Microstructure characterization of hypereutectoid aluminium bronze composite coating

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Abstract. Hypereutectoid aluminium bronze coating was deposited onto an E.N. 10503 steel substrate using plasma transferred arc welding (PTA). Microstructure characterisation of the coating and a section near the steel substrate joint was carried out using SEM, EBSD, EDS in conjunction with XRD and depth-sensing nano-indentation. The constituent phases in the coating were identified as: martensitic Cu\textsubscript{3}Al\textbeta, solid solution of Al in Cu\textalpha phase and the intermetallic Fe\textsubscript{3}Al\textkappa phase. The region near the steel substrate was characterised by high hardness, large grains and presence of Cu precipitates. No cracks were observed in this region.

The coating has high hardness of 4.9 GPa and Young’s modulus of 121.7 GPa. This is attributed to homogeneous distribution of sub microns size Fe\textsubscript{3}Al intermetallic phase. The implications of the coating to the engineering application of sheet metal forming are discussed.

1. Introduction
Hypereutectoid Cu-Al-Fe aluminium bronzes are known to have high hardness and wear resistance. However, production of these alloys using conventional sand casting is difficult due to the complications associated with the narrow range of solidification and the eutectoid reaction which can lead to embrittlement\textsuperscript{[1]}. These manufacturing difficulties can be overcome by using rapid solidification techniques such as plasma transferred arc welding (PTA). The high cooling rate can lead to novel properties due to a microstructure that deviates substantially from thermodynamic equilibrium. The microstructure of Cu-Al-Fe alloy is diverse and highly dependent on the cooling rate. An ordering reaction\textsuperscript{[2]}, martensitic transformation\textsuperscript{[3]} and formation of intermetallic have been reported. This makes the microstructure highly complex. Several phases are known to exist; these are listed in table 1. The microstructures of as-cast and heat treated Cu-Al-Fe alloys are well studied. However, there are few reports on the phases present in Cu-Al-Fe coatings, particularly those with high Al content. In the present study, the microstructure and mechanical properties of a Cu-11Al-7Fe (in wt.\%) aluminium bronze coating produced by PTA was assessed using SEM, EBSD, EDS, XRD and depth-sensing nano-indentation.
Table 1: Possible phases in rapidly solidified Cu-Al-Fe alloy in the composition range 9-14 wt.% Al

| Phase                  | Composition | Crystal structure | Reference |
|------------------------|-------------|-------------------|-----------|
| β’ disordered martensite | Cu$_3$Al   | Cubic             | [2]       |
| β'$_1$ ordered martensite | Cu$_3$Al   | Orthorhombic a=0.449nm, b=0.519nm, c=3.820nm | [4]       |
| Γ' ordered martensite  | Cu$_3$Al   | Hexagonal a=0.2606nm, c/a = 1.619 | [5]       |
| α solid solution of Al in Cu | (Cu) | Cubic a=0.361nm | [6]       |
| Γ'$_1$ intermetallic    | Cu$_9$Al$_4$ | Cubic a=0.871nm | [6]       |
| κ$_1$ intermetallic     | Fe$_3$Al   | Cubic a=0.571nm  | [7]       |
| κ$_2$ intermetallic     | FeAl       | Cubic a=0.290nm  | [7]       |

2. Experimental

2.1. Materials

The hypereutectoid aluminium bronze powders were produced from component metals with an electrolytic purity of 99.98% by gas atomisation in nitrogen atmosphere and cooling water as detailed in reference[8]. The powders were then deposited onto an E.N. 10503 medium carbon steel by plasma transferred arc welding (PTA) using a current of 170A, 3-6l min$^{-1}$ plasma nitrogen flow rate, 1-3g s$^{-1}$ powder feed rate and stand-off distance of 5-10mm. The composition of the powder and coating are shown in Table 2.

Table 2: Composition of the hypereutectoid powders and coating (all in wt.%)

|        | Cu  | Al  | Fe  | Mn  | Ni  | Si  |
|--------|-----|-----|-----|-----|-----|-----|
| Powder | 78.9| 14.9| 4.4 | 1.4 | 0.5 | 0.3 |
| Coating| 78.9| 11.2| 6.9 | 0.9 | 0.3 | 0.2 |

2.2. Approach to characterisation

Specimens for characterisation were sectioned using electric discharge machining. Samples were ground up to 4000 grit SiC and either diamond polished or electro-polished, the former by using 1µm diamond polishing and the latter by electrolysing for ~15s in 20% HNO$_3$, 15% 2-butoxyethanol and 65% methanol solution (in volume) cooled to -30°C at 30V. All specimens for EBSD investigation were prepared by electro-polishing. EBSD mapping was carried out using a JEOL JSM-6500F FEG-SEM operating at an accelerating voltage of 15 keV and probe current of 0.1nA. The specimen was tilted to 60° with a working distance of 18mm. Step size of 0.5µm and 1µm were employed. Phase identification was performed using a Bruker D2 Benchtop X-ray diffraction machine. The hardness and Young’s modulus were evaluated using depth-sensing nano-indentation operating at 500nm depth control mode. A total of 196 indents were produced.

3. Results and discussion

An SEM image in backscattered electron (BSE) mode of an electro-polished specimen is shown in Figure 1(a). Precipitates (appearing dark) with a range of dimensions from sub-microns to tens of microns were clearly observed. Certain areas of the matrix were also selectively removed following the electro-polishing (appearing dark grey in Figure 1a). This suggests the presence of multiple phases in the matrix. Table 3 shows typical EDS analysis of the precipitates and the constituent phases in the matrix. The precipitates are rich in Fe and Al with stoichiometric ratio close to 3:1. In conjunction with XRD, the precipitates were identified as the κ$_1$ Fe$_3$Al$_4$ phase. EDS analysis of the unaffected area of the matrix shows that it is high in Cu and Al. The stoichiometric ratio of Cu to Al suggests that it is one of the martensitic phases. As shown in table 1 several martensitic phases have been reported. The disordered martensite is known to form at Al<11 wt.%,[2], which falls outside the composition of the coating. For alloys with Al>11wt.% an ordering reaction precedes the martensitic transformation into either β'$_1$, β''$_1$ + Γ' or Γ' [2][5]. The ordered Γ' with hexagonal structure has been reported to form at 12.9<Al<14.7 wt.%.[5].
Figure 1 (a) BSE image of the electro-polished specimen, (b) observed XRD spectrum. Based on this information and the observed XRD spectrum, the martensitic phase in the present coating was identified as the ordered $\beta_1'$ with orthorhombic structure. The structure identified is in agreement with previous TEM observation of water quenched Cu-11.7Al wt% alloy[4]. In summary, using XRD, SEM and EDS, the phases in PTA Cu-11Al-7Fe coating were identified as: martensitic Cu$_3$Al $\beta_1'$ phase, solid solution of Al in Cu $\alpha$ phase and the intermetallic Fe$_3$Al $\kappa_1$ phase.

Table 3: EDS analysis of the precipitates and the constituent phases in the matrix (all in at.%)

| Phases | Cu  | Al  | Fe  | Mn  | Ni  | Structure            |
|--------|-----|-----|-----|-----|-----|----------------------|
| $\alpha$ (Cu) | 79.1±0.6 | 17.8±0.3 | 2.1±0.3 | 0.6±0.1 | 0.4±0.2 | Cubic, cF4, a=b=c=0.365nm |
| $\beta_1'$ (Cu$_3$Al) | 74.4±0.5 | 22.6±0.6 | 1.5±0.4 | 1.0±0.1 | 0.5±0.2 | Orthorhombic, cP8, a=0.449nm, b=0.519nm, c=4.66nm |
| $\kappa_1$ (Fe$_3$Al) | 11.6±1.8 | 24.5±1.2 | 57.9±2.1 | 1.5±0.2 | | Cubic, cF16, a=b=c=0.579nm |

Figure 2(a) shows the EBSD phase map of the coating. As shown in the magnified area, EBSD is capable of identifying the $\kappa_1$ and the $\alpha$ phase but it was not possible to index the $\beta_1'$ phase.

Asymmetric broadening of the $\beta_1'$ phase peak was observed as shown in figure 1(b). This indicates crystallite smallness, presence of long-range internal stresses and chemical heterogeneity. Fine precipitates also contribute to broadening of the observed XRD peaks[10]. These factors affect the crystal structure, which can impede indexing. The pole figures and misorientation angle distribution indicate that there is no crystallographic texture. This is expected, as the turbulence generated by the
PTA process will result in a random orientation of grain growth. Fine precipitates (<1 μm) were also observed in BSE image shown in Figure 2(a). EDS analysis indicates that it is rich in Fe and Al with composition close to that of the κ₁ phase. The homogeneous distribution of the κ₁ phase and the predominantly hard martensitic β₁’ phase leads to a uniform hardness with an average of 4.9GPa and Young’s modulus of 121.7GPa. The martensitic structure such as the one found in this coating was reported to have higher wear resistance than a similar alloy with eutectoid structure[9]. Previous work[8] has also reported that due to the limited solubility of Cu and Al in Fe, the adherence tendency of Cu-Al-Fe alloys to steel is low. This makes the coating highly suitable as forming die materials. Figure 3(a) shows the EBSD orientation map of the joint between coating and the steel substrate. This area is characterised by large grains of ~17 μm in size. In this area the κ₁ phase and the grains in the joint were also observed to have the same orientation. This suggests that the region melted during deposition is thicker than the joint region. Dendrites were observed to extend from the joint region into the coating as shown in Figure 3(b). This increases the surface area of contact between the coating and the substrate, which increases the bond strength.

![Image](https://example.com/image1.png)  
![Image](https://example.com/image2.png)

**Figure 3:** (a) EBSD orientation map, (b) BSE image of the joint

The joint area is rich in Fe with significant amount of Al and traces of Cu as shown in Table 4. This suggests that during the deposition process part of the steel substrate was melted. For PTA process, melting of the substrate is not uncommon as droplet temperature can exceed 2000°C, which is well above the melting point of the steel substrate. The melting of the steel substrate is evidenced as an increase in the Fe content in the coating compared to the original powder as shown in Table 2 as well as the presence of large grains in the joint region as shown in Figure 3(a). The presence of Cu and Al in the interface layer leads to a hardness of 282HV compared to 195HV for the steel substrate. No cracks were observed in this region.

| Cu    | Al    | Fe    | Mn    | Ni    | Si    | Cr    |
|-------|-------|-------|-------|-------|-------|-------|
| 0.7±0.2 | 6.0±0.8 | 88.2±1.5 | 1.1±0.13 | 0.5±0.1 | 1.3±0.2 | 2.3±0.2 |

**Table 4:** Compositions of the joint area between the coating and steel substrate (all in at.%)

4. Conclusion

Microstructure characterisation of Cu-11Al-7Fe (in wt.%) coating identified the presence of 3 main phases, martensitic β₁’ phase, solid solution of Al in Cu α phase, and Fe₃Al κ₁ intermetallic phase. The presence of the martensitic and intermetallic phases leads to high hardness of 4.9GPa. The high hardness of the coating is expected to improve its wear performance, thus making it suitable for applications requiring wear resistance such as die for sheet metal forming.

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