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Dynamic recrystallisation and precipitation behaviour of high strength and highly conducting Cu–Ag–Zr-alloys

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ABSTRACT

Dynamic recrystallisation of CuAgZr alloys within a composition range of (3–7) wt% Ag and (0.05–0.3) wt% Zr is studied as a function of alloy composition, temperature and strain. Dynamic recrystallisation was investigated using hot-compression and hot-rolling experiments at temperatures between 500 °C and 850 °C. For CuAgZr with 7 wt% Ag and 0.05 wt% Zr, an optimised hot-rolling temperature of 750 °C was found and a mean grain size of 25 μm was established at a true strain of 2.2. Similar grain size distributions were found for the extended range of alloy compositions while the active mechanism for dynamic recrystallisation changes from necklace towards a particle stimulated nucleation mechanism. This change is driven by the volume fraction of the ternary phase Cu_4AgZr as these particles are identified to stimulate nucleation of dynamic recrystallisation in the samples with increased Zr content. The final tapes exhibit an outstanding combination of ultimate tensile strength of 1 GPa and an electrical conductivity of 70%IACS at a true strain of 4.8 of cold work being applied.

1. Introduction

Ultra-strong conductors are being developed with a focus on an exceptional combination of high mechanical strength and high electrical conductivity. In specialised applications a suitable mechanical and electrical reliability is needed to enable the implementation of technical designs. Examples include spring-loaded contacts/connectors/probes and micromechanical contacts/devices for industrial purposes as well as conductor materials for pulsed high-field electromagnets for academic application. In the latter case, a mechanical strength well above 1 GPa to resist the Lorentz force and an electrical conductivity of 60% IACS[1] in order to restrict Joule heating during pulsed operation are needed [1]. Since the early 1990s, Cu–Ag-based materials were investigated regarding their hardening mechanisms and their potential as ultra-strong conductors [2–4]. The strength of the Cu–Ag micro-composites is achieved by taking advantage of versatile basic hardening mechanisms: solid solution hardening, grain boundary hardening, work hardening and age hardening due to a strongly temperature-dependent solubility of Ag in Cu. The crucial point in the case of Cu–Ag-based materials is the tailoring of the precipitation mode to achieve a maximum precipitation hardening effect. The precipitation behaviour of binary Cu–Ag-alloys is well described in the literature [5–10]. Two different precipitation modes – continuous and discontinuous precipitation reaction – are observed in CuAg alloys during age hardening heat treatments. While continuous precipitates are formed within the Cu matrix, coarse discontinuous precipitates nucleate at high-angle grain boundaries – predominantly at Cu/Cu interfaces [11]. Since the resulting lamellar microstructure of decomposed Cu and discontinuously precipitated Ag is comparably coarse and limited to the vicinity of the grain boundary, discontinuously precipitated cells provide a limited hardening capability and possible sites for localised deformation and thus reduced workability. Hence, discontinuous precipitates have to be suppressed. When aiming at maximum hardness this can be achieved by changing interface characteristics or adding other alloying elements. If the Ag-content is increased up to 24 wt% the direct contact between two Cu grains is prevented by the formation of the Ag-rich eutectic [12,13]. In this case, the lack of potential nucleation sites will lead to a suppression of the discontinuous precipitation reaction. However,

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Cu–Ag alloys with high Ag contents tend to form shear bands due to localised deformation between Ag-rich eutectic and Cu grains. Besides, a decreased Ag content will enhance electrical conductivity and reduce the costs of the material.

It is well known that the discontinuous precipitation reaction strongly depends on the diffusion of Ag atoms along grain boundaries [9,10]. Therefore, it is possible to suppress the formation of discontinuous precipitates by changing the diffusion rate of Ag along the grain boundaries. This can be done by adding small amounts of Zr which changes the precipitation behaviour drastically and continuous precipitates are formed even at low Ag contents [14].

In previous investigations the fabrication of CuAg7-wires with small Zr additions [13,15,16] was optimised by age hardening treatment, wire drawing and intermediate heat treatments. Therefore, the production of CuAg7Zr0.05-wires with an ultimate tensile strength of 1.4 GPa and an electrical conductivity of 60%IACS was possible after cold drawing up to a true strain of 5.82. In the present investigation, we explore the possibilities of producing conductor tapes made of Cu–Ag-based materials for applications in contact devices. Since a rolling process requires a suitable fine-grained initial microstructure, the hot-rolling process in order to dynamically recrystallise the material prior to cold-working is studied in detail.

2. Experimental details

The composition of the alloy will be provided in the form of CuAgXZrY where X represents the mass fraction of Ag and Y the mass fraction of Zr. The alloys were melted in an induction furnace and cast into graphite mold. The purity of the starting materials was 99.99% and above. Zr addition was realised by adding a CuZr30 master alloy to the CuAg melt. The alloys in the range of CuAg(3–7)Zr(0.05–0.3) were homogenised at 850 °C for 5 h in an argon atmosphere and subsequently water-quenched. Surface near cast defects were removed by machining. Hot-working was carried out by hot-rolling up to a true strain of 2.2 at several temperatures between 600 °C and 750 °C with a true strain per pass of 0.2. In order to initiate the precipitation reaction, the samples were subsequently heat-treated at 400 °C for 18 h in an argon atmosphere. Finally, cold working was carried out to further strengthen the material by work hardening. Cold-rolling was applied with a strain per pass of 0.2 up to a true strain of 4.8. Parallel to the hot-rolling experiments, hot-compression tests up to a true strain of 1.1 with strain rates of 0.1-10/s were carried out in order to determine the appropriate working window on as-cast samples for dynamic recrystallisation during hot-rolling.

The microstructure was investigated by light optical microscopy (LOM) using a Nikon Epiphot 300, scanning electron microscopy (SEM) using a Helios NanoLab 600i, electron backscatter diffraction (EBSD) using a TSL Digiview system and energy dispersive X-ray spectroscopy (EDX) using an EDAX Apollo X system. All SEM images shown in this paper are backscattered electron (BSE) images obtained with a four diode detector. Samples were prepared by a standard metallographic procedure; final polishing was performed using Mastermet-2 (mechanical-chemical combination). Etching was done utilising a solution of 5 mg ammonium persulphate and 50 ml water. SEM was operated at 20 kV with the exception of the phase analysis of Cu_4AgZr which was carried out at 30 kV and high-resolution images which were taken at 10 kV. Hardness measurements (HV0.1 & HV0.01) were conducted on polished samples with a load time of 10 s, using a Vickers hardness tester Shimadzu HMV-2. The average hardness was obtained from a minimum of 9 indentations. The ultimate tensile strength was determined at room temperature on rolled tape pieces of a total length of 90 mm using an electromechanical Instron 8562 testing machine, at a displacement rate of 0.2 mm/min. The electrical conductivity was measured using a standard four-probe technique at room temperature and up to 750 °C utilising a set-up described elsewhere [16].

3. Results and discussion

3.1. Homogenisation

In order to achieve maximum strength of the final tape, continuous precipitates have to be formed homogeneously. Therefore, an initial homogenisation has to be applied to release the full potential of precipitation hardening. In this section the relevant peculiarities observed in CuAgZr-alloys during homogenisation are described.

3.1.1. Elimination of microsegregation

The as-cast microstructure of the base alloy CuAg7Zr0.05 is shown in Fig. 1(a). By etching, bright and dark regions in the grain interior of the cast alloy can be highlighted. These regions form a dendrite-like morphology. The element distribution across these structures was investigated by EDX line analysis which is shown in Fig. 1(c). It reveals different components of the microstructure. The main fraction of the microstructure, which is represented by the dark regions in Fig. 1(a), exhibits a high intensity of Cu and a low intensity of Ag, indicating the Cu–Ag solid solution. Within the Cu-matrix Ag-enriched regions are observed, which correlate with the bright regions in Fig. 1(a). This Ag-enrichment is known as microsegregation [17], which results from suppressed diffusion during the solidification of alloys. In order to achieve best properties and formability of the tape, microsegregation should be eliminated by a homogenisation treatment or during hot-working itself. Besides this, the two peaks of Ag intensity indicate Ag-rich precipitates, which correspond to the white particles shown in the BSE inset of Fig. 1(c). A homogenisation treatment has been suggested in previous work [15] to be sufficient for a complete dissolution of the Ag-precipitates. For both purposes a homogenisation at 850 °C for 5 h was performed. The homogenised alloy exhibits a homogeneous microstructure without microsegregation and Ag-precipitates, which is shown in Fig. 1(b). During homogenisation the lateral concentration variation within the Cu–Ag solid solution was eliminated by diffusion. The Ag-precipitates were completely dissolved. Therefore, all investigated CuAgZr-alloys were homogenised at 850 °C prior to hot-working.

3.1.2. Ternary phase Cu_4AgZr

As mentioned above, a homogenisation treatment leads to a dissolution of Ag-precipitates and the removal of microsegregations. However, the BSE image of the homogenised CuAg7Zr0.2 alloy in Fig. 2(a) shows white particles, which cannot be dissolved during annealing below 850 °C. These particles were analysed by means of EDX and EBSD. The EDX spectrum can clearly be matched by Cu, Ag and Zr and a quantitative evaluation leads to an element concentration of 69 at% Cu, 13.5 at% Ag and 17.5 at% Zr. This composition coincides with the solubility range of the ternary phase Cu_4AgZr. This phase was firstly identified by Zhou et al. [18] and is thermodynamically stable at room temperature. Using EBSD we were able to identify the Kikuchi pattern based on the space group and the lattice parameters given in Ref. [18]. In a previous investigation of different Zr additions to CuAg7 [15] it was shown that the area fraction of Cu_4AgZr strongly depends on the Zr content. High contents of the hard ternary phase can lead to a decrease of workability as found in the case of wire drawing of CuAg7Zr0.3 [15]. Therefore, the area fraction of Cu_4AgZr in the