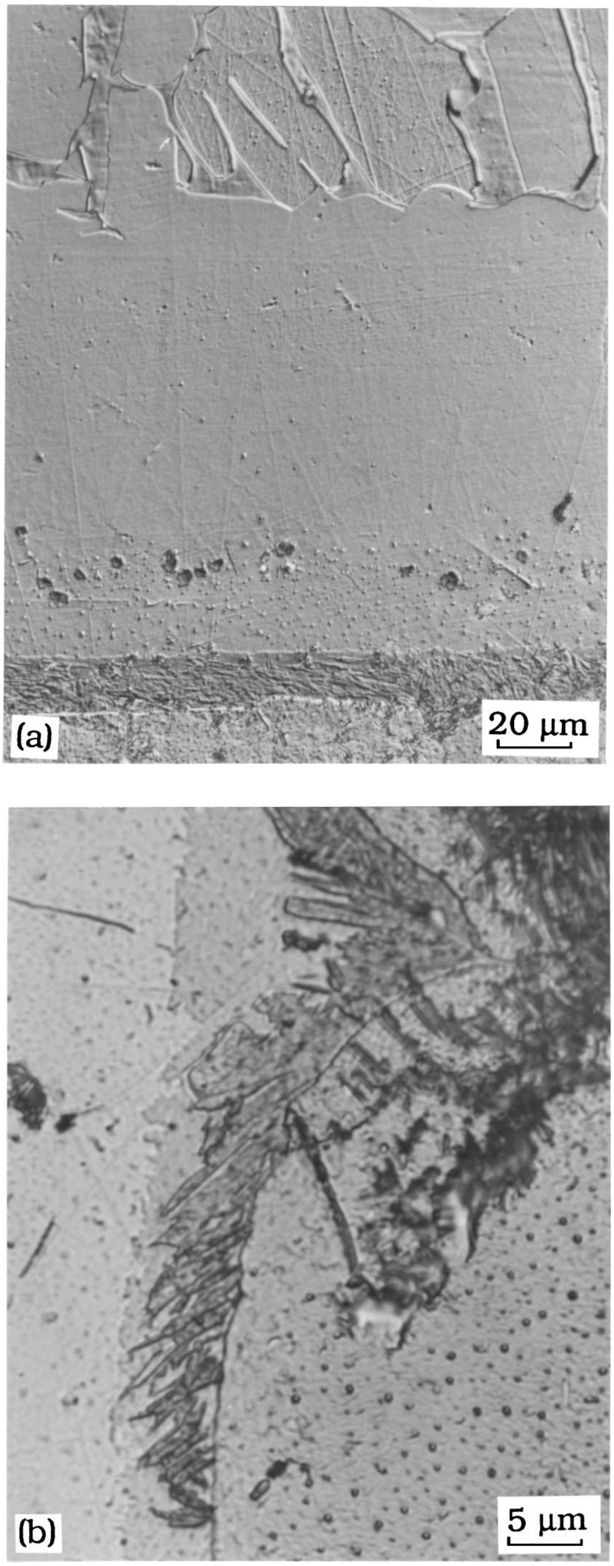


Figure 9 Optical micrographs showing the martensitic structure formed at the Ni_3Al-carbon steel interface.

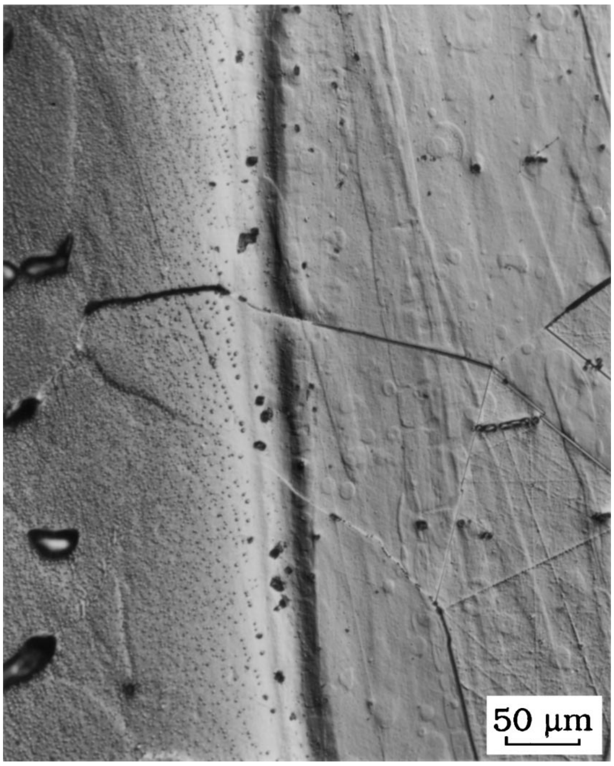


Figure 10 Optical micrograph showing the microstructural change across the Ni_3Al-stainless steel interface.

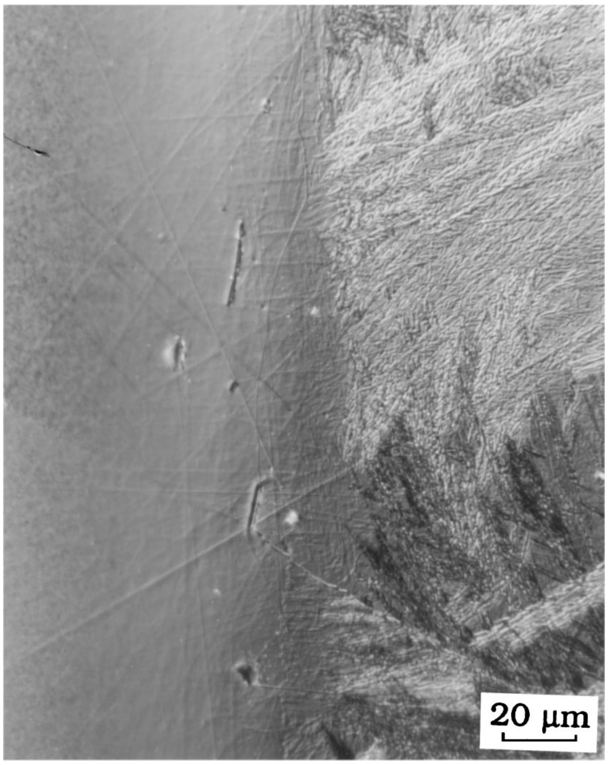


Figure 11 Optical micrograph showing the microstructural change across the Ni_3Al-tool steel interface.

couple after soaking at 1400 °C for 5 min followed by annealing at 1200 °C for 2 h. Fig. 4b shows another example of the interfacial bonding between the Ni_3Al intermetallic and the stainless steel, after soaking for 5 min at 1380 °C and then 2 h at 1200 °C.

The microstructural development of the *in-situ* synthesized Ni_3Al intermetallic is closely related to the diffusion process at the interface. Fig. 5 shows its characteristic microstructure with several layers, suggesting that different recrystallization and densification events have occurred during diffusion bonding. Along with the diffusion process at the interface during annealing, the recrystallization of the reaction-formed Ni_3Al intermetallic could be initiated at the interface and proceed, which involved the nucleation of new grains and

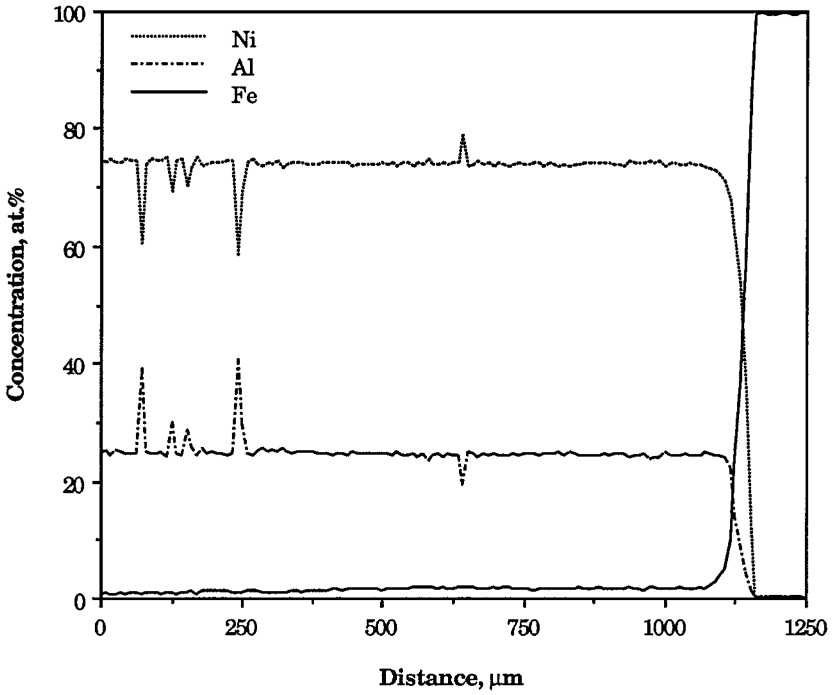


Figure 12 Chemical concentration profiles in the interfacial layer of the diffusion couple (Ni_3Al-carbon steel) after annealing at 1200 °C for 2 h.

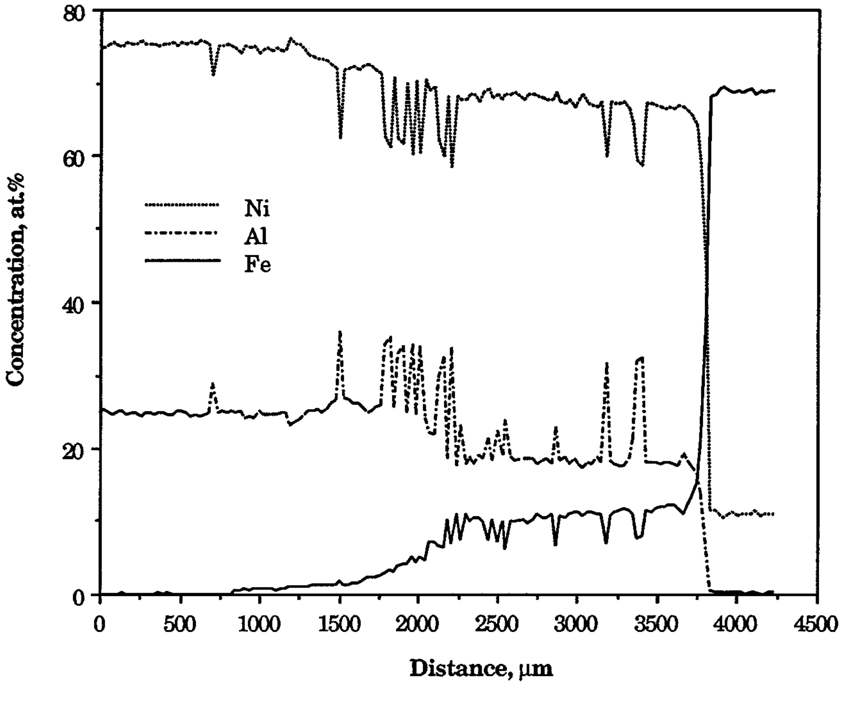


Figure 13 Chemical concentration profiles in the interfacial layer of the diffusion couple (Ni_3Al-stainless steel) after annealing at 1200 °C for 2 h.

then grain growth from the interface toward the intermetallic. The recrystallization of the intermetallic also resulted in its densification, thus changing its porous state to a fully or nearly fully densified state. Such a recrystallization process however did not occur throughout the whole volume of the reaction-formed Ni_3Al intermetallic, but was rather limited in the region close to the interface where diffusion during annealing took place. It may thus be defined as diffusion-induced recrystallization. With increasing distance away from the interface, the recrystallization became less completed. As a result, several layers with distinctive structures could be discerned: the unrecrystallized Ni_3Al phase with an as-reaction-formed fine crystal structure, the reaction-formed Ni_3Al intermetallic phase with a coarsened grain structure before recrystallization, the newly nucleated and recrystallized Ni_3Al intermetallic phase with a fine grain structure, and the recrystallized Ni_3Al intermetallic phase with a coarsened grain structure. It is thus the diffusion-induced recrystallization process that results in the variations in grain size and density in the intermetallic close to the interface, as can be seen in Fig. 5. One can further notice from Fig. 5 that there is a line dotted with pores between the fine recrystallized layer and the coarse uncrystallized layer. This is formed by pushing pores to the front of the interfacial

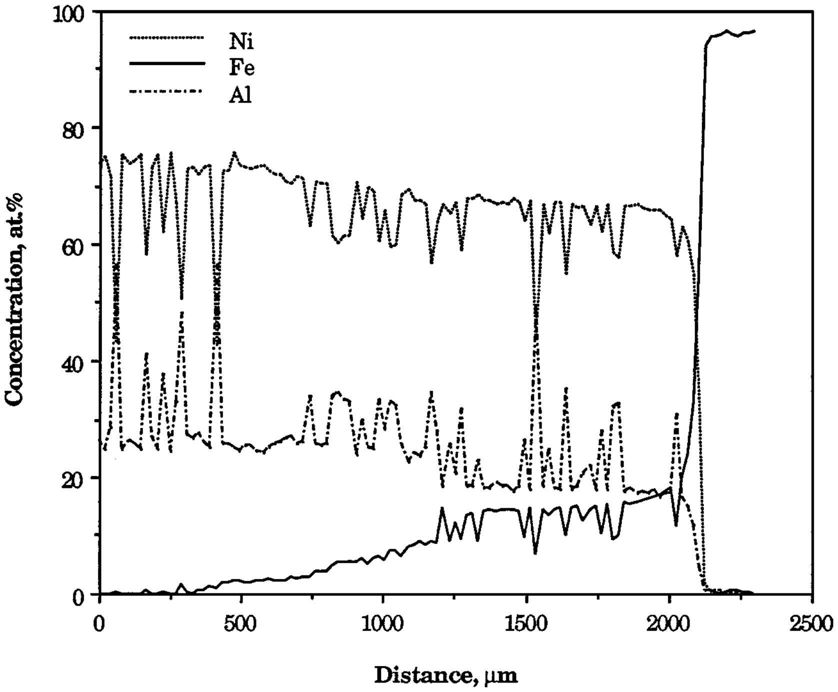


Figure 14 Chemical concentration profiles in the interfacial layer of the diffusion couple (Ni_3Al-tool steel) after annealing at 1200 °C for 2 h.

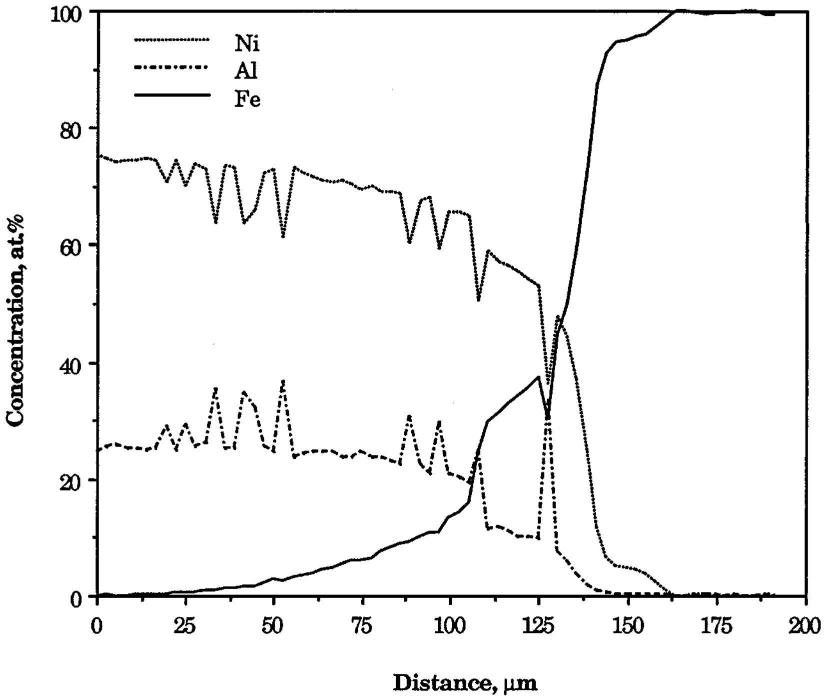


Figure 15 Chemical concentration profiles in the interfacial layer of the diffusion couple (Ni_3Al-carbon steel) after annealing at 1000 °C for 100 h under the external pressure of 2 MPa.

layer, or more specifically, to the front of the recrystallized material.

3.2. Microhardness across the intermetallic/substrate interface

The results of the microhardness measurements across the interfaces from the reaction-formed Ni_3Al intermetallic to the carbon steel, the stainless steel and the tool steel are given in Figs 6, 7 and 8, respectively. The measured variations in hardness across the interface could be used as an aid in determining the microstructure and the phases formed in the interdiffusion zone during annealing. The results indeed showed different interfacial mechanical properties related to different concentrations of the principle elements and microstructures at the interfaces in these three diffusion couples. The diffusion between the reaction-formed Ni_3Al intermetallic and the carbon steel resulted in interfacial hardening, as shown Fig. 6. The hardness continuously decreased from the reaction-formed intermetallic across the interface to the stainless steel substrate (Fig. 7). And the diffusion between the Ni_3Al intermetallic and the tool steel led to interfacial softening, as can be seen in Fig. 8.

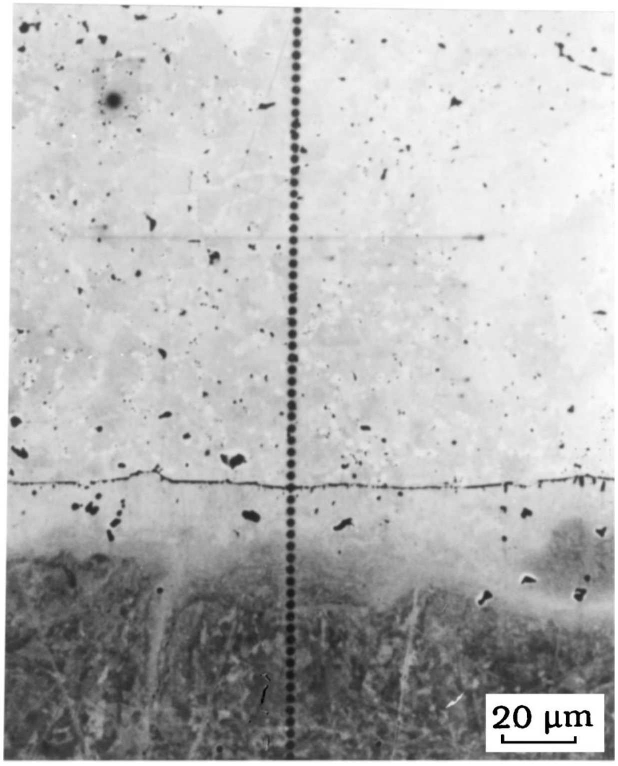


Figure 16 SEM micrograph indicating the measurements of chemical concentrations across the Ni_3Al-carbon steel interface, as given in Fig. 13.

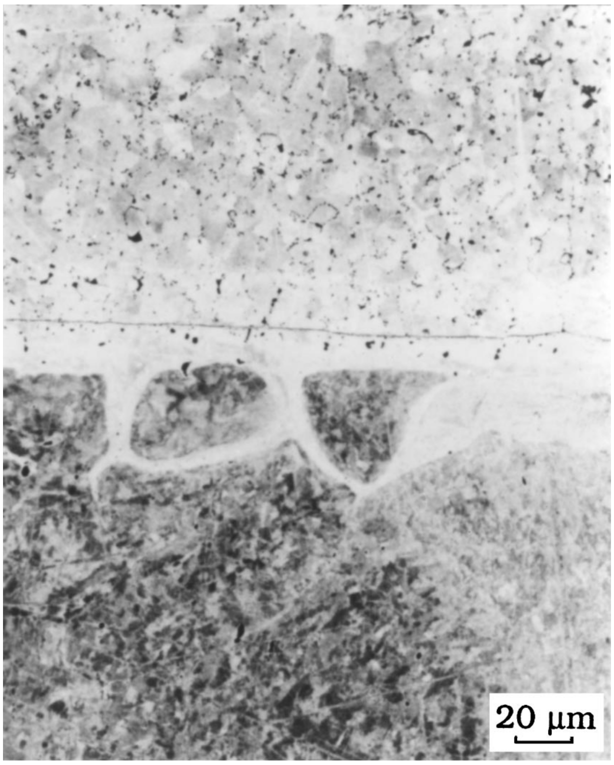


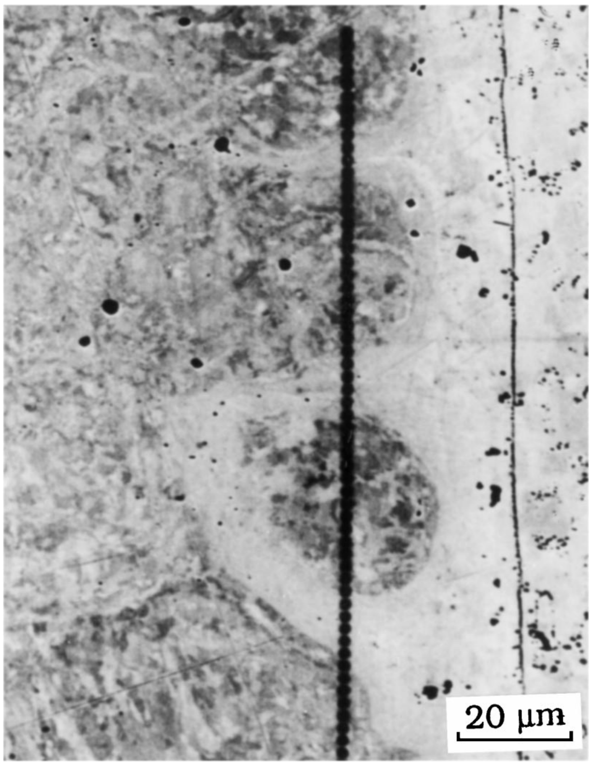
Figure 17 SEM micrograph showing the microstructure developed in the interfacial layer of the diffusion couple (Ni_3Al-carbon steel) following annealing at 1000 °C for 100 h under the external pressure of 2 MPa.

The reaction-formed Ni_3Al intermetallic in its fully densified state was measured to have a hardness value of about 400 Hv. Away from the interface, the intermetallic had decreasing hardness due to an increasing amount of porosity. After diffusion bonding, the substrates of the carbon steel, the stainless steel and the tool steel had the hardness values of 200, 220 and 500 Hv, respectively. In all the cases, within the interdiffusion zone from the intermetallic toward the interface, the hardness decreased from 400 Hv to about 215–230 Hv, which might be attributed to the disordering transition of the intermetallic, which was related to the concentration changes of the principle elements occurring during diffusion bonding. After reaching a minimum at the interface, the hardness varied in different ways, as a result of the microstructural development that had taken place in the interfacial layer linked to the different substrates. In the Ni_3Al-carbon steel couple, a hardness peak of about 500 Hv, being about the same as the hardness of the tool steel, appeared in a thin layer on the substrate side of the interface, see Fig. 6. In good agreement with this result, OM revealed a thin layer of the martensitic structure there, as shown in Fig. 9. After the peak, the hardness dropped to a stable level corresponding to the hardness of the substrate (carbon steel). In the Ni_3Al-stainless steel couple, the hardness decreased continuously from the intermetallic across the interface into the substrate. Consistently, OM showed a continuous, smooth transition of microstructure and the growth of grains from one side of the interface to the other without interruption, see Fig. 10. Both the ordered Ni_3Al intermetallic and the 316 stainless steel have the same crystal structure (f.c.c.) and thus the main change in microstructure is the order/disorder transition. This transition depends on the concentrations of the principle elementals in the interfacial layer, which is in turn dependant upon the diffusion process. In the Ni_3Al-tool steel couple, a minimum in hardness appeared in the interfacial layer, see Fig. 8. The change in hardness on the intermetallic side could be attributed to the disordering of the intermetallic, while on the substrate side the hardness would be controlled by the volume fraction of the martensitic phase formed in the tool steel. The microstructural changes across the interface of this diffusion couple are shown in Fig. 11.

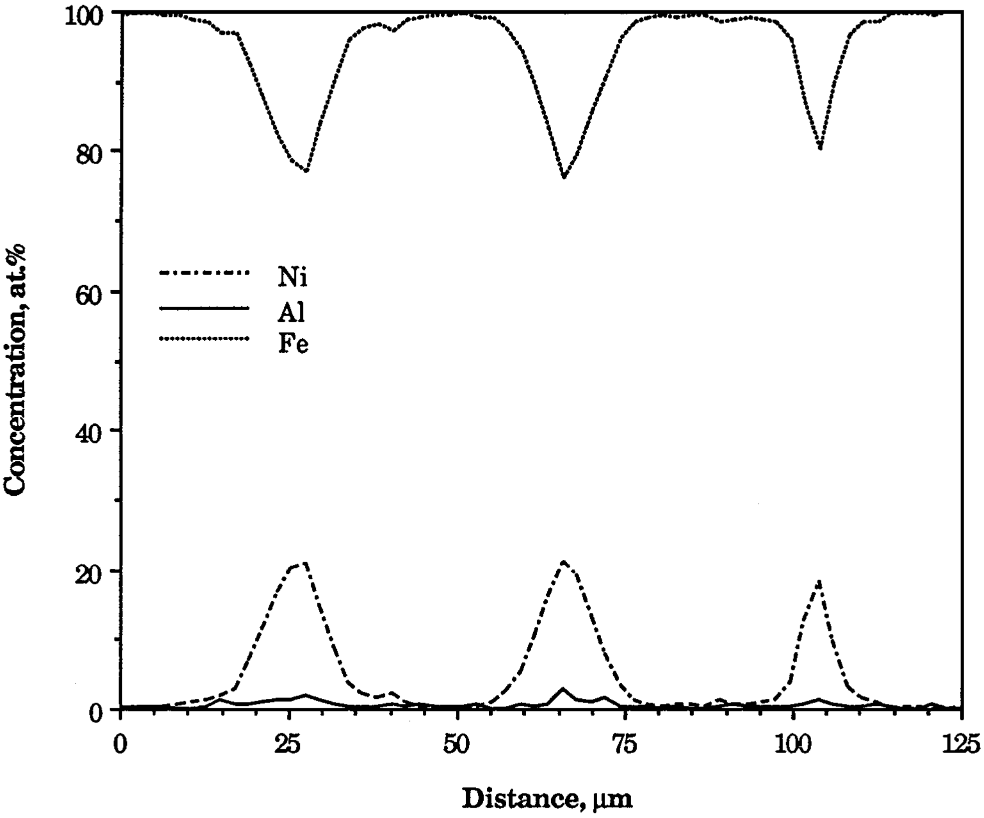
The results obtained in the present investigation indicate the possibilities to achieve the desired mechanical properties at the interface through proper design of diffusion couples. A proper variation of hardness or strength across the interface could provide an improvement in mechanical properties, e.g. fracture toughness, to the substrate material. In this regard, the diffusion couples of the Ni_3Al-carbon steel and the Ni_3Al-tool steel are of more interest. It is however important to note that the interfacial properties can be adjusted by varying annealing parameters such as temperature and cooling rate to result in interfacial hardening or softening even with the same substrate material.

3.3. Chemical concentrations across the intermetallic/subtract interface

The concentration profiles of the principal elements at the interface were determined with EDS linked to SEM to assist in estimating the thickness of the interdiffusion zone. Fig. 12 shows the concentration profile of the Ni_3Al-carbon steel couple which was annealed at



(a)



(b)

Figure 18 (a) SEM micrograph and (b) EDS concentration profiles of the elements in the region of the substrate parallel with the interface of the diffusion couple (Ni_3Al-carbon steel) following annealing at 1000 °C for 100 h under the external pressure of 2 MPa.

1200 °C for 2 h. It can be seen that the atomic concentrations of the reaction-formed intermetallic correspond well to the designed composition of Ni_3Al, i.e. 75%Ni + 25%Al. The concentration fluctuations of these two elements in Fig. 12 are caused by the concentration changes at the grain boundaries. In the region approaching the interface, the recrystallized grains are larger and thus less frequent fluctuations are observed. Furthermore, from the intermetallic to the carbon steel, a thin region can be noticed where there are substantial

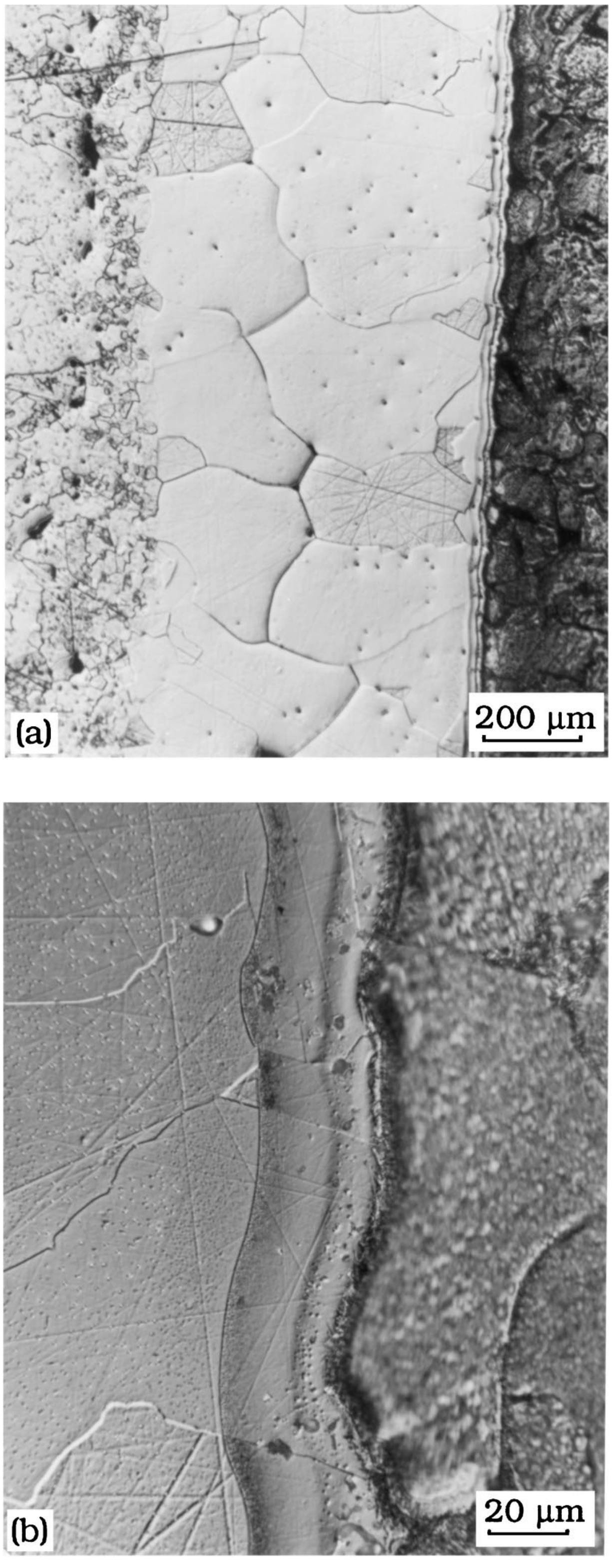


Figure 19 Optical micrographs revealing the interfacial diffusion layer in the Ni_3Al-carbon steel couple.

changes in the concentrations of nickel, iron and aluminium. Similar concentration profiles were obtained from the other diffusion couples having undergone the same annealing treatment, as shown in Figs 13 and 14. In those diffusion couples, however, the variations in chemical concentration appeared to be more complicated, probably due to the presence of other alloying elements in the substrate steels. The thickness of the diffusion layer with dramatic changes in chemical concentration was found to be about 20 μm for these three diffusion couples which had undergone the same annealing treatment, i.e. 1200 °C for 2 h.

The EDS analysis was also carried out of the samples which were diffusion bonded with the help of an external pressure. The diffusion couple of the Ni_3Al-carbon steel after annealing at 1000 °C for 100 h under a pressure of 2 MPa (without heating slightly above the melting point of Ni_3Al) had a good interfacial contact to allow the interdiffusion zone to establish, though not throughout the whole interfacial area. Fig. 15 shows its concentration profile across the interface, as indicated by the line in the SEM micrograph (Fig. 16). In this diffusion couple, the reaction product was still Ni_3Al, but little diffusion-induced recrystallization and then grain growth took place due to the low annealing temperature. As a result, more frequent concentration fluctuations can be observed in Fig. 15, in comparison with those in Fig. 12.

In addition, the lower temperature used in pressure-assisted diffusion bonding resulted in a different microstructure at the interface, especially on the substrate side (compare Fig. 17 with Fig. 3), suggesting a different operating mechanism of diffusion. At the lower temperature with an external pressure, the grain boundary diffusion would dominate the process, while at the higher temperature without any external pressure the grain boundary diffusion would only initiate the early-stage diffusion and the volume diffusion would be a more important mechanism for the development of the interfacial layer. Fig. 18 shows the concentration profiles on the carbon-steel substrate side in parallel with the interface. It can be seen that within the individual grains the material is basically a carbon steel. However, at the grain boundaries, extensive diffusion has taken place, especially of nickel, and even an intermetallic phase based on Fe_3Ni has formed. The maximum diffusion distance of nickel from the interface into the carbon steel was found to be about 100 μm and thus the diffusion coefficient could be estimated to be about 1.3×10^{-14} m^2/s. This value is in good agreement with the grain boundary diffusion of nickel in iron but much higher than that for the volume diffusion of nickel in iron (about 2.2×10^{-16} m^2/s at 1000 °C) [11].

3.4. Interface thickness and diffusion kinetics

The diffusion zone at the interface could be revealed through proper etching. An example is given in Fig. 19, clearly showing the interfacial diffusion zone in the Ni_3Al-carbon steel couple and allowing the measurement of its thickness. The measured thicknesses of the diffusion layers on the intermetallic side and the substrate side as well as the total thickness could be used to establish their relations with diffusion temperature/time. Fig. 20 shows such relations in the Ni_3Al-tool steel couple annealed at 1200 °C over the durations from 0.5 up to 18 h. The thickness of the diffusion zone appeared to be a linear function of the second root of time. In this case, the diffusion process would be controlled mainly by the volume diffusion. With such

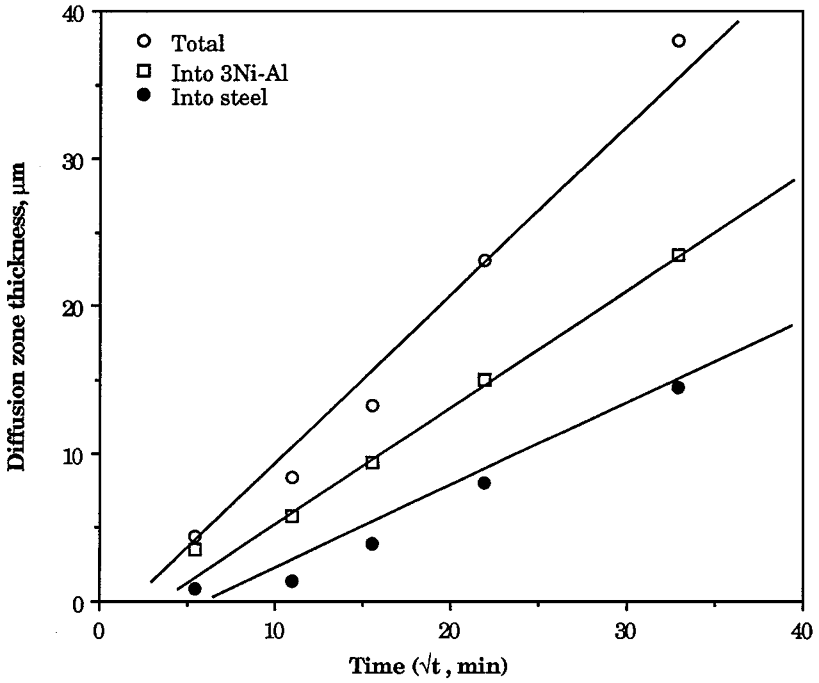


Figure 20 The relation between the diffusion layer thickness and time for the Ni_3Al-tool steel couple annealed at 1200 °C.

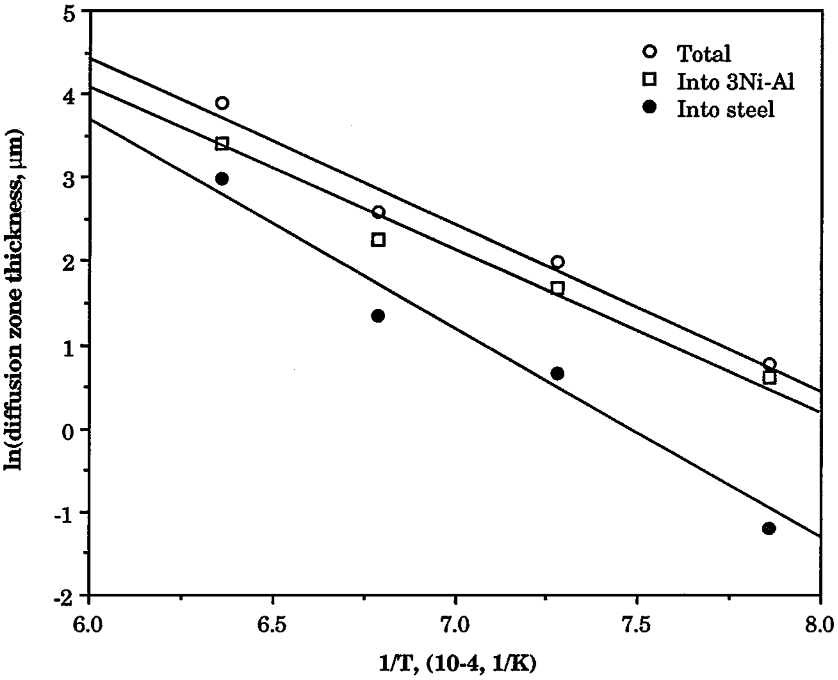


Figure 21 The relation between the diffusion layer thickness and temperature for the Ni_3Al-tool steel annealed for 4 h.

a plot, the diffusion coefficient of nickel in the tool steel could be estimated to be 2.3×10^{-15} m^2/s, that of iron in the intermetallic 4.7×10^{-15} m^2/s and that of interdiffusion 1.2×10^{-14} m^2/s. Also the activation energy for the diffusion process could be estimated by plotting the diffusion layer thickness against annealing temperature, see Fig. 21 for the diffusion couple of the Ni_3Al-tool steel over the range of annealing temperature from 1000 to 1300 °C at an annealing time of 4 h. The obtained activation energy for the diffusion of iron in Ni_3Al was 33 kcal/mol and that for the diffusion of nickel in the tool steel 46.2 kcal/mol. Unfortunately, little information is available to allow us to compare the obtained values with those in the literature and to evaluate the mechanism of the diffusion process in these complicated engineering materials.

4. Conclusions

The present investigation is part of a feasibility study on the *in-situ* synthesis of intermetallics for surface coating on conventional metallic materials. The procedures to prepare the Ni_3Al intermetallic coating on three representative types of steels for high-temperature corrosion/wear-resistant applications have been developed. More understanding of the microstructural development of the reaction-formed intermetallic and the diffusion process resulting in different microstructures and mechanical properties at the interface has been gained. The results obtained have allowed us to draw the following conclusions.

1. The microstructure of the reaction-formed Ni_3Al intermetallic in the front of the diffusion boundary is unstable at the early stage of the process. Recrystallization is initiated by diffusion at the intermetallic/substrate interface during subsequent diffusion bonding.

2. Strong bonding between the reaction-formed intermetallic and the substrate steels is the key to the processing of intermetallic coatings. A pre-condition is a conformable contact at the interface, which can be achieved through local melting for a short time before diffusion bonding.

3. During annealing for diffusion bonding, an interdiffusion zone between the intermetallic and the steel substrate is established. This zone can be divided into two layers, one on the intermetallic side with the elements diffused from the substrate and the other on the substrate side with the elements diffused from the intermetallic. The thicknesses of these two layers as well as the total thickness of the interdiffusion zone are largely a function of annealing temperature and time. However, the diffusion activation energy and diffusion coefficient affect the diffusion process in a given material system as a diffusion couple.

4. The microstructural development at the Ni_3Al-steel interface will result in different interfacial properties, depending on the diffusion couple. In the Ni_3Al-carbon steel couple, the diffusion leads to interfacial hardening due to the formation of a martensitic layer. In the Ni_3Al-stainless steel couple, the hardness decreases from the intermetallic crossing the interface into the substrate. In the Ni_3Al-tool steel couple, the diffusion brings about interfacial softening. These results suggest the possibilities to obtain desired interfacial mechanical properties according to the performance requirements through proper design of diffusion couples.

5. The present success in coating the typical carbon steel, stainless steel and tool steel with the Ni_3Al intermetallic shows a great potential to apply the technique of *in situ* reaction synthesis of intermetallic compounds and diffusion bonding to a wide range of conventional materials for various applications.

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