Colossal supersaturation of oxygen at the iron-aluminum interfaces fabricated using solid state welding¹

N.Sridharan^{1,2*}, D.Isheim³, D.Seidman³, S.S.Babu^{1,2}

¹Department of Mechanical Biomedical and Aerospace Engineering, University of Tennessee Knoxville; ²Manufacturing Demonstration Facility, Oak Ridge National Laboratory, Oak Ridge, TN 37831; ³Northwestern University Center for Atom Probe (NUCAP), Northwestern University

*** Corresponding Author**

Please direct all communication regarding this manuscript to niyanth.sridharan@gmail.com

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Abstract:

Solid state joining is achieved in three steps, (i) interface asperity deformation, (ii) oxide dispersion, followed by (iii) atomic contact and bonding. Atomically clean metallic surfaces without an oxide layer bond spontaneously. Despite its importance the oxide dispersion mechanism is not well studied. In this work the first ever atom probe study of the Iron-Aluminum solid state welds show that the oxygen concentration at the interface is 20 at.%. This is significantly lower than any equilibrium oxide concentration. We therefore propose that the high-strain rate deformation at the interfaces renders the oxide unstable resulting in the observed concentration of oxygen.

Key words: Solid state welding; oxide dispersion; Atom probe tomography

Solid state joining is perhaps the oldest welding technique, invented much before the invention of electric arc welding, for manufacturing similar and dissimilar metal combinations. Solid state joining is achieved by bringing atomic contact of similar or dissimilar metallic free surfaces, which is driven by the reduction of free surface energy (γ_0) of the material [1] in comparison to interface energy (γ_{int}), given by the following energy balance ($\Delta G = \gamma_{\text{int}} - 2\gamma_0$). Number of physical processes such as recrystallization [2, 3], surface diffusion [4] and grain rotation [5] may operate to achieve the reduction in ΔG during the welding process, it is accepted that solid state welding is in fact a three-step process, i.e., (i) collapse of surface asperities, (ii) removal of the naturally occurring oxide layer on metallic surfaces, and (iii) atomic contact between the atoms [4]. Interestingly, the exact mechanism(s) of oxide removal are not well understood and forms the motivation behind this research.

Pre-existing research [6],[7],[8, 9],[2],[10] suggests that the intense shear strains, during solid state welding processes, fragment and mechanical dispersal of the oxide layers. This conclusion was based on energy dispersive spectroscopy (EDS) results where the absence of oxygen peaks was interpreted as complete oxide dispersion. The absence of oxygen in the EDS spectrum could have been due to the quality and detectability of low energy of the characteristic X Rays for the Oxygen peaks. More sophisticated techniques such as 3-D atom probe and secondary ion mass spectroscopy are necessary to successfully detect and quantify trace oxygen concentrations. For example, atom probe has been used to rationalize the formation of non-equilibrium solid solutions in Cu-Ag interfaces fabricated using solid state welding [11]. This phenomenon was attributed to ballistic mixing facilitated by plastic straining at the interface [12]. By corollary, we hypothesize that the strains may dissociate the oxide layer and force the oxygen into a non-equilibrium solid solution by a similar mechanism. In specific, this dissociation and non-equilibrium dissolution is very different from the conventional mechanical dispersal mechanisms. However, fundamental understanding of oxide removal has been ignored in the literature. In addition to scientific curiosity, nature of oxide removal may provide a pathway to achieve solid-state bonding of other dissimilar metals [1].

Since the underlying requirements for all solid state joining are similar [1, 13, 14], we evaluated the oxide dispersion in solid-state joint made between Al-6061 to 4130 Steel using ultrasonic additive manufacturing (UAM). This technology combines ultrasonic seam welding and mechanized tape layering to fabricate Al-6061 to 4130 Steel welds [15-17]. The joints were made using a 9 kW UAM machine at The Ohio State University where the Al was the foil and steel was a substrate as shown in figure-1(a). Previous work has shown that

the joining at interfaces is achieved by at and above shear strain rate of 10^5 s^{-1} induced by 20 kHz vibrations of sonotrode. Following fabrication, the builds were sectioned and polished using standard metallographic techniques. Scanning electron microscopy was used to identify regions where bond formation (shown in figure 1(b) and (c)) was observed to extract samples for analysis. A region was considered bonded when no voids were present at the interface. An example of such an interface is shown in figure-1 (a) and a step-by-step illustration of our analysis methodology is presented in figure-1. The interface identified by electron microscopy (see Fig. 1c) was analyzed further using Local Electrode Atom Probe tomography (LEAP)[18]. LEAP was performed on a CAMECA LEAP 4000 in the laser atom probe mode. The analysis was performed after cooling the sample to 40K and by using laser energy of 30pico-Joules and a pulsing rate of 250 KHz. A total 32 million ions were collected from the region containing bulk and the interface. Visualization and data analysis was performed using IVAS 3.6.8, commercially available software from CAMECA. Data was reconstructed using the tip profile mode.

Tomographic reconstructions performed using the atom probe data show oxygen and magnesium enrichment at the interface as shown in figure 2(a)-(d). Interestingly, Cantin et.al observed qualitative enrichment of Mg and O co-segregation at Al-Al joints made by friction stir welding, which was interpreted as the formation of magnesium oxide [6]. Thermodynamic calculations were used to support the formation of MgO under low oxygen activity [6]. Since these measurements were not quantified, the conclusion of MgO formation is questionable. To answer the question, whether this region (see Fig. 2) is an oxide or not, quantitative analysis was performed using the proximity histogram with 6 at.% oxygen iso-concentration surface [see figure 3(a)]. The disruptions in the oxide film shown

in figure 3(a) and marked with a black arrow showed an oxygen concentration of 5 at% and the maximum oxygen concentration at the interface (marked using a red arrow) is close to 20 at%. The average oxygen concentration at the interface is close to 12.5 at%. In contrast, the oxides (Al_2O_3 , MgO) and spinels (MgAl_2O_4) need to have an oxygen concentration of 50 at% or more. Based on this data, it is concluded that the oxygen super saturation at the interface is indeed higher than equilibrium levels (3×10^{-8} at.%) [19]. The reason for the Mg enrichment at the interface is not yet understood. Though such enrichment could be rationalized by the increased mobility of the Mg atoms due to the increased defect densities, mass balance calculations are necessary to validate the hypothesis. Such calculations have not been performed and are outside the scope of the current paper.

Carbide dissolution and non-equilibrium super saturation within ferrite (BCC) matrix during heavy plastic deformation of pearlitic steels had been observed before [20]. This phenomenon was rationalized based on higher binding energy of carbon with point and line defects within ferrite matrix compared to carbides [12, 21]. Interestingly, decomposition of oxides to atomic oxygen has been documented during extensive plastic deformations such as mechanical alloying of oxide dispersion strengthened materials [22]. The decomposition of oxides to nano clusters with non-stoichiometric oxygen concentrations has been shown and interpreted as oxide decomposition [22][23-25] and segregation to dislocations and defects. First principle calculations also confirm the possibility of oxygen segregating to pre existing vacancies in iron due to the enhanced binding energy of the oxygen atoms with defects [26]. These published data and our results could be rationalized using the theory of ballistic mixing in metals [27]. The mechanism requires significant increases in the non equilibrium defect density resulting in mechanical mixing and dissolution of stable phases and

precipitates[28]. Though the oxygen solid solubility in Al (3×10^{-8} at.%) is insignificant, theoretical calculations suggest the oxygen super saturation at grain boundaries and defects can reduce the overall free energy [29-31] using the Gibbs adsorption theory. Gunduz et al theorized that prolonged ultrasonic vibrations (~ 1 s) may lead to high defect density (i.e. vacancy) in metal and eventually may modify the phase diagrams [32]. In our UAM process, higher-strain rate shear deformation (10^5 s^{-1}) occurs within [33] a small volume of the interface ($< 10 \text{ }\mu\text{m}$) under 0.1 s. This condition will lead to creation of abundant vacancies (point defect) and dislocations (line defects). We hypothesize that, in our experiments, before the annihilation of these defects due to the adiabatic heating, the oxygen dissolution and super saturation within matrix would have been triggered and frozen-in.

In this paper we present the first direct experimental evidence for complete oxide dissolution leading to non-equilibrium colossal super saturation of oxygen within the FCC matrix of aluminum driven by the high-strain rate plastic deformation process at interfaces during solid state joining.

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Figure-1: Shows (a) Schematic of the ultrasonic additive manufacturing process; The Substrate is a 4130 steel machined prior to fabrication (b) Shows the SEM micrograph of an interface which showed complete bonding from which samples were extracted (c) A tip that was used for analysis in the atom probe. Note the interface is marked using black arrows in the figure

Figure-2: Shows the reconstructed tips showing (a) Distribution of Al (b) distribution of Fe (c) O distribution (e) Mg distribution. The respective interfaces are marked using arrows

Figure-3: (a) Shows the 6% Mg and Oxygen iso surface. Note the region marked using the black arrow indicating a region where there appears to be a local perforation in the oxide film (b) Shows Proxigram analysis performed along the direction marked using the red arrow (c) Shows the Proxigram analysis performed along the direction marked using the black arrow. Note that there is still considerable ~5 at% oxygen present in the region

Figure-1

Figure-2

Figure-3

Specimen fabrication

APT sample preparation from the interface

*Reconstructed data showing
super saturation of oxygen at the
interface*