Synthesis of Copper Chromium Alloys by Alumninothermic Reduction

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Abstract

Due to the combination of high thermal and electrical conductivity, high strength and long term stability Copper-Chromium materials are widely used in high voltage applications as electrical high-power contacts and vacuum interrupters. The binary system of Copper and Chromium shows nearly complete immiscibility in the solid state. In order to obtain Copper-Chromium materials with a mass fraction of Chromium between 10 % and 55 wt.-%, extensive and cost-intensive production processes are required to obtain an uniformly distribution of Chromium particles in the Copper matrix. Currently Cu-Cr contact materials are produced by powder metallurgical or VAR technologies. The synthesis of copper-chromium alloys by a cost reduced aluminothermic reduction process is currently under investigation at IME, RWTH Aachen University.

Focussing on this new method, this paper presents the first approach to produce Copper-Chromium material with Chromium mass contents higher than 25 % by joint aluminothermic reduction of Chrom- and Copper-oxides in labscale. The aluminothermic reduction shows high-potential for an alternative production method for Copper-Chromium materials due to its high heating rates, high temperatures and short reactions times combined with its self-propagating behaviour. In order to define the process window parameters like intrinsic chemical energy (enthalpy of the reaction mixture), equilibrium temperature and physical properties (particle size and mixing degree) were optimized.

The full paper will be published soon in a scientific journal.

1 Introduction

Because of the superior mechanical properties in comparison to monolithic copper, CuCr alloys have many applications and are often used in vacuum switches like medium voltage circuit breakers (1 to 72.5/84 kV) and arc suppression chambers. [1] Full demixing metallic binary alloys like CuCr are most usually processed using powder metallurgy. However, the crystal grain structure of Copper and Chromium obtained from vacuum arc remelted CuCr alloys is more refined and the distribution of grains is more uniform. [2] The aluminothermic reduction offers a promising process to produce CuCr material suitable for electrodes for the vacuum arc remelting. The aluminothermic reaction is self-propagating and proceeds with very high reaction velocities and thus provides a least expensive process for synthesising CuCr alloys.

2 Fundamentals

An aluminothermic reaction is defined as the reduction of a metal compound in which aluminium is used as reducing agent. The reaction is possible when aluminium has a greater affinity for the non-metal element of the compound than the desired metal. Aluminothermic processes are usually applied to manufacture master alloys for the steel and superalloy industries by reducing mostly refractory metal oxides or ores. The greater the difference in oxygen affinity of aluminium and metal oxide, the higher is the ease of reaction. For the present investigation of synthesis of copper-chromium alloys copper and chromium are applied as oxides. The reactions of Al with Cr_2O_3 and CuO are given in Equations (1) and (2).

$$\frac{1}{2}Cr_2O_3 + Al \rightarrow Cr + \frac{1}{2}Al_2O_3 \qquad -\Delta H_{298} = 274 \text{ kJ} \tag{1}$$

$$\frac{3}{2}\,CuO + Al \rightarrow \frac{3}{2}\,Cu + \frac{1}{2}Al_2O_3 \qquad -\Delta H_{298} = 604 \text{ kJ} \tag{2}$$

Regarding the heat of reaction per mole reductant, $-\Delta H_{298}$ should be higher than 300 kJ/mol in order to ensure an adequate metal/slag separation. [3] At these conditions the reduction of CuO provides sufficient enthalpy for both reactions, thus making the process beneficial.

The desired chromium content of the alloys is highly dependent on the particular area of application and varies between 20 and 60 wt.-%. Alloys with a low Cr content are applied to operational conditions with high arc quenching and low current, whereas alloys with a high Cr content offer high erosion resistance and proper welding behaviour. [4] By combining the properties of copper and chromium, it is possible to obtain an alloy with high hardness, high melting point and an excellent electrical conductivity. Simultaneously, the combination shows the difficulty of a miscibility gap, that has a critical composition at 43.6 at.-% of chromium at 1 787 K [5] and expands considerably at lower temperatures (cf. Figure 1). Below the dashed line, the initially homogenous bulk alloy will be separated into a mixture of a Cr-rich and a Cu-rich liquid phase. [2][5]

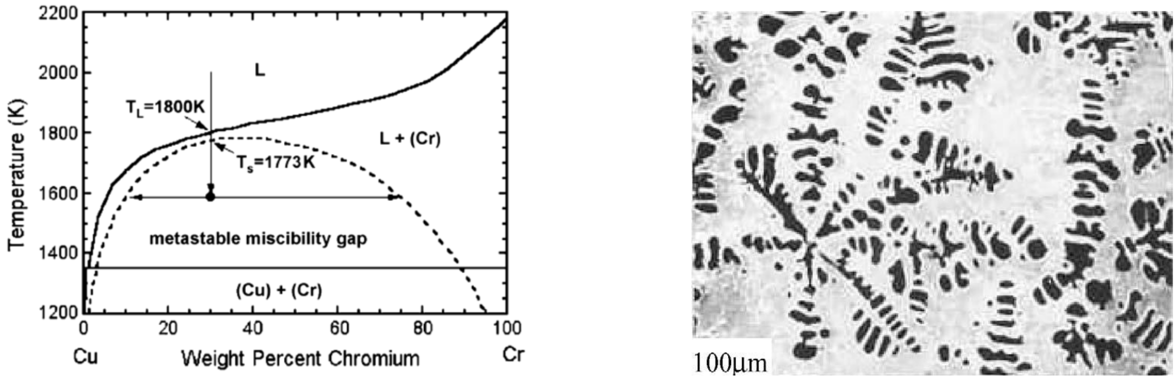

Figure 1: Binary Cu-Cr phase diagram (left) [5] and microstructure of CuCr25 alloy melted by a vacuum induction furnace (right) [6]

4 Experimental Procedure

The process temperature of an aluminothermic reaction strongly depends on the released energy during reaction including the effects induced by interatomic and intermolecular interactions, e.g. heat of mixing and heat of phase transformation. In previous research [7] a calculation model is developed using the theoretical process temperature to be reached as key criterion. Based on this calculation model the input mixture for the aluminothermic reduction of CuO and Cr_2O_3 is calculated. CaO is added as flux to decrease the liquidus temperature of the forming Al_2O_3-slag. The experiments are performed in an Al_2O_3 lined steel vessel with a filling volume of 25 liters. The charging material is 20 kg. The Chromium content is varied between 25 wt.-% and 40 wt.-%. In all conducted experiments an adequate phase separation between metal and slag is observed. Furthermore, the obtained metal ingot contains numerous cavities and shrinkages holes as illustrated by Figure 2 (right).

Figure 2: Metal phase and free cross-sectional area

5 Results

The trails show the feasibility of synthesizing CuCr-alloys by aluminothermic reduction. The metal ingot consists of one apparently homogenous phase, hence a separation of Copper and Chromium did not occur in a macroscopic scale. As demonstrated in Table 1 the composition of the metal phase of alloy CuCr25 nearly meets the values which were targeted during blending the input materials. However, the metal analysis indicates that the alloy contains a non-negligible amount of aluminum. With increasing content of Chromium within the alloy (cf. Table 1, CuCr40) a decreased excess amount of aluminum is observed.

Table 1: Metal compositions of the produced CuCr alloys

	Cu in wt.-%]	Cr in wt.-%	Al in wt.-%
CuCr25	73.2	22.5	4.3
CuCr40	62.1	32	2.9

In order to investigate the distribution of the chromium phase in the metal ingot metallographic methods were utilized. As shown in Figure 3 the chromium-rich phase (grey) is comparatively well distributed within the copper-rich matrix. Thereby, the dendritic structure of the chromium-rich phase in the CuCr25 alloy (left) is more pronounced as in the CuCr40 alloy (right). Additionally, the CuCr40 alloy contains a third phase, which is not present in the CuCr25 alloy. It can be assumed that this phase represents an eutectic composition. The round-shaped areas in the left image of CuCr25 are supposed to be non-metallic inclusions, whereas the dark field at the image border represents one of the previous mentioned cavities.

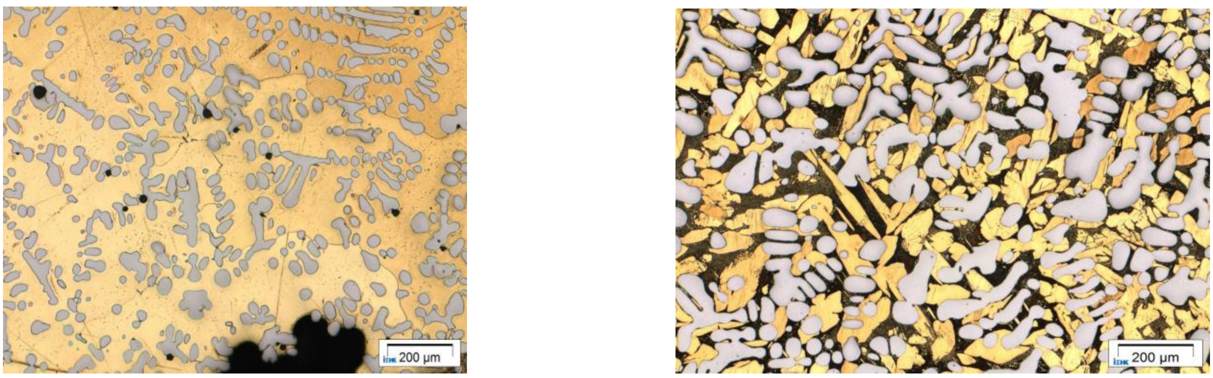

Figure 3: Metallographic images of CuCr25 (left) and CuCr40 (right)

References

[1] LESNIK N., ., MINAKOVA R. V., KHOMENKO E. V. (2001): Chromium – copper system: adhesion characteristics, doping, the structure of phase boundary and composites. Powder Metallurgy and Metal Ceramics 40, pp. 432 440

[2] SHIXIN X., SHENLI J., JIMEI W. (2002): Arc remelting experimental results and analysis on CuCr contact material" Proceedings XXth International Symposium on Discharges and Electrical Insulation in Vacuum

[3] DAUTZENBERG, W. (1974): Aluminothermie. In: BARTHOLOMÉ ET AL. (ED.) Ullmanns Encyklopädie der technischen Chemie, S. 351, 4. Auflage; Weinheim/Bergstr. (Verlag Chemie)

[4] KOWANDA C. et al. (2010): Netshape manufacturing of CuCr medium voltage circuit breakers. S Proceedings XXIVth International Symposium on Discharges and Electrical Insulation in Vacuum (2010), Braunschweig

[5] ZHOU et al. (2009): On the metastable miscibility gap in liquid Cu-Cr alloys" Journal of Materials Science 44, pp. 3793-3799

[6] ZHANG C., YANG Z., WANGY. (2006): Preparation of CuCr25 contact materials by vaccum induction melting. Journal of Materials Processing Technology, Vol. 178, pp. 283-286

[7] STOEPHASIUS J.-C., FRIEDRICH B. (2005): Modelling of metallothermic reactions - local reaction rates during aluminothermic –γ-TiAl-Nb production – World of Metallurgy - Erzmetall 2, pp 63-69, Clausthal-Zellerfeld