Grain Boundary Behavior of Copper with C45 Medium Carbon Steel

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Brazing is one of the most important techniques known in joining two similar/dissimilar metals/metal–nonmetal combinations for structural, mechanical, and aerospace applications. Brazing joints are formed by melting pure or alloyed foil called braze. Braze is melted in between the two substrates to be joined, and the joint is formed due to inherent adhesion and reactivity between braze and substrate. Copper and nickel are most commonly used brazes in the industry. Copper behavioral studies are mostly aimed at stainless steels (SS), and lot of research is carried out in Cu–SS systems. But, what is the copper behavior with medium carbon steels? What is the grain boundary behavior of copper and its mechanism when the alloying elements in steel are very low? Sandwich experiments were conducted with C45/Cu/C45 systems under an inert gas environment at 1100 °C. Cu was found to be wetting and penetrating the grain boundaries of medium carbon steel such as C45. The depth of penetration varied depending on holding times. The microstructure of the interface was characterized by SEM, and penetration depth was measured by image analysis software for better resolution and accuracy.

**Keywords:** C45 steel, medium carbon steel, brazing, copper foil, depth of penetration

1. Introduction

Joining is a physiochemical phenomenon of bringing two or more similar/dissimilar items together to make them one single component. The physiochemical joining processes are classified into welding, soldering, and brazing. The mode of classification depends on the temperature used. The temperature used in welding is above the melting point of both the substrates to be joined, and joint is formed due to melting of substrates. Soldering is a process where the solder is melted below a temperature of 450 °C. In brazing, the melting temperature of braze is lower than the corresponding substrate material but is generally above 450 °C. Solders differ from brazes at the temperature of application. Both brazing and soldering are used mostly for fabrication and packaging purposes in the industry. Soldering is used to make electrical contacts for electronic appliances. Brazing is used for fabricating heat exchanger joints used in refrigerators, air coolers, etc. Brazing has also inserted its foot in the door of aerospace applications by packaging various electronic equipments. Copper and copper alloys are most commonly used brazes for stainless steels. This has been the norm for over a century with studies starting with pure copper foil as braze to newly developed, tried and tested alloys like Cu–Ag, Cu–Ni, Cu–Sn–Ag, Cu–Ag–Ti, etc.

When copper is used as braze, or any braze is used for the fabrication, certain aspects like the wetting behavior of the metals to be joined, time of brazing, and temperature are crucial factors. The joint efficiency in the end is based on the wetting and interfacial behavior of braze material with the substrate. Copper when used with steel, the interfacial behavior, wetting ability, and penetration are of scientific interest for the last 50 years.

Ishida studied the effect/behavior of pure molten copper on cast iron systems. Good wettability and penetration were reported in the systems. They also opined that Cu wetting behavior increases with increasing temperature [1]. Rassoul et al. reported a study on copper diffusion in steel at the interface and showed that an inverse relationship exists between steel’s carbon composition and copper penetration. The diffusion of copper varies as an inverse function of carbon composition. Activation energies of carbon diffusion in steel are also found to increase with increasing braze temperatures and the corresponding carbon content [2].

Yoshida et al. [3] conducted a research in brazing of dissimilar carbon steels with copper as braze alloy. Normally in brazing, the copper melts and forms a diffusive dissolution with iron in both the substrates to form a joint. But in their study, they chose two steels of different compositions: a low carbon one and a high carbon one. They found that iron from low carbon steel dissolves in copper at the interface, and this iron reacts with carbon from high carbon steel on the other end of the interface to form a columnar Cu–Fe–C structure, which grows as column. This Cu–Fe–C column becomes stronger with brazing temperature and time, providing a good link up joint between the two substrates through the molten braze. The shear strength of the thus-formed joint was also checked, and it was close to the value of that of steel. There is a direct relationship observed between the difference in the carbon content in the steels used and the rate of formation of grooves at the grain boundaries.

Fredriksson et al. investigated the mechanism of copper penetration in steels and concluded that copper penetration in steel grain boundaries follows a two-step pattern. In the first step, copper diffuses from interface into the grain boundary of Fe with the help of Kirkendall vacancies. Kirkendall vacancies are vacancies formed due to the differences in diffusion coefficients of two reacting elements at the interface, and corresponding diffusion occurs from the element with a lower diffusion coefficient to the element with a higher diffusion coefficient. Simultaneous diffusion of Fe from grain boundaries to interface and Cu from interface to grain boundaries takes place. The diffused copper forms initial grooves at the grain boundary. In the second step, these grooves at the higher temperatures of brazing forms channels for copper to flow due to high energy of copper and helps in penetrating the grain boundary [4]. Protosenko et al. studied the interaction of SS304 with Pb as braze. They observed that the surface of steels gets deoxidized at high temperatures of brazing, and this change will accommodate the corresponding braze penetration observed [5–6]. Ding et al. studied the activated brazing of cubic boron nitride (CBN) abrasives to medium carbon steel with Ag–Cu as braze and Ti as an activator. The experiment of brazing was done under vacuum at higher temperatures. Ti was found to have a preferential mixing on the surface of grains with N and B from CBN [7].

Elrefaey et al. and Atasoy et al. used a copper interlayer to the diffusion bonding of dissimilar Ti–steel systems. The important parameter for successful bonding in this case was temperature.
No matter what the holding time is, if the brazing temperature is less than 800 °C, the bonding will not happen, whereas if the temperature is around 850 °C, the joint will form under brazing. This observation held true for all holding times at that temperature. Hence, temperature was a very important factor. The thus-added copper as an interlayer actually helped in inhibiting the reaction between Ti–Fe and C [8–9].

Although stainless steels are the frequent choice of material in the industry, low–medium carbon steels are also a focused area, particularly on the low–medium industry scale. Klucznick registered a patent on joining mild carbon steel with Ti on both sides, which has been detailed. One problem with brazing steels of different carbon contents is that at brazing temperatures, the carbon diffuses from high carbon steel to low carbon steel via molecular diffusion, and the joint efficiency is compromised. However, with Ti, this effect is mitigated as Ti and does not absorb carbon readily, and the steel can be heat treated for toughness. The experimental temperature was 760–870 °C. Cu and Cu–Ag were used as braze alloys foils [10].

Diffusion welding of mild steel and aluminum is carried out by using a Ni interlayer under vacuum conditions by Iwamoto et al. Mild steel and 1050 Al was brazed using a Ni interlayer and found that Ni at the interface has formed precipitation strengthening compounds and has improved the strength of the joint, compared to the strength of base metals under tension [11]. Murugan et al., Anand et al., and Yang et al. reported the studies on aluminum diffused by copper under various experimental methods, which were studied by the scientific community. Pure Ti and low carbon steel were brazed using various holding times. The joint was formed via diffusion bonding. 850 °C was found to be the optimum temperature of brazing when using this system for a holding time of 90 min. The strength of the joint and the system as whole depends on the diffusion time and temperature. Both hardness and joint strength were seen decreasing when both diffusion time and temperature are increased above the optimum time and temperature as mentioned above. Silver diffused into steel from the interface with increasing holding times. These were the various modes of research done in low–medium carbon steels with the following study focusing to address the issue of grain boundary behavior of copper in mild carbon steels [12–14]. Several investigations were made in the study of brazing characteristics of Sn–Ag–Cu and Cu–Ag alloys as braze foils at various compositions to check the microstructure of the thus-obtained joint [15–19]. The studies on electrical and thermal effects of multiple braze cycles on the joint performance were also performed by other study groups. The parametrical effect on the joints was investigated in oxygen-free electronic joints [20–22]. Miab et al. conducted research on low-to-medium carbon steels brazed to different ceramic substrates with Cu/Ni/Cu–Ni braze alloys. The joint efficiency of ceramic–carbon steels has been investigated thoroughly and cumulatively by other groups too [23–27].

2. Experimental Details

The material used in the study is C45 having the composition presented in Table 1. The trace impurities included are Si, P, and S amounting to 1%.

The experiment was a sandwich type, where two steels are placed one on top of each other with 99.99% pure Cu braze as interlayer (Figures 1 and 2). The thickness of the Cu foil is 70 μm. The experiment was carried out in a resistance tube furnace under inert gas (Ar) environment at a temperature of 1100 °C. The holding times were 5 and 10 min, respectively.

The C45 samples were cut to 10 × 10 × 5 mm size, followed by grinding and polishing. The grinding includes grit papers of 180, 320, and 500 μm. This was followed by a diamond finish polish by using alumina paste with a particle size of 3 μm. The samples were sonicated prior to experiment. The copper foil was also cleaned by using ethanol and sonicated as a pretreatment process.

The chamber of the furnace is pumped with vacuum initially up to 10⁻² bar, and then inert gas is pumped for 10 min. This process is repeated three times for consistency and to bring oxygen levels in the chamber to a bare minimum. The microstructure and depth of penetration are important for finding out the strength and efficiency of the joint. The post-experiment samples were taken out and placed in Bakelite resin and mounted. Later, they are cut for microstructure examination. Microstructure was studied by scanning electron microscopy using a Carl Zeiss EVO MA10 equipment at 20 kV using a Bruker microprobe. The pictures are taken under BSD-SE mode.

3. Results and Discussion

The joint formed between C45–Cu–C45 was a strong one. The interface was found to be completely wetted, and good joint aesthetic was observed. The copper at the interface has wetted the system perfectly forming channels, and penetration was also observed at the grain boundary with both 5 min and 10 min holding times.

Table 1. C45 steel composition

| Fe | C (%) | Si (%) | S (%) | P (%) |
|----|-------|--------|-------|-------|
| Balance | 0.45 | 0.3    | 0.30  | 0.4   |
The microstructure and penetration depth are important parameters for our study. Hence, we discuss about their characterization.

### 3.1. Microstructure

The microstructures of the samples are presented in Figures 3 (5 min holding time) and 4 (10 min holding time). The 5 min holding time samples show a clear penetration of copper into the grain boundaries of steel in all samples (Figure 3a, b, c, and d). The copper forms grooves at the grain boundary initially, forming a channel for further reaction. These channels encourage further penetration of copper deeper into the bulk of steel. The small black points visible in the bulk of steel are the inclusions formed from the deposition of silicon from the resin.

From above SEM analysis images, we can see that copper has a good wetting ability with medium carbon steel, and we can see the grooves formed, which lead to channel formation for penetration of copper in the grain boundaries [1].

As mentioned earlier, SEM is used to characterize the interface structure and composition. The wetting and penetration

![Figure 3. C45/Cu/C45 system at 5 min holding time. (a and b) Copper penetrated grain boundary of C45 steel at 500× magnification. (c and d) Copper penetrated grain boundary of C45 steel at 1000× magnification](image)

![Figure 4. C45/Cu/C45 system at 10 min holding time. (a and b) Copper penetrated grain boundary of C45 steel at 500× magnification. (c & d) Copper penetrated grain boundary of C45 steel at 1000× magnification](image)
of copper was observed with medium carbon steel. The carbon content and oxygen content in the sample when measured were very low at the interface supporting the observation that a good joint is formed. The EDS spectra of the joint are taken for both samples and presented in Figures 5 (5 min holding time) and 6 (10 min holding time).

The oxygen content is very minimal, and the interface is composed of copper and iron, as visible from the EDS spectra above. Keeping the oxygen content at a minimum is very important for our experiment as it decides the purity of the steel surface, which in turn helps in wetting and penetration of copper.

3.2. Penetration Depth and Measurement. The depth of penetration is defined as the length up to which copper can penetrate at the steel grain boundary at the given holding time and temperature. Since the steel does not have any alloying elements, the penetration was observed without any hindrance. The following is the idea of penetration measurement. The grooves are formed at the interface. The distance of the grooves from the top or bottom of the picture depending on the orientation is calculated by image analysis software. Before doing this measurement, the pictures from SEM are calibrated in the software for the magnification scale equivalence. The software used is Axiovision V4.8. The distance is taken at more places along the interface, and an average value is taken for all the noted values. A line is marked at that distance as the interface. Then, the copper channel distance is measured from the interface line and showed as penetration depth. The measurement was taken from two different pictures, so as to get a more accurate penetration depth, as more values to calculate would give us more precise value of the thus-obtained depth (Figures 7 and 8).

At time $t = 0$ min, there is no penetration or diffusion, and the penetration length is zero (Table 2). But as the process sets in, the diffusion takes place initially, making a pathway for copper to form channels and penetrate the grain boundary. We know that diffusion is proportional to the square root of holding time [28–31], and it gives us a linear graph when extrapolated (Figures 9 and 10). This will later increase exponentially with time once penetration kicks in and starts moving through the grain boundary of steel.

Figure 5. EDS Spectra and the corresponding composition of the C45–Cu–C45 system at 5 min holding time

Figure 6. EDS Spectra and the corresponding composition of the C45–Cu–C45 system at 10 min holding time

Figure 7. Penetration depth of copper at steel grain boundary for 5 min holding time

Figure 8. Penetration depth of copper at steel grain boundary for 10 min holding time
Table 2. Holding time and penetration depth of copper at steel interface

| S. no | Holding time (min) | Penetration depth average (μm) | Square of penetration depth (μm²) |
|-------|--------------------|-------------------------------|----------------------------------|
| 1     | 0                  | 0                             | 0                                |
| 2     | 5                  | 23                            | 529                              |
| 3     | 10                 | 33                            | 1089                             |

Figure 9. Penetration depth as a function of holding time

Figure 10. Penetration depth as a function of square root of holding time

4. Conclusions

From the experiments it was observed that C45 steel does not hinder the penetration by copper under the given experimental conditions. The wetting of copper and its subsequent penetration were carried out successfully, and the microstructure of the joint was characterized by SEM. The EDS spectra showed absolutely no oxidation on the surface and the richness of Cu joint to iron. The penetration depth was also measured using image analyzer software, and it was found to be increasing with increasing holding time. As we can observe from the microstructure, the 5 min samples show clear demarcation between the substrate and the braze interlayer. Also, the penetration could be seen clearly with grooving and channeling. This could be the effect of the holding time on the braze reaction. However, in the samples with 10 min holding time, the microstructure differentiation is not clear between the braze interlayer and the steel substrate. Moreover, a lot of grey areas in and around the interlayer, which were the zones of diffusion for copper in the bulk of steel, were observed.

One inference could be that as the holding time is increased from 5 min to 10 min, there is more time for the penetrated copper to diffuse further into the steel substrate bulk using the already formed channels of penetration. However, there are no reactive compounds formed in the bulk of the substrate due to this diffusion of copper.

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