NanoWorld Journal

https://doi.org/10.17756/nwj.2019-070

Research Article

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Investigation of the Copper Penetration and Joint Microstructure Observed in Low Alloyed Steels

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Received: April 10, 2019
Accepted: August 12, 2019
Published: August 14, 2019

Citation: Varanasi D, Szabo JT, Baumli P. 2019. Investigation of the Copper Penetration and Joint Microstructure Observed in Low Alloyed Steels. *NanoWorld J* 5(3): 36-40.

Published by United Scientific Group

Abstract

The study was aimed at investigation of the microstructural quality of the joint achieved in low alloyed carbon steels. Two steels were used here, C45 (C 0.45%) and 42CrMo4 steel (1%Cr, 0.45%C) with a pure copper (Cu) foil as the braze material. The experiments were conducted at 1100 °C in an inert gas environment. The results show good wettability and joint formation observed between the substrates. Dissolution of steel grain boundary by Cu and the immediate grain separation were observed at the interface. Grooving of the grain boundaries and subsequent channel formation filled with liquid Cu was achieved as evident from SEM-EDS micrographs. Besides the microstructure of the joint, penetration depth was also measured as function of time. Depth of penetration wasseen varying as function of cube root of holding time

Keywords

C45 steel, CrMo4 steel, Copper penetration, Copper wettability, Brazing

Introduction

Brazing is a simple joining technique used to fasten different components permanently using a combination of thermo-mechanical reactions between the braze filler and the substrate. Brazing is particularly useful in the industries for heavy machinery manufacturing, joint fabrications in heat exchangers, high temperature electronic packaging, etc. The efficiency and the longevity of the joints depend on time and temperature of the process coupled with elemental interplay. Our study focusses on the brazing of low alloyed steels with no or few alloying elements. This gives us an idea as to how holding time effects the joint obtained without any interplay of the alloying elements.

The behavior of Cu with iron (Fe)/steel was studied by Ishida et al. [1]. The study comprised of molten Cu interaction with solid Fe. Molten Cu wetting of Fe was observed in their case with an increase in wetting behavior as function of holding temperature. Yoshida et al. [2] performed experiments with steel/Cu/steel system where the steels used varied in their carbon composition. A patent has been registered by Kluczynski ML [3] to join two steels with varying carbon content with titanium (Ti) plates on both sides. Carbon diffusion was reported to occur from both sides of Ti. Fredriksson et al. [4] study on Cu penetration in iron grain boundaries is one of the most influential studies conducted in the field. They modelled a two-step process for the wetting and penetration observed. They successfully modelled the diffusion and penetration of Cu into pure Fe grain boundaries. Varanasi et al. [5] investigated the behavior of pure Cu with C45 medium carbon steel and confirmed a good wettability of C45 by molten Cu.

Grain boundary penetration of Cu and vice versa, diffusion of Fe into Cu is still a major issue in the brazing industry concerning Fe/steel-Cu joints. Benardini et al. and Ribbe et al. [6, 7] have studied the grain boundary diffusion of Fe in pure Cu using a radioactive tracer mechanism. Segregation of Fe at grain boundaries was reported by the group. Yukawa and Sinnot [8] studied the Ni diffusion and penetration into Cu. They inferred that the grain boundary diffusion is function of grain groove angle and temperature. The penetration was thought to be the result of grain boundary mismatch. Interfacia segregation of Cu with low carbon steels was reported by Isheim et al. [9].

Brazing of low alloy steels like 42CrMo4 has also been investigated. Li et al. [10] vacuum brazed CrMo steel with TiAl using Ag-Cu/Ti/Ag- Cu as filler braze. An increase in time and temperature lead to an increase in formation of Al-Ti phases in interface. He et al. [11, 12] extensively studied the microstructure of the brazed joints obtained between various ceramic/steels with CrMo steels using Ag-Cu-Ti braze fillers. They found defect free brazed joints between various combinations of steels with CrMo steels when Ag-Cu-Ti-Mo filler was used. The interfacial joint however, consisted of various intermetallic compounds of Cu-Ti-Mo. Divinski et al. [13] investigated the GB melting phase transition in Cu-Bi system. They discovered the segregation of Bi at the Cu GB and formation of a liquid like layer of Bi at GB interface.

The current investigation focuses on the wetting behavior of Cu on carbon steels with low alloying elements. The onus was to observe if a low Cr steel has almost no infiltration/penetration of Cu at the grain boundaries. If it did, to what depth does the penetration occur as function of time in comparison to mild carbon steel like C45.

Materials and Methods

The steel substrates used in the study are C45 and 42CrMo4. The composition of the steels was tabulated (Table 1). Both C45 and CrMo4 steels were cut into the required shape of 10 x 10 x 5 mm samples. The samples were then ground using 180, 240, 360 and 500 grit size papers and later polished with 3 μ paper using an alumina paste to get the smooth finish. The braze filler used was a 99.99% pure Cu foil of 70 μm thick, cleaned in an acetone bath and subjected to polishing. The samples were later arranged in such manner that Cu foil was sandwiched between the two steel substrates. A steel wire was tightly wound around the samples to hold them in place prior to placing them in furnace (Figure 1).

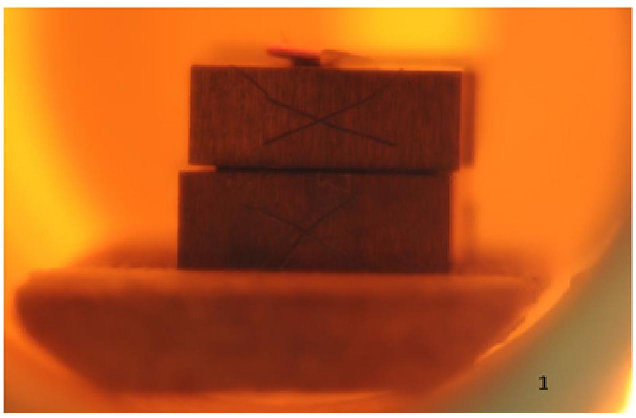

Figure 1: Sandwich arrangement of the samples placed inside the furnace. We can see two steel substrates and a Cu foil arranged to form a sandwich. A small Cu piece placed on top of the substrate to indicate Cu melting during experimentation.

Experiment was carried out in a vacuum furnace under an inert gas (Ar), at holding temperature of 1373 K (1100 °C). The holding times for the experiment were kept at 5, 10, 15, 30, and 60 minutes, respectively.

Results and Observations

Post experiment, the samples were allowed to cool down within the furnace. Later, they were taken out, cut and mounted for microstructure investigation. The scanning electron microscopy analysis of the obtained joint was carried out by using Carl Zeiss EVO MA10 equipment. The accelerated voltage of 20 KV was used for BSD microscopy of the joint. The microstructure showed good wettability and joint formation in samples of both the steels.

C45 Steel/Cu/C45 Steel

The composition of C45 steel used was as tabulated in Table 1. As we see it is medium carbon steel with C at 0.45 wt%. A good joint can be observed between steel/Cu/steel sandwich at all holding times (Figure 2).

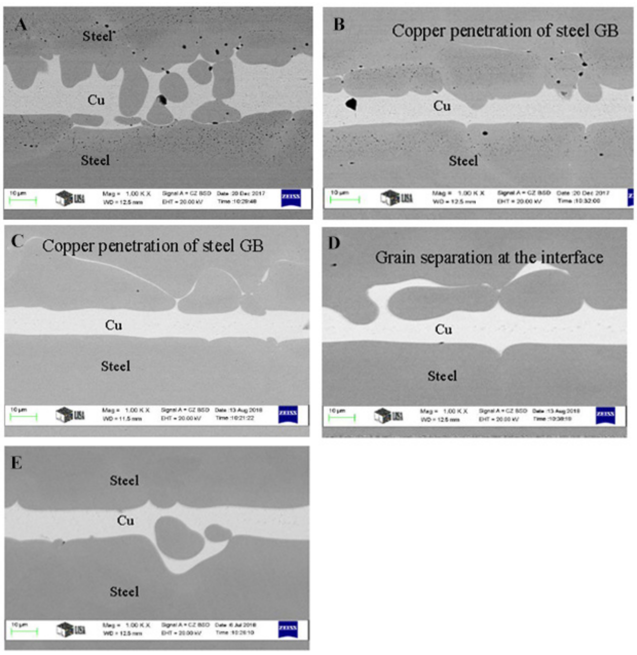

Figure 2: The joint microstructure obtained in a C45/Cu/C45 sandwich system. Cu wetting of the steel interface and formation of good quality joint can be observed. Additionally, Cu penetration of the steel grain boundaries can also be seen along with grains of steel separating from the steel boundary at steel/Cu interface. Pictures **(A-E)** are the joint microstructures at 5, 10 15, 30, and 60 minutes, respectively.

CrMo4 Steel/Cu/CrMo4 Steel

Table 1 provides us the composition of the steel used,

Table 1: Composition of the steels used in the study.

Steel	Fe	C wt%	Cr wt%	Si wt%	S wt%	P wt%	Mn wt%	Mo wt%	Source
C45	rest	0.45	-	0.3	0.030	0.04	-	-	XRF
42CrMo4	rest	0.40	1.3	0.40	0.030	0.04	0.75	0.30	XRF

with 1% Cr, 0.30% Mo and 0.75% Mn as the major alloying components. Cu showed very good wettability with CrMo4 steel and Cu penetration of the grain boundaries was also observed (Figure 3).

Penetration depth measurement

Before going any further, it is important to note that in the first-hand measurements of penetration depth, most of the measurements we perform are on a surface while penetration is a 3-dimensional process. Due to this mismatch, the complete picture is seldom revealed.

For penetration measurements in our study, we have used Image-J image analyzer with SEM images taken from Hitachi series machine. The scaling was done manually prior to the analysis using the set scale option embedded in the software. All the images were converted to 8-bit for the ease of operation with the said software. The length of channels was measured using the length scale and the penetration depth was taken. The sample length measurement was shown below highlighting the penetrated channel in red (Figure 4).

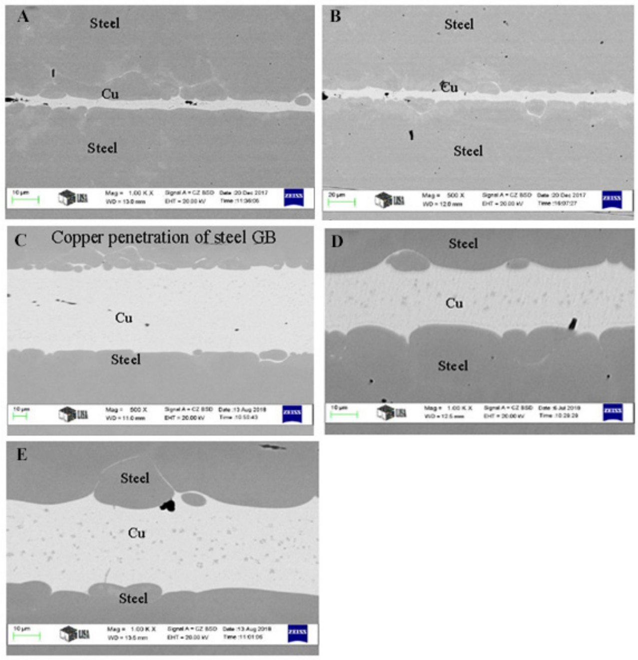

Figure 3: Brazed joint obtained in a CrMo4/Cu/CrMo4 sandwich system. Cu wetting of the steel interface and formation of good quality joint can be observed. Cu penetration was also achieved at the steel grain boundaries with Cu interface. Pictures **(A-E)** are the joint microstructures at 5, 10 15, 30, and 60 minutes, respectively.

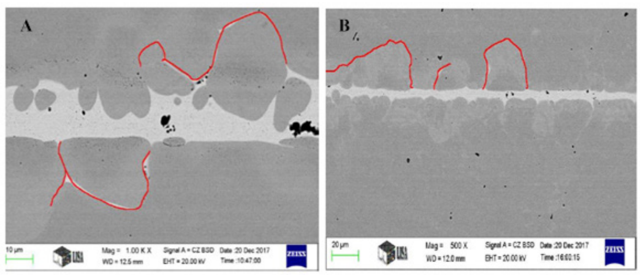

Figure 4: Penetration length as measured by Image-J analyzer software. **(A)** represents penetration in C45/Cu/C45 system. **(B)** represents penetration in CrMo4/Cu/CrMo4 system.

Discussion

Wetting

The term wetting is defined as the spread of a liquid on the surface of solid material. Depending on the extent of spreading, it is classified as good wetting and bad wetting. Wetting is understood in terms of wetting angle/contact angle θ and interfacial energies in play as given by Young.

$$\mathrm{Cos}\,\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \qquad (1)$$

Where, θ is the contact angle, σ_{sv}, σ_{sl} and σ_{lv} are the interface energies of between solid-vapor, solid-liquid and liquid-vapor phases, respectively.

It is also characterized by Young-Dupree equation given as below:

$$W_a = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} \qquad (2)$$

W_a is the adhesion energy

All other quantities are as previously defined.

Dissolutive wetting is one of the many ways in which wetting can take place in a system. In this case, liquid dissolves a little portion of substrate allowing the liquid to penetrate the substrate grain boundary. Various studies were undertaken on the penetration occurring during dissolutive wetting with Cu and Cu-Si as liquid melts [14-18].

Whenever there was complete wetting, there were two processes happening in the system – diffusion and penetration as illustrated in Figures 2 and 3. Low alloyed steels like medium carbon steels or low Cr steels have a good wetting property with Cu. The system shows a perfect joint under the experimental conditions. Although this is a general tendency among S-L interactions, grain boundary grooving has been observed furthering the wetting between the steel and Cu melt. Grain boundary wetting occurs when the wetting angle was between 0 - 90°. The grain groove angles were much lesser than 90°. The diffusion occurs governed by Fick's law of diffusion. Applying the diffusion laws shows us steel takes not more than 1s for diffusion. The diffusion between Cu and steel GB was almost instantaneous and results in spontaneous wetting. The energy balance was negative and driving force free Gibbs energy change ΔG was negative. These channels have zero angle grooves at the grain boundaries as observed from SEM pictures Figures 2A-E and 3A-E supporting the theory.

Copper Penetration

Grain boundary penetration of liquid melt follows the diffusion process. After diffusion coupled with dissolution of elements involved, the penetration becomes the next logical step. The drive for penetration comes from the difference in surface energies of the solid-liquid interface and grain boundary. Penetration occurs when grain boundary energy is greater than twice the surface energy of solid-liquid interface [19].

$$\sigma_{GB} > 2\sigma_{SL} \qquad (3)$$

Where, σ_{GB} is the grain boundary energy

σ_{SL} is the surface tension between solid and liquid phase.

From Brandes and Brook [20], we have σ_{GB} for steel is 0.88 J/m^2 and $\sigma_{Fe/Cu}$ is 0.43 J/m^2. By substituting the values in equation 3, we see that the above condition was valid in both the cases presented here.

Let us now discuss the formation of channels and the depth of penetration. For penetration let us assume a channel groove formation of length L and radius r. Penetration starts at the groove formed between the two grains at the interface and proceeds along the grain boundary into the linear three grain boundary in the bulk of steel. The shape of penetrating channel was difficult to predict as it depends a number of factors, but for consideration the channel shape was assumed to be tubular with a moving tip as shown in Figure 5. The penetration depth analyzed for two steels was shown in Table 2 and Figure 6.

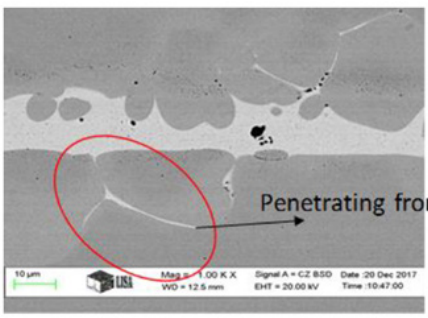

Figure 5: Illustration of the penetrating front and the grooves formed in the steel grain boundary.

The penetration behavior here can be understood in two parts. The behavior at shorter holding times (5 and 10 minutes) and longer periods (15, 30, and 60 minutes). The behavior varied significantly in CrMo4 steel compared to C45 steel as holding time was increased from 5 minutes to 60 minutes. While $L \propto \sqrt{t}$ was still perfectly valid for C45/Cu system across all holding times, in CrMo4/Cu system, this relation held good only until 10 minutes. Beyond 10 minutes, at longer holding times, the penetration depth increased exponentially as evident from Figure 6.

Table 2: Tabulated data of penetration depth as function of time.

Time (minutes)	Depth of penetration in C45 steel (µm)	Depth of Penetration in CrMo4 steel (µm)
0	0	0
5	65.31	44.99
10	89.27	70.66
15	81.82	76.95
30	83.19	87.25
60	90.78	82.733

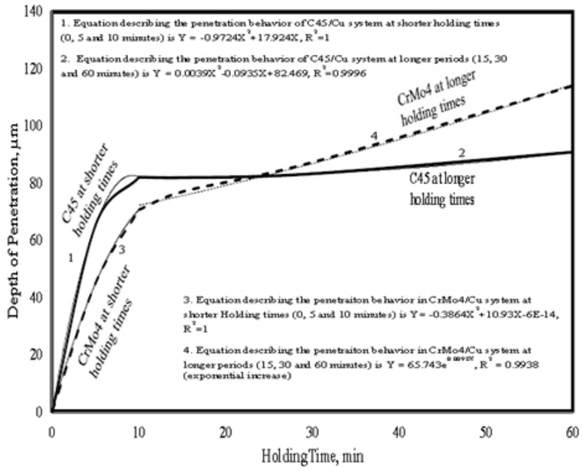

Figure 6: Depth of penetration as function of holding time for both the steels with the equation describing the fit of each curve. The penetration of Cu in C45steel is higher at shorter holding times whereas the penetration of Cu in CrMo4 steel increases exponentially at longer holding times.

Conclusion

The brazing study of low alloyed steels like C45 and 42CrMo4 using Cu as braze filler was conducted at various holding times. Following conclusions can be drawn from the experiments on the joint quality.

- Wettability and joint formation in all steel/Cu/steel systems at all holding times was found to be good. The grain boundary grooving has been achieved showing the good measure of spread and wetting of the surface by Cu melt.
- There was grain dissolution from grain boundary of the steel associated with diffusion of steel into Cu and consequential grain separation specially at longer holding times.
- The grain dissolution further leads to groove and channel formations in the steel which were later filled with molten Cu. The underlying mechanism was discussed.
- The penetration of Cu was observed along the length of joint microstructure and the depth of penetration

was measured by image analyzing software. The average depth of penetration for C45/Cu system reaches a value of 90 µm and up to 114 µm for CrMo4/Cu system as the time was increased from 5 minutes to 60 minutes (Table 2).

- Penetration depth behavior in C45 and CrMo4 steels vary at holding times higher than 10 minutes (600 s). The penetration behavior follows the usual square root relation with holding time at 5 and 10 minutes in both the steels. But beyond 10 minutes, the penetration in CrMo4 steel increases exponentially, contrary to the square root pattern observed in C45 steel. This was backed by the observed trendline fit.

Acknowledgement

The authors would like to thank Dr. Daniel Koncz-Horvath and Dr. Anna Sycheva for their contribution in providing us with microstructure measurements on SEM, and Mrs. Aniko Markus and Mrs. Napsugar Nyari Bodnar for sample preparation. We are also thankful to Innovacios Laboratorium Ltd., (Miskolc, Hungary) for support of Field Emission Scanning Electron Microscope (SEM) Hitachi S-4800 equipped with Bruker AXS Energy-dispersive X-ray Spectrometer (EDS) system.

Conflict of Interest

There is no conflict of interest in regard to this publication as presented research is an original work with original findings. It was submitted only to NanoWorld Journal for peer review and publication with consent of all the authors involved and we reaffirm that this article was not submitted to any other journal.

Funding Source

The research work presented are based on the results achieved within the GINOP2.3.2-15-2016-00027 “Sustainable operation of the workshop of excellence for the research and development of crystalline and amorphous nanostructured materials” project implemented in the framework of the Szechenyi 2020 program. The realization of this project is supported and funded by the European Union.

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