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HRTEM Observations and Simulations of the S''-Phase in Al-Mg-Cu Alloys and Implications for Al-Cu-Mg Alloys

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Abstract

An Al-Mg-Cu alloy was artificially aged in order to facilitate formation of homogenously dispersed S-phase in the microstructure. The rod-shaped S-phase was examined using high resolution transmission electron microscopy (HRTEM) in three different orthogonal directions with respect to the Al matrix $<100>_{Al}$ zones. When viewed in a direction perpendicular to the rod shaped S-phase, the variants that had $[021]_S$ closely aligned with the viewing direction showed a contrast that is similar with the previously published work in the literature, but was previously interpreted as having a crystal structure fundamentally different from that of the S-phase. By comparison of HRTEM observations and simulations, it is shown that all of these observations can be rationalized based on the S-phase having modified lattice parameters and orientation relationship with respect to the matrix. In order to maintain consistency with the early work of Bagaryatsky, we adopt the S"-phase notation to identify this S-phase.

1. Introduction

During artificial aging of Al-Cu-Mg alloys (i.e. those with Cu/Mg ratios in wt.% greater than one), it has been well established that metastable GPB zones with a rod-like morphology form in the microstructure [1, 2]. Kovarik et al. [3] has recently shown that alloys with significantly smaller Cu/Mg ratio form different GPB zones, both in terms of crystal structure and morphology. Another intermediate phase reported to form in Al-Cu-Mg alloys is the S"-phase. The existence of the S"-phase was first proposed by Bagaryatsky more than 50 years ago [4]. Bagaryatsky considered the S"-phase to be a monoclinic version of the S-phase that has a modified orientation relationship, being about 5 degrees off the now well established S-phase/Al orientation relationship. Much more recently, Cuisat et al. [5] proposed a different crystal structure for the S"-phase based on the detection of a set of diffraction satellite spots around the forbidden (110) spots. In later work by Gupta et al. [6], it was shown that the need to invoke the existence of a new structure was unsubstantiated since the diffraction satellites spots can be explained in terms of variants of the S-phase.

New debate regarding the existence of an S"-phase having a very different crystallographic structure than that of the S-phase has arisen recently once again. This

debate initiated with a paper by Zahra et al. [7] who presented HRTEM and DSC evidence in favor of such an S”-phase. However, the authors interpretations were strongly argued against in a response paper by Ringer et al. [8]. Despite these objections, Charai and Zahra at al. [9] recently restated that their HRTEM observations cannot be understood simply in terms of a variant of the S-phase. From their observations they proposed a monoclinic crystal structure for the S”-phase with a=0.32 nm, b=0.40 nm, c=0.254 nm, β=91.7°.

The purpose of this paper is to show that the HRTEM observation published by Zahra et al. [7] and Charai, et al. [9] in fact can be understood in terms of variants of the S-phase with a modified orientation relationship. The existence of such a modified orientation relationship has been previously reported in the literature and found to be metastable. Moreover, we also try to relate these observations to the work of Bagarystaky [4], and Shchegoleva et al. [10] and demonstrate that our present observations are consistent with their early interpretations of the S”-phase.

2. Experimental Procedures

The alloy was obtained in a form of 1 mm thin sheet from Alcan International Ltd. The composition of the alloy is shown in Table 1. Heat treatment of the alloy included solutionizing at 550°C for a period of 15 minutes, quenching in a water bath and subsequent artificial aging for 16 h at 200°C. Aged samples were then conventionally prepared for TEM observations. This included grinding and electropolishing in a 25% of nitric acid and 75% of methanol solution. Conventional and HRTEM observations were performed on a Tecnai TF20. HRTEM image simulations were performed with EMS software package [11].

Table 1: Composition of the alloy studied (in wt.%).

	Al	Mg	Cu	Si	Mn	Fe	Zn	Ti
Wt(%)	Bal.	2.96	0.42	0.12	0.25	0.21	0.007	0.002

3. Results

After 16 h of aging, the microstructure consisted of GPB-II zones and S-phase. Only the homogeneously dispersed S-phase is further discussed in this paper. A HRTEM observation from the S-phase viewed along the $[100]_S//[100]_{Al}$ is shown in Figure 1(a). Along this direction, the morphology of the S-phase was found to be faceted or polygonal. From the Fourier spectrum shown in Fig 1(b), the lattice parameters are measured as b=9.09Å, c=7.10Å, which is quite consistent with previously published work on the S’-phase [6]. From the Fourier spectra, it was also possible to measure that the orientation relationship is modified by about 4.5 degrees from the well known $[100]_S//[100]_{Al}$ and $[010]_S//[021]_{Al}$.

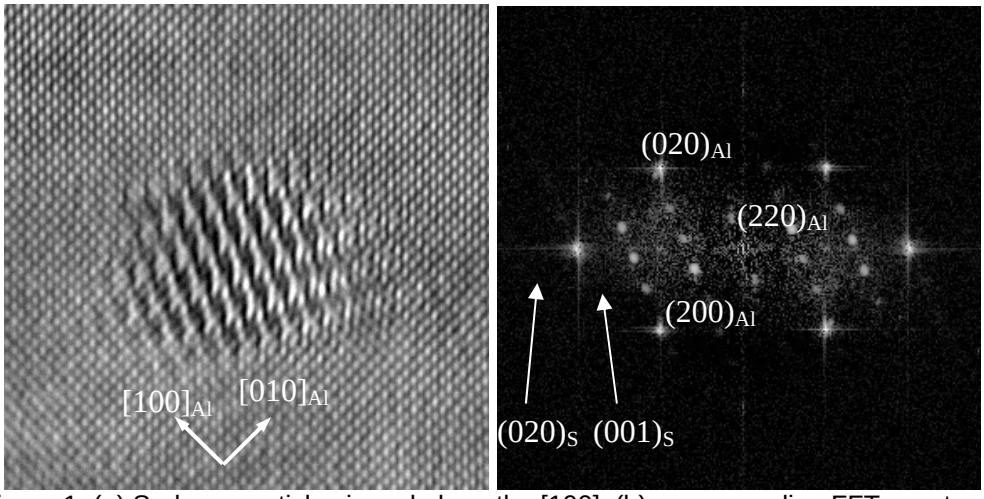

Figure 1: (a) S-phase particle viewed along the [100]. (b) corresponding FFT spectrum.

Along any given $[100]_{Al}$, there exists four variants such as the one shown in Figure 1(a). Apart from these four variants, the microstructure contains 8 additional variants, four of which are nearly aligned along the $[013]_S$ and four of which are nearly aligned along the $[021]_S$ direction. Given the Al/S-phase orientation relationship and considering the equilibrium S-phase lattice parameters, it can be calculated that the $[013]_S$ is about 3.2º away and the $[021]_S$ is about 5.4º away from the matrix $<100>_{Al}$ direction. The orientation of the S-phase and the important crystallographic directions is shown schematically in Figure 2(a). Due to the modified orientation relationship, the alignment of the $[013]_S$ type and $[021]_S$ variants improve with respect to the Al matrix. A plot showing misorientation of the $[013]_S$ and $[02\text{-}1]_S$ from the $<001>_{Al}$ for a range of possible orientation relationships is shown in Figure 2(b). Based on our present observations, the average misorientation value is about 0.9º for [021] and 1.3º for [013]. But it should be noted that the misorientation values will vary depending on the size of S-phase particles, as discussed in the work of Majimel et al. [12].

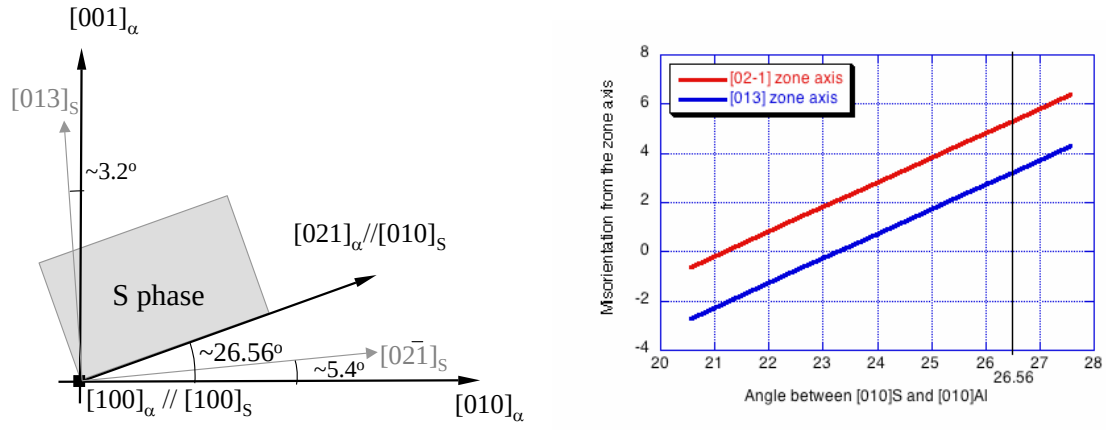

Figure 2: (a) Schematic of orientation relationship of the S-phase with Al matrix. (b) plot showing the mis-orientation of the $[013]_S$ and $[02\text{-}1]_S$ from the $<001>_{Al}$

HRTEM observations from one of the $[02\text{-}1]_S$ variants is shown in Figure 3(a). In this figure, the S-phase particle is elongated along the $[100]_{Al}$ direction, extending diagonally across the whole length of the image. The thickness is only several nanometers. Although the contrast from the particles changes along its length, it can be qualitatively described as having a periodic variation of intensity across the thickness of the particle. To properly interpret the image contrast, and the characteristic reciprocal space spots shown in Figure 3(b), it must be considered that the observation in Figure 3(a) was not made in the

immediate vicinity of the sample hole, but rather in a slightly thicker region. As such, it is likely that the particle is not extended through the entire thickness of the sample, but instead that Al matrix is superimposed on top and/or below the particle. Hence, the possibility of double diffraction must be considered. In the Fourier spectra shown in Figure 3(b), we therefore observe the presence of not only the $\{112\}_S$, but also their double diffraction counterpart. These spots are centered around the forbidden $g(110)_{Al}$ reflections, forming "satellites". These satellite spots are separated by 0.112 $Å^{-1}$, which compares very well with a measurement that can be made on Fourier spectra published by Charai et al. [9].

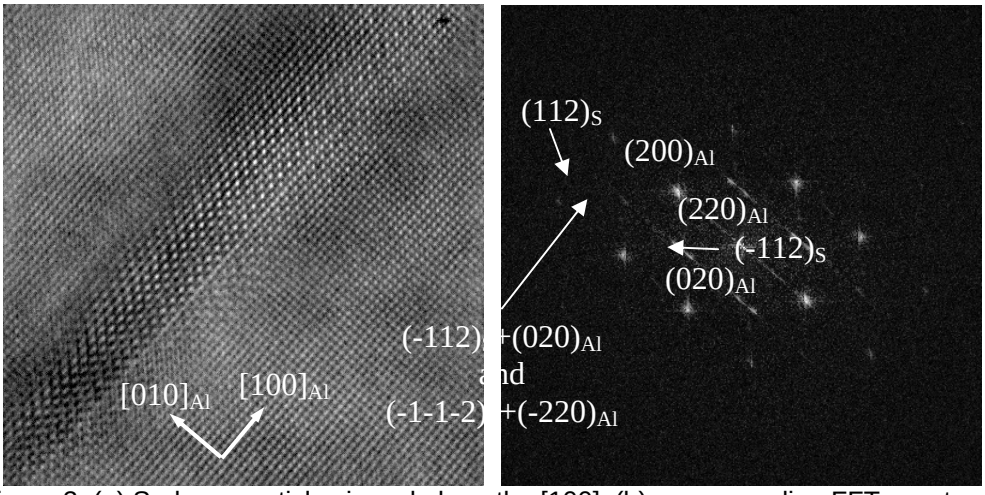

Figure 3: (a) S-phase particle viewed along the [100]. (b) corresponding FFT spectrum.

To support this interpretation, we also performed HRTEM image simulations based on the geometry shown in Figure 4(a) in which a 4 nm thick layer of S-phase is superimposed on top of a 4nm thick Al slab. The angle between the $[010]_{Al}$ and $[010]_S$ was 22.5°, which is consistent with the measured, modified orientation relationship. The lattice parameters were also modified to the values a=4.04Å, b=9.09Å, c=7.10Å, consistent with our experimental observations. The HRTEM image simulation is shown in Figure 4(b), and the image characteristics compare very well with the experimental observations in Figure 3(a). (Figure 4(b) also contains an inset from Al matrix simulation for a comparison). In fact, the similarity may be more easily recognized from the images shown in Figure 3 in Charai et al. [9] due to the larger width of the particles in their work. This similarity includes the presence of the "Moire alternation" along the $[010]_{Al}$, which has a wavelength of exactly 8.92 A ($1/(0.112A^{-1})$, where $0.112A^{-1}$ is equal to $|2g\{112\}_S-g\{220\}_{Al}|$). In this "Moire alternation" we see that intensities associated with $(020)_{Al}$ alternate in brightness along $[100]_{Al}$, forming a pattern resembling a checker-board. With respect to the simulations, it should be mentioned that the image in Figure 3(b) corresponds to the first indirect transfer condition. The Fourier spectrum of the simulated image is seen in Figure 4(c). The presence of the $g(112)_S$ and the double diffraction spot can be seen. The separation of the satellite spots is 0.112 $Å^{-1}$, which agrees exactly with the experimental observations. From performing a series of computer simulations, it was found that this separation is achieved only if the lattice parameters are modified to the values determined from the experiment.

4. Discussion

As already mentioned, a different interpretation of observations very similar to this study can be found in the work of Charai et al. [9]. Their HRTEM observations and Fourier spectra were identified in terms of S"-phase with a primitive monoclinic lattice: a=0.32 nm,

b=0.4 nm, c=0.254 nm, β=91.7°. The examined microstructure also contained the S-phase (in [9] shown in Figure4 and termed as S'-phase) with a modified orientation relationship. Thus we propose that the existence of such a phase is unsubstantiated and the authors findings can be explained adequately in terms of a $[021]_S$ variant with a modified orientation relationship, provided that the moiré effects discussed above are considered.

In fact, Gupta et al. [6] have previously shown that the $[021]_S$ variants can explain electron diffraction patterns that are identical to the Fourier spectra in Figure 3(b). However, the change in the orientation relationship has not been considered in this explanation and the HRTEM observations in Figure 3(a) or those of Charai, et al. [9] could not be accounted for without considering the modified orientation relationship.

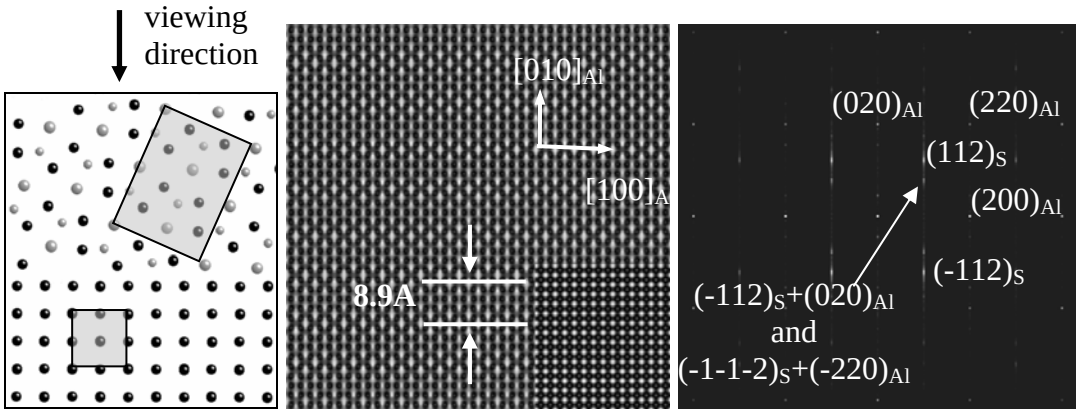

Figure 4: (a) A schematic of an overlay of Al and S-phase used in the computer simulation, (b) HRTEM simulations, for comparison an insert from the Al matrix is also shown, (c) Corresponding Fourier spectrum.

We would like to point out that the observed S-phase in our work has very similar characteristics to the S"-phase described by Bagaryatsky [4] and later also by Shchegoleva et al. [10]. Bagaryatsky considered the S"-phase to be a slightly distorted, monoclinic version of the S-phase, with a modified orientation relationship. The monoclinic distortion was considered 88.66º. The orientation relationship was then described as 4-5.5º degrees away from the well known $[100]_S//[100]_{Al}$ and $[010]_S//[021]_{Al}$, $[010]_S$ rotated towards the $[010]_{Al}$ while keeping the $[100]_S//[100]_{Al}$ [4].

The change in the orientation relationship is now well established experimentally. It was first reported by Radmilovic et al. [13] and later by Majimel et al. [12]. Both authors identified it as S-phase of type II, rather than the S"-phase. From the work of Majimel et al. [12], it can be seen that this modified orientation relationship is valid for particles that have the longest segment of the $(001)_S/(012)_{Al}$ interface not exceeding 50 Å, as projected along $[100]_S$. The average misorientation angle was observed to be a ~4.5°, which is actually in very good agreement with Bagaryatsky's proposition. It is also very interesting to note that for larger S-phase particles, the misorientation gradually decreased to the "standard" S-phase/matrix orientation relationship.

The monoclinic distortion as predicted by Bagaryatsky [4] has not been confirmed in the literature. Indeed this may be difficult considering that the proposed angle is 88.6°. Indirect evidence for the monoclinicity has nevertheless been provided by our HRTEM simulations, for which we noticed that streaking of $(112)_S$ reflection can be minimized, and thus made more consistent with our experimental observations, by imposing the monoclinicity of the S-phase. It should also be mentioned that the lattice parameters are also modified from those of the S-phase, which is in fact in quite close agreement with previously reported values for S'-phase [6]. Based on this analysis, we therefore suggest using the S"-phase

notation for a crystal structure of S-phase with such modified lattice parameters and modified orientation relationship.

5. Conclusions

HRTEM observation from $[001]_{Al}$ of artificially aged microstructure showed the presence of particles elongated along $[100]_{Al}$ with a contrast that gives rise to “Moire alternation” along the $[010]_{Al}$. It has been shown that the $[021]_S$ S-phase variant embedded in the Al matrix gives rise to this contrast rather than the previously proposed crystal structures in the literature. In the Fourier spectrum of the HRTEM images we see the presence of $(112)_S$ as well as spots from double diffraction. The observed S-phase has a modified orientation relationship with the matrix that closely resembles that which Bagaryatsky originally identified as S”-phase. Due to this resemblance, we adopt the S”-phase terminology to identify the observed S-phase.

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