STRUCTURE AND PROPERTIES OF PRECIPITATION-HARDENED Cu–Ni–Mn–Fe BINDERS FOR COMPOSITE COATINGS

O.V. Sukhova, K.O. Vashchynska

Oles Honchar Dnipro National University, Dnipro, Ukraine
e-mail: sukhovaya@ukr.net

The structure and properties of Cu–Ni–Mn–Fe alloys within the concentration range of 19.3–21.0 % Ni, 19.5–20.5 % Mn, 0.6–2.7 % Fe, Cu – the balance (in wt. %) were studied in this work. Quantitative metallographic, X-ray, and differential thermal analyses were applied. Two α-Cu solid solutions that differ in composition and microhardness were revealed in the structure of the investigated Cu–Ni–Mn–Fe alloys. These solutions were formed at 1010 ± 10 °C and 890 ± 10 °C, correspondingly. Besides, hardening NiMn phase was precipitated at 405 ± 15 °C due to ageing. In the Cu–Ni–Mn–Fe alloys annealed at 900 °C for 60–750 hours, the volume fraction and size of NiMn precipitates increased with increasing holding time. When iron content was raised from 0.6 up to 2.7 wt. %, the amount of NiMn precipitates increased, especially during first 60 hours of annealing at 900 °C. Brinell hardness of the Cu–Ni–Mn–Fe alloys with higher iron contents increased by 10 HRB on average. At that, as test temperature was raised up to 400 °C, tensile strength decreased by ~1.3 times and elongation dropped markedly by ~10 times. The investigated Cu–Ni–Mn–Fe alloys containing up to 2.7 wt. % may be applied as binder materials for composite coatings provided that working temperature does not exceed 400 °C.

Keywords: Cu–Ni–Mn–Fe alloys, annealing, ageing, structure, volume fraction, mechanical properties.

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1. Introduction

Macroheterogeneous composites produced by a furnace infiltration find the wide application as coatings to protect and restore the quick-worn parts of the machine-building and metallurgical equipment [1]. The widest use has found a coating, whose composition consists of the W–C eutectic alloy as a filler and Cu–20Ni–20Mn alloy as a metal binder. This composite material was designed for facing equipment, which work under the conditions of abrasive and gas-abrasive wear. The use of the composite coating made it possible to increase operating life by a factor from 3 up to 15.

The elevated strength of the Cu–20Ni–20Mn alloy is achieved by precipitation hardening [2]. This process involves the formation of θ-NiMn phase from a supersaturated solid solution of α-Cu. The precipitation occurs during the cooling of the alloys because the solubility of Ni and Mn in α-Cu decreases with lowering temperature. The evolution of NiMn precipitates dispersed in the α-Cu matrix is responsible for the achievement of the material's final strength.

Commercially fabricated Cu–20Ni–20Mn alloy contains foreign additives of up to 2.7 wt. % of Fe [3]. But the conducted research of the iron effect on precipitation hardening of the Cu–Ni–Mn alloys was concentrated basically on the alloys doped with more than 2.7 wt. % Fe [4]. Although precipitation hardening of the Cu–Ni–Mn–Fe alloy may allow mechanical strength and wear resistance necessary for functional applications of the composite coatings.

Thus, the control of the precipitation of the NiMn phase in commercially fabricated Cu–Ni–Mn–Fe binders for composite coatings will ensure wider applicability of the promising surface strengthening technology [1]. Therefore, the effects of iron content and annealing conditions on changes in microstructure and mechanical properties of the precipitation-hardened Cu–Ni–Mn alloys were investigated in this work.

2. Experimental procedure

The studied Cu – Ni – Mn – Fe alloys containing 19.3 – 21.0 % Ni, 19.5 – 20.5 % Mn, 0.6 – 2.7 % Fe, Cu – the balance (in wt. %) were prepared of high purity (99.93 – 99.99 %)

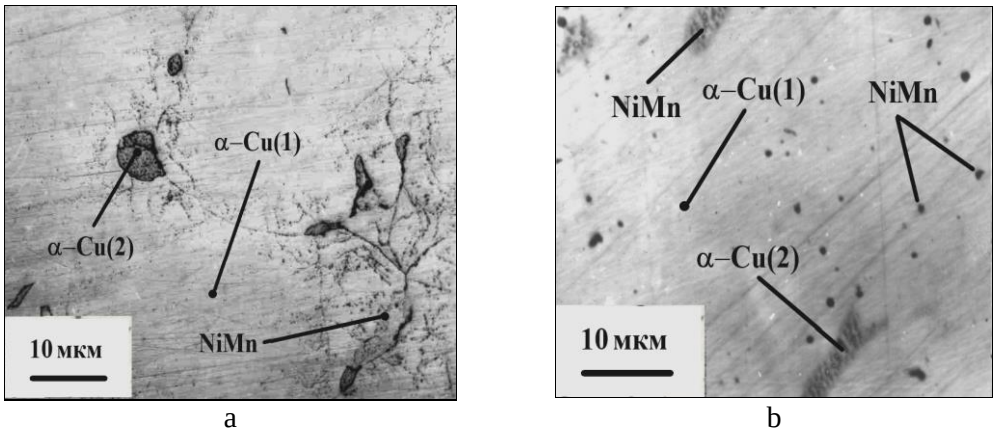
components and melted in alumina crucibles using Tamman furnace. The cooling rate of the alloys was 50 °C/min. To investigate ageing, the samples of Cu–Ni–Mn–Fe alloys were annealed at 900 °C for 60–750 hours.

The alloys were examined by light-optical microscope Neophot. Quantitative metallography was carried out with structural analyzer Epiquant. X-ray diffraction analysis was done to identify the existing phases in produced samples on an X-ray diffractometer ДРОН-УМ-1 with CuK_α source. The phase transformations were investigated by means of differential thermal analysis (DTA). Cooling curves were recorded for each sample at a cooling rate of 5 K/min.

The Vickers microhardness (H_μ) was measured from at least 10 different indentations using ПМТ-3 device. Brinell hardness of the alloys was determined by ТК-2М tester. Tensile strength and elongation to failure were evaluated by standard tests at 20 °C and 400 °C using ИМАШ 20-78 stretching machine.

3. Results and discussion

Most of the structure of the investigated Cu–Ni–Mn–Fe alloys comprise two solid solutions based on alpha-copper. As DTA measurements evidence, first of them (further referred as α-Cu(1)) primarily crystallizes within the temperature range of 1000–1020 °C and contains 84–85.4 % Cu; 7.8–9.0 % Mn; 7.3–4.9 % Ni; 0.6–0.7 % Fe (in wt. %) (Fig. 1, a) [3]. After that, at 880–900 °C secondary solid solution based on alpha-copper (referred as α-Cu(2)) is formed. Its composition falls within the concentration range of 72.3–77.5 % Cu; 13.1 %–3.8 % Ni; 8.4–10.5 % Mn; 6.2–8.2 % Fe (in wt. %). Both the solutions are found to differ in microhardness – 1.72 ± 0.1 GPa (α-Cu(1)) and 2.32 ± 0.2 GPa (α-Cu(2)).



a b

Fig. 1. Microstructure of the Cu–19.5Ni–19.3Mn–2.7Fe alloy: a – before annealing; b – after annealing at 900 °C for 750 hours.

The last to crystallize is NiMn phase that appears in the structure of the Cu–Ni–Mn–Fe alloys due to precipitation hardening within the temperature range of 390–200 °C (Fig. 1, a). With iron content of the alloys increasing from 0.6 up to 2.7 wt. %, thermal effect corresponding to the starting temperature of NiMn formation is shifted to 420 °C.

After annealing at 900 °C for 60–750 hours, in the structure of all investigated alloys, the crystals of α-Cu(2) secondary phase observed at the grain boundaries of α-Cu(1) matrix solid solution have non-homogeneous structure (Fig. 1, b). In the interior of this phase of grey color, a light-grey region is revealed. The increase in the annealing

time is found to give rise to the decrease in the amount of α-Cu(2) phase. After annealing for 750 hours, this phase almost completely disappears (Fig. 2, a, curve 2).

The observed structural changes may be attributed to the α-Cu(2) phase dissolution at annealing temperature. Therefore, non-homogeneous structure of these crystals is revealed since in their interior remain the regions of non-dissolved phase. On the periphery of these crystals, solid solution based on α-Cu contains less iron as compared with the crystals prior to annealing but more iron than primary α-Cu(1) matrix solution.

Annealing at 900 °C brings about the increase in the volume fraction of NiMn precipitates of dark color in the structure of the Cu–Ni–Mn–Fe alloys (Fig. 1, b). They are observed both at the grain boundaries and throughout matrix of alpha-copper solution.

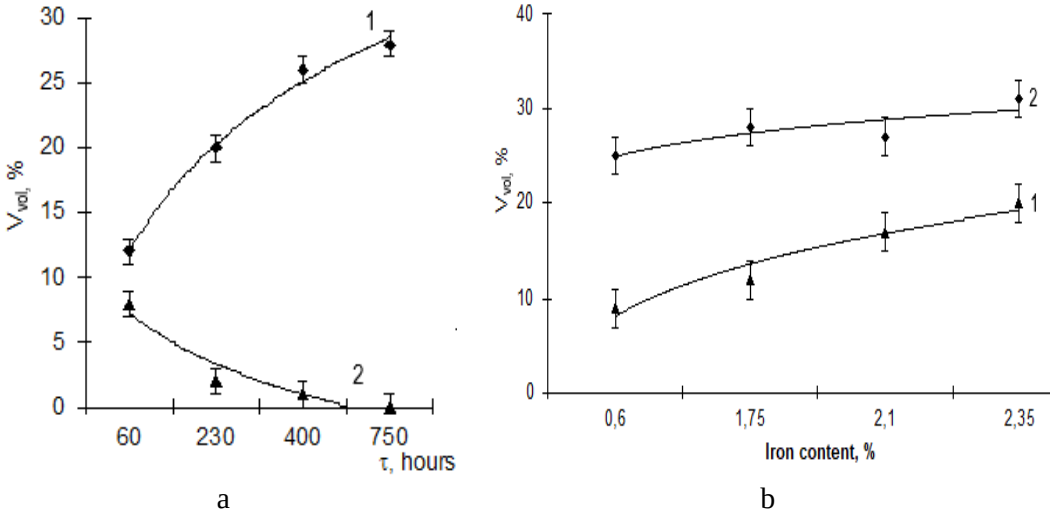


Fig. 2. Results of quantitative metallography: a – effect of annealing time on volume fraction of NiMn (curve 1) and α-Cu(2) (curve 2) phases of Cu–21Ni–20.5Mn–1.75Fe alloy; b – effect of Fe content on volume fraction of NiMn after annealing at 900 °C for 60 hours (curve 1) and 750 hours (curve 2).

Due to precipitation hardening, amount and size of NiMn precipitates increase. An average size of precipitates ranges from 5 до 10 μм. The longer annealing time, the more NiMn phase precipitates (Fig. 2, a, curve 1). As DTA results evidence, the thermal effect at 390–420 °C attributed to NiMn precipitation in the Cu–Ni–Mn–Fe alloys is significantly stronger with increasing NiMn volume fraction.

As Fe content of the Cu–Ni–Mn–Fe alloys is raised up to 2.7 wt. %, the volume fraction of NiMn phase slightly increases after annealing at 900 °C for 60 hours (Fig. 2, b, curve 1) and does not noticeably change after annealing for 750 hours (Fig. 2, b, curve 2). Volume fraction of NiMn precipitates is higher where α-Cu(2) phase was located before its dissolution during annealing (Fig. 1, b). So, it may lead to the conclusion that α-Cu(2) acts as nucleation site for NiMn precipitates. Addition of up to 2.7 wt. % Fe accelerates the ageing of the Cu–Ni–Mn–Fe alloys accompanying by NiMn precipitation. The effect tends to be more marked after first 60 hours of annealing.

Brinell hardness of the Cu–Ni–Mn–Fe alloys increases as the iron content increases (Table 1). After precipitation treatment at 900 °C for 500 hours, Brinell hardness decreases, which may be caused by overaging of the samples. Tensile strength at 20 °C and 400 °C decreases with increasing iron content and increases upon annealing at 900 °C for 500 hours (Table 1).

Table 1

Mechanical properties of the Cu–Ni–Mn–Fe alloys before and after annealing at 900 °C for 500 hours

Iron content, wt. %	Brinell hardness, HRB		Tensile strength, MPa			
	before annealing	after annealing	Test temperature		Test temperature	
			20°C	400°C	20°C	400°C
0.6	61.0±3.0	46.8±1.8	654±6	664±6	451±39	480±10
1.75	67.0±1.0	54.0±1.0	637±10	657±8	360±24	394±14
2.1	68.0±2.0	66.0±2.8	–	–	–	–
2.35	70.5±1.5	67.0±3.5	–	–	–	–
2.7	72.5±0.5	71.0±4.3	555±9	568±4	338±34	423±24

After annealing at 900 °C for 500 hours, elongation at room temperature of alloy with iron concentration of 0.6 wt. % decreases by 3 % (from ~32 to ~29 %), that of alloy containing 1.75 wt. % Fe is reduced by 5 % (from ~30 to ~25 %), and elongation of alloy with 2.7 wt. % Fe lowers by 10 % (from ~23 to ~13 %). Elongation determined at temperature of 400 °C is further down from ~ 15 % up to ~1.5 % (by 10 times) as iron content of the Cu–Ni–Mn–Fe alloys increases from 0.6 to 2.7 wt. %. These results indicate that iron has negative effect on elongation of the Cu–Ni–Mn–Fe alloys, primarily as test temperature is raised up to 400 °C.

3. Conclusions

In the structure of the studied Cu–Ni–Mn–Fe alloys two solid solutions based on α-Cu are observed, one of which primarily crystallizes at 1010 ± 10 °C and the other forms due to limited solubility of the components at 890 ± 10 °C. The secondary solid solution contains more iron and has higher microhardness as compared with primary solid solution. In addition, within the temperature range of 405 ± 15 °C, the NiMn phase precipitates through ageing of the alloys.

Upon precipitation treatment at 900 °C for 60–750 hours, the secondary solid solution based on α-Cu is re-dissolved into the matrix of primary α-Cu. More NiMn precipitates appear as the annealing time increases. The higher content of Fe added to the Cu–Ni–Mn alloys accelerates precipitation hardening during first 60 hours of annealing, and then Fe slightly affects the rate of NiMn precipitation.

The tensile strength of the Cu–Ni–Mn–Fe alloys annealed at 900 °C for 500 hours increases by ~15 %, but elongation decreases by ~1.9 times, specifically with increasing Fe concentration in the alloys.

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