



Effect of Re addition on the crystallization, heat treatment and structure of the Cu–Ni–Si–Cr alloy

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Abstract

For determination of the structure and properties of those alloys, the following investigations were carried out: scanning microscopy and EDS X-ray analysis. Investigations concerning the optimal chemical composition and production method of Cu–Ni–Si alloys modified by Cr and Re as well as the improved properties in comparison with traditional alloys contribute to better understanding of mechanisms influencing the improvement of mechanical properties of the newly developed alloys. Thermal analysis of the crystallization process allows for accurate calculation of latent heat of various phases developed during solidification. Based on the assumption that the latent crystallization heat is proportional to the share of various phases in the alloy, the thermo-derivative analysis also allows the calculation of the amount of crystallized phases. Calculation of the properties as mentioned earlier is based on the characteristic points determined in a derivative curve. The adequately selected chemical composition of the alloy, as well as the appropriate cooling rate and heat treatment conditions, leads to improvement of functional properties of manufactured elements. For the analysed alloys, a thermal derivative analysis was used to determine the kinetics of crystallization and the temperature of the beginning and the end of a phase and eutectic crystallization, mainly the liquidus temperature (T_L) and solidus temperature (T_{SOL}). The T_{SOL} temperature determined on thermal derivative analysis is the upper limit of supersaturation of the tested alloys. The conductivity and microhardness of the tested alloys were also measured in the function of the chemical composition and the state (i.e., heat treatment).

Keywords Copper alloy · Microstructure · Thermal derivative analysis · Crystallization kinetics

Introduction

Intensive development of industry enforces the need for the development of materials engineering and continuous improvement of the existing materials and the development of entirely new classes of materials. Requirements for the resulting materials are increasingly high and precise. To improve the mechanical properties of alloys, a modification of the chemical composition is used, which allows alloy strengthening as a result of reinforcing phases, by fragmentation of the structure as a result of heterogeneous nucleation of phases with a higher solidification

temperature than the matrix of the alloy, as well as the result of plastic forming allowing the grain to grind, but also as a result of the disadvantages of the point and line construction created in the alloy, which increase the possibility of dissolving the supersaturating phase and then separating the strengthening phases in the grain increasing the strength properties as a result of the heat treatment [1–3].

Knowledge of the phenomena occurring in solidifying copper alloys is of great importance because it allows to create the microstructure and thus the functional properties of alloys and also affects the technological parameters of heat and plastic treatment, including temperature and time. Increasing the cooling rate will support avoiding segregation (block and dendritic), obtaining a beneficial phase dispersion (fragmentation of multi-component eutectics and more even distribution at the interface) [2–7].

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The durability and operational reliability become a priority objective and force the need to search for materials with more favourable and more precise sets of usable features and high and stable mechanical, electrical or thermal properties during operation. A significant part of these properties is fulfilled by the alloys from precipitation-hardened copper alloys, such as Cu–Fe, Cu–Cr, Cu–Co, Cu–Ni–Si and Cu–Ni–Si–Cr [2–4].

The subject of research is increasingly becoming the CuNi2Si1 alloy, whose mechanical properties can be shaped by heat and plastic treatment [5–9]. In the study of CuNi2Si1 alloys, Cr and sometimes Cr and Mg or Cr and Ti are often introduced into the alloy. In the obtained Cu–Ni–Si–Cr, Cu–Ni–Si–Cr–Mg or Cu–Ni–Si–Cr–Ti alloys, the research results indicate the occurrence of phase transformations and change of morphology and, as a result, achieve more favourable mechanical properties and in some part also changes in conductivity [10, 11].

Analysis of the CuNiSiCrMg alloy showed that the stability of mechanical properties is determined by their microstructure which consists of inter alia the primary precipitation of the Cr₃Si phase and Ni₂Si formed during decomposition of the supersaturated solid solution [2, 10, 11]. Study of the CuNi2Si1 alloy revealed that the formation of coherent Ni₂Si precipitates is formed during solution and ageing process of the alloy. Too long ageing time causes coagulation of these precipitates [11, 12].

Material and investigation methodology

The purpose of the study was to determine the effect of Re addition on the kinetics of crystallization and alloy structure CuNiSiCr.

The interdependence between the chemical composition and the structure of the Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re is shown in Table 1. The cast alloys were made at 1500 °C in the high-temperature vacuum furnace HT-2100-G-Vac-Graphite-Special type—in graphite crucibles Ø25. Alloy elements were placed in a crucible in a pure form.

In order to determine the relationship between the crystallizations kinetics of the alloy and the chemical composition and microstructure of Cu alloy the following investigations were performed:

Table 1 Chemical composition of the analysed copper alloys

	Mass concentration of the element/% mass				
	Ni	Si	Cr	Re	Cu
Cu–Ni–Si–Cr	2	1	Up to 0.8	–	Rest
Cu–Ni–Si–Cr–Re	2	1	Up to 0.8	Up to 0.5	Rest

- Thermo-derivative analysis using the UMSA device equipped with a computer-controlled cooling system, which allows to set flexible the cooling rate applied to the Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys. The samples for thermo-derivative analysis were prepared with a diameter of Ø8 mm and a height of 10 mm. There have also been made holes for thermocouples, in the samples were the thermal node occurs for this type and arrangement of the sample geometry. The investigated samples were characterized with a mass of 8.16 g ± 3 g for this type of geometrical dimension.
- The supersaturation temperature of Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys was 900 °C, with a heating time of 1 h in a protective argon atmosphere.
- Measurement of electrical conductivity was taken on Sigmatest Foerster device.
- Microstructure and chemical composition investigations were carried out using EDS microanalysis on the scanning electron microscope Zeiss Supra 25.
- Alloy structure using MEF4A optical microscope supplied by Leica together with the image analysis software as well as scanning electron microscope using Zeiss Supra 25 device within high-resolution mode.
- The microhardness test was performed on the hardness tester Vickers FUTURE-TECH (FM-ARS9000) with a load of 100 gf for 15 s.
- Samples prepared for observation of the microstructure were ground and polished mechanically and then etched:
- Electrochemically in an electrochemical reagent consisting of ethanol, phosphoric acid, propanol, urea and distilled water.
- Or in a reagent with the following composition: iron chloride, hydrochloric acid and ethyl alcohol.

Investigation results

In the microstructure of CuNiSiCr alloys, there are two types of precipitates: primary precipitations of Cr₃Si and Ni₂Si phase resulting from decomposition of solution [2, 3, 11].

The results of microstructure observation performed using the Olympus light microscope are shown in Figs. 1 and 2. It can be observed that the α -matrix and the phases with chromium are solidified.

Primary phases of Cr₃Si (10 μ m) (Fig. 2 #1) do not melt and do not solidify during the crystallization process of the alloy. The Ni-containing phase is flushed through the front of crystallization of the α phase into the interdendritic areas (Figs. 2, 9).

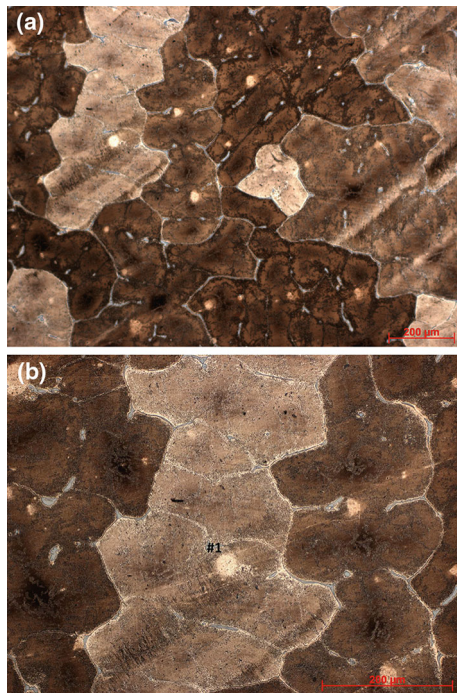


Fig. 1 Microstructure of the Cu–Ni–Si (a, b) as cast (#1—separation with Ni)

This is unconfirmed by ATD studies, but the EDS analysis shows that Re is concentrated at areas with higher content of Cr and Ni (Figs. 1, 2, 3, 4, 9).

However, on the derivative curve, no clear bends indicating the presence of the Re phase were observed.

Cooling and crystallization curves of the investigated Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys freely cooled are shown in Figs. 3, 4. As a result of the thermal

derivative analysis, T_L and T_{SOL} temperatures were determined (Table 2).

Comparison of the presented graphs allows observing the shift of the solidus temperature of analysed copper alloys. As a result of the Re addition, the melt temperature was supercooled and the T_{SOL} temperature decreased by 160 °C. The determination of T_{SOL} allowed to determine the supersaturation temperature and to state that the supersaturation temperature of the alloys with the addition of Re is lower than the temperature of the alloys without the Re.

The thermal derivative analysis also allowed the determination of the fraction solid of analysed alloys (Fig. 5). An evident change in the course of the solid fraction curve for alloys with the addition of rhenium is visible. It can be

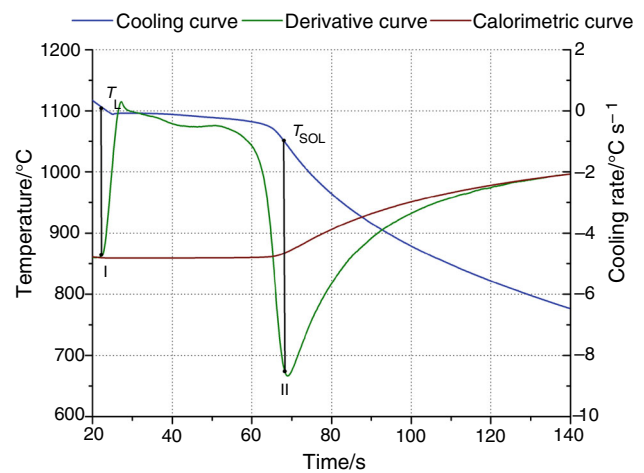


Fig. 3 Cooling and derivative curves of Cu–Ni–Si–Cr alloy

Fig. 2 Microstructure **a** of the Cu–Ni–Si–Cr (#2—as cast separation with Ni); **b** of the Cu–Ni–Si–Cr as supersaturated (#1—phases Cr_3Si); **c** of the Cu–Ni–Si–Cr–Re as cast; **d** of the Cu–Ni–Si–Cr–Re as supersaturated

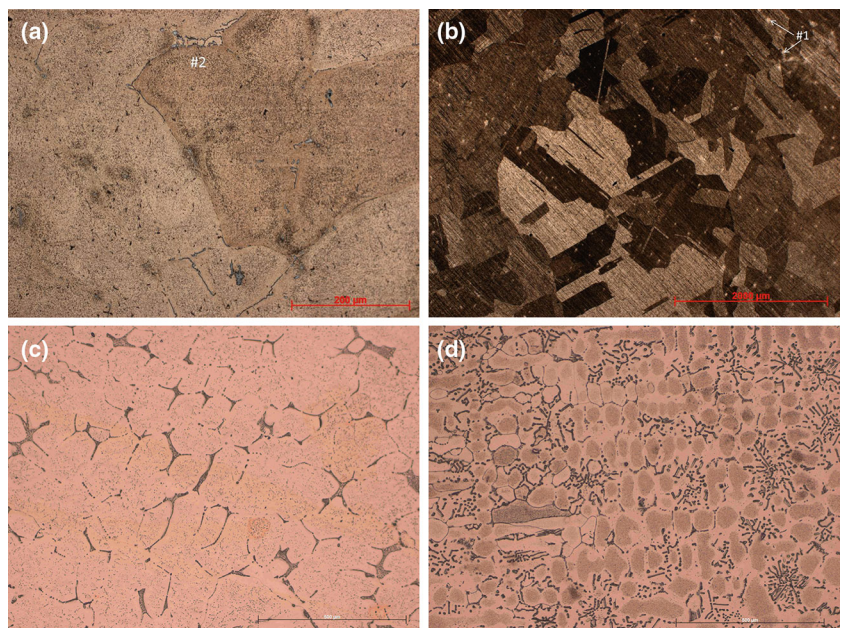


Fig. 4 Cooling and derivative curves of Cu–Ni–Si–Cr–Re alloy

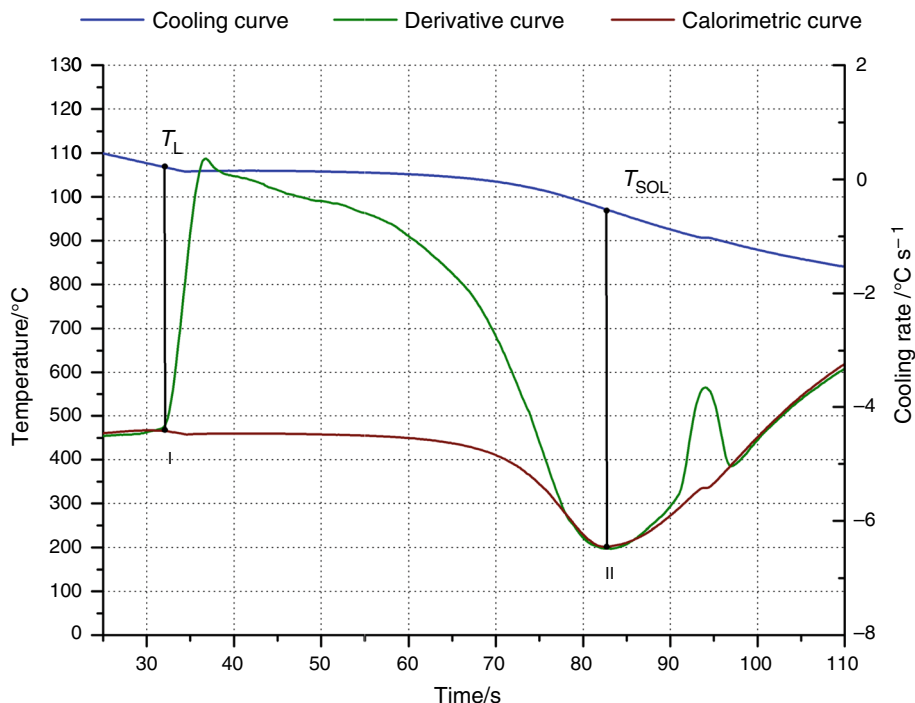


Table 2 Results from thermal derivative analyses of Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys

Analysed alloy	Temperature/°C	
	T_L	T_{SOL}
Cu–Ni–Si–Cr	1109	1145
Cu–Ni–Si–Cr–Re	1070	973

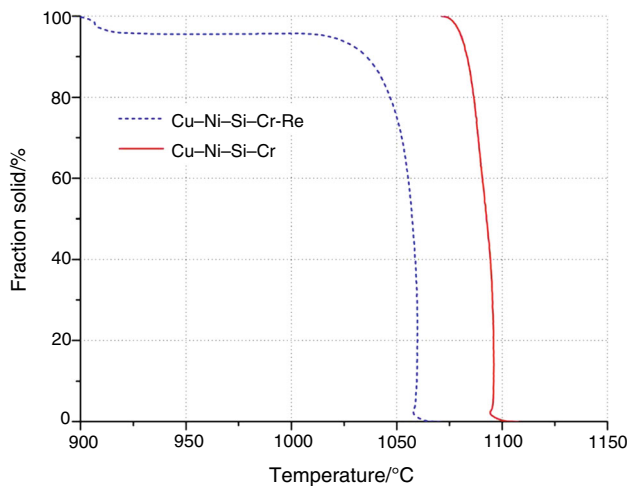


Fig. 5 Fraction solid during the crystallization of the particular compounds of the Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys

noticed that in a non-Re alloy the curve has a mild course and crystallization phases that contain the Cr and Ni elements can be observed. However, the analysis of the course of the alloy curve with the addition of Re showed a rapid increase in the fraction solid in the temperature range of 1060–1020 °C.

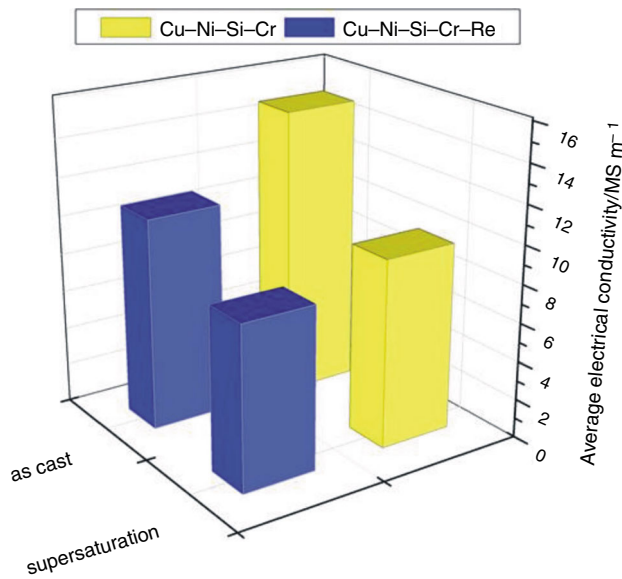
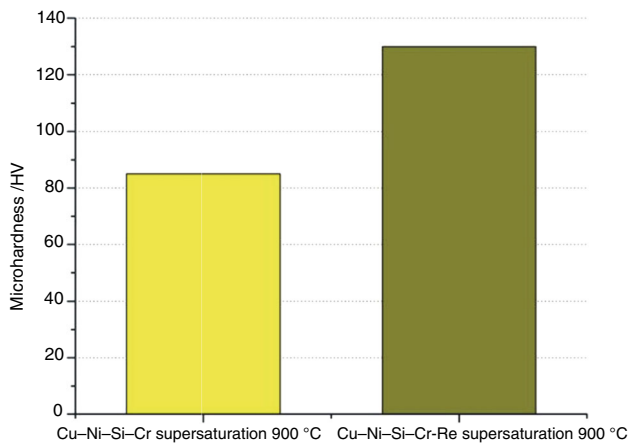
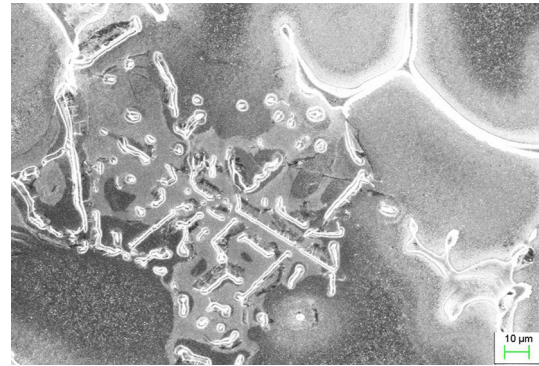
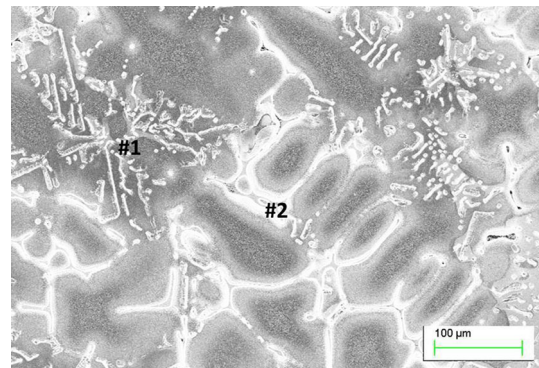
The saturation of alloys at designated temperatures (Table 3) was performed as a result of a thermal derivative analysis. Then the conductivity and microhardness were measured. The results of the electrical conductivity of the analysed Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys in as-cast condition and after saturation are presented in Fig. 6, which shows that in Cu–Ni–Si–Cr and Cu alloys Ni–Si–Cr–Re, saturated at 900 °C, the average electrical conductivity decreased. The results of microhardness are shown in Fig. 7, where it can be observed that the alloy with a small addition of Re (0.3%) is characterized by higher microhardness about 45HV.

Analysis of chemical composition in microareas and scanning electron microscopy showed that in the test alloy the α -phase and eutectics occur (Figs. 8, 9).

Figure 10 represents the distribution of the elements which are the main components of the Cu–Ni–Si–Cr–Re alloy.

Table 3 Parameters of the supersaturation process of Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys

	Supersaturation temperature/°C	Holding time/h	Cooling rate/°C s ⁻¹	Protective atmosphere
Cu–Ni–Si–Cr	900	1	1000	Ar
Cu–Ni–Si–Cr–Re	900	1	1000	Ar

**Fig. 6** Average electrical conductivity of Cu–Ni–Si–Cr and Cu–Ni–Si–Cr–Re alloys**Fig. 7** Microhardness of tested alloys after supersaturation from temperature determined by the thermal derivative analysis**Fig. 8** Microstructure of the Cu–Ni–Si–Cr–Re**Fig. 9** Microstructure of the Cu–Ni–Si–Cr–Re. The X-ray diffraction pattern of Cu–Ni–Si–Cr–Re alloy (point #1: Si = mas. 2.9%, Ni = mas. 3.7%, Cu = mas. 61.3%, Cr = mas. 30.2%, Re = mas. 1.6%—phases with Cr and Re; point #2: Si = mas. 1.267%, Ni = mas. 21.82%, Cu = mas. 65.51%—phases with Ni)

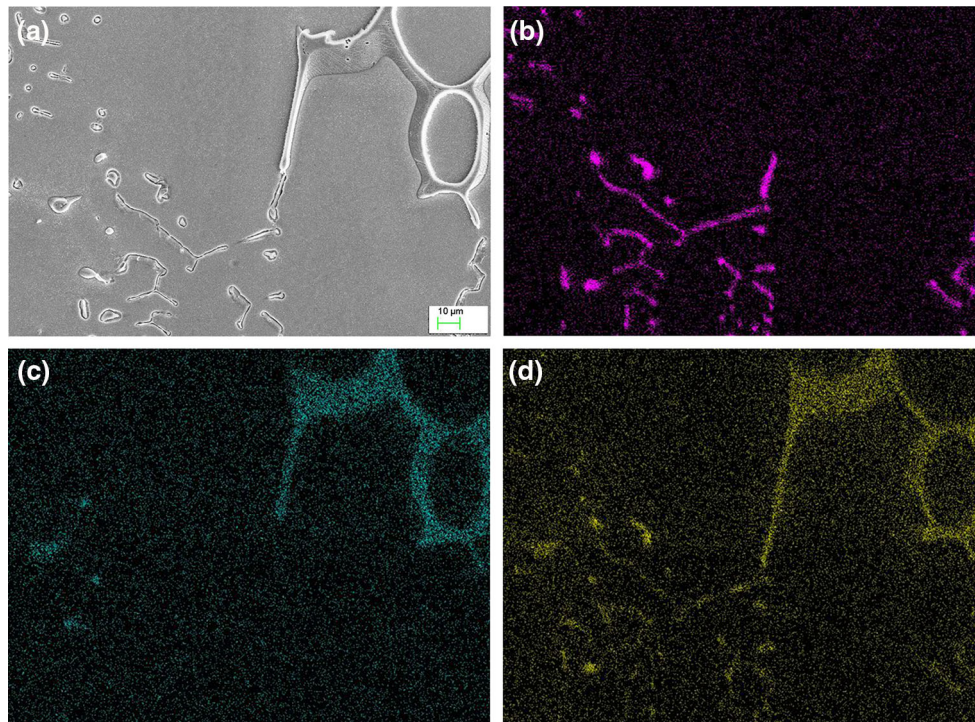


Fig. 10 Structure of the Cu–Ni–Si–Cr–Re alloy (a—#1 phases with Ni, #2 phases with Ni)—image obtained using the secondary electron (SE) and the distribution of elements: **b** Cr, **c** Ni, **d** Si

Conclusions

The application of thermal derivative analysis allowed to determine the temperature of the beginning of the solidification (T_L) and the beginning and end of the eutectic and phase crystallization as well as the solidus temperature (T_{SOL}) of the tested alloys.

The results can be summarized as follows:

1. The addition of Re to the alloy resulted in increased undercooling of the alloy and decreasing of the T_{SOL} temperature from 1060 to 896 °C.
2. Decreasing the T_{SOL} temperature is associated with the Ni–Si–Re phase coagulation most likely at the boundaries of α -phase.
3. In the tested alloys supersaturated at the temperature determined as a result of the thermal derivative analysis, it was found that the conductivity of the alloy with the Cr addition decreased by 5.25 MS m^{-1} , while the Re caused a decrease of 2.5 MS m^{-1} .

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