

Nucleation of ferrite at ceramic/steel interfaces

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SYNOPSIS

To understand the way in which complex non-metallic inclusions in steel weld deposits influence the nucleation behaviour of ferrite, controlled experiments have been carried out in which pure ceramics were diffusion bonded to steels. The diffusion bonded composite samples were then subjected to heat treatments in which the steel transforms from austenite to ferrite. By comparing ferrite formation events at the ceramic/steel interface with those within the bulk of the steel, it was possible to identify the mechanism by which ceramics influence ferrite nucleation. It is found that chemical reactions at the ceramic/steel interface can be extremely powerful stimulants for the austenite to ferrite transformation.

INTRODUCTION

In fusion welding processes involving steels, the use of strong deoxidising elements such as silicon, aluminium and titanium together with protective slag forming compounds causes the entrapment of complex multiphase non-metallic inclusions in the solid at the advancing δ -ferrite/liquid interface. The inclusions may be oxides or other compounds but they can under some circumstances influence the subsequent development of microstructure during cooling of the weld deposit. For example, the intragranular nucleation of bainite (known as *acicular ferrite* in welding terminology) is usually attributed to the presence of inclusions as heterogeneous nucleation sites [1].

It is established theoretically [2] that inclusions are less effective in nucleating ferrite when compared with austenite grain surfaces and indeed experiments show that ferrite formation first begins at the γ -grain surfaces. Subsequent intragranular nucleation on inclusions occurs when the austenite grain size is large so that events within the grain are not swamped by transformation products originating at the grain surfaces. Ferrite formed on such inclusions is better for weld properties so that an understanding of the nucleation mechanism on inclusions is an essential requirement for attempts at inoculating the intragranular formation of ferrite.

However, because of the complexity of the inclusions and the difficulty in conducting controlled experiments with welds, the nucleation potency of inclusions is not understood. In this work, we report experiments in which ceramics of well defined composition, purity, crystallinity and structure were diffusion bonded to steels which were then heat-treated within the diffusion bond. It was hoped that a comparison of events at the ceramic/steel interface with those within the steel at a distance from this interface would allow the ferrite nucleation potency of a variety of ceramics to be characterised in detail, using both microscopy and microanalysis techniques. The results of such experiments should allow various hypotheses for the nucleation ability of inclusions to be tested in an unambiguous way. These include the suggestions that: a) inclusions simply provide an inert surface for nucleation, b) those inclusions with good lattice fit with ferrite should be more potent nucleating

agents, c) inclusions which cause matrix deformation stimulate nucleation. These ideas originate from numerous reports in the literature, based on work done on inclusions in actual weld deposits. However, weld metal inclusions are extremely complex in shape, are multiphase and can be mixtures of amorphous and crystalline material. It is therefore difficult to identify a mechanism by which the inclusions enhance the nucleation of ferrite. This is why we chose a more controlled experimental approach to the problem.

It should be noted that the present work does not address the possibility that an inclusion which is surrounded by a solute depleted region stimulates the nucleation of ferrite because the austenite then may have a lower hardenability.

EXPERIMENTAL PROCEDURES

In order to cope with the limitations of the diffusion bonding apparatus used, and to ensure only limited transformation from ferrite, two extremely high hardenability steels were chosen for the experiments: Fe-0.3C-4.08Cr wt.% and Fe-0.31C-30.5Ni wt.%, both of which were prepared as 10mm diameter rods, sealed in quartz tubes under a partial pressure of pure argon, and homogenised at 1300°C for 3 days. 10mm lengths of rods were then cut, and the resulting fresh surfaces were prepared by mechanically polishing, degreased and used to form the bond with the ceramic powder.

The ceramics used were obtained as powders of 99.9% purity.

The diffusion bonding apparatus is illustrated in Fig. 1. The radio frequency induction heating coil, having a negligible thermal mass, permits fast temperature changes. The specimen temperature is monitored directly by an attached thermocouple which also provides feedback to a controller, so that heat treatment temperatures can be maintained to an accuracy of $\pm 2^\circ\text{C}$. A preset load of 12.5MPa was applied throughout the bonding process. The heat treatments used are summarised in Table 1.

Samples were prepared by placing the ceramic powder between two steel rods, evacuating the assembly to a pressure of $\approx 5 \times 10^{-5}$ mbar before austenitising at 900°C, the temperature at which the load was applied. The specimen was then argon quenched to the isothermal transformation temperature after which the load was removed. After heat treatment, the specimens were sectioned across the ceramic/metal interface and examined metallographically and with the help of microanalysis techniques.

RESULTS AND DISCUSSION

The bonds obtained between the Fe-Cr-C steel and a variety of Si based ceramics are illustrated in Fig. 2. Ferrite formation was not observed with Si_3N_4 or SiO_2 , but both pure Si and SiC caused the formation of very broad allotriomorphs of α at the interface.

Examination of the SiC bonds revealed a five layer structure consisting of the unreacted SiC, an allotriomorph of ferrite containing precipitates in the form of bands parallel to the advancing α/γ interface, a precipitate free zone (PFZ) in the α ,

a region with profuse precipitation of Cr-rich carbides and finally the unreacted austenite (which transforms to martensite on cooling to ambient temperature). That the SiC stimulates α formation is established by the fact that no ferrite formation was observed in the steel beyond the diffusion bond.

The precipitation within the ferrite caused its hardness to rise dramatically, to $\approx 700\text{HV}$ (normal hardness $\approx 200\text{-}300\text{HV}$) and microanalysis revealed that this region also contains $y_{\text{Si}} \approx 0.25$ of Si (Fig. 3), where y_{Si} is the ratio of the number of Si atoms to the number of iron atoms (the energy dispersive X-ray analysis technique is unable to cope with light elements such as carbon, so that the actual concentration of silicon is likely to be somewhat lower). The value of y_{Si} decreased continuously as the PFZ was traversed, until it reached zero in the unreacted austenite. The nature of the precipitation found within the ferrite is not clear, but it has tentatively been identified as an iron/silicon carbide.

The way in which the SiC stimulates the formation of ferrite is by *chemical reaction* with the steel. The SiC actually dissolves (if the bond is held at the isothermal transformation temperature for long enough, then all the SiC vanishes, Fig. 4), according to the reaction:



where the subscripts indicate that the element concerned is dissolved in the γ -iron. On cooling the silicon and carbon enriched austenite then transforms to ferrite. The Fe-Si carbide precipitates, probably at the α/γ interface by an "interphase precipitation mechanism" since the bands of particles are parallel to the advancing α/γ boundary. The formation of the carbide seems to be limited to regions within the ferrite where a critical Si concentration is exceeded, so that eventually, a PFZ is found. As the ferrite grows, it rejects excess carbon into the austenite, and when its growth ceases because austenite of low-Si content is encountered, chromium rich carbides form in the carbon-enriched austenite. This process is summarised in Fig. 5.

These results are consistent with diffusion bonding experiments in which the SiC was replaced by particles of pure Si. The results obtained in this case were similar but with the significant absence of precipitation within the ferrite and only limited precipitation within the austenite, presumably because of the absence of carbon enrichment of the type associated with the dissolution of SiC. The Si dissolved by chemically reacting with the steel to induce ferrite formation.

To confirm the effect of chemically active inclusions, similar experiments were done on the Fe-30.5Ni-0.31C wt.% steel which on its own simply does not transform to ferrite (Fig. 6). Both SiC and Si gave the same results with this steel, the precipitates in this case being FeSi.

Experiments were also carried out using the two steels bonded to Si_3N_4 and SiO_2 , and no ferrite nucleation could be detected in these cases. There was no chemical reaction either. Table II gives thermodynamic data for the Si family of ceramics; the results indicate that the compounds which are thermodynamically more stable do not react with the steel. This has been confirmed using a wide range of ceramic powders (Table III).

Space considerations prevent detailed discussion of all our results, but our general conclusion is that only the ceramics which are chemically active (Table III) are effective in stimulating the formation of ferrite for the circumstances of the present experiments. Of course, the mechanism of the chemical reaction concerned is different for the different ceramics. In Table III, the ceramics cover a wide range of lattice matching characteristics, differences in thermal expansion coefficients and crystal structure; we find no correlation between these factors and the tendency to nucleate ferrite.

CONCLUSIONS

A method has been developed which enables controlled experiments for the study of nucleation of ferrite at inclusions in austenite. It is found that for high hardenability steels, it is the chemical reaction between the ceramic and the steel which is responsible for the stimulation of ferrite nucleation and growth.

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REFERENCES

- 1 D. J. ABSON, R. E. DOLBY and P. H. M. HART, "Trends in Steels and Consumables for Welding" The Welding Institute, Abington, 1978.
- 2 R. A. RICKS, P. R. HOWELL and G. S. BARRITTE, J. Mat. Sci., 1982, 17, 732.

Steel	Ceramic	Austenitising		Quench Time/s	Isothermal	
		Temperature/°C	Time /mins		Temperature/°C	Time/s
4857	SiC	900	1	100	505	60
4857	Si	900	1	81	505	60
4857	Si ₃ N ₄	900	10	101	502	60
4857	SiO ₂	900	10	112	505	60
4863	SiC	900	10	Quenched to room temperature		
4857	SiC	900	10	35	700	120
4857	SiC	-	-	-	500	600

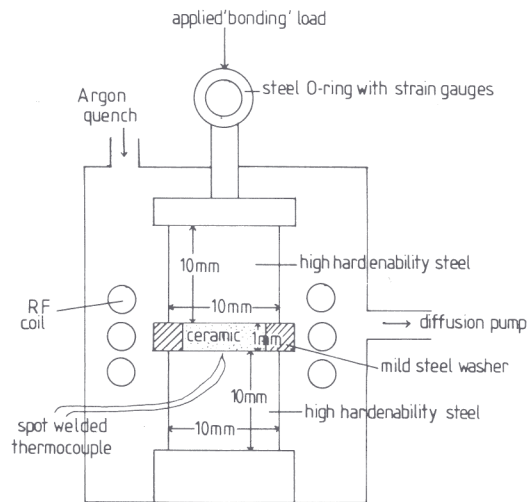
Table I, Summary of heat treatments applied to silicon based ceramic / steel couples

Ceramic	$\Delta H_{298}^{\circ} / \text{kJmol}^{-1}$	$S_{298}^{\circ} / \text{JK}^{-1} \text{mol}^{-1}$
Si	0.0	0.0
SiC	-63.0	16.6
Si ₃ N ₄	-740.5	107.5
SiO ₂	-909.5	42.8

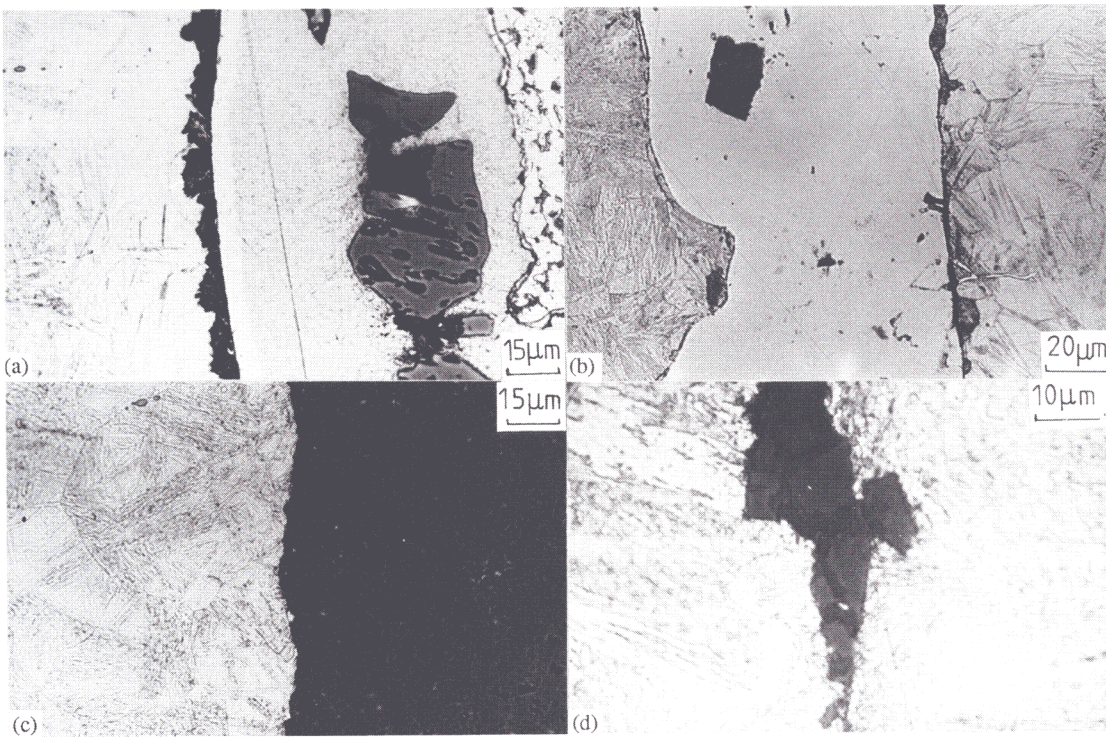
Table II, Standard enthalpies and entropies of formation of silicon based ceramics

Chemically Active	Chemically Inactive
TiO ₂	TiO, Ti ₂ O ₃ , TiC, TiN, TiB ₂
Al ₂ Si ₂ O ₇	Al ₂ O ₃
MnO ₂	MnO
SiC, Si	Si ₃ N ₄ , SiO ₂
CoO, V ₂ O ₅	ZrO ₂ , FeS, Y ₂ O ₃

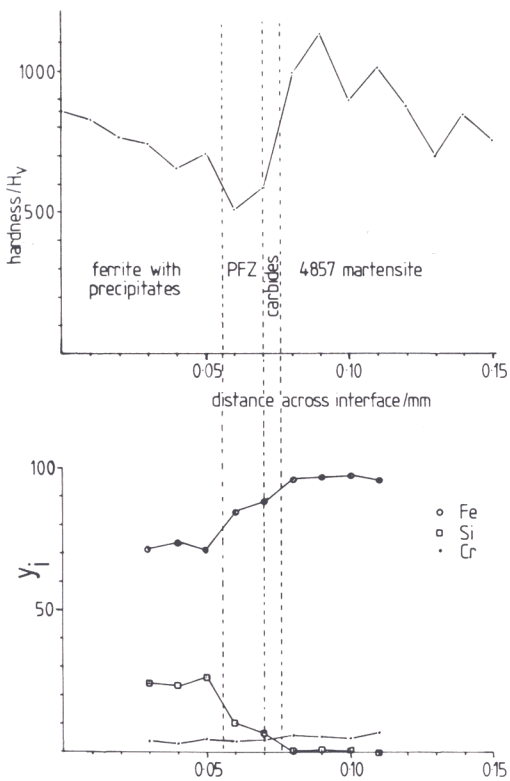
Table III, Complete listing of ceramic / steel interfaces studied indicating which are chemically active



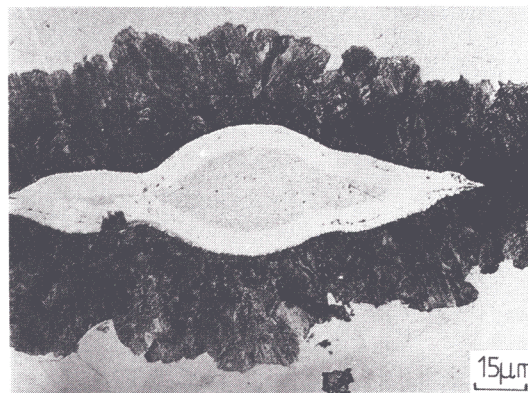
1. Schematic diagram of diffusion bonding apparatus



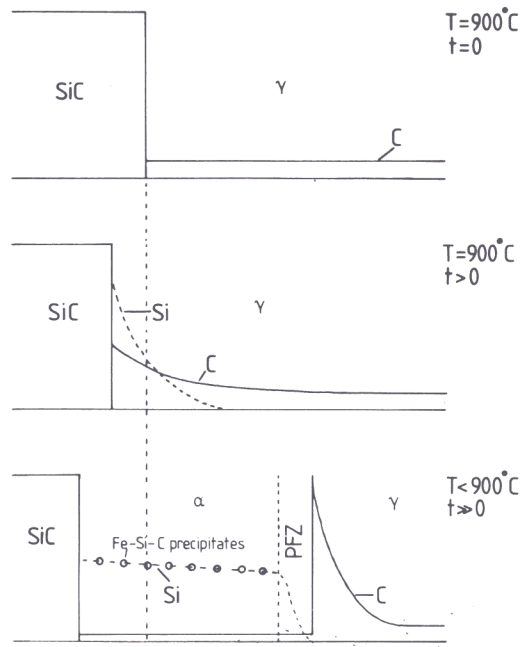
2. Ceramic/steel interface regions after heat treatment at 505°C for 60s, (a) SiC, (b) Si, (c) Si₃N₄ and (d) SiO₂



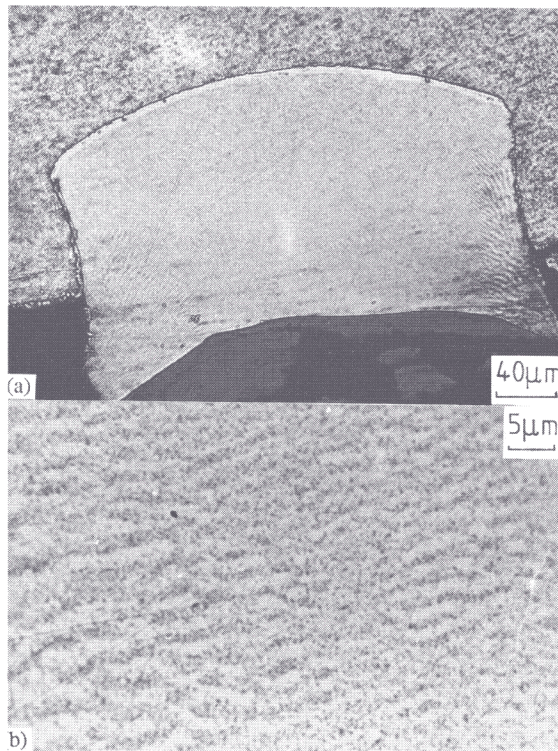
3. Microhardness and microanalytical traces across the steel/SiC interface after 60s at 505°C



4. Interface region of 4857/SiC after extended heat treatment at 900°C to fully dissolve the ceramic



5. Proposed model of SiC dissolution in steel



6. (a) Ferrite allotriomorph emanating from SiC into 4863 and (b) detail of banded precipitates in ferrite