Internal oxidation of Cu-C and Ag-C composites

Notranja oksidacija Cu-C in Ag-C kompozitov

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Abstract: The internal oxidation in copper-carbon and silver-carbon composites occurs when they are exposed to air or oxygen at high temperature. Solubility of carbon in copper or in silver is very low. The kinetics of oxidation at high temperature and activation energy were determined and the mechanism of internal oxidation was analysed. The kinetics of internal oxidation was determined for both cases and it is depended from the diffusion of oxygen following parabolic time dependence according to Wagner's theory. The activation energy for Cu-C composite is 70.5 kJ/mol, and for Ag-C composite is 50.1 kJ/mol, what is in both cases close to the activation energy for the volume diffusion of oxygen in copper or in silver. In both cases gas products are formed during the internal oxidation of composites. In the internal oxidation zone pores, bubbles occur. The carbon oxidates directly with the oxygen from solid solution as long there is a contact, which breaks down with the presence of gas products. Then the oxidation occurs over the gas mixture of CO and CO₂.

Izvleček: Pri visokih temperaturah kompoziti bakra in srebra z ogljikom na zraku ali v kisiku reagirajo po mehanizmu notranje oksidacije. Topnost ogljika v trdnem bakru in trdnem srebru je zelo majhna. Analizirali smo kinetiko oksidacije kompozitov, določili aktivacijsko energijo in mehanizem notranje oksidacije. Kinetika oksidacije je pri obeh skupinah materialov odvisna od difuzije kisika in sledi parabolični odvisnosti od časa v skladu z Wagnerjevo teorijo. Aktivacijska energija procesa je za kompozit Cu-C enaka 70,5 kJ/mol, za kompozit Ag-C pa 50,1 kJ/mol, kar je blizu aktivacijski energiji za volumsko difuzijo kisika v trdnem bakru oziroma srebru. Pri
Internal oxidation is a general term for the process taking place under the surface of alloys and including the selective reaction of a less noble composite constituent with oxygen\[^{[1,2]}\]. The phenomenon of internal oxidation was first noticed in copper alloys with silicon, nickel, tin, manganese and zinc, but it is also seen in silver alloys with additions of less noble alloy constituents\[^{[3]}\]. The oxidation of these alloys results in the zone with a typical heterogeneous composition, the so called internal oxidation zone (IOZ)\[^{[4,5]}\].

The internal oxidation is a phenomenon that includes several elementary processes with oxygen transmission as the most important factor of growth and morphological characteristics of the oxidized zone.

Conditions for the process of internal oxidation are\[^{[4,6]}\]:
- larger electronegativity of alloy constituent from the basic metal,
- larger oxygen solubility in basic metal, and
- higher diffusion rate of oxygen in basic metal in comparison with the diffusion rate of alloy constituent.

Special examples require additional conditions like the maximal concentration of alloy constituent, oxidation temperature and partial oxygen pressure in atmosphere. All these influence the transmission process from the internal to external oxidation or passivation.

Theoretical principles

The first theoretic analysis being the principle of further research was made by Wagner\[^{[4]}\] who used his own principle mathematic pattern for the calculation of process kinetics to explore typical examples of internal oxidation in different alloys.

The discussed examples of oxidation of Cu-C and Ag-C composites belong to the examples of internal oxidation of two-phase alloys. Copper and silver dissolve a small portion of carbon in both liquid and solid state, and do not create compounds with carbon. Therefore their composites are two-phase composites and consist of a matrix and carbon particles.

Copper and silver meet the conditions that are necessary for internal oxidation:
- both metals are more noble than carbon,
- oxygen solubility in both metals is relatively high, and
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- diffusion rate of oxygen exceeds the diffusion rate of carbon.

Internal oxidation of two-phase alloys and composites runs according to one of Kapteijn and Meijering mechanisms\(^\text{[6,7]}\) or follows the mechanism that is a combination of both\(^\text{[8]}\) (Figures 1 and 2).

**Experimental Work**

For testing purpose, samples made of copper with 1 and 2 m.% carbon and samples made of silver with 1, 2, 5 and 10 m.% carbon were prepared\(^\text{[9-11]}\). Cu-C and Ag-C composites were made using the process of powder metallurgy. Mixtures of metal and graphite powder were compacted in a rigid hydraulic tool on the hydraulic press. They were subjected to sintering under vacuum and then to hot isostatic process. As a result, materials reached a practically theoretic density with no porosity. Cu-C composites were oxidized in a mixture of Cu\(_2\)O and Cu powders so that the oxygen partial pressure equalled Cu\(_2\)O dissociation pressure. Therefore, no copper oxide was created on the surface of Cu-C composites and internal oxidation was released. In case of Ag-C composites, internal oxidation was released also in the air or in pure oxygen as silver oxide disintegrates completely already at temperatures around 453 K\(^\text{[12]}\).

We cut samples from both materials and prepared them for a metallographic analysis using an optical microscope (OM) and scanning electronic microscope (SEM).

**Results and Discussion**

After the internal composite oxidation, the zone of internal oxidation (IOZ) consists of a matrix and scattered oxide particles (bubbles, pores) of composite constituent. A comparison of morphological characteristics of the internally oxidized zone in different composites shows essential differences in the size, form and distribution of oxide particles in the matrix. We noticed no resi-
dues of porosity at the microscopic level. We found that the thermodynamic condition for the internal oxidation is met in the Cu-C and Ag-C composites.

Metallographic characteristics of internally oxidized Cu-C composites show that internal oxidation is running primarily with a direct carbon oxidation (Figure 3). Metallographic characteristics of internally oxidized Ag-C composites show that oxidation of these type of composites is probably running directly out of a solid solution (Figures 4 and 5).

On the basis of kinetics of growth of the internal oxidation zone (Figures 6 and 7) we calculated the activation energy of process. The activation energy for Cu-C composites is 70.5 kJ/mol which is close to the activation energy for a volume diffusion of oxygen in copper between 1023 and 1323 K that amounts to 67.2 kJ/mol.

For Ag-C composites, the calculated activation energy is 50.1 kJ/mol which is close to the activation energy for a volume diffusion of oxygen in silver between 1023 and 1173 K that amounts to 46.1 kJ/mol.

In both examples, the activation energies are very close to the activation energy for a volume diffusion of oxygen in copper and in silver. This makes us conclude that kinetics of the internal oxidation in both composite groups primarily depends upon oxygen diffusion.

**Conclusions**

Ag-C and Cu-C composites meet all necessary conditions for internal oxidation. They
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In case of Ag-C composites, we noticed some similarity between the geometry of pores and carbon particles only with small concentrations of carbon (0.5 to 2 m.% C). Differences are obvious with large carbon concentrations. In the discussed example, oxygen diffusion in silver is the most essential parameter for the control of oxidation kinetics.

Carbon oxidation is carried out directly with oxygen out of solid solution and - when the creation of gas phase this contact is interrupted - over a gas mixture of CO and CO₂.

**Povzetek**

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Kompoziti bakra in srebra z ogljikom v kisiku ali na zraku reagirajo pri visokih temperaturah po t.i. mehanizmu notranje oksidacije. Topnost ogljika v trdnem bakru in trdnem srebru je zelo majhna.

Analizirali smo kinetiko oksidacije kompozitov, določili aktivacijsko energijo in mehanizem notranje oksidacije. Kinetika oksidacije je tako pri kompozitih Cu-C kot tudi pri kompozitih Ag-C odvisna od difuzije kisika in sledi parabolični odvisnosti od časa v skladu z Wagnerjevo teorijo.

Aktivacijska energija procesa je za kompozite Cu-C enaka 70,5 kJ/mol, za kompozite Ag-C pa 50,1 kJ/mol, kar je zelo blizu aktivacijski energiji za volumsko difuzijo kisika v trdnem bakru oziroma srebru.
Pri oksidaciji kompozita nastajajo plinski produkti. Oksidacija ogljika poteka neposredno s kisikom iz trdne raztopine, ko pa se zaradi nastanka plinske faze stik prekine, pa preko plinske zmesi CO in CO₂.

V okviru predstavljenega dela so bili izdelani in analizirani kompoziti Cu-C z 1 oziroma 2 m.% C ter kompoziti Ag-C z 1, 2, 5 in 10 m.% C. Vsi kompoziti obravnavani v priopisnem delu so izdelani po postopkih metalurške prahov. Z uporabo optične in elektronske presevne mikroskopije so bile izvedene metalografske analize vzorcev obeh navedenih skupin kompozitnih materialov.

REFERENCES


